

CHEMISTRY AND STRUCTURE OF SPUTTER DEPOSITED BORON-CARBON-NITROGEN THIN FILMS

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ABSTRACT

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PhD. in Chemistry

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There is a growing interest in synthesizing new materials with unique mechanical properties like hardness or electrical and optical properties. For this purpose, Boron-Carbon-Nitrogen (BCN) ternary phase diagram promises new materials with potentially unique properties, such as variable band gap semiconductors or phases with extreme hardness. On the other hand, the physical or mechanical properties of these new BCN materials strongly depend on the chemical environment of the atoms and their atomic structure. In this thesis, atomic structure and chemical environment of the atoms in BCN thin films were investigated. BCN films were synthesized by Reactive Magnetron Sputtering (RMS) technique from a B₄C target. Various process parameters of synthesis were changed during deposition, such as the substrate bias, substrate-to-target distance and N₂ flow.

The effect of process parameters are investigated with respect to their fundamental effects on the growing BCN films. Several sets of experiments were planned and conducted in order to gain insight as per their effect on the final chemistry and atomic structure. The characterization of the chemical composition of the films was done using data from Infrared Spectroscopy,

Raman Spectroscopy, X-ray Photoelectron Spectroscopy, X-Ray Diffraction, and Electron Energy Loss Spectroscopy. Also, electron transparent thin cross-sections from the BCN films were prepared using focused-ion beam technique for conducting High Resolution Transmission Electron Microscopy analysis for the verification of atomic structure.

In the first series, named B series, the energy is supplied to growing film by applying a radio frequency generated d.c. bias on the substrate. Magnitude of the applied bias was changed throughout the series. In the second and third series, namely P and D series, the effect of substrate-to-target distance was investigated. In these series, BCN and BN films were deposited on substrates that were located at different distances from the target surface. In sub-series, effect of, i) the magnitude of applied bias, ii) type of applied substrate bias on the chemistry of the BCN films were scrutinized. In addition, the effect of atomic composition on the bonding preferences was studied. For this purpose, a series of BCN films were r.f. sputter deposited from B₄C target with different N₂ flow rate at the process gas.

After the careful analysis of the data from mainly the spectroscopic techniques, several important results were obtained. First, a prevailing bonding preference, i.e. phase segregation, was observed in the films deposited regardless of the process parameters used, such that a dominant presence of B-N and C-C or C-N bonding were observed in the films. Furthermore, increasing the substrate bias or decreasing the substrate-to-target distance resulted in the atomic ordering and layered (turbostratic) BCN films. Examination of the spectroscopic data in detail also indicated that the individual layers were made out of separate domains of h-BN like and graphitic like carbon regions, which supports the phase-segregation assertion.

Two main regimes are identified for the growth of BCN films; thermodynamically or kinetically controlled regimes. BCN films synthesized with large substrate bias or close to target surface were overall more ordered as the adatoms arriving on the substrate surface had enough energy to diffuse and find energetically most favorable sites. Such a case could be termed as thermodynamically controlled regime. In the opposite case, where adatoms were in a diffusion-limited environment, the final chemistry and structure was dictated by the kinetics. However, the prevalence of B-N bonding in both cases, and failure to observe hybridized chemistry suggests that bonding energy consideration is the major deciding factor for the chemistry of BCN films.

As a conclusion, the work presented herein suggests that phase segregation in BCN films reveal as an innate character, while hybridization is not observed in the process parameter space explored. The main reason for this is the relative energies of the B-N and C-C bonding.

Key words: Boron Carbon Nitrogen, Thin Film, Reactive Sputter Depositions, XPS, IR, Raman Spectroscopy, Biasing, r.f. sputtering, B_4C

ÖZ

SAÇTIRMA BİRİKTİRME YÖNTEMİ İLE ELDE EDİLEN BOR-KARBON-AZOT İNCE FİLMLERİN KİMYASI VE YAPISI

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Eşsiz elektriksel, optik veya mekanik özelliklere sahip yeni malzeme sentezine ilgi büyümektedir. Bor-Karbon-Azot (BCN) üçlü faz diyagramı potansiyel olarak benzersiz özelliklere sahip, değişken band aralığına sahip yarı iletkenler veya çok sert fazlar gibi yeni malzemeler vaat etmektedir. Diğer yandan, bu yeni BCN temelli malzemelerin fiziksel ve mekanik özellikleri malzemedeki atomların kimyasal çevresine ve atomik yapısına bağlıdır. Bu tezde, B_4C hedeften reaktif magnetronlu saçtırma (RMS) tekniği ile sentezlen BCN filmlerdeki atomların bağ yapıları ve kimyasal çevreleri araştırılmıştır. Biriktirme sırasında farklı işlem parametreleri değiştirilerek, örneğin alttaş meyillendirmesi, alttaş-hedef mesafesi ve N_2 akış miktarı gibi, bunların sentezlenen filmin özelliklerine etkisi incelenmiştir.

İşlem sırasında kullanılan parametrelerin kimyasal ve atomik yapı üzerine nihai etkisini anlamak için birçok deney seti planlanıp ve uygulanmıştır. Filmlerdeki kimyasal çevrenin karakterizasyonu için, Kızılötesi Spektroskopisi, Raman Spektroskopisi, X-ışını Fotoelektron Spektroskopisi, X-ışını Kırınımı ve Elektron Enerjisi Kayıp Spektroskopisi kullanılmıştır. Ayrıca, yapıdaki atomik

değişiklikler için, Odaklanmış İyon Demeti tekniği ile hazırlanan, elektron geçirgen, ince, yan kesit BCN örnekleri Yüksek Çözünürlüklü Geçirgenli Elektron Mikroskopu`nda incelenmiştir.

B serisi olarak isimlendirilen ilk deney serisinde, alttaş üzerinde büyümekte olan filme enerji, alttaşa uygulanan radyo frekansı ile oluşturulmuş doğrusal akım meyillendirmesi ile sağlandı. Uygulanan meyillendirmenin şiddeti seri içinde belli bir aralıkta değiştirilmiştir. P ve D serisi olarak isimlendirilen ikinci ve üçüncü serilerde, alttaş-hedef mesafesinin etkisi incelendi. Bu serilerde BCN ve BN filmler hedefin yüzeyine göre değişik mesafelere yerleştirilen alttaşlar üzerine biriktirilmiştir. Bu serilerin alt-serilerinde ise alttaşa uygulanan meyillendirmenin şiddeti ve tipinin BCN filmlerin kimyasına etkisi detaylı olarak incelenmiştir. Ayrıca, G serisinde de atomik kompozisyonun bağlanma tercihleri üzerine etkisi çalışıldı. Bu seride değişik miktarda N₂ içeren çalışma gazı akışı altında radyo frekansı saçtırmasında tabii tutulan B₄C hedeften değişik uzaklıklara yerleştirilen alttaşlar üzerine BCN filmler biriktirilmiştir.

Yukarıda bahsedilen serilerden sentezlenen BCN filmlerde çoğunluğu spektroskopik tekniklerle elde edilen bilgiler dikkatlice analiz edildikten sonra birçok önemli sonuç elde edilmiştir. İlk olarak, biriktirilen filmlerde kullanılan işlem parametrelerinden bağımsız bir şekilde bağlanma tercihinin faz ayrışmasından yana olduğu gözlemlenmiştir. Örneğin, filmlerde baskın biçimde B-N ve C-C veya C-N bağları gözlemlenmiştir. Ayrıca, uygulanan alttaş meyillendirmesinin arttırılması veya alttaş-hedef mesafesinin azaltılmasının BCN filmlerde atomik düzenliliği arttırarak ve tabakalı (turbostratic) BCN yapısının gözlemlenmesine yol açmıştır. Spektroskopik datanın detaylı incelenmesi de; herbir tabaka ayrılmış h-BN ve grafitik karbon benzeri kümeler içeren bölgelerden oluştuğunu, bu durumun ise faz ayrışması iddiasını desteklediğini göstermiştir.

BCN filmlerin büyümesinde, termodinamik ve kinetik olarak kontrol edilen iki ana rejim tanımlanmıştır. Yüksek alttaş meyillendirmesi ile veya hedef yüzeyine yakın alttaşlar üzerinde sentezlenen BCN filmlerin atomik yapısı genel olarak daha düzenlidir. Buna neden olarak alttaşa ulaşan iyonların yüzeyde film büyümesine katılan saçtırılmış ve eklemlenen atomlara, enerji olarak en uygun pozisyonu yüzeyde bulmaları için gerekli enerjiyi sağlaması gösterilebilir. Bu ve benzer durumlara termodinamik olarak kontrol edilen rejim denilebilir. Tam aksi durumda ise, eklemlenen atomların yüzeydeki hareketlerinin sınırlandırıldığı rejim, elde edilen son kimya ve yapı kinetik tarafından belirlenmiştir. Ancak, her iki durumda da egemen olan B-N bağı ve melezlenmiş kimyanın gözlemlenmemesi, BCN filmlerde bağlanma enerjisinin belirleyici ana unsur olduğunu işaret etmektedir.

Sonuç olarak; sunulan çalışma, uygulanan işlem parametresi uzayı veya kümesinde, faz ayrışmasının BCN filmler için tabii bir karakter olduğunu ve melezlenmenin mümkün olmadığını ileri sürmektedir. Bunun temel nedeni, B-N ve C-C bağlarının görece kararlılığı ve enerjisidir.

Anahtar Kelimeler: Bor Karbon Azot, İnce Film, Reaktif Saçtırma Biriktirme, XPS, IR, Raman Spektroskopisi, Meyillendirme, r.f. Saçtırma, B₄C

To my mother, my wife and our unborn baby

X

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1. INTRODUCTION

Thin film technology has been one of the most important fields of science and technology after the advent of semiconductors. One of the earliest reports regarding thin films synthesized under vacuum conditions was made by Drude in 1889¹. Drude, in his work, reported that he encountered deposits with unusual properties on the walls of glass discharge tubes. This could be suggested as the start of a new area of science; thin film technology.

Major progress in thin films technology was fueled with the advent of vacuum technology following the early 1940's and gained significant speed since 1960's. This technique allowed for the coverage of large areas using relatively small amounts of material. Therefore, in principle properties of very large areas could be easily altered by the thin films. For example, glass is a good electrical insulator but a few microns thick gold coated glass surface can become as conductive as gold. In addition to this, obtaining metastable phases at low temperatures was another advantage of thin films synthesis. Especially, with plasma involved techniques, like plasma assisted chemical vapor deposition (PACVD) and sputter deposition techniques, thermodynamically metastable phases at room temperature conditions, like diamond and cubic boron nitride, could be synthesized at lower temperatures and pressures than bulk synthesis methods of these materials.

Synthesis of polycrystalline diamond films merit further discussion. The phase diagram of carbon was indicated that for synthesizing diamond high pressures (more than 5GPa) were needed according to Berman-Simon line². For kinetic purposes of phase transformation, high temperatures (few thousands Kelvin) were also required³. However with the help of activated species created in the

plasma environment, polycrystalline diamond films could be synthesized at lower than 1000 K and at 20 mbar pressure using PACVD technique⁴.

Thin films technology has been applied to multitude of other technologically crucial areas such as semiconductor technology, cutting tool technology, and photovoltaic cell technology⁵⁻⁷. It is well known that compounds between IIIA and VA groups and elemental solids of group IVA (e.g. Si and Ge) are commonly used in the aforementioned technologies for their unique electrical and physical properties. Some of these materials in question display a wide range of range electrical properties, furthermore these materials posses' distinct physical properties, such as high hardness and optical transparency. One of the reasons for these unique properties is the highly covalent character and short bond lengths between the basic building blocks (atoms) for these materials.

One example for the application area of thin films technology is the synthesis of compounds and elemental solids in the B-C-N ternary system. The ternary compounds that are composed of boron, carbon, and nitrogen atoms can be called BCN compounds. The importance of these ternary compounds could be seen easily when the ternary phase diagram of boron, carbon, and nitrogen is investigated. In Figure 1, the ternary phase diagram of boron, carbon and nitrogen systems is given. Materials with unique and dissimilar properties are rather abundant in this ternary phase diagram. Diamond, graphite, cubic boron nitride (c-BN), hexagonal boron nitride (h-BN), boron carbide (B_4C) and β - C_3N_4 are some examples. Three of these, namely diamond, c-BN and B_4C are the hardest materials known. β - C_3N_4 is also expected to be harder than diamond⁸. Furthermore, graphite is used in battery cells as anode material and also as dry lubricants, h-BN a wide band gap semiconductor and also used as a mold-release agent in glass and plastics industry.

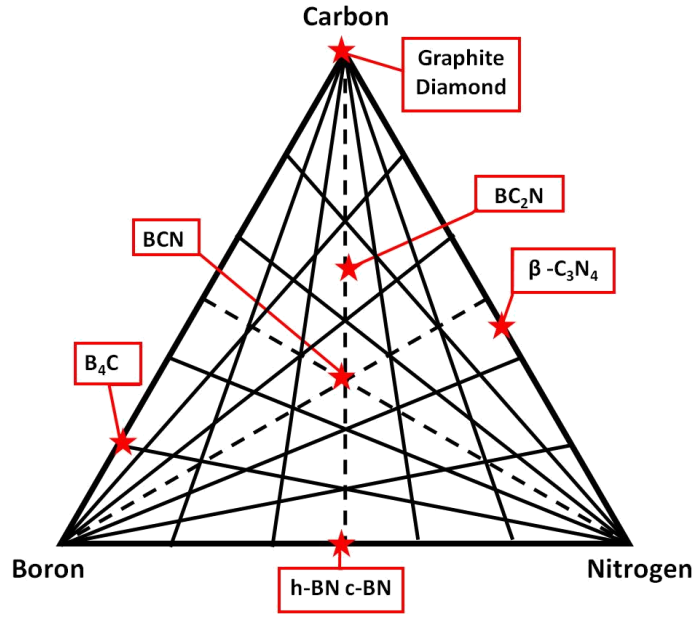


Figure 1: Ternary phase diagram of Boron, Carbon and Nitrogen

Solozhenko et al.⁹ was able to synthesize bulk cubic BC_2N (c- BC_2N) and Vickers hardness tests on this compound indicated a hardness of 76 GPa which is higher than that of single crystal c-BN (62 GPa). Motivation of the work of Solozhenko was based on a computational study by Liu and Cohen⁸. Their calculations showed that the bulk modulus is directly proportional to covalent character in bonding and, is inversely proportional to the bond length in covalent materials. For tetrahedrally bonded covalent solids, a simple semiempirical expression was derived;

$$\mathbf{B} = \frac{(19.71 - 2.20\lambda)}{d^{3.5}} \quad (1)$$

B is bulk modulus, λ is a measure of the ionicity of the compound, λ is 0 for group IV compounds, 1 for III-V and 2 for II-VI compounds and d is bond length in angstroms. Bulk modulus is proportional to hardness as strength and

compressibility of the bond are significant factors in the resistance of a structure to deformation.

Because of their short bond distance and structural similarity, hybrid compounds of IIIA-IVA-VA groups are potential candidates for hard materials following the postulate put forth by Liu et al.⁸. Hence, there is a similarity in the atomic structures of elemental solids and compounds in the B-C-N ternary, as well. For example, the structure of diamond and the structure of c-BN are cubic and are very similar to each other. In Figure 2, the structure of diamond and c-BN are provided. Accordingly, potential compounds of B, C, and N can exhibit exceptionally high Bulk Modulus values. For instance c-BC₂N synthesized by Solozhenko et al.⁹ is a good example, it is likely that this is not the only compound in this ternary to have such high hardness values.

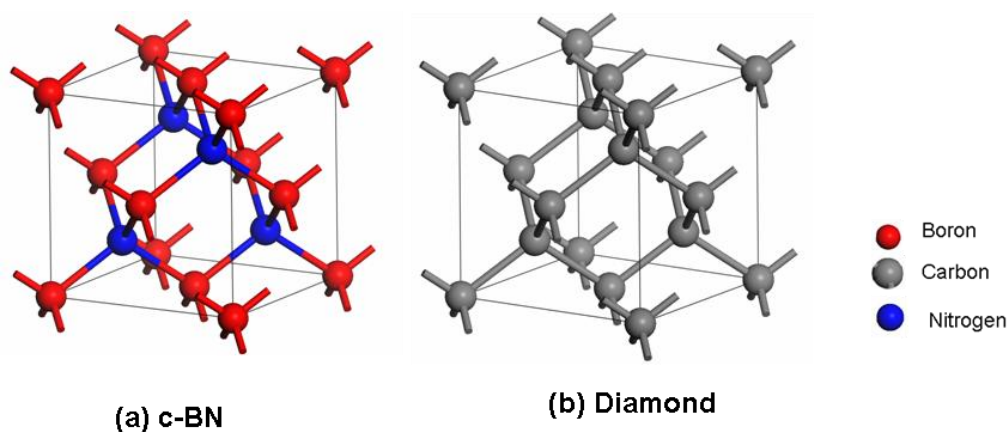


Figure 2: Crystal structure of (a) c-BN and (b) diamond.

In addition to studies on the hardness and related attributes, another study by Liu et al.¹⁰ examined the electrical properties of layered BCN compounds through pseudo-potential local-orbital calculations on hexagonal BC₂N (h-BC₂N). The structure of the graphite and h-BN are counterparts of each other, shown in Figure 3. Both of them are layered structure and there are weak van

der Waals interactions between the layers. In the case of electrical properties, the graphite is a semimetal, whereas h-BN is an insulator.

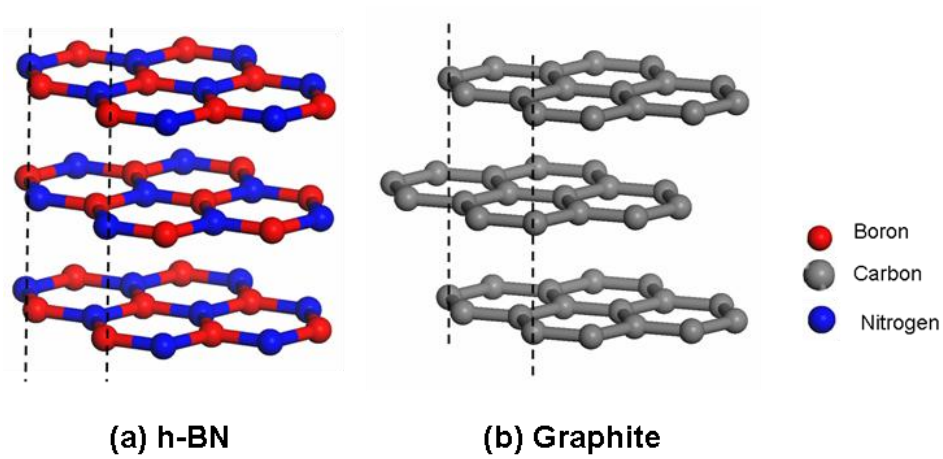


Figure 3: Crystal structure of (a) h-BN and (b) graphite.

Liu et al.¹⁰ considered the combination of these two similar structures and three different atomically arranged h-BC₂N single layer atomic models for their calculations. In Figure 4, the atomic arrangements used by Liu et al.¹⁰ are given. It is reported that the total energy of B-C-N layers decreased with the increase in the number of C-C and B-N bonds. Moreover, the calculated electrical properties were shown to be drastically influenced by the change in the atomic arrangement of atoms in the layers. These findings suggest that if the atomic arrangement could be tuned the electrical properties can be controlled without changing the atomic composition. In other words, these materials have variable band structures and they can be used as versatile semiconductors in a range of applications¹⁰.

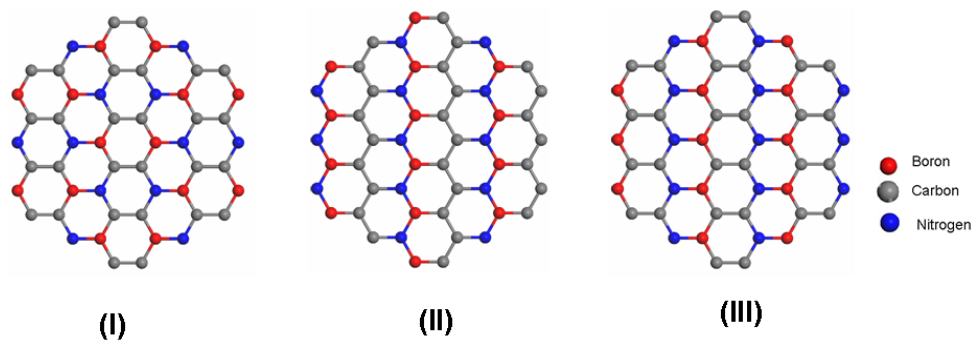


Figure 4: Layered h-BC₂N structures that are considered by Liu et al.¹⁰.

The Nobel prize for physics in 2010 was given to Andre Geim and Konstantin Novoselov for their study on the single-layered carbon sheets, also known as graphene¹¹. Hybridized graphene and monolayered h-BN (also known as White Graphene) is also a very active topic in the recent literature¹². There have been theoretical works on the electronic properties of such mono-layered hybrid structures¹³, besides various investigation on their synthesis¹⁴ and characterization, i.e. atomic resolution imaging of 2-D structures¹⁵.

Nanotubes were also studied intensely during the last two decades, as well. There is a large literature about carbon nanotubes and BN nanotubes. The structural similarities between layered carbon and layered BN make it possible to synthesize BCN nanotubes which were first reported by Weng-Sieh et al.¹⁶ through arc discharge method. The increase in the importance of BCN related works could be observed better when the numbers of publications that are related with BCN compounds, throughout the years are compiled. The plot in Figure 5 shows total number of articles where “boron, carbon, nitrogen”, “boron carbonitride” and “BCN” were used as keywords versus the publication years for the corresponding work. The data presented here was obtained from Web of Science¹⁷. In 1989 two very important articles were published; one of them was about the band gap variation in monolayer h-BC₂N related with intralayer

atomic arrangement¹⁰. Second one is related to the effect of bond distance and ionicity on bulk modulus of tetrahedrally coordinated solids¹⁰. The significant effect of those can be easily observed as a break point in the plot shown in Figure 5. Between 1990 and 2000, there has been a steady increase in the number of papers on BCN, mainly fueled by the work on developing a hard, stress free c-BN or β -C₃N₄ coatings with reproducible performance. Nonetheless, partial motivation from the 1991 paper by Sumio Iijima on carbon nanotubes should not be counted out¹⁸. Hence, in 1995 the first paper on BCN nanotubes was published, as well¹⁶. While, a stagnation period followed this region of high activity starting from year 2000 on, nevertheless first synthesis of a hard, crystalline BCN compound, c-BC₂N was announced in 2001⁹.

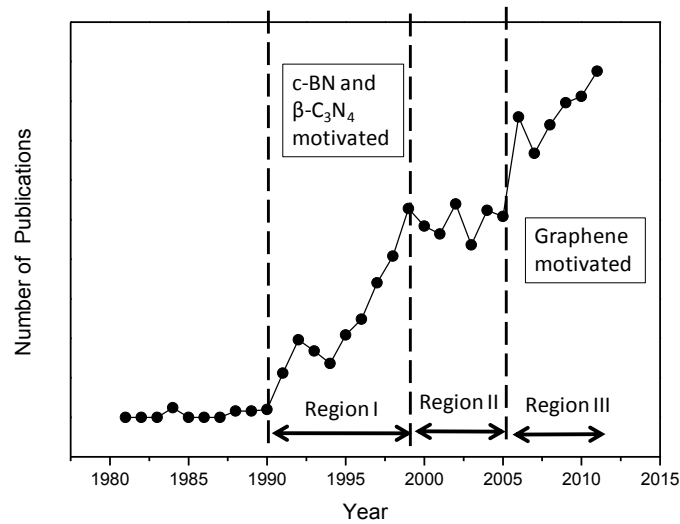


Figure 5: Number of BCN related publications vs. publication year. Three main periods are observed; region I motivated by c-BN and β -C₃N₄, region 2 stagnation period, and region III the onset of graphene and other 2-D structures era. (Data obtained from Web of Science)

In the third period starting with 2007, landmark papers regarding graphene were published which caused a renewed interest on BCN structures but this time the focus was on the mono-layered or 2-D structures and on optoelectronic properties thereof¹¹.

Until now, only the most recent advances and studies during the last two decades on B-C-N ternary were mentioned in this section. However, the history on B-C-N solids dates back to late 60's. During the space race era, the refractory materials for space vehicles become important for re-entry stage. Lightweight and high temperature resistant materials received significant attraction, thus BCN ceramics were studied for that purpose. The first report on BCN system was published at 1969 by Gingerich K.A.¹⁹. In that study, Gingerich attempted to measure the heat of atomization of BCN molecules using mass spectrometry. The main purpose of the study was to investigate the stability of BCN at high temperatures. Kosolapova et al. studied synthesis bulk boron carbonitride with solid state reactions, in 1971, the motivation of this work was develop new high-temperature electrical insulators²⁰. First thin film synthesis of B-C-N materials was reported by Badzian et al.²¹. In this work, BCN films were deposited by chemical vapor deposition technique and their hardness and high temperature stability was the focus.

There is a large body of work about the deposition of BCN films. Upon the compilation of various deposition techniques used in the literature, one can easily group these methods under four main classes: chemical vapor deposition (CVD), ion beam assisted deposition (IBAD), pulsed laser deposition (PLD) and magnetron sputter deposition techniques (MS). As an example for the CVD technique, a work published by Polo et al. could be mentioned²². In this study, BCN thin films were synthesized by radio frequency plasma assistance chemical vapor deposition where B_2H_6 - N_2 - CH_4 gas mixture was used as a precursor. The atomic composition of the film was controlled by controlling the

partial pressure of the gases used during deposition. For the case of IBAD, the work reported by Gago et al. could be given as an example²³. In this study, BCN films were deposited by co-evaporation of boron carbide and graphite using electron beam evaporation, while the growing film on the substrate was bombarded with nitrogen ions of energy between 200 eV and 2 keV from an ion gun. PLD was used by Wada et al.²⁴. In this study, a stoichiometric hot-pressed BC₂N target was ablated with a Nd:YAG laser. As an example for the MS deposited BCN films, the work published by Essafti et al., could be mentioned²⁵. In this work, BCN films were deposited from a boron carbide target material with the radio frequency generated plasma in argon and nitrogen flow. The nitrogen gas flow was adjusted to keep N₂ amount in the gas environment at 50 %. No bias voltage was applied to the substrate during film growth.

As indicated earlier, properties of the BCN thin films were directly related with the atomic structure and chemical environment of the atoms in the thin film. Although, there were numerous publications about the chemical make-up of the atoms in the BCN thin films, there is not a consensus on the bonding chemistry between boron, carbon and nitrogen in the films. Some studies on these films suggest that boron, carbon and nitrogen are hybridized; that is bonding exists between all three of the components without preference in the films. While, there is another school of researchers claiming otherwise, suggesting that phase segregation causes a phase mixture of BN and C-rich phases to be formed in these films. Interestingly, both sides depend heavily on x-ray photoelectron spectroscopy and infrared spectroscopy while supporting their claims. Moreover, in many cases the data reported as evidence are almost identical for both opposing groups, yet only with a strong dissent on interpretation of data at hand.

Hence, the objective of this thesis is to provide an accurate understanding of the local chemistry of BCN films using high precision characterization techniques, and ways to control the bonding chemistry in order achieve enough insight to tune properties of BCN solids. In this thesis, BCN films were deposited using reactive magnetron sputter deposition technique using various process parameters, such as changing substrate bias and flow rate of synthesis gas. The resulting films were investigated using transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) for the confirmation of the film chemistry. Detailed information about the composition of the films and the local coordination of boron, carbon and nitrogen was collected using *ex situ* X-ray photoelectron spectroscopy (XPS). Also, infrared spectroscopy was employed to collect similar information about the bonding chemistry. Further analyses on the films were done using Raman Spectroscopy as well. All of the data from the aforementioned analytical tests was used to explain the change in the composition and local chemistry in the deposited films depending on process parameters used. Several hypotheses were built through the elaboration of the data at hand.

In this thesis, the literature review is given in chapter 1.1. In the chapter 2, information about synthesis and characterization techniques and equipments used thereof are mentioned, the experimental procedure is also part of this chapter. In chapter 3, results obtained from the experiments and the related discussions are mentioned. The summary and the discussion relating to the data are given in the chapter 4. In the Appendix, brief information about the thin film technology is given and the final part is about the references.

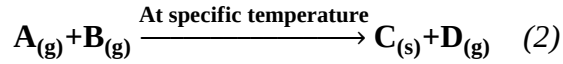
1.1 Literature Review: BCN Thin Film Synthesis

In this part of the chapter, a general review on the BCN thin films synthesis is provided. The literature on BCN thin films are grouped with respect to deposition techniques used for synthesis; CVD, IBAD, PLD and sputter deposition. Amongst the various techniques for thin films synthesis of BCN, major emphasis is kept on sputter deposition as in this study, the same technique is employed for the synthesis of BCN films, as well. There are numerous studies on BCN thin films, however in these sections only ones with significant scientific impact and relevance to the current studies are covered.

In the studies about BCN thin films, while most reports were concerned with the synthesis, characterization, and understanding of the physical properties, industrial applications of BCN thin films were also considered. One of the most important points about industrial application of thin films in general is to formulate a cost effective and reliable synthesis technique. In the following sections, the techniques utilized are not only considered from a scientific perspective, also analyzed is the applicability of the process in question to high volume manufacturing.

1.1.1. Chemical Vapor Deposition (CVD)

In this technique, the reactant gases are sent through a reaction chamber. The main purpose for this is to induce a reaction between the reactant gases, which will result in the formation of solid-products on a heated substrate. A sample reaction path is shown below:



The reaction is expected to take place only above a certain temperature and only on the substrate. Often, the substrate temperatures used in CVD reaches several hundreds of degrees in Celsius. In some cases, r.f. or microwave excited or ignited plasma is used to drive the reaction at lower substrate temperatures. This also has the added benefit of increasing the deposition rate of the desired thin film. In Figure 6, a schematic representation of plasma enhanced-CVD (PECVD) or plasma assisted-CVD (PACVD) technique is shown.

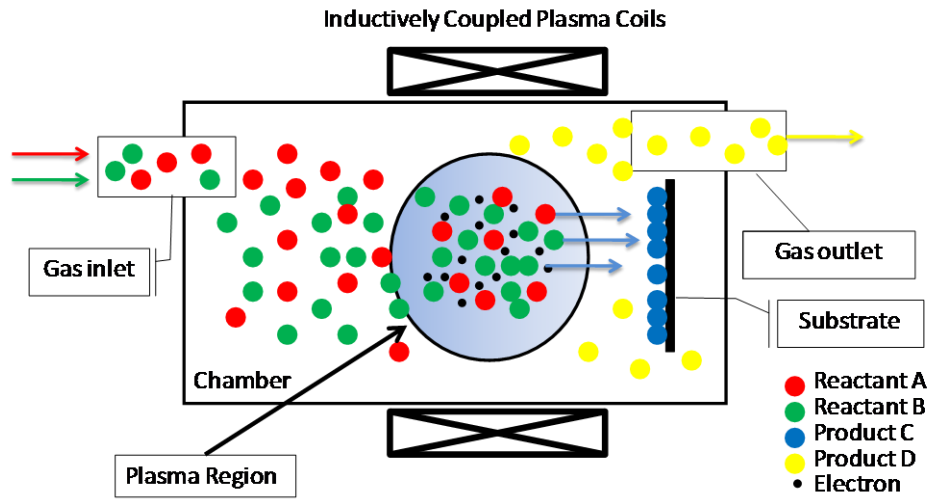


Figure 6: Schematic representation of PECVD.

As mentioned earlier, the first work about the synthesis of BCN thin films were published in 1972²¹. Badzian et al.²¹ synthesized BCN films using a hot-wall CVD technique. There are many other studies on BCN thin films synthesized using CVD in the literature²⁶⁻²⁹. In particular, Sugino and his colleagues investigated properties of BCN thin films that were deposited by PACVD³⁰⁻⁵⁴, field emission properties⁵⁰, optical and electrical conductivity³⁷. In these studies, a mixture of B₂H₆, CH₄, and N₂ were used as precursor gas during

PACVD process. Through IR and XPS analysis, it was found that these films were found to be a mixture of h-BN and graphite, thus phase segregation was observed. In addition to Sugino and co-workers, Mannan and co-workers also conducted a series of studies on the BCN thin films synthesis using CVD techniques. In these works, the BCN films were synthesized with a microwave or radio frequency plasma assistance. N_2 or $CH_4 + H_2$ mixture was used as carrier gas and a single source molecular precursor (tris(dimethylamino)-borane) was used. The substrate temperatures were between 650-750°C. In these studies, effects of applied power and types of plasma on the atomic arrangement of the films with different compositions were examined. Again, XPS and IR were used for the characterization of the chemistry and atomic structure of the films. Mannan and co-workers concluded that their BCN films were hexagonal with c-axis parallel to the substrate surface (turbostratic-BCN) while further asserting that there was full hybridization between atoms in the same layer⁵⁵⁻⁶⁰.

Although, this technique has been used widely for the deposition of BCN thin films, there are no reports on successful synthesis of metastable phases, e.g. c- BC_2N or c-BN. Furthermore, as the substrate has to be heated during this process, substrate choices are limited with the high temperature durability of the relevant materials. In addition to these, during CVD as the chamber pressures are kept relatively high, the reaction byproducts are inevitable. Hence, the deposited BCN films were sometimes called B-C-N-H materials due to significant amount of hydrogen incorporation to the growing film. Furthermore, the reactants used for CVD during BCN synthesis are generally highly toxic such as B_2H_6 , dangerous for humans and the environment. These render CVD techniques for BCN growth not very suitable for high volume manufacturing.

1.1.2. Ion Beam Assisted Deposition (IBAD)

In ion-beam involved techniques, basic components of the films are vaporized using electron beam evaporators. However, the evaporated atoms leave the bulk with very low kinetic energy and cannot be accelerated toward the substrate because of their neutral character. Energetic ions that are used for the structural modification of films are generated and accelerated in ion-guns.

The working principle of the electron beam evaporators is described with a schematic representation of an electron beam evaporator in Figure 7. An electron beam is generated by heating up a tungsten wire, the heated wire starts emitting electrons over a specific temperature range. Emitted electrons are then directed to the material that is to be evaporated. Because of the applied electric field, the electrons gain kinetic energy, as well. When the electron beam hits the target material, this kinetic energy will be converted into heat and the target material will eventually start evaporating.

On the other hand, in the ion gun the desired gas is ionized and the ions are then accelerated towards to the substrate. The ions that are impinging to the substrate surface help to manipulate the structure of the deposited film. The detailed information about effect of ion bombardment on deposited films is mentioned in the Appendix. If the ionized gas is a reactive gas, the vaporized material and the ions are co-deposited on the substrate generally forming a compound through a chemical reaction. If a novel gas used as ion source, it will mostly affect the physical processes taking place during the deposition process of the thin film. In Figure 8, a schematic representation of IBAD technique is shown.

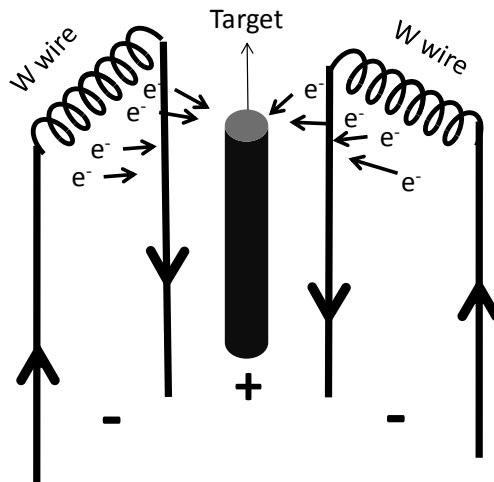


Figure 7: Schematic representation of an electron beam evaporator.

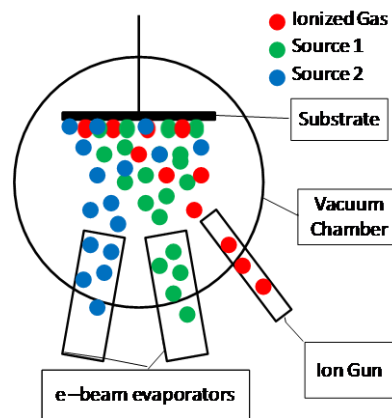


Figure 8: Schematic representation of IBAD.

There were many publications about the IBAD synthesized BCN thin films from many groups. Jimenez and colleagues⁶¹⁻⁶⁸, studied synthesis of BCN films primarily with IBAD technique. The boron and the carbon source of the atoms in the BCN films synthesized in these works were electron beam evaporated graphite and B₄C and source of the nitrogen atoms was the ion gun. In these works, Ar:N₂ mixture or Ar:N₂:CH₄ mixtures were used in ion bombardment.

The substrates were kept electrically grounded and were not heated in these experiments. The purposes of these works were to understand the chemistry of the atoms in BCN films with different deposition parameters. The compositions of the films were changed by changing the evaporation rate of the materials or changing the composition of the ionized gas. The effect of accelerating voltage of the ionized gas and the effect of ion flux on the chemical structure were also investigated. The chemical structure in the films was explored using IR, XPS and X-ray absorption near edge spectroscopy (XANES). In addition to chemical analysis, some of the mechanical test were also applied; hardness, coefficient of friction etc. The conclusion of these works about the chemistry of the BCN films, was that the BCN films were phase-segregated as h-BN/CN_x and in layered sp² hybridized structure. In addition to Jimenez and co-workers, Zhou and colleagues also studied on the IBAD synthesized BCN thin films. BCN coatings were deposited on Si wafers and Si₃N₄ disks by evaporating B₄C target, with simultaneous N₂ ion bombardment⁶⁹⁻⁷¹. The substrates were electrically grounded and not heated during the depositions. The effect of ion energy and the ion flux on the roughness of the film, the mechanical properties like hardness and tribological properties like wear resistance were tested. The chemical composition and bonding were analyzed by using only XPS. The conclusions of the Zhou and co-workers about the chemistry of the atoms in IBAD synthesized BCN films were that the atoms in the films were hybridized but no conclusion about the atomic structure of the films was given. In addition to these groups, some other groups worked on IBAD synthesized BCN films and published these works⁷²⁻⁷⁴.

Although, the major deposition parameters were independently controllable for this technique, IBAD is not a widely adapted technique in the industry because of several serious disadvantages. The main shortcomings of the IBAD systems are as follows : a- the coated area is not as wide as the other methods, b- the need for high vacuum during process, < 10⁻⁶ mbar, c- for evaporation of

refractory materials significant amount of energy is consumed thereby rendering IBAD a very expensive technology.

1.1.3 Pulsed Laser Deposition (PLD)

In this technique high power, high frequency lasers are used to vaporize target material, when the focused laser interacts with the target material, it heats up a small area, thus the material vaporized from surface of target material. In some cases, reactive gases are inserted in to the reaction chamber for co-deposition of the materials. If plasma assistance is used during PLD process, it is called plasma assisted PLD (PAPLD). In Figure 9, the schematic representation of PAPLD system was represented.

For example, Castillo et al. synthesized BCN film from B₄C target. Ablation was performed by KrF excimer laser ($\lambda=248$ nm). The chamber was full with N₂ gas and the pressure of the chamber was kept at 60 mbar. These films were analyzed *in situ* by XPS and reflection electron energy loss spectroscopy (REELS). The mean free paths of the electrons in the deposited BCN films were investigated for electronic applications. However, there was not any information about chemical environment of the atoms in the films⁷⁵. In addition to this work, also a group of scientists from Institute of Atomic Physics, Bucharest, Romania, had a series of publications about PLD synthesized BCN thin films at late 1990s`. In these studies, BCN thin films were synthesized from hot pressed h-BN and graphite. The reaction chamber was fed with reactive gas, N₂. Materials were ablated from target materials with XeCl excimer laser $\lambda=308$ nm. The atomic compositions of the films were changed by changing the h-BN/graphite ratio of the target materials and pressure in the chamber (1-100 Pa). The characterization of the films was done with secondary ion mass spectroscopy (SIMS), IR, XPS, scanning electron microscopy (SEM), transmission electron

microscopy (TEM), atomic force microscopy and micro hardness. The results indicate that crystals of c-BCN, h-BCN and h-BN are formed^{76, 77}. The main disadvantage of this technique is that the deposition rates of the films were low and PLD is an expensive technique. Due to laser involvement, experienced personnel are required.

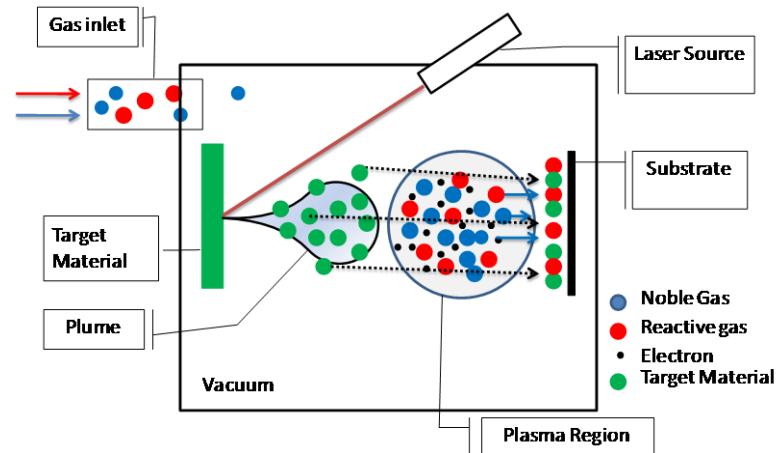


Figure 9: Schematic representation of PAPLD.

1.1.4. Magnetron Sputtering (MS)

During sputter deposition, target materials are vaporized with ion sputtering. Ions are created in the plasma environment and these created ions are directed to a target material by using electric field. Because of the electric field, these ions gain significant kinetic energy. When the energized ions hit the surface, their effects on the target material are different than electrons. In addition to kinetic energy-heat conversion, a successful momentum transfer occurs because of the similarity in the mass of the ion and atoms in the target. This process will create removed atoms from the surface of the target materials. If the plasma contains reactive gas, the deposited film consists of not only target material but also the atoms of the reactive gas. These types of depositions are called reactive

sputter deposition. Detailed information about sputtering and deposition are given in the Appendix. In Figure 10, a schematic representation of reactive sputter deposition is given.

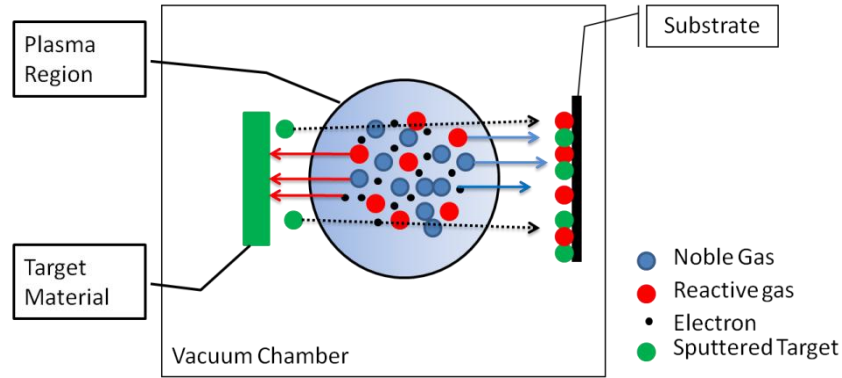


Figure 10: Schematic representation of reactive sputter deposition technique.

Early sputter deposition synthesis works on BCN were published at 1990's. Motivation for these studies were c-BN coatings. There had been number of studies about sputter deposited c-BN coatings until 1990's⁷⁸⁻⁸⁷. The problem in the c-BN coatings was the residual stress in the films⁸⁸. This compressive stress was the reason of the delamination of the c-BN films. The sputter deposited c-BN films were r.f. sputtered from h-BN or boron targets⁸⁹⁻⁹³. R.f. plasma has to be used because of the nonconductive properties of h-BN and boron targets.

During this period where c-BN was the most sought after material as a thin film, Luthje et al. were the first to publish on sputter deposited BCN thin films⁹⁴. Again, the motivation of the synthesis was deposition of low stressed c-BN thin films; actually "BCN" was not used for naming such films. These BCN films were deposited from a B₄C target with r.f. plasma. The study claimed that the cubic phase was achieved when the substrate temperature was 300°C and the applied r.f. generated d.c. bias was between 450 V and 550 V range. The evidences for cubic phase formation were obtained from infrared spectroscopy

and transmission electron diffraction pattern of the samples. The residual stress of the film was found to be decreasing with inclusion of the carbon in to the system. The work contains data from series in where only one parameter was changed in each set. In these series, the effect of; (i) gas content in the chamber, (ii) applied substrate bias, (iii) substrate temperature, (iv) oxygen content in the film on the c-BN/h-BN structure in the film were investigated.

The studies about deposition of BCN thin films with sputter technique can be investigated easily by classifying them into three separate groups with respect to the major experimental parameters controlling the structure of the films and the chemical environment of the atoms in BCN films; (i) ion flux and energy, (ii) target composition, (iii) substrate bias and temperature during process. (Further information about thin film deposition phenomena that covers the effect of the above-mentioned process parameters on the final film properties are mentioned in the Appendix)

A) Ion flux and energy:

The above mentioned work⁹⁴ marks the beginning of studies dealing with the sputter deposition of BCN thin films. In following years, the main emphasis was on the understanding of the effects of process parameters promoting c-BN growth. Especially, the crucial role of energetic ion bombardment during the cubic phase formation was investigated^{80, 82, 95-97}. After Luthje et al.⁹⁴, there were a number of published studies which investigated the role of ion bombardment on the growth mechanisms of cubic phase of the BN thin films^{88, 98-101}. Although, in these studies, the deposited films contained significant amount of carbon, thus the films synthesized could be termed as BCN, the authors were only focused on the c-BN phase growth and the experimental parameters, which affect stabilization of the cubic phase. The main reason for

the carbon inclusion was the ease of using B₄C targets instead of the highly dielectric and low-yielding BN targets.

In order to investigate energetic ion bombardment effects, the ion density over the substrate was controlled and increased by the help of an external magnetic field perpendicular to the substrate surface. This can be attained by the use of a solenoid placed around the substrate¹⁰¹. The resulting external magnetic field is then used in order to change the electron motion from linear to an helical path. Therefore, the path length of the electrons would be increased so that the larger probability of the collisions will induce an increased ion density above the surface of the substrate. Thus, the ion flux reaching the substrate could be improved significantly. Hence, together with the applied bias on the substrate, this external magnetic field will affect the number of ions impinging on the growing film above the substrate.

The films synthesized using an externally applied magnetic field above the substrate were characterized for confirming the c-BN formation and its relative amount with respect to the h-BN phase using IR, XRD, TEM and other related techniques^{88, 98-101}. The phase separation between BN and retained C was not directly a concern for the authors but nevertheless the resulting films were defined as “c-BN:C”. While, their analyses suggested that the boron and nitrogen in the deposited films were sp³ hybridization, no conclusions were provided regarding the chemistry of the films including the state of carbon. When the microstructure of the films were investigated using TEM¹⁰⁰, the HRTEM images indicated that the structure of the c-BN:C films were very similar to those observed for c-BN. In the c-BN:C films, first, an amorphous thin layer is observed over the substrate which is followed by a turbostratic-BN (t-BN) structure. Finally, a cubic phase was observed at the top layer over the turbostratic phase. In these studies, it was shown that to attain a cubic phase “momentum flux” of the impinging ions should be above a certain limit without

increasing the average ion energy. In other words, the ion flux impinging on the substrate surface must be increased without increasing the applied bias. If the ion energy is increased in order to increase the “momentum flux”, re-sputtering mechanisms could become dominant rendering very thin films.

B) Target composition

The studies in the literature about sputter deposited BCN thin films can be classified into two groups with regards to targets used as the source for boron, nitrogen and carbon; single-phase targets sputtering and multi-phase target co-sputtering.

B.1. Reactive single source sputtering

In these studies, BCN thin films were reactive sputter deposited from a single target material. These studies can be separated into three group with respect to used target materials:

(a) B_4C targets

Several studies reported about the reactive sputter deposition of the BCN thin films from a B_4C target^{25, 88, 94, 98, 100-112}. The source for the boron and carbon atoms was B_4C . As for the nitrogen source for the synthesis of BCN films, N_2 gas with varying flow rates was used. In these studies, Ar was used as the inert gas. The results from these studies can be summarized as follows:

-At approximately 10 % and over N_2 flow, the films saturated with nitrogen and the stoichiometry of BCN thin films became approximately B_4CN_4 .

-Boron to carbon ratio indicated some fluctuation. A decrease in the carbon content of the films was observed increasing the N₂ flow. This was explained by the formation of volatile carbon-nitrogen compounds, especially (CN)₂.

Although, nearly all of the studies under this category used the same characterization techniques, e.g. IR, XPS and XRD, there was not a consensus about the chemical environment of the atoms. Some of the studies claimed that atoms in the deposited films were showing no preferences for bonding, so the atoms in the films can be bonded to any of the other atoms. This type of films are called atomically hybridized in the literature and in the context of this thesis^{104, 105, 109}, whereas others claimed that the films were the mixture of two phases; h-BN and graphite^{25, 98, 102, 103}.

(b) BN target sputtering

In another group of studies, sputter targets made of h-BN were utilized as the source for boron and nitrogen atoms. As for the source of carbon, carbonaceous gases such as CH₄,^{113, 114} and C₂H₂⁹⁹ were used. In these studies, the main attempt was to control the carbon content independently of other parameters. Hence, the carbon content in the films was adjusted by the proportion of the carbon containing reactive molecular gas in the gas flow with respect to the inert gases. These studies concluded that; the boron to nitrogen ratio was larger than unity, causing a boron rich or nitrogen deficient system. The main reason for this observation was the recombination of N atoms sputtered from BN target as N₂ molecules. Moreover, the synthesized BCN films stoichiometry was in the carbon rich region in the ternary phase diagram of BCN. Still, the researchers, leaving the topic a controversy, did not reach a consensus in the chemical environment of the atoms. Some of the studies claimed that there was phase segregation such as BN/carbon⁹⁹, others claim that the atoms in the films were atomic level hybrids composed of B, C and N atoms.^{113, 114}

(c) Boron target sputtering

In order to induce further independence to process parameters controlling the BCN film composition, some studies followed the route of using targets made out of elemental boron¹¹⁵. The nitrogen and argon gas flows were kept constant in the experiment series and the CH₄ content in the flow was increased stepwise. IR, Raman and XPS techniques were used for the characterization. The chemical compositions of the BCN films were found to vary between BN to BC₂N. Chen et al.¹¹⁵ claimed that the BCN films were composed of a hybrid B-C-N structure.

B.2. Multi-phase target co-sputtering

In this synthesis route, thin films were deposited multiple targets or a single target which is composed of multiple compounds (composite target) such as graphite/BN with a set ratio. Generally, BN was used as the source for boron and nitrogen and a carbon or graphite target was used for carbon. The atomic composition of the films was controlled by controlling the target powers for two separate target cases, and in the composite target case by controlling the relative ratios of the compounds. In order to eliminate nitrogen loss -due to of N₂ and/or (CN)₂ formation- N₂ gas was added to the flowing gas¹¹⁶⁻¹²¹. The films were characterized by using IR, XPS, Raman, TEM, transmission electron diffraction and reflection electron energy loss spectroscopy (REELS) techniques. Again, there was not a consensus in the chemical environment of the atoms; some of the studies claim that there were phase segregation occurred in the thin films and opponents claimed that films were consisting of atomically hybridized boron, carbon and nitrogen atoms.

In addition to hot pressed composite BN/C targets, hot pressed elemental boron and carbon targets were also used¹⁰⁶⁻¹⁰⁸. In these studies, several targets with varying compositions were used (B, 4B:C, B:C, B:4C, C). Source of the nitrogen atoms in the BCN films was N₂ in the flowing gas. Linss and co-workers published these papers, The film structure in these published studies concluded phase segregation like h-BN/CN_x.

C) Substrate biasing and substrate heating

In order to control the flux and energy of the impinged ions on the substrate of the film the applied voltage on the substrate was used. The significance of the ion bombardment and substrate temperature on the film structure is covered in the Appendix. Briefly, extra energy imparted to the growing films due to energetic ions or by the heat supplied through heating of the substrate. Both of these could initiate or trigger various chemical or physical processes on the surface such as diffusion or chemical reactions. Hence, the effect of heating^{103, 109, 117, 120-122} and ion bombarding^{106, 116, 119, 123-125} the substrate were investigated widely. On the other hand, even though the studies used same characterization techniques, the conclusions of the studies about effect of bias and temperature of substrate on the chemistry of the atoms in the sputter deposited films did not agree.

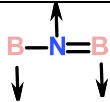
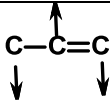
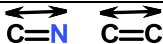
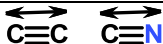
1.2. Literature Review: Characterization Techniques

In the remaining portion of this chapter, results of the works focused on the characterization of the chemistry and physical properties of BCN thin films are described. The focus is particularly kept on studies where infrared (IR) spectroscopy -related techniques and X-ray photoelectron spectroscopy (XPS) have been heavily used; nevertheless, other techniques are also covered. Brief information about the theory of the techniques and advantages and shortcomings with respect to related research will be mentioned. The depth of coverage provided for individual techniques is proportional to the frequency of usage; thus, more detail will be provided for IR and XPS.

1.2.1 Infrared Spectroscopy (IR)

IR is one of the most frequently used techniques for the characterization of bonding in BCN thin films^{112, 126, 127}. As a cheap, easy to implement and quick technique IR can easily provide a wealth of information about the system such as the bonding characteristic, e.g. single or double bond. Table 1 shows a list of possible bonding types and their assigned vibrational frequencies from literature on BCN thin films. Generally, the references used for identifying IR bands and positions are obtained from binary or molecular solids; thus, peak positions are not a universal constant for these chemical bonds. The shifts in vibration frequencies of the bonds are possible and common.

Table 1: IR peak positions for relevant bonds for BCN coatings compiled from literature.

Type of Bond	IR position (cm^{-1})	References
	780	128, 129
	680	130, 131
	1360	132, 133
	1080	134
	1150	135
	1350	130, 136, 137
	T.O. mode @ 1380, L.O. mode @ 1510	128, 134
	1580	137-139
	2200	137, 138

Although IR technique is a powerful technique to understand the bonding types and types of atoms involved, there are some disadvantages and shortcomings:

(i) This technique is very useful for gases, molecular solids and liquids, but there are some difficulties for using non-molecular solids.

(ii) The absorption coefficient of the bonds depends on the polarity of the bond. The polarities of the possible bonds for BCN films are significantly diverse. Hence, the signal originating from a less polar bond may be overwhelmed by

the signal coming from a more polar bond. In other words, the intensity of the absorption signal is not related with the abundance of particular bonding.

(iii) If the solid is amorphous having only short range order, the bond strength/length may vary causing a broadening for the related band.

In conclusion, IR technique is a simple, non-destructive and cheap technique, but by itself IR cannot be a definitive technique for the characterization of BCN films. Nevertheless, IR technique can provide useful information that could be combined with data obtained from other techniques to understand the chemistry involved in the BCN thin films.

1.2.2. Raman Spectroscopy

Raman spectroscopy (Raman) is also related with the vibrational motion of bonds. Raman scattering is the name given to inelastic scattering of light. Most of the light scatters from materials elastically. Therefore, the energy of the incident light is the same as scattered light. On the other hand, very small amount of the incoming light, 1 in 10^7 , can inelastically scatter from the material where the energy of the scattered photon is different from the incident photon. During Raman scattering, photons either lose energy or gain energy. The amount of energy change (the *shift*) is the same with the energy required to change vibrational state of bonds.

Inelastic light scattering occurs when there is a change in "polarizability" of the material. *Polarizability* is the measure of the change in a molecule's charge distribution like the electron cloud of an atom or molecule, to be distorted from its normal shape by an external electric field. It is a property of matter. Polarizabilities determine the dynamical response of a bound system to external

fields, and provide insight into a materials internal structure¹⁴⁰. By the vibrational motions of atoms in bond, the charge distribution so, the polarizability of bond is changed. Thus, the Raman scattering occurs, as Raman scattering is related with the change in polarizability of the bonds. Furthermore, IR is related with dipole moment change in the bond. The similarity between IR and Raman is that both of them are related with the vibrational frequency. As mentioned in the IR technique section, Raman also provides valuable information about the chemistry and in some cases bond ordering in the films. In Table 2, Raman shifts values, which were assigned in literature for some of the related materials, are given.

Table 2: Raman peak positions of relevant bonding for BCN coatings compiled from literature.

Material	Peak positions (cm ⁻¹)	References
c-BN	L.O. mode @ 1055, T.O. mode @ 1304	141
h-BN	1364	128, 141
Diamond	1332	130
Graphite	G Band @ 1580 D Band @ 1350	130
CN _x	G Band @ 1580 D Band @ 1350	131, 142, 143

Some of the relevant shortcomings of the Raman spectroscopy can be listed as:

(i) Raman scattering ability of the bonds are variable. In some cases, the Raman scattering from a bond is so high that the signal from the bonds with weak scattering are screened.

(ii) Scattering intensity is related with the symmetry in the material if the material is amorphous the probability of Raman scattering decrease¹⁴⁴.

However, the main advantage of the Raman is that it can provide valuable information about non-polar bonds especially carbon-carbon bonds. In this regard, brief information about the structure and Raman data in relation to carbonaceous materials will be mentioned in the following paragraphs.

The Raman data of the disordered carbon based materials generally displays two main peaks, G and D, 1580cm^{-1} and 1350cm^{-1} , respectively. G peak is related to a stretching mode of two sp^2 bonded carbon atoms and D mode is belongs to the so-called *breathing* modes of the 6-fold carbon rings. The vibrational mode of the G and D peaks are shown in Figure 11.

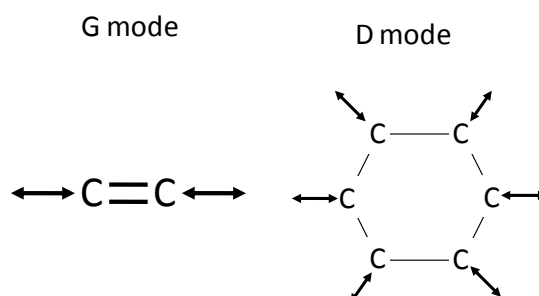


Figure 11: Schematic representation of D and G vibration modes for carbonaceous materials.

The π conjugation of this sp^2 hybridized structure can create long-range polarizability. This effect can intensify the Raman scattered light from the G and D modes and dominate the Raman spectra for carbonaceous materials. The ratio between the intensity of the D and G peaks, $I(\text{D})/I(\text{G})$, and relative position of the G peak provides evidence about the atomic structure of the carbonaceous

materials, as well. By the help of these, the size of the sp^2 domains can be estimated¹³⁰.

1.2.3 X-Ray Photoelectron Spectroscopy (XPS)

Photoelectrons are electrons that are ejected from a material when a photon of energy higher than binding energy of the electron is absorbed by the atoms in that material. In the XPS technique, a sample is illuminated with X-rays of known energy and the resulting photoelectrons from the sample are captured and analyzed with respect to their energies.

During the propagation of X-rays in the solid material, X-ray photons interact with the present atoms core electrons. Some of the energy of the incident X-ray photons gets consumed for the excitation of the core electrons from their orbital to the vacuum level and the rest is converted to escape energy, kinetic energy. As the energy of the incident X-ray photons are known, thus the binding energy of the ejected electrons can be obtained by the subtraction of the measured kinetic energy of the electrons from energy of the incident light.

The X-rays used in XPS have energy levels around 1000 eV and during the process, the core-shell electrons are ejected from the atom. Hence, for each type of atom a characteristic binding energy for each core shell electrons exist. Thus, the data from the XPS provides information on the elemental make of the surface. Moreover, quantitative measurements regarding the elemental composition of the surface can be done as the photoelectron response from each element is unique and related with amount. In addition, as the binding energy of core-shell electron is influenced by the change in the chemical environment of the atom, so shifts in the binding energy of the core shell electrons can be detected and correlated to the local chemistry. In summary, XPS gives

information about the type of atoms, quantity of the atoms and the chemical environment of the atoms on the surface. Thus, XPS technique was used very widely to characterize BCN thin films^{127, 145, 146}.

Although this technique gives very valuable information about the chemical environment of the atoms, there are some disadvantages of this technique. Here are the disadvantages:

(i) Photoelectrons have a certain mean free path in solids depending on the type of atoms in the solid. Typical mean free paths of electron are on the order of nanometers. Photoelectrons created deeper in the solid, lose their kinetic energy through collisions. Thus, only the photo-electrons created very close to the surface, generally within a depth corresponding to couple of mean free-paths can reach the detector without losing their kinetic energies, hence XPS is a very surface sensitive technique providing chemical information from the first several monolayers on the thin films. In other words, XPS data from the bulk of the material is hard to obtain, unless some the top layers are *removed*. This is generally achieved by sputtering the top layers with the help of a separate ion-gun.

(ii) As indicated above, XPS is a surface sensitive technique; hence, the interaction of the films with the ambient environment is also a problem. In air, any surface will be covered by a layer of oxygen and other contaminants in the atmosphere, generally carbonaceous materials. This is not only undesirable in terms of creating a layer blocking the escape of photo-electrons from the film, also the detrimental effect of the photo-electrons from various unrelated oxide and carbon-containing molecules will make it harder to analyze the XPS data from a carbon and/or oxygen containing film.

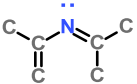
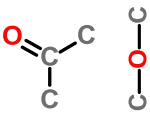
(iii) For dielectric materials or for materials with low electrical conductivity, pseudo shifts in the binding energy positions will occur because of the charge accumulation on the surface of the sample.

(iv) Reference data in the literature are generally collected from an elemental sample or a binary compound of element in question. However, in multi-component systems the chemical environment of the same element will be rather unique. Hence, reference peak positions in the literature should be used with great care to analyze materials in a multi-component system such as BCN thin films.

In conclusion, useful and valuable data can be obtained from XPS technique, so XPS technique was used widely in the BCN thin film characterization. However, XPS also has shortcomings. The data from XPS provides insufficient data about the atomic structure. Also, one has to be very careful about peak position assignments due to possible charging effects. Hence, data from XPS has to be processed very carefully.

The assigned peak positions in XPS for boron carbon and nitrogen atoms in possible chemical environments are given in Table 3.

Table 3: Binding energy list of B 1s, C 1s and N 1s core electrons for various bonding environments acquired from literature.

Atoms and chemical environment	Definition	Peak position (eV)	Reference
	N 1s: Three carbon coordinated nitrogen	400	147
	N 1s: Two carbon coordinated nitrogen	398	147
	N 1s: Nitrogen in BN matrix	398.4	148, 149
	C 1s: Carbon in carbonyl position in the carboxylic acid or ester	288.9	150
	C 1s: Carbon in carbonyl position in the ketone or ether	287.2	147
	C 1s: Two nitrogen coordinated carbon	286.8	147
	C 1s: One nitrogen coordinated carbon	285.6	147
	C 1s: Carbon in amorphous carbon, DLC, Diamond, graphite	284.7	147, 150, 151
	C 1s: Carbon in BC ₃ matrix	284.2	151

	C 1s: Carbon in B ₄ C matrix	282.9	151, 152
	B 1s: Boron in B ₂ O ₃	192.3	76
	B 1s: Boron in BN matrix	191	153, 154
	B 1s: Boron in carbon environment	189.5	151
	B 1s: Boron in B ₄ C	188.5	151, 152
	B 1s: Boron in Elemental Boron	188.1	155

1.2.4 X-Ray Diffraction (XRD)

The most common technique for the investigation of crystal structure of materials is the XRD technique. In this technique, an x-ray beam of known wavelength (monochromatic, Cu K_α = 1.5405 Angstrom) is used to illuminate the sample in question. The planes of atoms will act as mirrors to the incident X-rays “reflecting” them very strongly under certain few conditions. This is called diffraction. The diffraction of X-rays will take place only at particular angles of incidence, which has to satisfy a well-known condition called Bragg’s Law, which is given in Equation 3:

$$\lambda = 2d\sin\theta \quad (3)$$

In this equation, λ is the wavelength of the incident X-rays, and θ is the angle of incidence. In this expression, d is the distance between “parallel” planes of atoms that is causing the “diffraction” of incident X-rays. In order to satisfy the diffraction conditions, there should be significant amount of order in the bulk for atoms. The XRD patterns of amorphous materials or nano-crystalline materials do not contain dominant sharp peaks in the θ - 2θ scans. Only a broad peak appears in the diffraction pattern for such materials¹⁵⁶.

XRD technique was used to find out whether there were new and unique crystalline compounds in BCN thin films^{25, 127}. Also, it has been used to understand what other crystalline phases existed in these films. In the following section, cross-sectional TEM images from c-BN thin films will be discussed in detail where it will be shown that BN films indicate a specific growth pattern. In these films, the structure is dominated by a “turbostratic” layer where single atomic layers of h-BN e.i. “basal planes” were found to grow perpendicular to the substrate surface. Furthermore, these poorly crystalline films consist of atoms with low atomic numbers with weaker scattering cross-sections for x-rays. Therefore, typical θ - 2θ scan geometry was relatively unsuccessful for the XRD characterization BCN thin films. Hence, instead of θ - 2θ scan geometry, some studies involved the use of grazing-incidence XRD (GI-XRD) geometry¹⁵⁷⁻¹⁵⁹, which is a surface sensitive technique where crystallographic information from the first several atomic layers is captured using brighter x-ray sources. Typical d -spacing for the basal planes in these “turbostratic” films (d_{002}) were found to be between 3.40 and 3.55 Å¹⁵⁷. The variation in this d -spacing is sometimes used to differentiate and poorly-crystallized and ordered BCN thin films¹⁶⁰.

1.2.5 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) has been heavily used in materials science as it can provide very precise information about the atomic structure and the local chemistry about the materials^{161, 162}. High Resolution TEM (HRTEM) images can supply the information even at sub-angstrom resolution¹⁶³. Also, with proper analytical attachments, characteristic x-rays produced during electron-matter interactions (EDS) or energy loss induced in the transmitted electrons (EELS) can be utilized to obtain chemical information on the sample being imaged. Hence, these analytical capabilities make TEM a unique and powerful technique for the investigation of materials. TEM techniques were also widely used in the characterization of BCN thin films^{101, 145, 164}. There are a number of TEM studies investigating the thin film growth mechanisms of diamond-like carbon and c-BN thin films¹⁶⁵⁻¹⁶⁹. The cross-sectional HRTEM images obtained from the deposited samples shows that first, an amorphous layer was formed and a layered structure, which was perpendicular to substrate surface, was grown over amorphous structure. The cubic structure starts growing over that perpendicular layered structure¹⁷⁰. The plane view of this layered structure was also investigated and fullerene like structures were observed¹²². EELS has also been used to understand the atomic structure and also the local chemistry of BCN films. The presence of a 1s to π^* transition structure before the K-edge of carbon, boron or nitrogen indicates that the atomic structure of the film to be layered, e.g. turbostratic or hexagonal¹⁰⁷. Schematic representation of turbostratic-BN is shown in Figure 12. Although, TEM is a powerful characterization equipment, TEM related techniques have some disadvantages for BCN thin film characterization. Some of the shortcomings of TEM related techniques are;

-Sample preparation could be a long and very difficult process. Also, artifacts during -sample-preparation can complicate analysis.

- Electron-beam induced damage; extended exposure to electron beam can induce artifacts in the films.
- Operator impact; experience and skills of the operator can influence the quality of the data collected.
- TEM analysis is could be time-consuming.

In spite of these disadvantages, the TEM related characterization could provide valuable information about the BCN thin films that cannot be matched by other techniques.

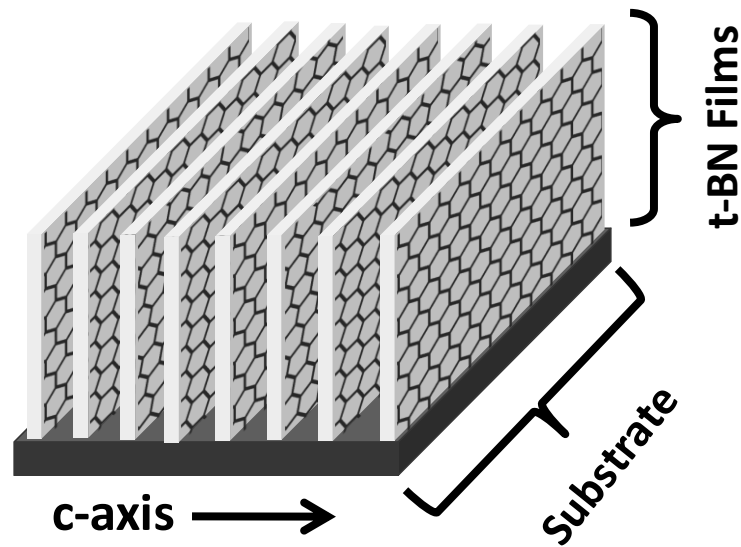


Figure 12: Schematic representation of the alignment of basal planes for turbostratic-BN.

2. EXPERIMENTAL

The first section of this chapter encompasses the equipments used during deposition, synthesis and characterization of BCN thin films during the work presented in this thesis. Thorough descriptions of the systems are made for each of the sputter deposition equipment used during this work. Also, essential details for the ion-implanter used during the implantation series in this work. In the following section, characterization equipment employed for the chemical and physical analysis of the films is described briefly. Also mentioned is the nano-indentation equipment that has been used for the mechanical testing of the thin films. In the final section, detailed descriptions of the synthesis and deposition parameters used during film growth are provided.

2.1 Equipment

2.1.1 Deposition and Synthesis Equipment

During the studies, two separate deposition systems were used. A detailed description of the systems is provided below:

Deposition Systems

System A:

This system was designed and constructed by the VAKSIS A.Ş. (Ankara, Turkey). A simple schematic representation (inset) and photograph of the system are shown in the Figure 13. This sputter deposition system was comprised of two 2-inch magnetrons. Both of the magnetrons were r.f. powered.

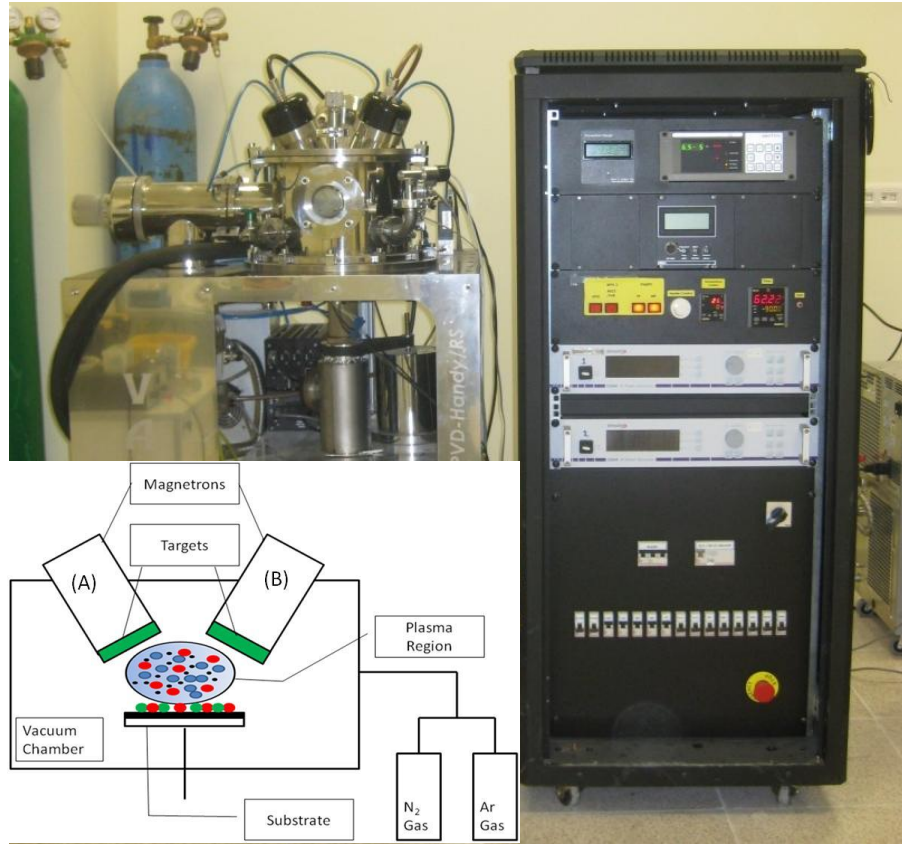


Figure 13: Schematic representation (inset) and photograph of VAKSIS Deposition system.

Magnetron A (on the left) was unbalanced and magnetron B (on the right) had a balanced magnetic field set up. More detailed information about the balanced and unbalanced magnetron set-ups are given in the Appendix. The positions of the magnetrons were fixed. The substrate holder allowed for the change of the height of the substrate from the bottom of the chamber, hence substrate surface to target distance could be adjusted. However, during the experiments in this system, the height of the substrate was kept constant and the distance between substrate and magnetrons were approximately 7 cm. Two r.f. power supplies (AE Cesar 600, Colorado, USA) were used on the system with separate matchboxes for each power supply. Two mass flow controllers (MKS, 1079 type, Massachusetts, USA) managed gas flow in the system. A calibrated cold

cathode gauge with a high vacuum range, manufactured by Varian Company, controlled the pressure of the system. Also for the low vacuum range a calibrated convectron type gauge was used, manufactured by Kurt J. Lesker Company. The pressure of the chamber was controlled by the use of a manual throttling gate valve. In this remainder of thesis, “VAKSIS” will be used for depicting the first deposition system.

System B

This system was designed and constructed by Mantis Deposition Inc. (Thames, UK). The schematic representation (inset) and photograph of the system was shown in the Figure 14. This system has three balanced 3-inch diameter circular magnetrons built by Angstrom Sciences Inc. (Pennsylvania, USA); two of them were d.c. / d.c. pulse and one was a r.f. type. The height of the magnetron could be adjusted through the stem flange and also these magnetrons were of swivel head type which allowed the head of the magnetrons to be bent up to 45 degrees. The d.c. pulse power supply was manufactured by Advance Energy company (DC Pinnacle-plus model) capable of providing up to 5kW on a dual outlet. The r.f. power supply (R601 type) and its matchbox (MC2 type) were bought from SEREN industrial power systems. Another smaller the d.c. power supply manufactured by TDK-Lambda Company (Genesys 600-1.3 type) was used for biasing the substrate. The pressure of the system was monitored through a compact gauge system that is manufactured by Inficon Company. During the deposition process, pressure is controlled by a precision baratron type gauge. Gas flow was again managed by four mass flow controllers (MFC) for use with Ar, N₂, O₂, low flow N₂. With the help of a butterfly valve in front of the pumping system, pressure of this system could be set and controlled automatically at given gas flows. The distance between substrate holder and magnetron surface was variable in a wide range 30cm - 3cm. In this thesis, “MANTIS” is used to describe this system throughout the text.

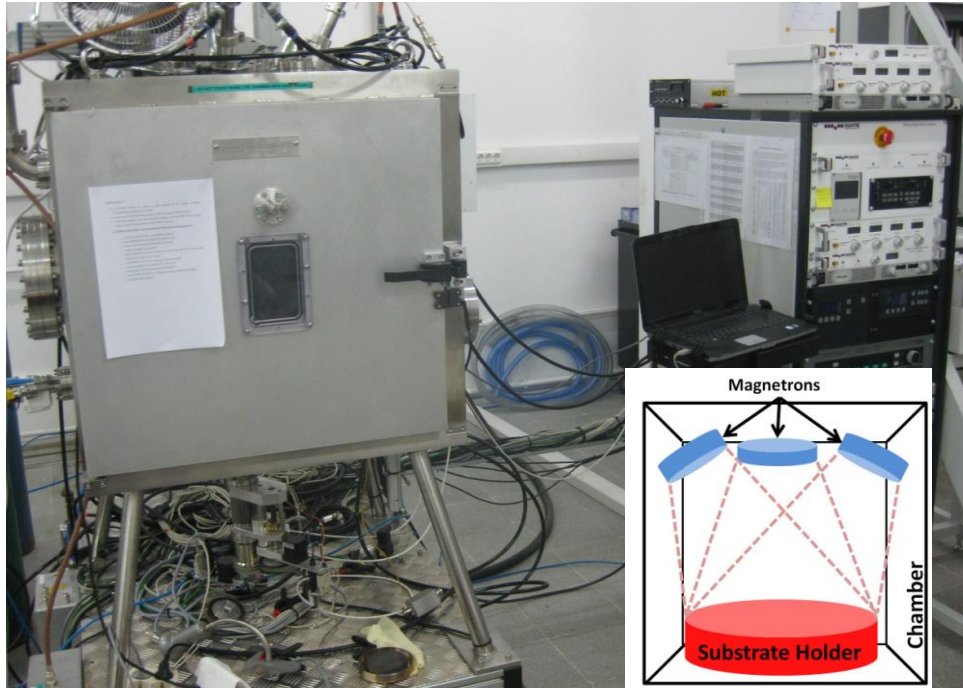


Figure 14: Schematic representation of magnetron configuration (inset) and photograph of MANTIS deposition system.

2.1.2 Characterization Techniques and Equipment

A) Infrared Spectroscopy (IR)

For IR spectroscopy analysis, Fourier transform infrared (FTIR) type IR spectroscopy (Bruker Corporation, Tensor27 model, Massachusetts, USA) equipment was used. The FTIR data was collected from regular spectral transmittance, in other words, data collected from transmitted light. The intensity change in the transmitted light at a range of the photon frequencies of interest is recorded. Absorbance data was obtained by comparison of the intensity of the initial light, which reaches to sample, and the transmitted light, which passed through the sample. In order to obtain initial light intensity a background spectrum was collected. During background data collection section, thin film free or “clean” Si wafer was put in front of the light direction so the

absorption and scattering effect of the Si wafer, environment and equipment was eliminated and initial light intensity was obtained. The resulting data is given as a plot of wavenumber vs. absorbance. While representing the IR data in the proceeding section, normalized IR data are used. Normalization is done by the division of all data by the maximum value of the relevant data array.

In spectroscopic techniques, the sample holder, which has a minimum interaction with the examined light, was preferred. Thus, for FTIR measurements, BCN thin films were deposited on the high resistance Si (100) wafers. Although, the Si wafers are from same batch, some deviations in the absorption spectra can be encountered. Thus, background spectrum from each Si wafer was recorded from virgin part of the deposited Si wafer.

B) Raman Spectroscopy (Raman)

In order to obtain Raman spectroscopy data micro Raman equipment (Horiba Ltd., LabRAM HR model, Kyoto, Japan) was used. The wavelength of the laser used during data collection was 532.6 nm. Power of used laser source is 40 mW. All data was collected with 600 groove /cm grating mirror. Before and after each data collection section, in order to be sure about the peak positions, the calibration of the instrument was done by adjusting the laser as zero wavenumber. All data were collected with the 50X objective.

C) X-Ray Photoelectron Spectroscopy (XPS)

The XPS data were obtained from two different XPS equipment; First, Thermo Scientific, K-Alpha model is used. This instrument uses monochromated Al K α radiation as X-ray source (1486.6 eV). The power set point of the source was adjusted for 72 W. In order to overcome charging effect dual source flood gun were used; in addition to emitted electrons with very low energy, Ar⁺ ions were generated and emitted to chamber in order to overcome overdosing the sample

with of electrons; negative charging effect. The system also houses a separate ion etching gun, which is used in order to remove carbonaceous species adsorbed on the surface of the samples due exposure to air. These carbonaceous species were ion etched with the ion-gun; during ion-cleaning of the substrate surface 1000 eV ions with a flux of 19 μA was used for 2 minutes. XPS data from the samples were collected by using 25 eV pass energy with a 0.05 eV step size. The energy resolution of the instrument with the data collection parameters mentioned above was obtained from the deconvolution of the Au 4f_{7/2} peak. The full width half maximum of Au 4f_{7/2} peak was measured to be 0.75 eV with the as-mentioned parameters.

The second equipment used for XPS analysis during this study is a custom design system with XR50M X-ray Source, Focus 500 monochromator and a Phoibos 100 analyzer by Specs GmbH. Again, in this system a monochromated Al K α line was used as the X-ray source. The power setting for this source was 400 Ws. A flood electron gun was again used in order to overcome charge accumulation on the sample surface. The system also has a rastering ion gun that is used to clean sample surfaces off contaminants. Ions with 750 eV and 3000 eV were used with a flux of 20 μA . The spectral data were collected with 25 eV pass energy and 0.05 eV step size. The energy resolution of the equipment with those parameters was checked with Ag 3d_{5/2} peak. The full width half maximum of Ag 3d_{5/2} peak was 0.89eV.

Before every detailed scan a rough survey scan on the surface of the samples were done on both systems. In survey scans, the contaminations on the surface were identified and the optimum sample positioning is performed before the detailed scans. After detailed scans of the B 1s, Ar 2p, C 1s, N 1s and O 1s regions, the surface was cleaned with Ar ion- etching to remove (if exists) excess surface carbon and oxygen. Hereafter, a detailed scan was performed on the same region in order to better understand the chemical composition of the

film. The detailed scans after the ion etching may induce a change in the chemical environment of the atoms in the films because of the energetic ion bombardment. This phenomenon, ion mixing, is mentioned with some detail in the Appendix chapter.

Quantification of the XPS spectra for atomic concentrations was done by first normalizing the peak areas by using corresponding Scofield factors (0.486 for B 1s, 1.0 for C 1s and 1.8 for N 1s). Although, a flood gun was used during data collection in order to prevent charge accumulation on the substrate, each binding energy was recalibrated by shifting XPS data with respect to Ar 2p_{3/2} peak position.

D) X-Ray Diffraction (XRD)

For XRD diffraction pattern, Rigaku Corporation, Miniflex model (Tokyo, Japan) equipment was used. The X-ray source of the equipment was Ni edge filtered Cu K_α radiation. Data were collected between 10°-60° as 2θ values. Step size of the detector was 0.05° and data collection speed was 3° per minute.

E) Transmission Electron Microscopy (TEM)

The energy filtered transmission electron microscopy (EFTEM) images, high-resolution transmission electron microscopy (HRTEM) images and electron energy loss spectroscopy data were collected from JEOL JEM 2100F TEM equipment at the Department of Material Science and Engineering, Anadolu University, Eskisehir, Turkey. The samples were prepared by using dual beam focused ion beam instrument.

2.2 Experimental Procedure

As mentioned in the introduction chapter, although the same well-known characterization methods were used in the studies for the understanding the chemistry BCN thin films, the interpretation of the data in each study was grossly differing. Hence, in order to understand the film chemistry, the effect of each parameter was studied in a serial experiment, the characterization data were collected from the samples obtained from serial experiments. In that series, one of the deposition parameters were changed and the change in the data were compared.

In all deposition experiments, the base pressure of the system was always better than 2/1000th of deposition pressure which means if the deposition pressure is 5×10^{-3} mbar, base pressure was less than 1×10^{-7} mbar. Depositions were made on 300 μm thick, single crystal Si wafers with (100) or (111) surface. The resistivity of the Si wafers were between 1-9 ohm/cm. Ar gas (99.999% purity) was used as inert gas and N_2 gas (99.999% purity) was used for nitrogen source during the deposition of the BCN films. Unless it was indicated, N_2 during depositions were adjusted to be 10% of the total gas flow in the experiments by default. The applied pulsed-d.c. potentials in all experiments were set at 250 kHz frequency and 0.4 μsec reverse time. In reverse time, it applies positive 30 V. Pulsed d.c. bias is mostly utilized when the growing film or the substrate has low electrical conductivity. Hence, pulsed d.c. helps driving away the accumulated charge and eliminate its undesired effects. In Table 4, the other deposition parameters used in the experiments are given.

All substrates and targets were plasma cleaned before deposition process. The surface of the substrates and targets were subjected to energetic Ar^+ ions created in the plasma ignited on the substrate and target. The plasma cleaning of the target and substrate surface were made simultaneously at an Ar pressure of

2×10^{-2} mbar in both VAKSIS and MANTIS systems. The substrates before the coating process in the VAKSIS were cleaned with r.f.-generated plasma, 2.5 W/cm^2 power applied the surface. The substrates, deposited in the MANTIS, were cleaned with pulsed-d.c. (p-d.c.) generated plasma. - 400 V d.c. bias was applied to substrate. Targets were cleaned with the same power of deposition procedure. Depositions start with adjusting the pressure of the chamber to desired value while sustaining the plasmas, then the bias to the substrates were set to the working value.

Table 4: Deposition parameters that were fixed and kept constant during all of the following experimental series:

Process Parameter	VAKSIS	MANTIS
Base Pressure	$< 5 \times 10^{-6}$ mbar	$< 5 \times 10^{-6}$ mbar
Deposition Pressure	2.5×10^{-3} mbar	2.5×10^{-3} mbar
Applied Power on Target	(r.f.) 12.5 W/cm^2	(p-d.c.) 9 W/cm^2
Plasma Cleaning Pressure	2×10^{-2} mbar	2×10^{-2} mbar
Substrate Bias	(r.f.) 2.5 W/cm^2	-400V p-d.c.*
Substrate	Si (111)	Si (100)

*The applied pulsed-d.c. parameters in all experiments were 250 kHz frequency and 0.4 μsec reverse time. During the reverse time, a positive 30 V is applied to the substrate.

The overview of the experiments series are given in the flow chart provided in Figure 15. The detailed experimental parameters for deposition experiments are also given.

2.2.1. Effect of Bias (B Series)

In B series (B is due to biasing), the effects of r.f. generated d.c. substrate bias on the atomic structure and chemistry of the atoms were investigated. Deposition experiments in this series were done in VAKSIS system. These films were deposited from 2" diameter, copper back-plated B₄C target which was supplied from Kurt J. Lesker. It's purity was 99.9 %. During deposition processes, the pressure was kept at 9×10^{-3} mbar. Target power was 250 W in all depositions. Distance between the substrate and target was set to 7.5 cm. On the other hand, r.f. generated d.c. bias on the substrate was changed; r.f. generated d.c. bias used were 50, 100, 150, 200, and 400V dc. These values were generated by applying 1 W, 3 W, 7 W, 22 W and 38 W of r.f. power to the substrate during deposition, respectively. In the "grounded" case, BCN film deposition was carried out while the substrate was grounded through the chamber to earth.

2.2.2. Effect of the type of bias applied to substrate and target to substrate distance (P Series)

In this series, the effect of the magnitude of the applied bias, type of bias and the distance between target and substrate were investigated. The films in this series were deposited in the MANTIS system. An r.f. power of 400 W was applied to B₄C target for sputtering. In this series, experiments can be divided into two sub-groups: The first, P8 series ("8" denotes that the substrate to target distance is 8 cm), the films were deposited on grounded, d.c. and pulse- d.c. biased substrates. The substrate was 8 cm away from target; hence, the substrate was subjected to an intense bombardment of ions as the plasma-plume on the target extends up to 10 cm from the surface of the target. In the second series, called P18 series ("18" denotes that the substrate to target distance is 18 cm),

films were deposited again on grounded and pulse- d.c. biased substrates. Hence, in this case, substrate was positioned well away from the plasma-plume in front of the target indicating that the interaction of the ions with the depositing film on the substrate was significantly limited.

2.2.3. Effect of the substrate-to -target distance (D series)

In D series (D is due to distance), the effect of substrate-to-target distance was investigated exclusively. During the deposition processes, pressure in the chamber was kept at 2.5×10^{-3} mbar. In these series, a special substrate holder was designed and used in order to investigate the effect of substrate-target distance during deposition. It is well known that substrate to target distance controls the ion-flux impingent on the substrate. Thus, this will have a profound impact on the growing film which is mentioned in sufficient detail in Appendix. The schematic for the substrate holder is shown in Figure 16.

Nine different substrate-target distances can be set-up and tested in one deposition experiment. The closest substrate to target distance was 7.5 cm and the farthest was 27.5 cm. Depositions in D series can be divided in to 2 groups; one for the experiments conducted for the deposition of BCN films with varying substrate-to-target distances, called BCND series, the other is BND series, effect of substrate target distance on deposited BN film was investigated.

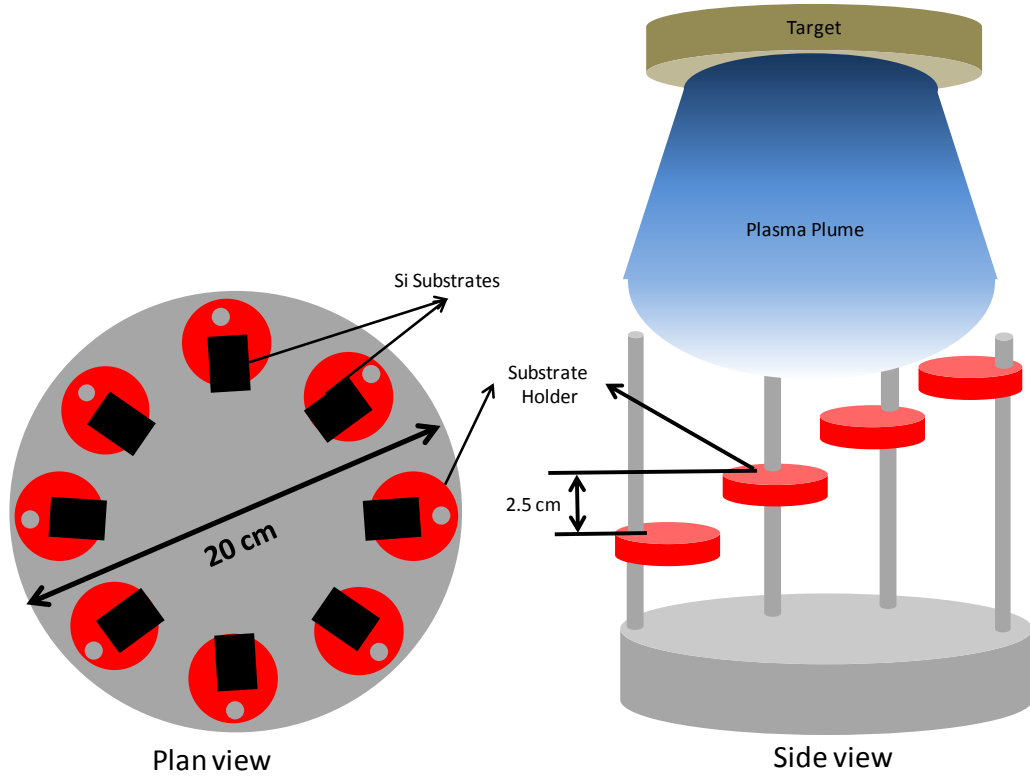


Figure 16: Schematic representation of the substrate holder designed and built for experimental series D.

Effect of substrate-to-target distance on BCN thin films that deposited from B_4C (BCND Series)

These deposition experiments were carried out in the in MANTIS system. The thin films in these series were deposited from a copper back-plated B_4C (99.9 % purity) 3" circular target which is supplied from Plasmaterials Inc. (California, USA). During all of the BCND experimental series target power was set to 400 W of r.f. power. The BCND Series can be further divided in to 3 groups with respect to the type of substrate bias applied. In Table 6 the name of the subsets and details on the applied substrate bias are given.

Table 5: Experimental parameters used for the BCND subsets.

Subset Name	Bias type	Applied Bias
BCND50	p-d.c.	50V
BCND50DC	d.c.	50V
BCNDGr	Grounded	Grounded

Effect of substrate target distance on BN films that deposited from BN target (BND Series)

In this experimental series, thin films were deposited from copper back plated, 3", circular BN target supplied from Plasmaterials Inc. (California, USA). The purity of the target was 99.9 %. Depositions made with 10 % N₂ gas flow and a constant 50 V pulsed-d.c. bias was applied to the substrate holder.

2.2.4. Effect of reactive gas flow rate (G series)

In this series the effect of nitrogen content in the film was investigated (G stands for “gas”) through the change of the N₂ flow during deposition. The thin films in this series were deposited in the MANTIS system. In the deposition processes, pressure in the chamber was kept at 2.5×10^{-3} mbar. In this series, experiments can be divided into two sub-groups: The first, GT series (T indicates “thermodynamics”), the films were deposited on a substrate with a 50 V p-d.c. bias applied which was positioned 8 cm away from target. Hence, thermodynamical preferences were control the growth mechanism due to intense and energies ion bombardment. In the second series, called GK series (K denotes “kinetics”) films were deposited on grounded substrates located 18 cm away from the target surface.

3. RESULTS and DISCUSSION

The work presented in this thesis has two main starting aims; (a) investigating the atomic structure and chemical environment of the atoms in the BCN thin films and, (b) understanding the effect of deposition parameters on the final atomic structure and chemical environment of the atoms in BCN thin films. As mentioned in the Appendix, during deposition several parameters have great influence on the final atomic and microstructure of the thin films. Briefly, competition between nucleation and growth during synthesis determines the final properties of the films. If equilibrium thermodynamics dominates the film growth mechanisms, in general films will assume energetically more stable phases and grow with few defects with a relatively long-range order. However, due to kinetic limitations for reaching the equilibrium conditions, films with metastable phases with highly defected atomic structures are also observed. For instance, adatoms on the surface contributing to the film growth may find energetically more favorable sites under conditions favoring high diffusion rates, such as higher substrate temperatures. On a colder substrate, as the mobility of adatoms is limited, eventual resting sites of the atoms would not be far away than the actual landing sites. Final microstructure of the films grown under these two distinct situations will be markedly different while the overall crystal structure might very well be the same. Furthermore, changes in the microstructure will significantly affect the resulting physical and chemical properties of the films, such as through the well-known Hall-Petch effect¹⁷¹.

In this thesis, an attempt has been made to probe the thermodynamically and kinetically controlled processes deciding the final atomic structure and chemistry of BCN films. In this attempt, a careful selection of process parameters that will be used to investigate the above-mentioned points was

conducted in order to isolate their effects on BCN growth. In the first group of experiments, the composition of the films were kept constant while the ion flux and energy reaching the growing BCN films were manipulated through the substrate bias and type, also through target to substrate distance. In the second set of experiments, effect of the relative abundance of reactive components were adjusted to investigate the energetically stable chemical configuration of individual boron, carbon and nitrogen atoms through varying the reactive gas flow and selective ion-implantation. Hence, the chemistry and atomic structure were probed in two mutually exclusive approaches. In one case, the effect of extra energy pumped into the system through intensified non-thermal energy transfer via ion bombardment on the final local atomic configuration is investigated while keeping the composition of the films constant. In the other complimentary approach, effect of the relative arrival rates of film forming components on the surface are manipulated to understand the bonding preference of atoms.

The following sections in this chapter are arranged to reflect the two distinct approaches explained above. The first section is focused on analyzing the experimental results of changing the substrate bias and type of bias used, and the substrate to target distance. In the second section, the results from the atomic composition changes induced by the N₂ gas flow and selective ion-implantation are provided.

3.1. Investigation of the effect of ion bombardment on the atomic structure and chemistry of BCN thin films

In this part, the main focus is on the non-thermal energy supplied to the growing film. Non-thermal energy is provided by the bombardment of the surface with the energetic ions. In sputter deposition, this is achieved by attracting some of the ions in the plasma to the substrate by the application of a negative bias imposed on the substrate with respect to ground. The bias is created by the use of a separate d.c. or r.f. power generator.

As mentioned in the surface-particle interaction section, there are several different types of surface-particle interactions. The common point of these mechanisms is that kinetic energy of the ion is transferred in to thermal energy on the surface. Then, this thermal energy propagates through the bulk. However, the real effect is on a pack of atoms surrounding the point of impact where the energy of ion is released. The energy transferred from the impinging ion, generally larger than the bonding energies of the atoms in the film, causes a rearrangement of the atoms in the vicinity of the impact. In some cases, the transferred energy per atom is in the order of several thousands of Kelvin enough to break all of the bonds in this small pocket of atoms such as the case of sputtering action. This extra energy provided by the ions bombarding the growing film could have effects ranging from densification of the films, heating, enhanced diffusion, activation of chemical processes on the surface, and also re-sputtering. In the following sections, the effect of average ion energy (bias) and ion-flux is summarized for BCN films.

3.1.1. B series

In B series, the effects of applied bias were investigated. The effects of the applied bias on the substrate during deposition of BCN films were studied in the literature extensively^{88, 98, 99, 116, 119}, especially in those studies trying to address the phase segregation question. However, still in others on the same topic did not provide much information even about the bias settings^{25, 105, 113, 114, 118}.

The experimental parameters in this series of runs were given in the Table 4 and Figure15. During these depositions only r.f. generated d.c. negative bias was changed. The resulting films were characterized using IR spectroscopy, XPS, XRD, EELS and HRTEM.

First, the atomic compositions of the films generated in series B are presented with respect to changing bias conditions in Figure 17 (a), (b) and (c). Atomic compositions for B, C, and N are obtained from the detailed scans of XPS results. Only a relatively minor difference between the compositions of films pre- (a) and post (b) ion-etching is observed, The data presented are collected from the same films but (a) being "pre-etching" from the raw, as-is surface, and (b) is from the surface of the films collected "post-ion etching". The XPS measurements were done *ex situ*; during the period between deposition and XPS analysis the films were exposed to ambient atmosphere. This exposure causes film surfaces to be contaminated by the environmental factors such as carbonaceous materials in ambient atmosphere, even if utmost care is taken.

As XPS is a surface sensitive technique, where nearly ~90% of the data originates from the top few monolayers of atoms, film surfaces has to be "cleaned" in order to avoid interfere data from the "impurity layer". Hence, in order to clean surface of the films, generally low energy ions of inert gases are used, e.g. Ar^+ , Xe^+ and etc. These ions are used to remove oxides and carbonaceous species that are physisorbed on the surface as impurities. If these

physisorbed species were not removed, analysis of the data for the identification of compositional and chemical state of the surface could be misleading. Especially, in the case of BCN samples, carbon contamination is particularly problematic^{107, 147, 172}. On the other hand, the only way for cleaning the surface, namely ion-etching, could also lead to significant issues during analysis of the data. This is due to the ion-mixing of atoms on the surface by energetic Ar⁺ ions. As B, C, and N are close to each other due to similar atomic mass, ion-mixing effect during surface cleaning is not expected to cause compositional variations as also shown in Figure 17 (a) and (b), where trends are very similar. However, ion-mixing changes the local chemical environment of atoms. This is a very serious issue when XPS is used to probe local coordination of atoms in a films such as the case covered in this thesis.

The effect of ion etching on the chemical environment was clearly depicted when the XPS data from pre- and post ion-etched C 1s spectra were considered, as shown in Figure 18 (a) and (b), respectively. The shape and positions of the peaks were changed drastically after the films were subjected to ion-etching. It looks as if ion-etching caused a re-arrangement in the local coordination of carbon atoms and the final configuration is different than the original environment that the carbon atoms were in right at the end of deposition. Hence, this is the effect of ion mixing on the surface of the film. As the ion-etching is done using the same parameters (750 V, 19 μ A, 50 sec) on every film, the final chemical state of the surfaces after ion-mixing due to ion bombardment looks the same. Hence, this also explains the reason for using "as-is" films for XPS characterization in spite of the fact that the surfaces are contaminated with some carbon and oxygen in many studies.

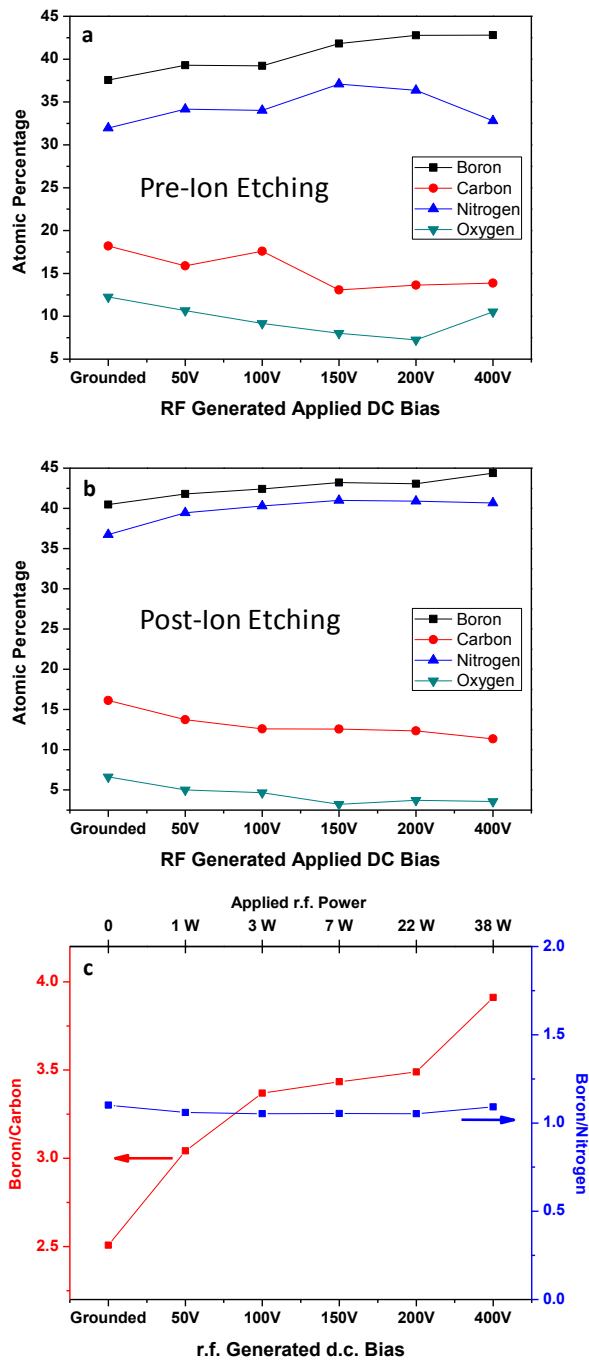


Figure 17: Atomic composition of the B series films with respect to applied bias on the substrate during deposition; (a) pre- and, (b) post ion etching obtained from XPS analysis, (c) B:C and B:N atomic ratios after ion-etching.

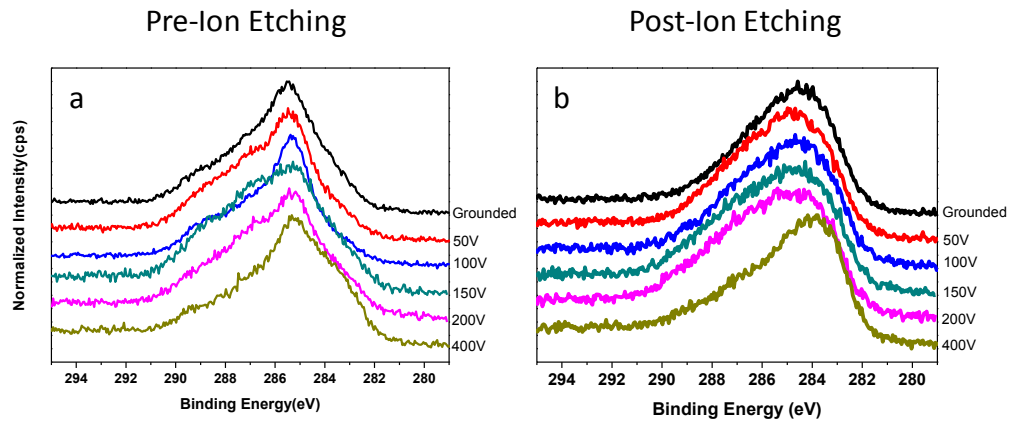


Figure 18: The effect of ion etching on the C 1s region from BCN films deposited in B series; (a) pre ion-etching and (b) post ion-etching. (Ion-etching parameters: using Ar gas, 750 V at 19 μ A for 50 sec.)

Furthermore, XPS analysis in this work indicated that the effect of contamination due to atmospheric exposure is most severe for the C 1s spectrum as the largest contribution to surface contamination is from ambient carbon and oxygen. The data in Figure 18 (a) and (b) shows ion-etching has a profound effect on the oxygen content but a limited one on carbon content, while boron and nitrogen amount looks like increased in the films. In several other studies, a similar conclusion has been reached suggesting C 1s spectra to be the most sensitive for contamination^{108, 147, 172}. Hence, considering the effect of contamination to be limited with the C 1s spectrum and not seriously undermining the quality of data from B 1s and N 1s, in the following sections only data from pre-ion-etched films were used to analyze the chemical environment of the atoms. Briefly, the XPS data collected from "as-is" surfaces were used to investigate the chemistry of atoms in BCN films while the spectra collected post ion-etching were used for the chemical composition analysis.

Boron and nitrogen atom ratio in the films were found to be relatively stable with increasing substrate bias through the analysis of the post ion-etching data, as shown in Figure 17 (c). On the other hand, the carbon content and the oxygen content of the films decreased with the increase in substrate bias. When compound targets are used, the ratio of the components in films should be the same as in the compound, unless a volatile product is produced. Otherwise, the chemical composition must be the same in the sputtered target and the deposited film. However, the boron to carbon ratio (B:C) in the films was reported as lower than the target material in the all series. This ratio was found to increase with an increase in the applied bias. For the experiment with the largest substrate bias, B:C reaches to four which also was the B:C ratio in the target. Interestingly, while B:C ratio is dependent on the applied bias boron-to-nitrogen ratio (B:N) is rather stable. Both plots are shown in the Figure 17 (c). In addition to these, oxygen content of the film also decreased with the increasing applied bias. From these findings, it can be easily concluded that the source for the extra carbon and oxygen in the films were due to surface contamination. It is also apparent that higher bias settings resulted in "less" contamination due to lowered concentration of oxygen and impurity carbon from the ambient. Perhaps, higher bias settings induced configurations chemically more stable due to less defect and dangling bonds, which enable a surface to stay cleaner over a longer period.

In the following part, the focus will be on the understanding of the local chemistry of boron, carbon and nitrogen atoms in the deposited films. Thus, a detailed XPS analysis for the 1s regions of boron, carbon and nitrogen in BCN films will be presented. As mentioned before, the XPS data from the BCN films were collected from the as is surfaces.

In Figure 19 (a) and (b), the data obtained from XPS of the B 1s region is presented. The position and the shape of the peaks for B 1s from the deposited

films in series B indicate that the overwhelming majority boron atoms were in a nitrogen-rich environment. Thus, the position of the B 1s peak observed for films in the B-series corresponds to B 1s peak position for B atoms in h-BN, Table 3. In the spectrum, a shoulder on the lower binding energy side of the main peak is not observed, which would have meant that some of the boron atoms were coordinated with a less electronegative element than nitrogen, such as carbon. Two separate hypothetical conditions were used to investigate such an effect, in Figure 20 (a) and (b). In the case represented by the inset in Figure 20 (a), the binding energy of B is expected to appear at 191 eV just as in h-BN as majority of boron atoms are in a nitrogen rich environment. For the case representing carbon-coordinated boron, in addition to the major component - boron in BN network, another coordination of boron is observed as shown in the inset for Figure 20 (b). In the hypothetical XPS spectrum for this one, a main peak at 191 eV with an asymmetry due to the existence of carbon coordination (~ 189.2 eV) would be expected as shown in Figure 20 (b). However, for the spectra shown in Figure 19 (a) and (b), even if there was a trace amount of B-C bonding, it could not be detected by the energy analyzer used ($\sim <1\%$). Nevertheless, a closer look at the B 1s spectrum from the grounded BCN film, in figure 19 (b), an asymmetry toward the higher binding energy is observed (~ 193 eV). It is likely that for this film some of the boron bonded to a more electronegative element than nitrogen. The grounded film contains the most oxygen relatively. Therefore, a respectable amount of the boron in the grounded films was bonded with oxygen. The position of the shoulder also matches to that for B-O bond (193 eV)¹⁷³.

In Figure 21 (a) and (b), the XPS data from the N 1s regions of the films from B series experiments are given. The positions and the shapes of the N 1s peaks indicate that the nitrogen atoms were mainly surrounded with boron atoms. The counter effect was also seen in B1s region in Figures 19 (a) and (b). On the other hand, the effect of the incremental increase in the applied bias is also

readily observed in the overall narrowing of the N 1s peak. This is due to the gradually diminishing intensity of the shoulder located at higher binding energy side of the N 1s at 398.4 eV. This shoulder has been often identified as nitrogen atoms in a carbon rich environment such as in CN_x ¹⁴⁷. The decrease in the intensity of this shoulder through increasing the substrate bias suggests that nitrogen atoms can find energetically more favorable arrangements under a more intense ion bombardment. As indicated earlier, a higher bias causes an increase in the average energy of the ionic species; in this case it is Ar^+ and N_2^+ ions providing more energy for atoms in the growing film to re-arrange themselves through diffusion. Another implication for this suggestion is that B-N bonding being energetically more favorable than B-C and C-N^{12, 145}. Other studies based on *ab initio* density functional theory calculations also reported B-N bonds to be more stable than C-N¹⁶³.

Composition of the films in Figure 17 shows that boron and nitrogen accounting for nearly 85 % at. of the films and the rest were carbon. Analysis of the B 1s and N 1s regions suggested that the peak shapes and positions were consistent with a predominant boron type as in BN network. Even if, there existed some signal under the B 1s and N 1s peaks for carbon bonded nitrogen and/or carbon bonded boron, they were hardly observable possibly due to the lower carbon content of the films. Naturally, existence of C-N and/or B-C could be better examined in the C 1s spectra of the BCN films. In the literature, two types of B-C bonding has been reported; a- in a boron rich environment (B_4C) C 1s is expected at 282.9 eV for the C 1s peak, b- in a carbon rich environment (BC_3) C 1s is expected at is 284.2 eV. Conversely, N bonding to carbon all cause shifting of the C 1s with respect to carbon in carbon environment (284.7 eV) to a higher binding energies (285.6 eV to 288 eV). The contamination of the films is mainly due to physisorbed hydrocarbons and oxidized carbons meaning that the possible effect would be a shift to higher binding energies up to 287.2 eV. Nevertheless, at least lower energy portion of C 1s spectrum could be used to

investigate possible effect of B-C bonding on C 1s spectra. In Figure 22 (a) and (b), the detailed scans of C1s region from the BCN films deposited during B series experiments are shown. The shapes of the peaks in these plots suggest a significantly complicated bonding environment for carbon atoms. The effect of the substrate bias is rather ambiguous due to the effect of contamination, and there is not systematic change in the peak shape or positions.

Overall, the analysis of the XPS data indicated that the atomic compositions of the BCN films deposited during B series were not affected with incremental increase in the applied substrate bias. With respect to the chemistry in the films, boron atoms in the films were found have a strong preference toward bonding with nitrogen atoms. This was also confirmed through the counter-analysis of N 1s spectra from the same films. In addition, the some of the nitrogen atom was coordinated with carbon atom according to the shoulder in the higher binding energy side of the N 1s peak. The intensity of the high-energy shoulder was decreased with increasing applied bias. The increase in the average ion-energy, therefore, caused adatoms to find a more thermodynamically stable resting position, which seems to be coordination of nitrogen with boron instead of carbon atoms. The data about the carbon atom were not very helpful in providing useful info regarding the chemistry of BCN films deposited in B series because of the physisorbed carbonaceous impurity layer.

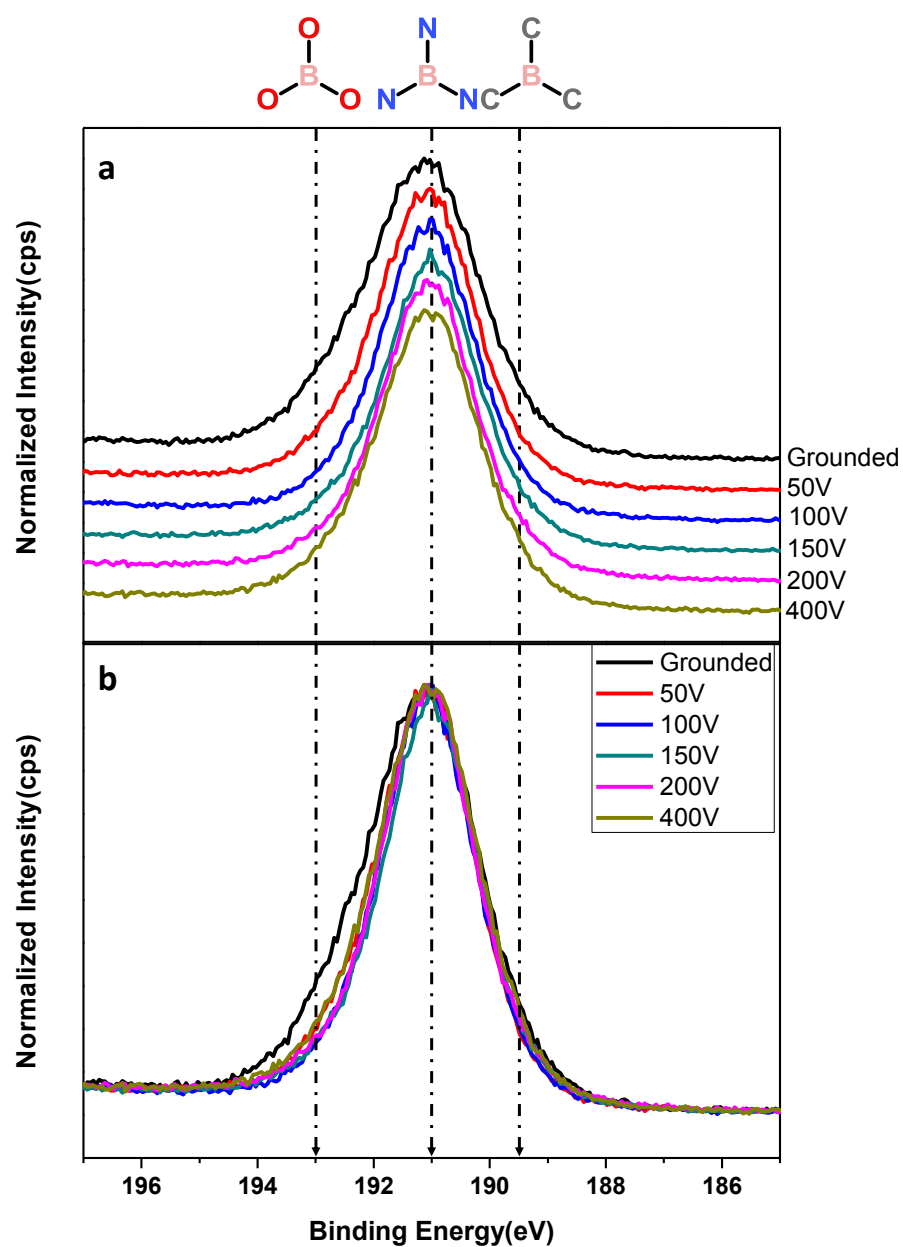


Figure 19: XPS spectra of the B 1s region of BCN films deposited on substrate with different r.f. generated d.c. biased in B series, (a) waterfall representation (b) overlap representation.

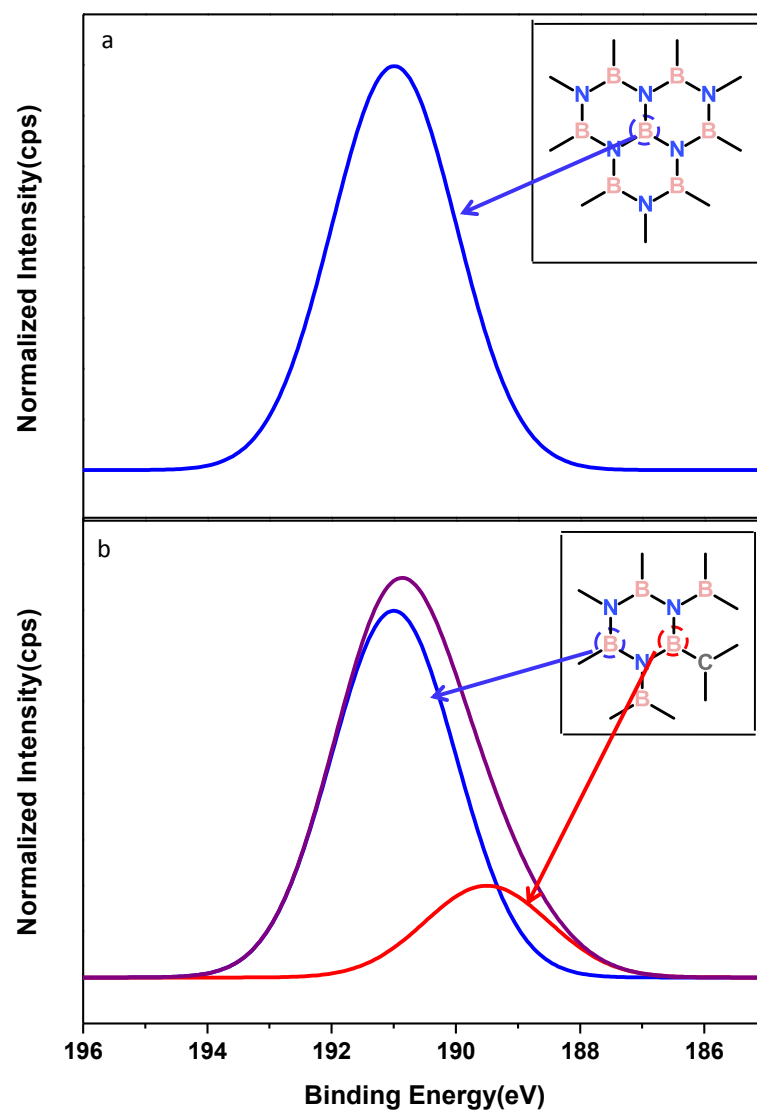


Figure 20: Hypothetical XPS spectra for (a) boron in BN environment, (b) carbon coordinated boron in BN environment. Insets show the corresponding atomic configurations.

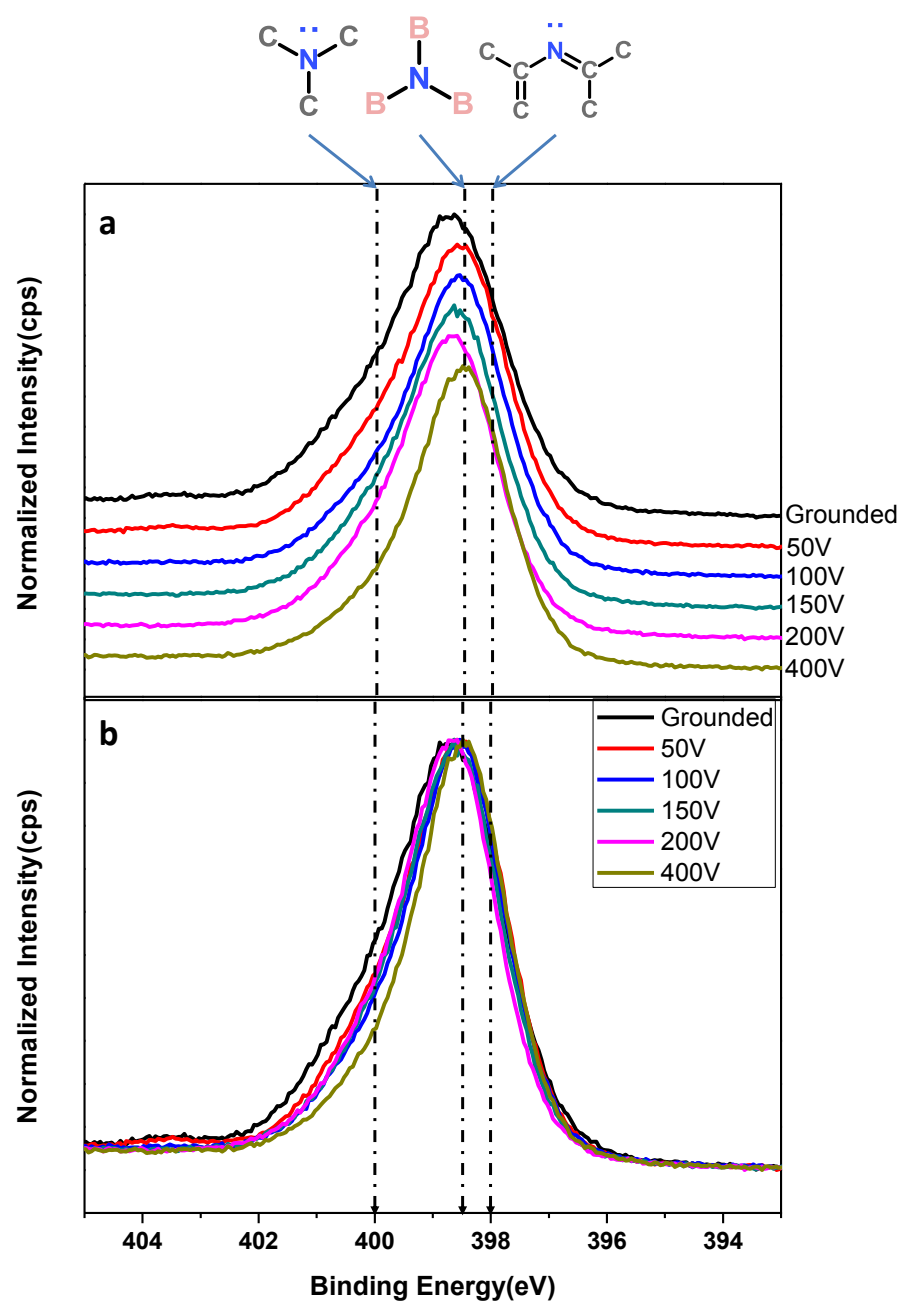


Figure 21: XPS spectra of the N 1s region of BCN films deposited on substrate with different r.f. generated d.c. biased in B series, (a) waterfall representation (b) overlap representation.

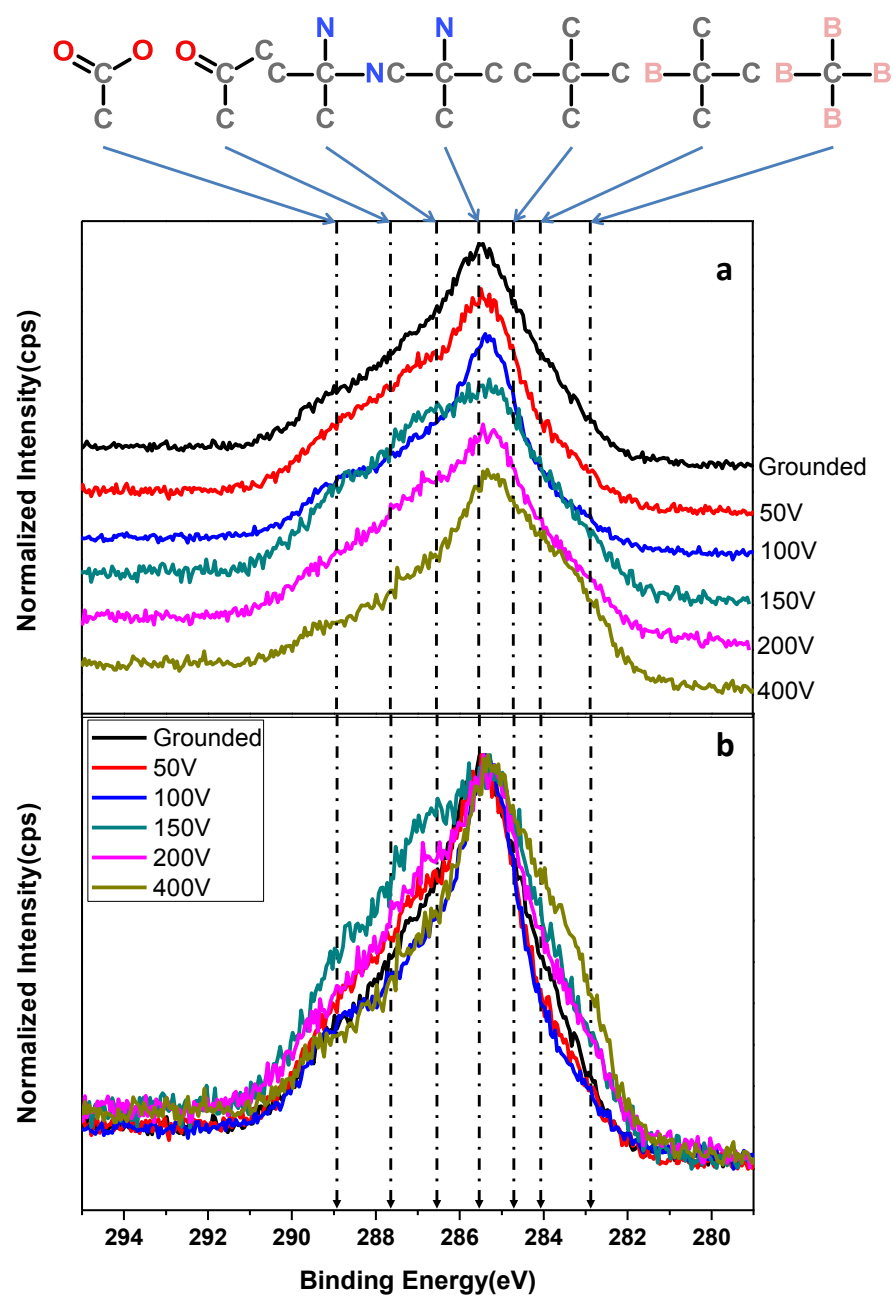
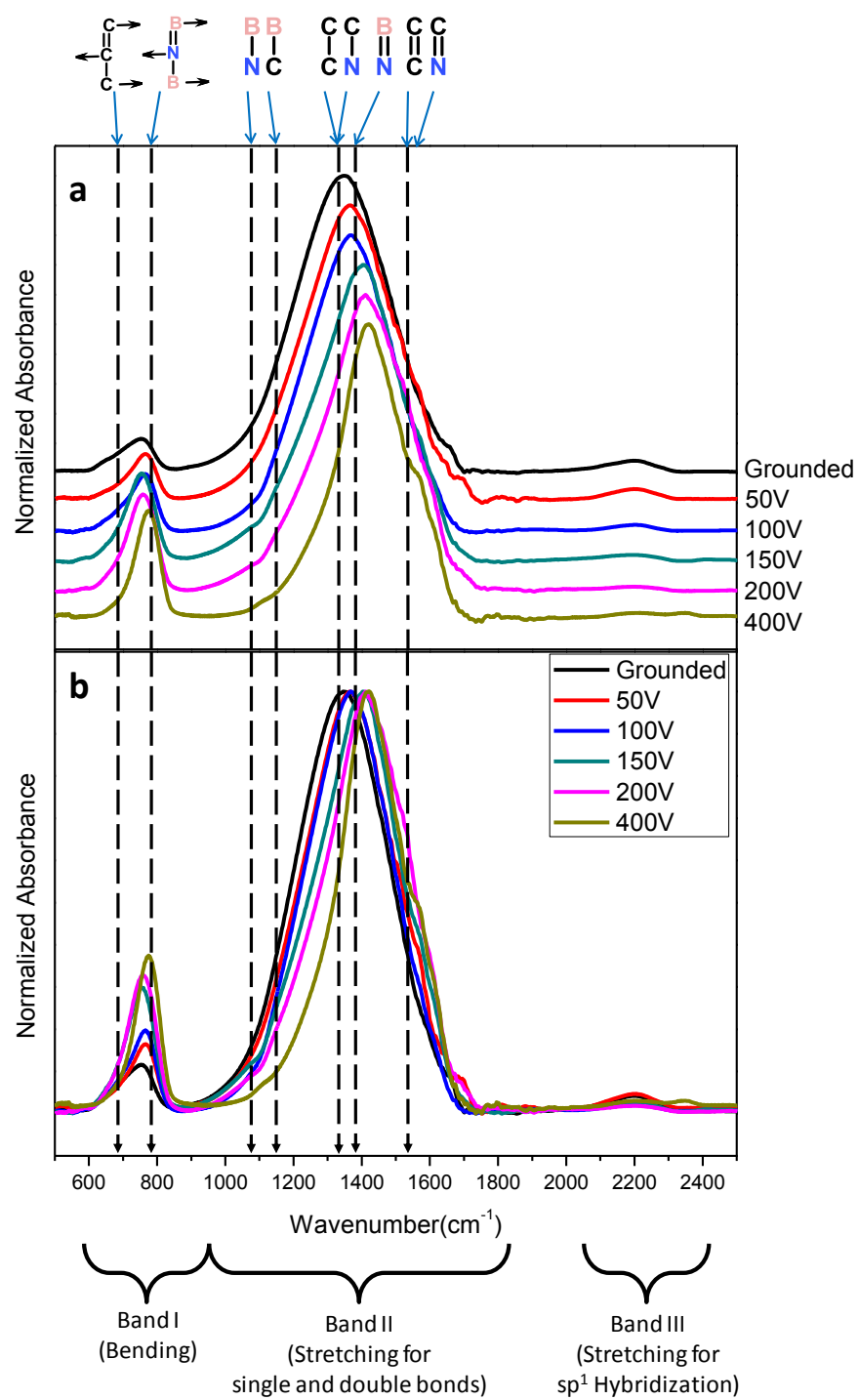


Figure 22: XPS spectra of the C 1s region of BCN films deposited on substrate with different r.f. generated d.c. biased in B series, (a) waterfall representation (b) overlap representation.

Complimentary to the XPS data, IR spectra from the BCN films were also collected. In the Figure 23 (a), (b), (c) and (d), IR spectra of the B series are shown. In the spectra, bands related to stretching and bending of the modes were identified using prior studies in the literature, mentioned in Table1. Analysis of the XPS data shown in Figure 17 indicated that B:N ratio of the BCN films in question remained the same which make up nearly the 85-90 % of the films in B series. Yet, XPS data did not provide evidence suggesting striking changes taking place in the chemistry of the films. Thus, the changes in the IR data as shown in Figure 23 are directly related with the change in the atomic bonding and chemical environment of the atoms. Three major changes are observed when the IR data from films deposited with increasing substrate d.c. bias. First, the intensity of the Band I was found to increase with substrate bias, secondly Band II shifted to higher frequencies and the shoulder in the lower frequency side diminished, and finally the intensity of the Band III deceased with the increase in applied bias and over -150 V, it was lost.



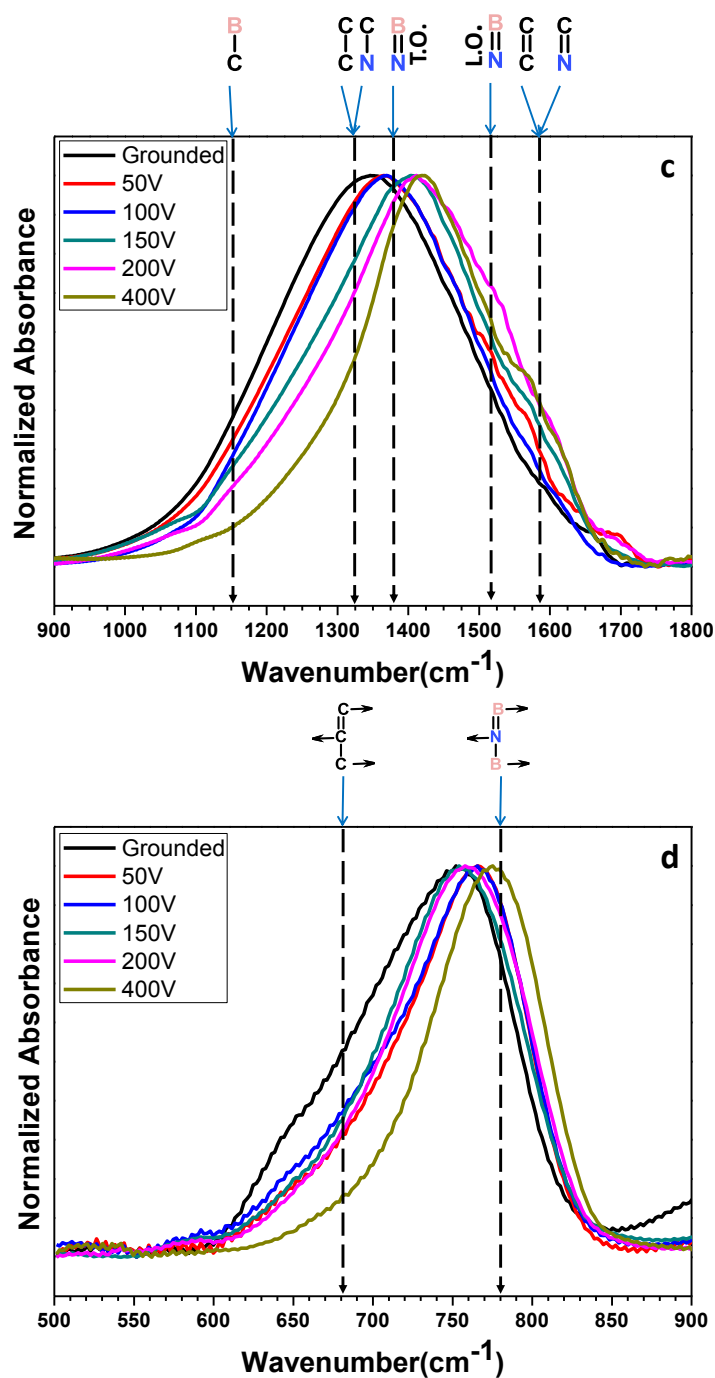


Figure 23: IR spectra of BCN film deposited on substrate with different r.f. generated d.c. bias; (a) waterfall representation, (b) overlap representation of the overall spectrum. In (c) and (d) are showing the detailed regions for Band II and Band I, respectively.

Numerical values about intensity and area changes are given in Table 6. Data presented in Table 6 suggests that Band II-to-Band I ratio (both area and intensity) decreases with increasing bias. The increase in the relative intensity and relative area of Band I with substrate bias is an evidence for the structure of the films evolving from a low-range order system to a moderately ordered, layered structure. The source of Band I is actually the B=N-B bending out of plane, so the relative increase of the intensity would be an indication of the increase in the amount of the bending mode with respect to stretching mode.

Table 6: Area under the peaks and intensity of bands in the IR spectra of BCN films deposited for B series.

Bias	Areas				Relative Intensity of Bands with respect to Band II	
	Band I	Band II	Band III	Band II/ Band I	Band I	Band III
Grounded	4.37	101.96	1.75	23.33	0.11	0.06
50 V	4.5	123.01	1.15	27.34	0.16	0.04
100 V	7.27	89.83	1.35	12.36	0.19	0.03
150 V	8.13	80.98	0	9.96	0.29	0
200 V	10.39	101.04	0	9.72	0.32	0
400 V	8.97	63.96	0	7.13	0.37	0
h-BN	16.13	222.10	NA	13.76	0.22	NA

The blue shift in the Band II means that the bonds between the atoms are getting stronger. Thus, the shift in the band positions and decrease in the shoulder intensity at lower frequencies can be explained by change in the bonding strength and change in the local coordination of atoms. In this case, higher bias

values drives the atomic configuration to be a more ordered, layered structure with double-bonds, hence the blue-shift in Band II is a result of this. The shape of the Band II with a significant component between 1000-1200 cm^{-1} for BCN films deposited with lower bias values indicate presence of additional bonding schemes which are predominantly single-bonds. In addition to these, the change in the intensity of the Band III can be explained by the increased applied bias suggest the quantity of the sp hybridized carbon or nitrogen decreased.

IR technique has been used in the literature for the characterization of BCN films^{146, 174, 175}. Most of the related analysis focused on the Band II region (1000-1500 cm^{-1}), stretching band of the single and double bonds. As mentioned previously in Chapter 1.2.1, there are several shortcomings in the interpretation of the IR peaks. These are;

- overlapping vibrational bands,
- broadening of the bands due to short-range order or amorphization,
- variation of IR absorption response for bonds.

In spite of these shortcomings, band information and positions obtained from the literature on binary compounds can be applied to the interpretation of the IR spectra of the BCN films. In BCN film characterization, IR technique was mainly used to understand the sp^3 to sp^2 ratio in the early c-BN synthesis studies^{88, 94, 98}. For the identification of BN bonds by using IR spectroscopy, a study by Geick et al has been commonly used¹²⁸ in addition to a recent one by Jager et al.¹³⁴ emphasizing on the IR spectra from thin films of c-BN and h-BN. With the help of XPS data, chemical composition (Figure 17) and the chemical shifts in boron (Figure 19), carbon (Figure 22) and especially N 1s peaks (Figure 21), IR spectra from films synthesized in series B can be easily attributed to a predominantly BN-type configuration for the BCN films in series B as shown in Figure 23 (a) and (b).

With the increase in the bias, the blue shift in Band II and the increase in the signal strength of Band I suggests a sp^2 hybridized bond type and the formation of a layered structure within BCN films as displayed in Figure 23 (c) and (d). While analysis of the B-N bonding in the BCN films were relative easy due to use of well-established literature above, identification of C-N or C-C bonding in such films has been a subject of intense debate. The shoulder on the high frequency side of the Band II, Figure 23 (c), has been considered as an evidence for hybridization through identification of this band as C-N by G. Bejarano et al¹²⁶. However, it is possible that longitudinal optical mode of B-N double bond at 1510 cm^{-1} could be gaining intensity due to the ordering of c-planes of the BCN films perpendicular to the substrate surface at the applied substrate bias increases¹³⁴. On closer investigation, a roughly 40 cm^{-1} shift in the Band II of the films deposited with -150, -200, and -400 V d.c. bias is also observed with respect to that for h-BN stretching band suggested by the literature. Hence, the shift in the Band II can be interpreted as the contribution from several other types of double bonds; C-C or C-N, or perhaps due to the longitudinal optical (L.O.) mode of B-N double bond suggesting the c planes of the BCN films ordering perpendicular to the substrate surface¹³⁴. The intensity ratio of Band II to Band I, presented in Table 6, can be used as an indicator for understanding the texturing of t-BN films¹³⁴, although this fact has been ignored or overlooked by many researchers in the field. Arguably, a ratio larger than 0.22 (measured for h-BN powders in this study) can be attributed to significantly textured films. However, as it is hard to isolate the longitudinal optical (L.O.) contribution, it is difficult to determine the major contributor for the shift or the shoulder directly using the IR data.

Concerning the possible carbon-nitrogen and carbon-carbon bonding in these films, it is useful to investigate the literature concerning the characterization of CN_x / N-doped DLC films^{132, 139}. The discussions in CN_x literature are based on the fundamental assertion of IR spectroscopy that the condition for the infrared

absorption of a bond is the existence of a change in dipole moment during vibration. Thus, many of the studies suggested bands observed for CN_x films in the 1000-1800 cm^{-1} range was due the polar single ($\sim 1300 \text{ cm}^{-1}$) or double ($\sim 1600 \text{ cm}^{-1}$) CN bonds¹⁷⁶. This point was investigated using ^{15}N isotope insertion in the CN_x films¹⁷⁷. Unfortunately, isotope insertion did not induce isotopic shifts in the stretching band position of the IR spectra from the films, which was expected to be about 15-20 cm^{-1} due to the change in the effective mass. Hence, the source of the IR bands in the 1000-1800 cm^{-1} range was interpreted as the sp^2 hybridized Raman active (D and G modes) C-C bonds that are normally inactive for IR mode for DLC films. The reason that the Raman active D and G bands for DLC films became IR active due to the breaking of the symmetry by the insertion of nitrogen in the hexagonal structure¹⁷⁷. The position and the intensity of that D and G bands are dependent on the structure and disorder of the DLC films. D band corresponds to *breathing* modes of the 6-fold sp^2 hybridized carbon rings. G band belongs to stretching of sp^2 hybridized C-C bond. The vibrational mode of the G and D peaks are shown in the Figure 11. The π conjugation disperses the effect of the symmetry breaker, inserted N (or even B) into the hexagonal C network, over a long range and the vibration signal of the double bonded structures become dominant in the IR spectrum^{131, 132, 138, 139, 142, 143, 178-180}.

Thus, in the light of the discussions presented above, the shoulder on the higher frequency side of the 1400 cm^{-1} peak can be attributed to polarized C=C double bonds. In addition, the Band III observed in the spectra for BCN films deposited with substrates bias up to -150 V d.c. in Figure 23 (a) around 2200 cm^{-1} is assigned to sp hybridized triple CN bond (nitrile). Similar band structures were also observed for CN_x films¹⁸¹. As shown in Table 6, the intensity of the Band III diminished as the energy impingent on the system due to ion bombardment. This finding is also supporting the assertion made earlier based on the XPS data

from BCN films of series B that BCN films preferred BN type bonding rather than CN type bonding.

Further evidence for the preference of the C-C bonding over C-N bonding is also observed in the red shift of Band I as shown in Figure 23 (d). At first impression, the shift and shape change in Band I could appear contradicting to the interpretations made for Band II. It may be concluded from the shift in Band I that as the substrate bias was increased the contribution from the C=C-C bending is decreasing, which is against the assertion made earlier regarding the contribution of C=C on the Band II increasing with increasing bias. However, the change in Band II to Band I intensity ratio with respect to applied substrate bias presented in Table 6 has to be reconsidered carefully to understand this effect. As the texturing in BCN films gets stronger due to increased bias, the B=N-B bending mode gets significantly strengthened nearly tripled in intensity which nearly completely drowns the effect from C=C-C bending. Interestingly, Band I region has not been investigated at all in the literature on CN_x and/or BCN films.

In the literature, the interpretations for BCN films IR spectra provided are often rudimentary or lacking detailed analysis. Some of the more careful analysis has been provided by Linns et al^{106-108, 182} where spectra from films deposited by sputtering targets with the following B:C ratios, 4:1, 1:1 and 1:4, with a Ar:N₂ gas flow of 1:1 using floating^{106-108, 182} or varying substrate bias settings^{106-108, 182}. Overall, observed variations in the band shape and position for the provided spectra were very much similar to this study, however detailed analysis was not provided. For instance, a similar shoulder on the Band II region was also observed^{106-108, 182}, and their conclusion regarding the shoulder was in support of our findings as well.

As a summary, IR data shows that the bonding type and bonded atom pairs were changing with applied bias. The BCN thin films deposited with grounded and

lower substrate biases were found to contain several different types of single bonds (B-C, C-C, C-N) together with the predominant B-N double bonding. As the applied bias increased, the amount of the single bonds in Band II region and the triple bond in the Band III were found to decrease. Also, the increase in the Band I-to-Band II intensity ratio suggests that the order and texturing in the BCN films improving with increasing bias. Finally, in support of the conclusion from the XPS data, IR spectra also suggested phase segregation due to increased substrate bias going from partially hybridized amorphous BCN films to a h-BN/C type.

The XRD patterns (θ - 2θ) collected from the films were identical to each other, so θ - 2θ scan from the film deposited with a substrate bias of -200 V d.c. is shown in Figure 24. The Figure 24 also shows the scan from the un-deposited substrate. The scan contain only two features; a hump around $2\theta=30^\circ$ and peaks from the Si (100) substrate. In Chapter 1.2.3, the literature review, it was already mentioned that BCN films grow turbostratically with the basal planes perpendicular to substrate. Due to this strong directionality, θ - 2θ scan geometry is not an effective technique for probing the crystal structure for BCN films.

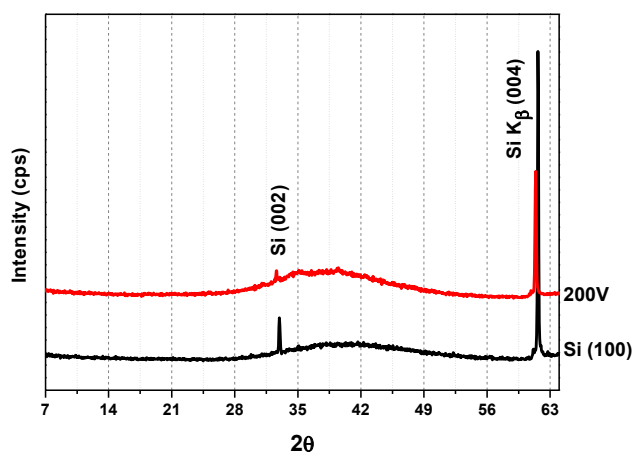


Figure 24: XRD pattern of thin film deposited with -200 V r.f. generated d.c. bias and substrate.

In the following part of this section, TEM images and the analysis of these images are discussed. The TEM imaging were done on BCN films deposited with grounded, -200 V d.c. and -400 V d.c. substrate bias settings. Focused ion-beam technique has been utilized for the preparation cross-sectional TEM samples. In Figure 25, the HRTEM image from the cross-sectional TEM sample from the grounded sample is shown. Two sections from this lattice image are Fourier transformed to create power spectra of these sections. In these power spectrum images, the repeat frequency and the direction of the repeating structure in the original image can be observed, as shown Figure 26 (a) and (b). In the inset of Figure 26 (a), spots due to the lattice planes of the crystalline titanium buffer layer can be observed. In the inset of Figure 26 (b), power spectrum image from the BCN film is shown. The HRTEM image in Figure 25 and the diffuse ring in the power spectrum image from Figure 26 (b) suggest that the BCN film does not have long range order; similar to an amorphous material. In Figure 27, the HRTEM image of the BCN film deposited with -200V d.c. bias was shown. This image shows a structure very similar to that observed during the HRTEM analysis of c-BN films⁸⁰; the c-planes of the BCN films are grown perpendicular to the substrate surface. Hence, BCN films deposited with a substrate bias were essentially displaying a turbostratic texturing. The Fast Fourier Transformed (FFT) sections from the Figure 28 show two diffuse spots perpendicular to each other, in the inset of Figure 28. The spots on the ring of the inner circle are due to the 0002 planes (c-planes) and the ones on the outer circle is due to 1020 planes (prism planes) of the hexagonal structure. Hence, this is a strong indication that the films deposited with -200 V d.c. bias were well ordered and also are turbostratic.

In Figure 29, HRTEM image of the BCN film deposited with -400 V d.c. bias is shown. The image from this BCN film indicates a structure similar to that observed from the TEM sample of the BCN film deposited with a substrate bias of -200 V d.c. Thus, the c-planes of the BCN film were found to be growing

perpendicular to the substrate surface. Again, this is a very strong evidence for the turbostratic texturing of the BCN film. The Fourier transformed sections from the Figure 29 is given in the inset of Figure 30 which shows two reasonably diffuse spots corresponding to the (0002) planes (c-planes) of the hexagonal structure. However, the sharpness of the spots in the FT of BCN film synthesized at -200 V d.c. suggest a relatively better ordered film with respect to one deposited using a substrate bias of -400 V d.c., see Figure 31 for a comparison.

The TEM equipment used for the HRTEM imaging was also equipped with a GATAN Tridiem EELS attachment for the analysis of inelastically scattered electrons therefore allowing for the chemical analysis of the samples. The same equipment can be used for energy filtered-TEM (EF-TEM) imaging. In Figure 32, the EF-TEM images and high angular annular dark field (HA-ADF) images from the BCN film deposited with a -400 V d.c. substrate bias. In Figure 32 (a), an image of the BCN film formed by electrons which are transmitted through the BCN film without losing any energy are given that shows the Si substrate, Ti-buffer layer and the BCN film with reasonable contrast. In addition, in Figure 32 (b), for imaging the BCN film electrons that are scattered at very high angles are used. These electrons are mainly the ones that interacted with atoms with larger Z (atomic number), therefore this image indicates brighter contrast for regions which are made up of atoms with a larger atomic number. In the following (c), (d) and (e), pseudo-colored energy-filtered images which are composed of electrons that have interacted with boron, carbon and nitrogen are provided, respectively. These images show that only the BCN film contains homogeneously distributed boron, carbon and nitrogen atoms.

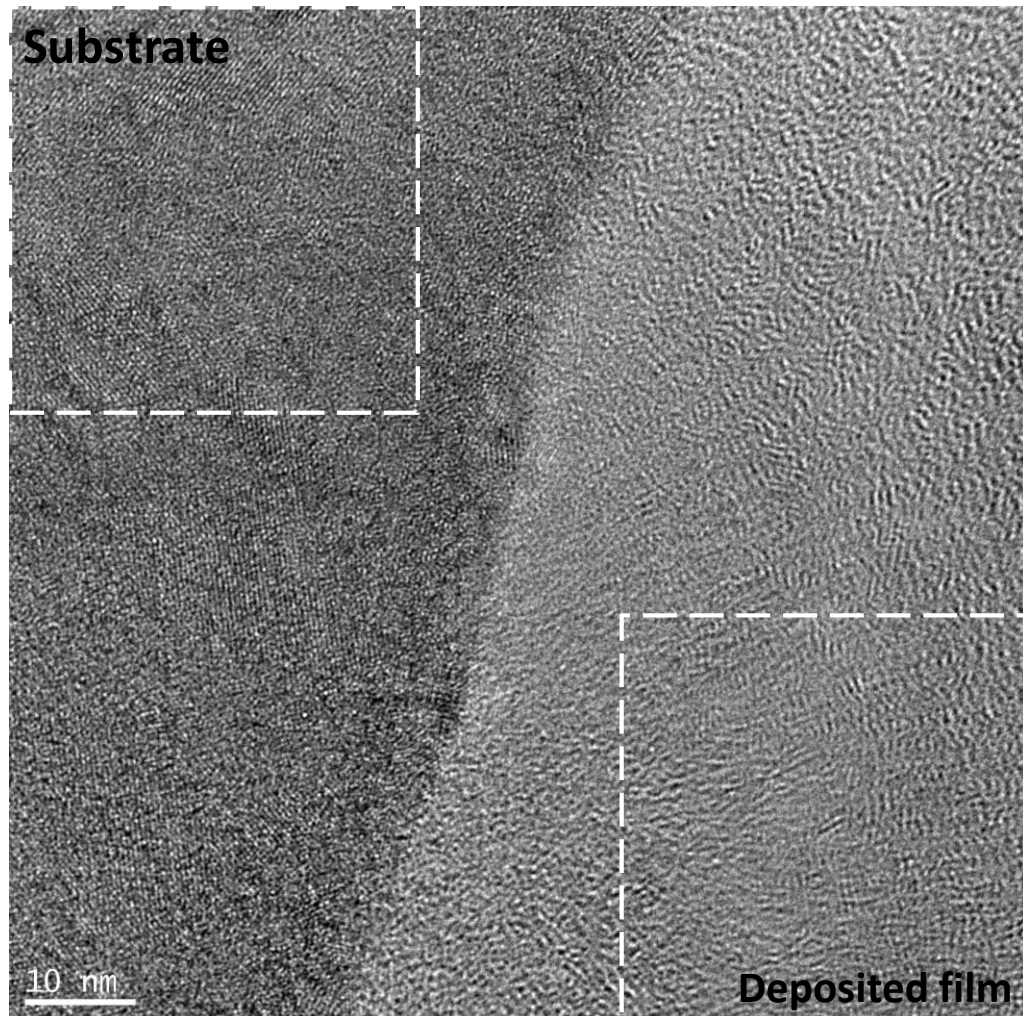


Figure 25: HRTEM image of BCN film deposited on the grounded substrate and substrate. The squares, defined with dashed lines are the image areas where the FFT process was applied.

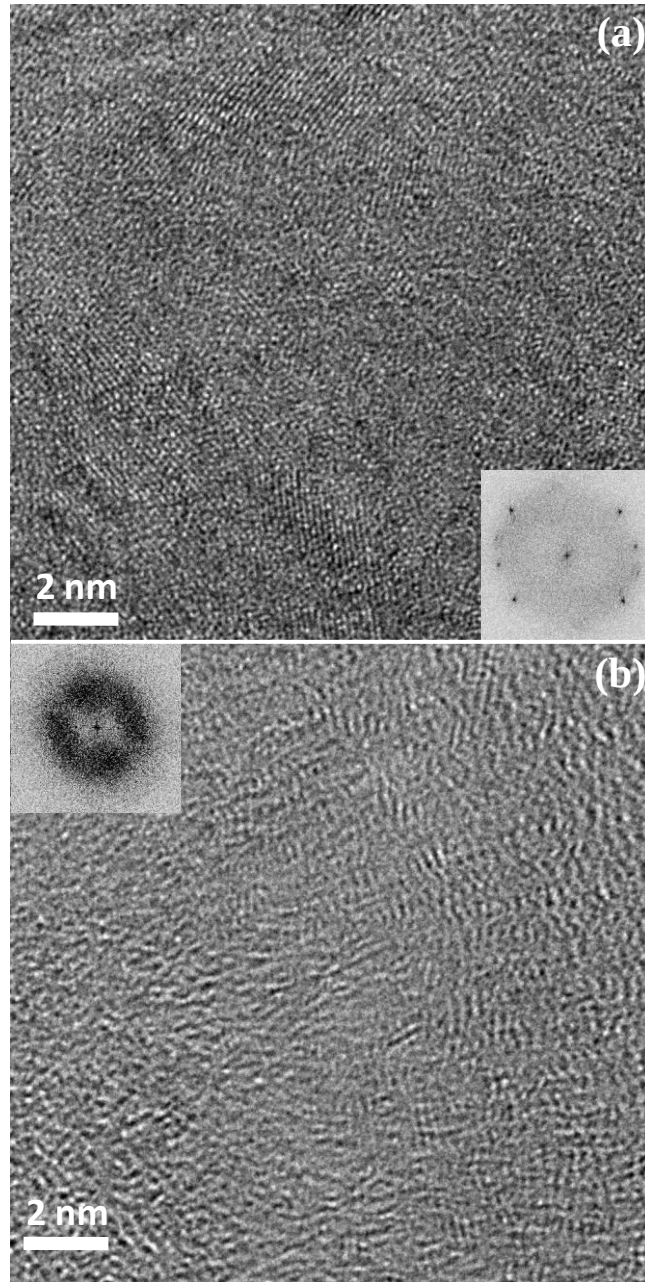


Figure 26: (a) HRTEM image cropped from the substrate region of HRTEM image obtained from grounded sample of B series with (inset a) FFT image of substrate, and (b) HRTEM image cropped from BCN film part of the HRTEM image collected from the grounded sample of B series, with (inset b) FFT image of thin film.

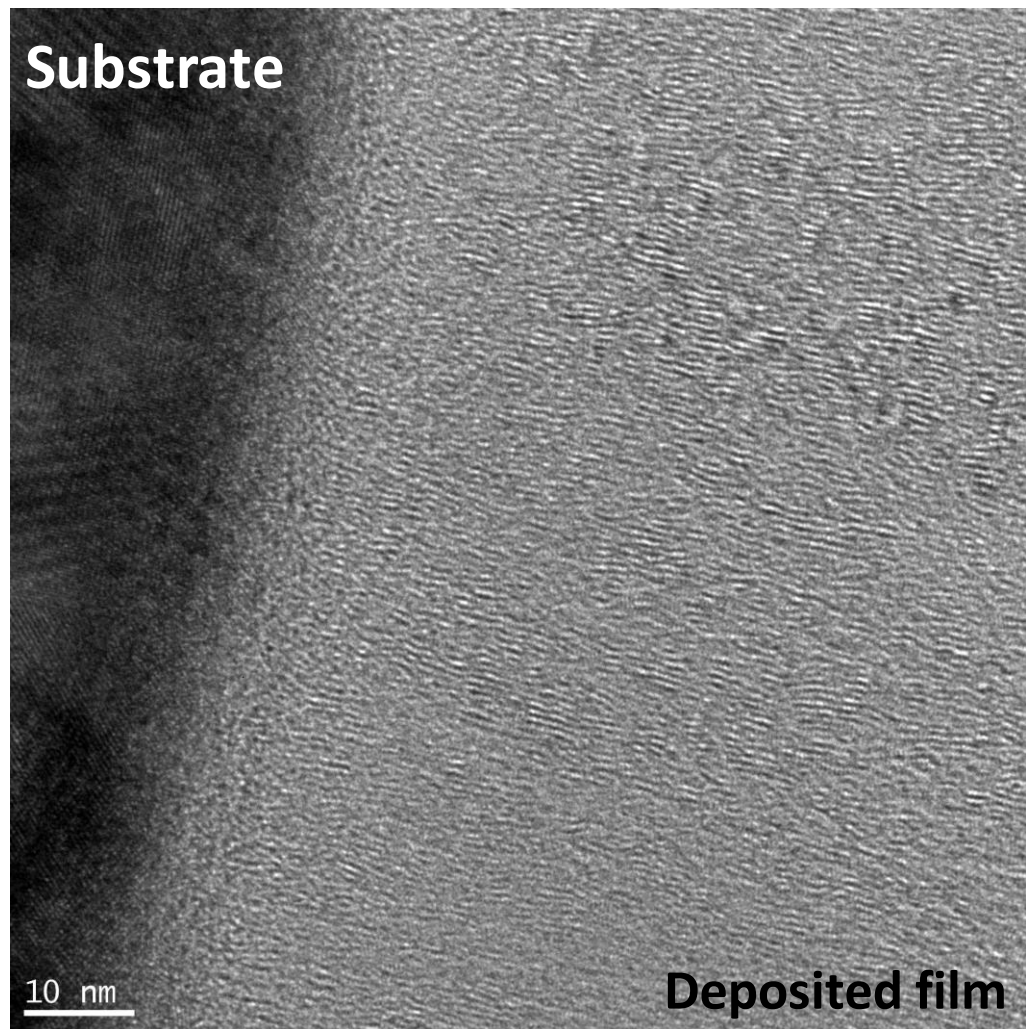


Figure 27: HRTEM image of the film deposited on substrate -200 V r.f. generated d.c. bias and the substrate.

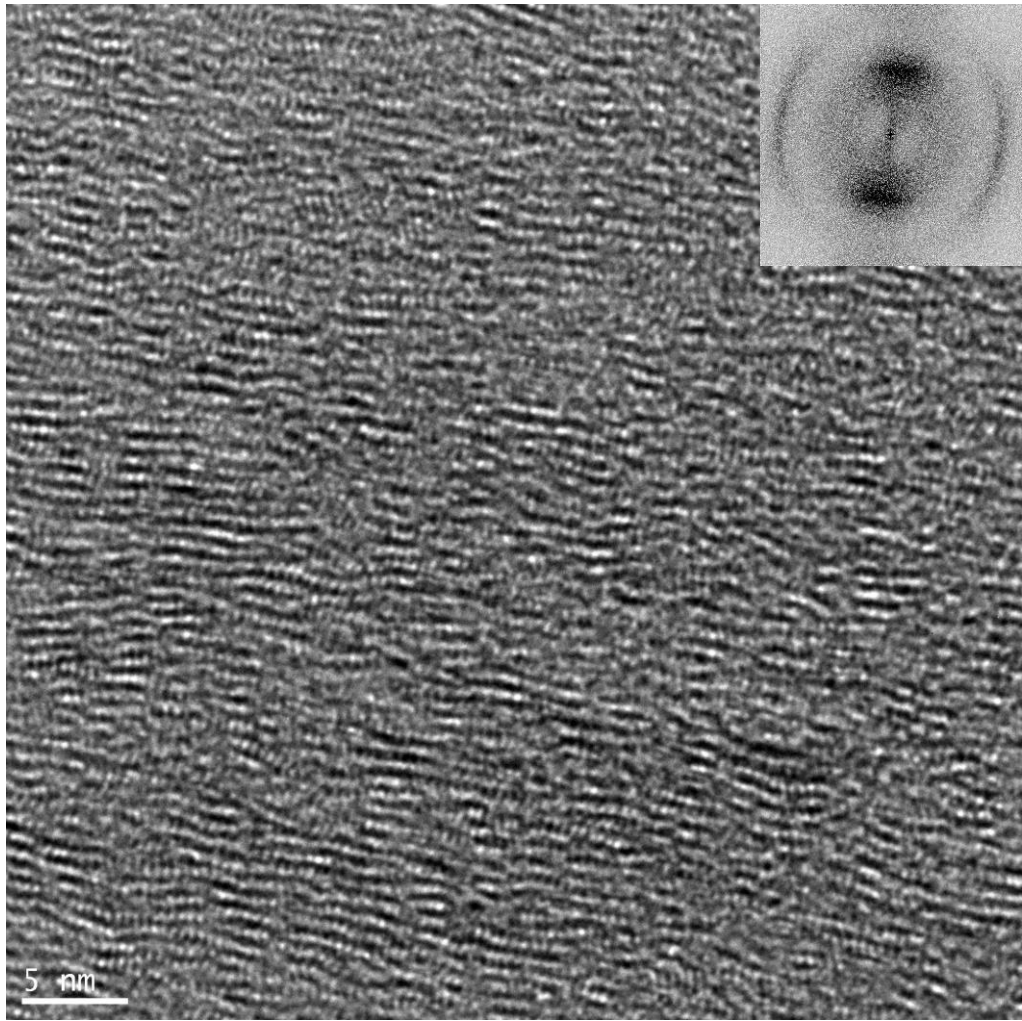


Figure 28: HRTEM image of the BCN film deposited on -200 V r.f. generated d.c. biased substrate and inset is the FFT of the image.

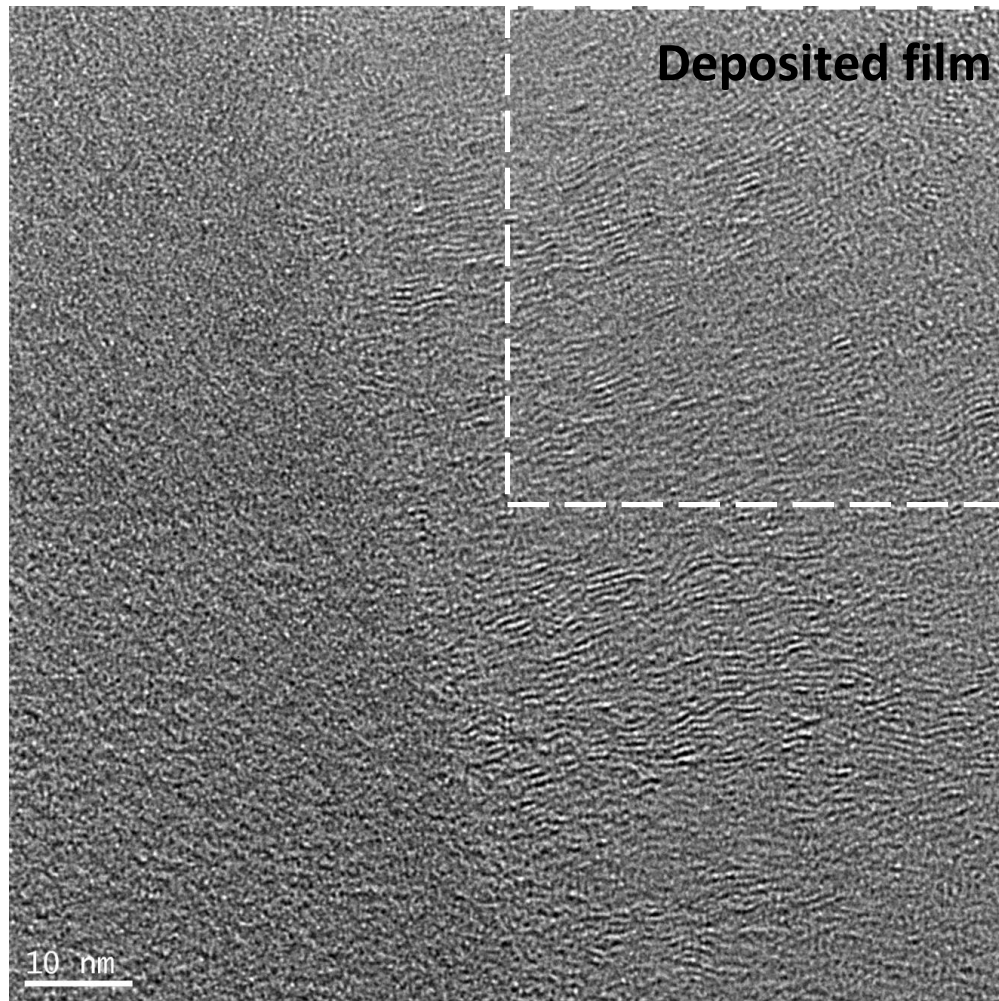


Figure 29: HRTEM image of the BCN film that was deposited on -400 V r.f. generated d.c. bias applied substrate. The square defined with dashed lines is the image area where the FFT process was applied.

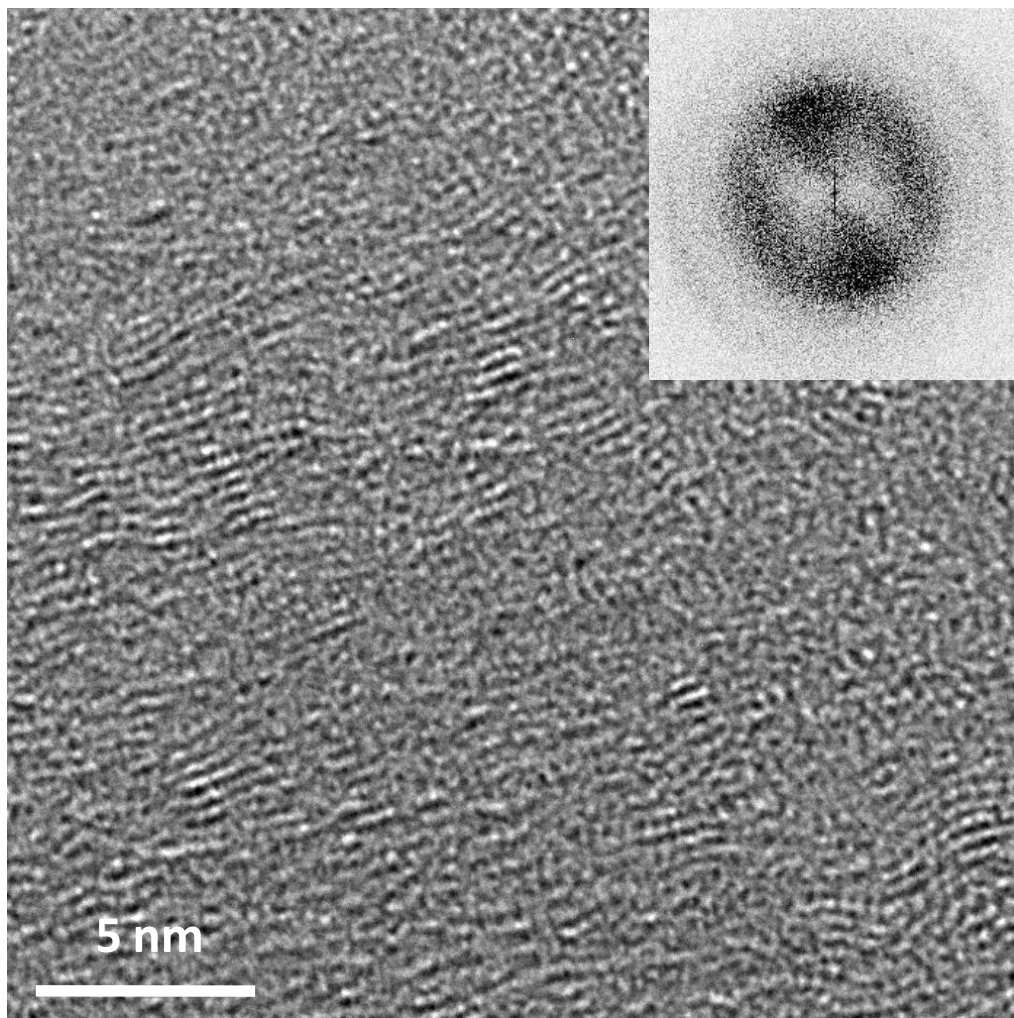


Figure 30: HRTEM image cropped from HRTEM image of BCN film deposited on -400 V r.f. generated d.c. biased substrate and inset is the FFT image.

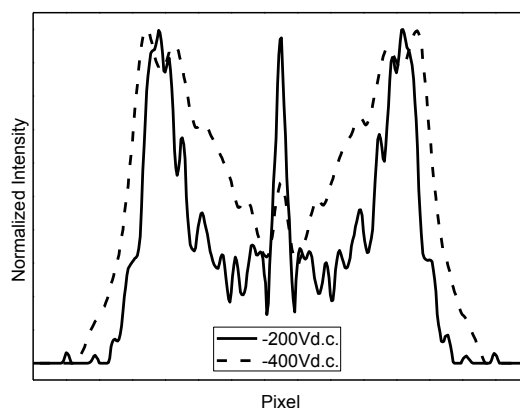


Figure 31: Comparison of line plot obtained from of FFT images of -200 V d.c. and -400 V d.c. biased sample in B series

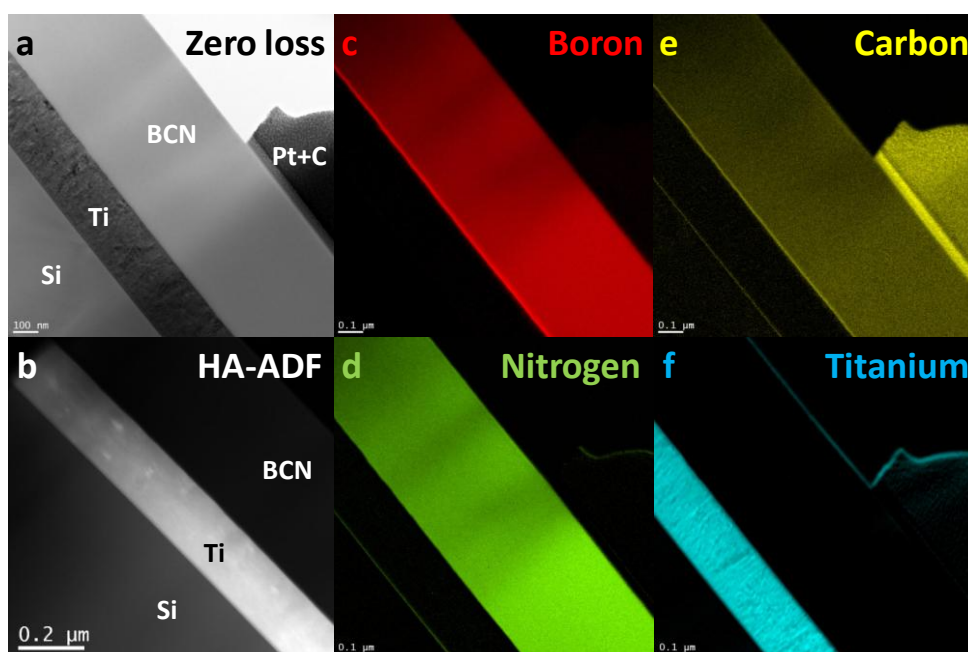


Figure 32: Energy filtered TEM analysis of the BCN film deposited on -400 V biased substrate; (a) Zero energy loss image, (b) HA-ADF image, (c) Boron K edge image, (d) Nitrogen K edge, (e) Carbon K edge, (f) Titanium K edge image.

As mentioned before by EELS data, the presence of a $1s$ to π^* transition structure before the K-edge of carbon, boron or nitrogen indicates that the atomic structure of the film to be layered, e.g. turbostratic or hexagonal¹⁰⁷. In

the Figure 33, the change in the structure before the K edge of the atoms are compared with in the change applied r.f. generated d.c. bias. The spectra in the graphs are normalized and shifted vertically in order to overlap 1s to σ^* transition edges. The transition from 1s to π^* is an evidence for the layered 6-fold hexagonal BN structure. As the applied r.f. generated negative substrate d.c. bias increased the intensity of the 1s to π^* transition increases in the B K-edge and N K-edge suggesting increase layered ordering of the BCN films. No change in the intensity of C K-edge was observed with the increasing applied r.f. generated negative d.c. bias. However, changes in the extended edge structure of the C K-edge are observed.

In summary, HRTEM images are related with atomic structure. Therefore, the FT images that were obtained from HRTEM images indicate the structure in the films. Although no diffraction pattern observed in the XRD of the films, there were structures in biased films but the film deposited on grounded substrate shows no structure. The structures in the biased films were perpendicular to substrate like turbostratic structures. Thus, with help of the literature about structure of the deposited BCN film, the films were grown turbostatically and perpendicular to substrate¹²².

Overall, the IR, XPS data and TEM images and data of the B series indicate that increasing the applied bias to the substrate during the growth of BCN films induce drastic changes in the chemistry and structure of the films. HRTEM, EELS and IR data suggest the atomic structure of the films grown under ion bombardment are ordered with a sp^2 hybridized layered structure. XPS and IR data also display that boron and nitrogen bonding is preferred when the films are provided with enough activation energy, thus interaction between carbon and nitrogen is weak. Simply, the energy provided to the growing film in the deposition process helps promote more oriented and phase segregated BCN films.

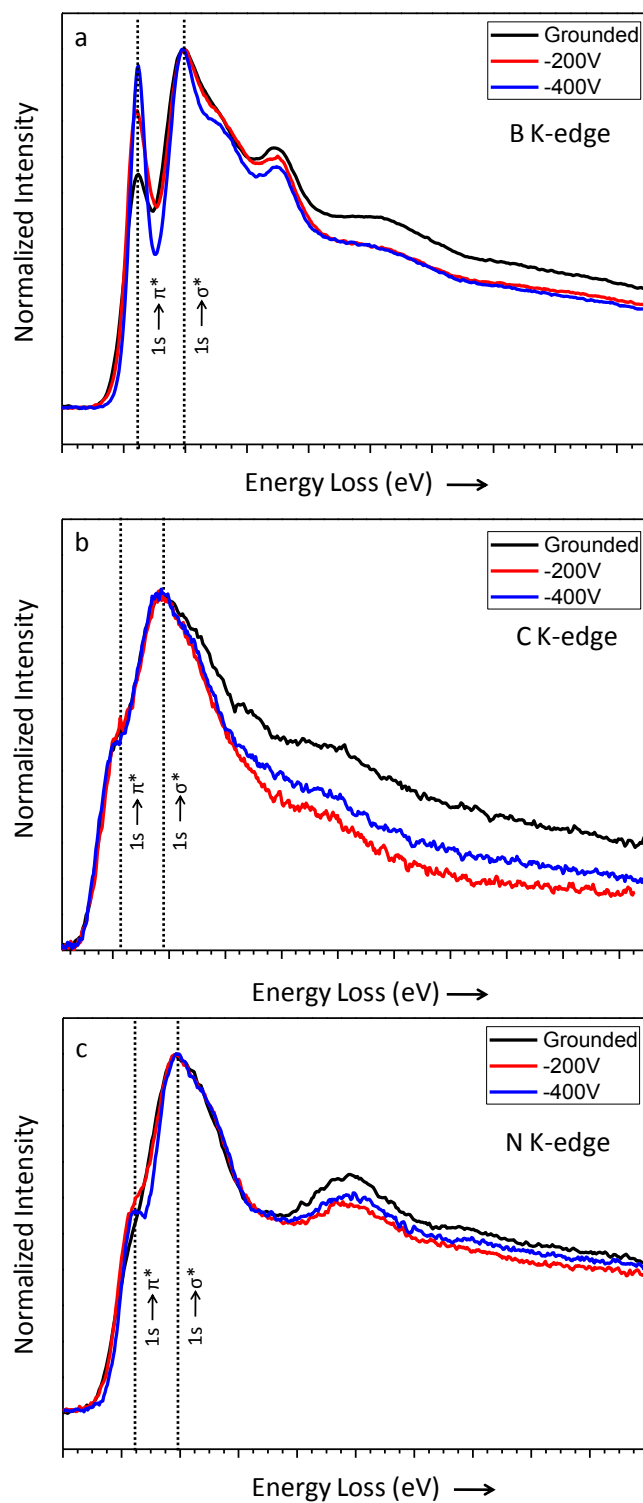


Figure 33: EELS spectra of the BCN films in B series; (a) Boron K-edge, (b) Carbon K-edge and (c) Nitrogen K-edge region.

3.1.2. P Series

In the experiments for P series, the effect of bias type and the distance between target and substrate were investigated. This series experiments can be divided in to two groups: P8 and P18 group of experiments. In P8 series, the BCN films were deposited on a grounded, d.c. or pulsed-d.c. (p-d.c.) biased substrates which were located 8 cm away from the target. Therefore, substrates were very close to the plasma region formed above the target surface due to the confinement of electrons by the magnetic field caused sputtering cathodes. Hence, they are almost immersed in this plasma plume region where the density of electrons and ions is large. In P18 series, BCN films were deposited on the pulsed-d.c biased or grounded substrates, which were located 18 cm away from the target surface. In this case, the substrates were far away from the densest part of the plasma environment. The BCN films deposited in these two series were characterized using only IR spectroscopy technique.

P18 Series

In P18 series, films were deposited on a substrate which was located 18 cm away from the target. Only the values of applied p-d.c. bias were changed. The IR data obtained from the BCN films deposited from this group are shown in Figure 34. Band I, Band II and Band III can be observed in the spectra. The area and the intensity ratio of Band I to Band II are given in Table 7. In Figure 34, the bands related to stretching and bending of the atoms were identified using prior studies in the literature, for references see Table 1. Contrary to IR data of series B, the effect of increased applied bias on the substrate during film growth did not seem to induce a significant effect on the chemistry of the BCN films deposited in series P18. The shape and the positions of the peaks were nearly unaffected from the bias applied on the films. It is as if none of the deposition

parameters used were changed. This observation can be explained by that at the substrate-to-target distance used in P18 series applied bias was insufficient. Thus, one can suggest that the change in the ion-flux at the substrate and the average energy of the ions reaching the growing film are not capable of inducing a respectable change in the chemistry of the BCN films.

The main ion source in the deposition chamber is the plasma on the target. As the distance of the substrate from the target increases, the number of ions reaching the substrate due to the electrical field induced between the plasma and substrate decreases. Combination reactions between ions moving toward the substrate and the stray electrons are one path explaining the decreasing number of ions at the substrate. In addition, the electromotive force exerted on the ions decrease as the distance increases; this force at a large separation between the ion source and substrate could be insufficient for diverting ions toward the substrate. Hence, the effect of ion bombardment cannot be observed in the IR data for the BCN films.

P8 Series

In P8 series, the effect of applied bias and bias type were examined on the chemistry of the atoms in BCN films deposited on substrates located 8 cm away from target. The IR data obtained from the films are shown in Figure 35. In the graphs, bands related to stretching and bending of the atoms were identified using prior studies in the literature, given in Table 1. The area and the intensity ratio of Band I to Band II are given in Table 7. Contrary to IR data of BCN films deposited in the P18 series, the graph shows that at 8 cm away from target films growing on the substrates which were d.c. and p-d.c biased displayed a change in their IR spectra.

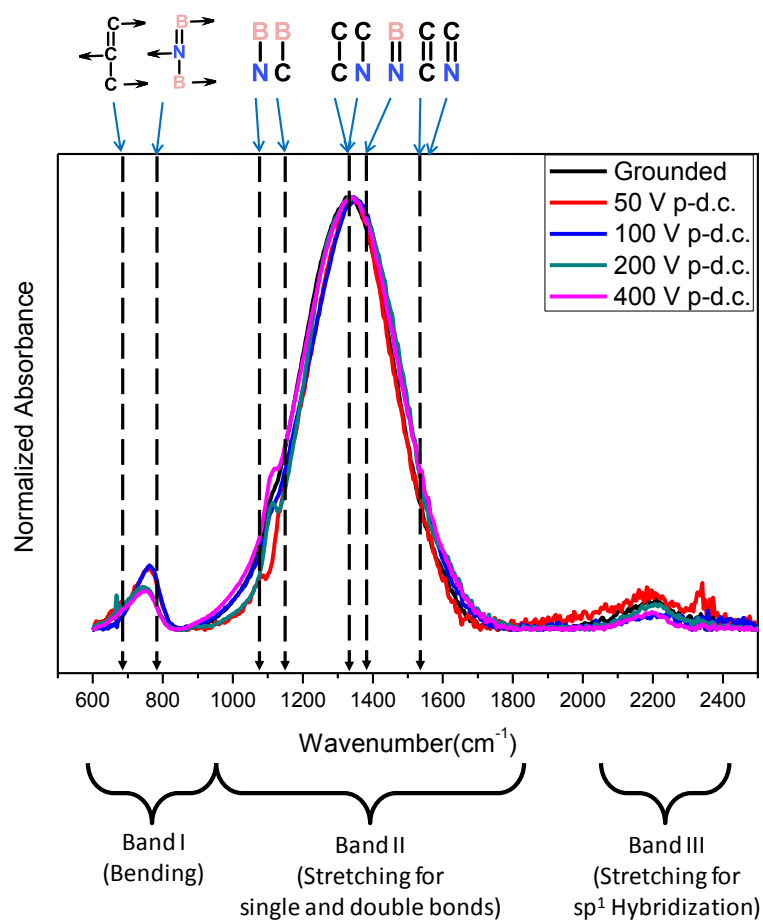


Figure 34: IR spectra of BCN films deposited on different magnitude p-d.c. biased substrate in P18 series. (Target-to-substrate distance is 18 cm)

The data has two regimes; grounded film and the biased films. First, the Band II of the grounded film is at lower frequency than the biased films suggesting that the bonds between the atoms were weaker than the biased films. Furthermore, the intensity of the Band I is lower than the Band I of biased films.

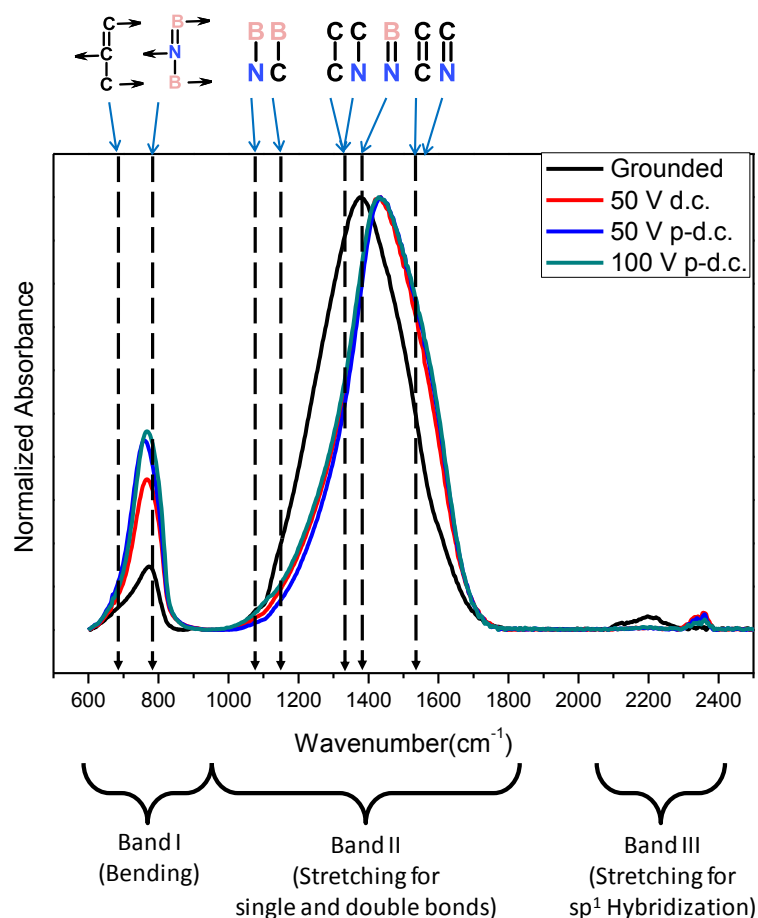


Figure 35: IR spectra of BCN films deposited on, different magnitude and type biased substrate in P8 series. (Target-to-substrate distance is 8 cm)

The increase in the Band I indicates the change in the atomic structure of the films, a tendency to a more ordered, layered structure. Thus, applied bias drives the atomic configuration to be a more ordered, layered structure with double-bonds within the layer. The blue shift in Band II for biased films is an indication of relaxation of BN double-bonds with the ordering of atomic arrangements in the film. Finally, Band III vanishes with applied bias. These observations were similar to those observed for the BCN films deposited in series B. When the biased films were examined as group, the spectra show that the data collected from the biased films so similar that the amount of the applied bias did not seem

to affect the atomic structure of the deposited film. This observation can be explained by the atomic structure of the film reaching to the maximum possible ordering even with -50 V of bias. In other words, applied bias attracted enough ions that can provide enough driving force for the growing film to arrange its atomic structure in order for reaching a minimum energy state. It is arguable that this new atomic arrangement is a global minimum energy state.

Table 7: Band areas and intensities of P series IR spectra

	Areas				Intensity	Peak positions (cm ⁻¹)	
	Band I	Band II	Band III	Band II/ Band I	Band I/ Band II	Band I	Band II
P18 Grounded	3.00	93.72	3.28	31.21	0.10	750	1335
P8 Grounded	4.47	94.55	0.97	21.14	0.15	775	1380
P8 -50V d.c	11.10	88.89	NA	8.01	0.35	770	1420
P8 -50V p-d.c.	8.13	80.98	NA	9.96	0.45	760	1420
h-BN	16.13	222.1	NA	13.76	0.22	810	1380

The effect of substrate-to-target distance on the chemistry of the atoms in the BCN thin films can also be scrutinized through the contrasting of the IR data from the films synthesized in series P8 and P18. In Figure 36 (a), (b) and (c), the IR spectra of the films deposited on grounded, -50 V, -100 V pulsed d.c. biased films in series P8 and P18 were compared one to one, respectively. As demonstrated comparatively in the respective figures, the IR bands positions and shaped are changing noticeably with the target-to-substrate distance for

films at the same bias settings. In general, it is observed that decreasing the target-to-substrate distance induces a blue shift in the Band II and decreases in the intensity of the Band I and Band III.

In Figure 36 (a), the IR spectra of the BCN film deposited on grounded substrate at two separate substrate-to-target distances are shown. It is observed that Band II is shifted approximately 45 cm^{-1} toward higher frequency values, as shown in Table 1. In addition, a decrease in the intensity of Band I and Band III with decreasing substrate-to-target distance are observed. In both cases, as there were no substrate bias applied to the substrate the expectation was to observe no difference in the IR spectra. Naturally, the flux of “stray” ions escaping from the plasma generated by the r.f. power applied to the target will be larger as the distance-from the target surface decreases. The fact that the substrate is grounded will not induce any hindrance to ions traveling toward the substrate surface. The ion flux impinging on a flat surface can be approximated by the inverse square relationship of the surface-to-source distance, Appendix. Thus, it is expected a surface placed at 18 cm away from the ion source will receive approximately 20% of the ion flux of another one placed at 8 cm away. Furthermore, this simple calculation does not consider the recombination reactions that an ion may undergo on its way to the substrate surface.

In -50 and -100 V d.c. bias cases, the shift in the position Band II and the intensity changes measured in Band I and Band III were larger than the grounded case, see Table 7. This could be because in biased cases the ions were directed toward the substrate following the electrical field lines due to the potential difference created by the applied bias between the substrates and the plasma above the target. Therefore, in P8 series the flux of ions on the substrates is expected to be larger than for P18 series, so the overall energy transfer from the ions to the growing film were more effective.

The BCN thin films deposited on the substrates located 18 cm away from the target surface were affected minimally from the applied bias. The IR spectra from these films suggest that several different types of single bonds (B-C, C-C, C-N) existed together with the predominant B-N double bonding. As the substrate target distance decreased, the amount of the single bonds in Band II region and the triple bond in the Band III were found to decrease. Also, the increase in the Band I-to-Band II intensity ratio suggests that the order and texturing in the BCN films were improving with increasing bias, thus suggesting that total number of impinged ions provided enough energy for the system to re-arrange its structure for a lower energy state. The increase in the applied energy, therefore, caused adatoms to find more thermodynamically stable resting positions, which seems to be coordination of nitrogen with boron instead of carbon atoms. Finally, in support of the conclusion from the B series, IR spectra of P series also suggested phase segregation due to increased applied non-thermal energy going from partially hybridized amorphous BCN films to a h-BN/C type. As a summary not only the amount of the applied bias is important but also the ion flux on to the substrate was found to be playing a crucial role.

As a summary not only the amount of the applied bias is important but also the ion flux on to the substrate was important. If the bias could not generate its own plasma as in case of p-d.c bias the distance between the substrate and plasma source became important. Furthermore, the applied bias type is also important especially for the film that probability of electrically low conductivity.

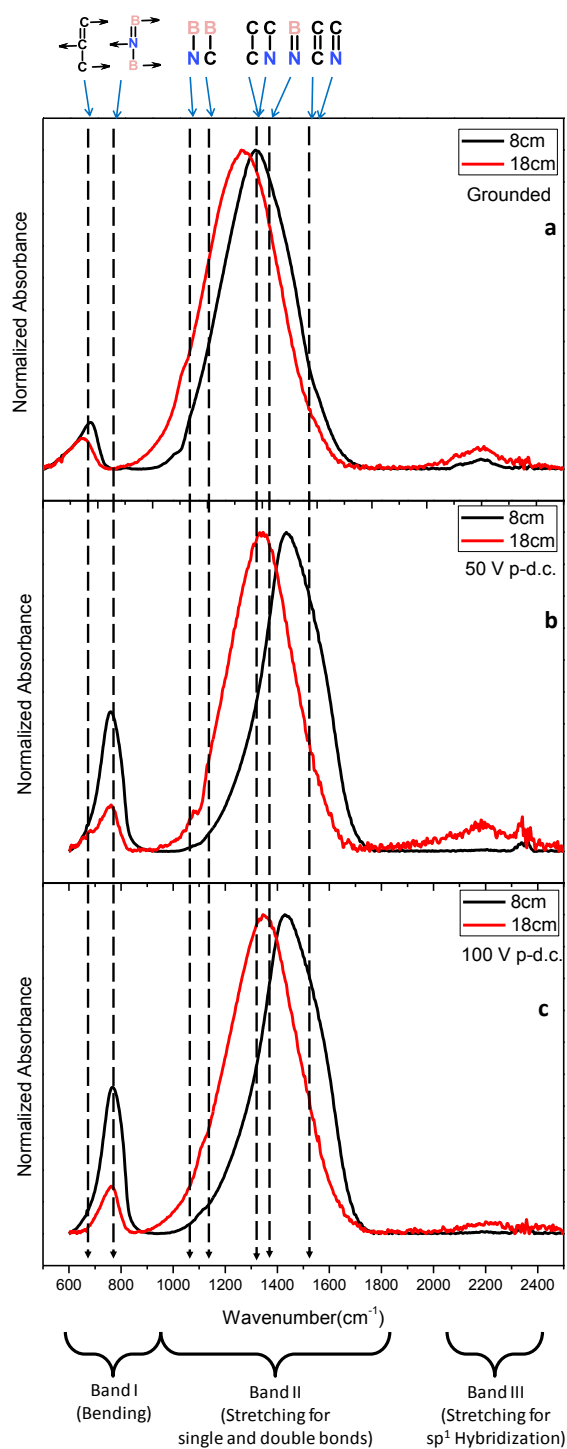


Figure 36: Comparison of IR spectra of BCN films deposited with same bias magnitude in P8 and P18 series, (a) Grounded films,(b) -50 V and (c)-100 V p-d.c. biased films

3.1.3 D Series

In the P series, the effect of the substrate-target distance on the chemical environment of the atoms in the sputter deposited films is examined over the use of IR spectroscopy. However, there was not a thorough examination of the effect of target-to-substrate distance in the literature. Moreover, in some studies there was no mention of the location of the substrate with respect to target. Thus, in the D series, a detailed analysis of the substrate-to-target distance and its effect on atomic structure and chemical environment of the atoms was studied. For this purpose, a special "adjustable substrate holder", Figure 16, was designed. For the characterization of BCN films, XPS, IR and Raman were used. In the D series, two types of films were synthesized; BCN films and BN films. Hence, the results and discussion regarding these films are grouped in two separate sections; BCND series and BND series.

BCND series

In this series, BCN films were deposited on nine substrates with each substrate having a unique target-to-substrate distance. During the deposition step, a B₄C target was sputtered by using an Argon-N₂ mixture with 10% N₂ flow. A separate bias setting and type were used in each run, as shown in Table 5

BCND50 series

In BCND50 series, samples were deposited using a substrate bias of -50 V p-d.c on nine different substrates located at unique but fixed substrate-to-target distances. The resulting BCN films were characterized using XPS, IR and RAMAN techniques. XPS data collected from "as-is" surfaces were used to investigate the chemistry of atoms in BCN films, the spectra collected post ion-

etching were actually used for the chemical composition analysis. The atomic compositions of the pre- and post etching were found to be differing from each other. The atomic composition of the films obtained from the analysis of XPS data are shown in Figure 37; (a) pre-etching and (b) post ion-etching data. This issue was emphasized and an explanation was given in the section for B series (Chapter 3.1.1). However, the variation was not as large as the one observed for series D.

XPS data obtained from *as is* BCN films shows that the carbon and oxygen content of the films to be increasing with increasing distance, while the boron and nitrogen contents were decreasing. Boron and nitrogen atomic compositions behaves the same way keeping the B:N ratio relatively insensitive to changing substrate-to-target distance, see Figure 37 (a). On the other hand, the carbon and the oxygen content of the *as is* films were observed to be increasing with the substrate-to-target distance.

When compound targets are used, the ratio of the components in films should be the same as in the compound, unless volatile products are produced. Otherwise, the chemical composition is expected to be the same in the sputtered target and the deposited film. However, B:C ratio in the films were measured to be ranging from approximately 2.5 to 0.8 with increasing substrate-to-target distance which is substantially different than that B_4C target material. In addition, oxygen content of the films also increased with the increasing substrate-to-target distance, while smaller substrate-to-target distances resulted in "less" contamination. The handling of the BCN films pre- and post-deposition process and during loading of the films to XPS chamber were carefully planned; it was ensured that all films received the same treatment. The type and amount of background gases before and during the deposition were monitored by using a residual gas analyzer (SRS Inc., RGA200). It was found that residual oxygen and carbon content never exceeded ppm levels.

The findings summarized above imply that the extra carbon and oxygen in the films were likely due to contamination from exposure to ambient atmosphere. The increase in the contamination level for films at larger distances could be attributed to the surface chemistry, such that these films may have a more active surface with more atoms with dangling bonds. It is possible that films on substrates located closer to the targets were chemically more stable due to intense ion flux, which provided enough activation energy to surface adatoms to find themselves energetically more stable regions. Therefore, surface defects and dangling bonds were reduced on such films enabling these surfaces to stay relatively clean.

The XPS data from the BCN films obtained post ion-etching, Figure 37 (b), indicate that level of oxygen content together with the carbon content were significantly lowered. One of the reason for this could be that most of the oxygen and carbon observed on the as is surface are physisorbed rather than strongly bonded to surface atoms. In Figure 37 (c), the change in B:N and B:C ratio with respect to substrate-to-target distance, in the post ion etching data are shown. B:N ratio in the films were found to be relatively stable with increasing substrate-to-target distance through the analysis of the post ion-etching data. The B:C ratio of the films were significantly higher than the ratio in the target up to 20 cm of substrate-to-target distance. BCN films growing on the substrates which are close to the target are likely to get subjected to influx of excessive N_2 ions enabling the formation of volatile CN_x compounds¹⁰⁷. Therefore, films grown closer to the plasma plume formed on the target could be carbon deficient.

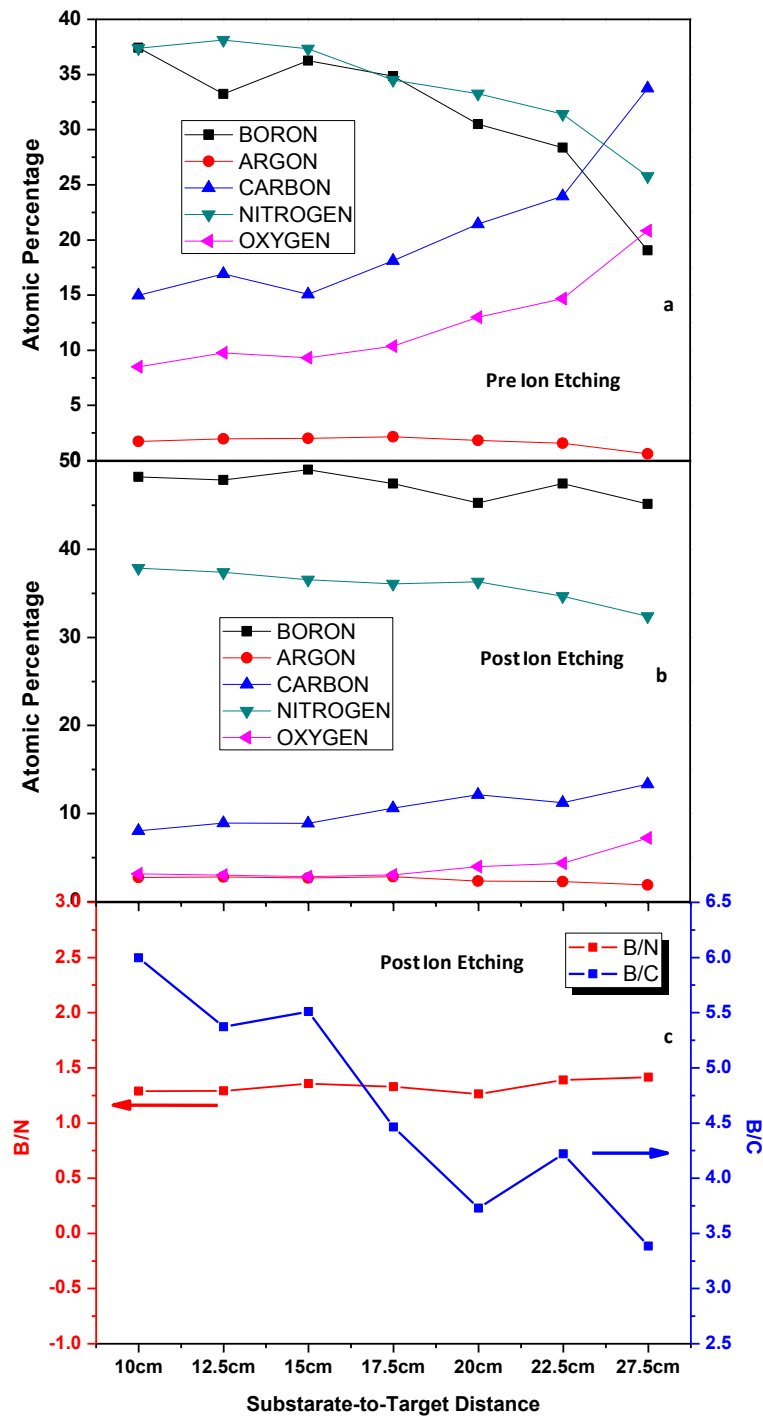


Figure 37: Atomic compositions of the BCND50 series obtained from the XPS data obtained from (a) pre- (b) post- ion etching surfaces and (c) comparison of atomic composition of data in (b).

In the following section, the focus will be on the understanding of the local chemistry of boron, carbon and nitrogen atoms in the deposited films, so XPS data from the *as is* film surfaces are going to be used. A detailed XPS analysis for the 1s regions of boron, carbon and nitrogen in BCN films will be presented. As shown in the Figure 37 (a), films deposited on the substrates that were located 25 and 27.5 cm away from the target were contaminated severely, and thus the XPS data from these films were not included in the following analysis.

In Figure 38 (a) and (b), the data obtained from the B 1s region is presented for the films in BCND50 sub-series. The position of the B 1s peak observed for films in the BCNG50 series corresponds to B 1s peak position for B atoms in h-BN. Hence, the overwhelming majority of boron atoms were in a nitrogen-rich environment. The relative stability of the B 1s peaks also emphasizes that the substrate-target distance is not a factor in defining the chemical environment of boron atoms in BCN films. Therefore, boron coordination can be said to be relatively independent of ion-flux, and under the conditions valid for this series boron prefers to bond with nitrogen atoms.

In Figure 39 (a) and (b), the XPS data from the N 1s regions of the films from BCND50 series experiments are given. The positions and the shapes of the N 1s peaks indicate that the nitrogen atoms were mainly surrounded with boron atoms. The counter effect was also seen in B 1s region in Figures 38 (a) and (b). On the other hand, the effect of the incremental decrease in the substrate to target distance is also readily observed in the overall narrowing of the N 1s peak. This is due to the gradually diminishing intensity of the shoulder located at higher binding energy side of the N 1s (398.4 eV) at 400 eV.

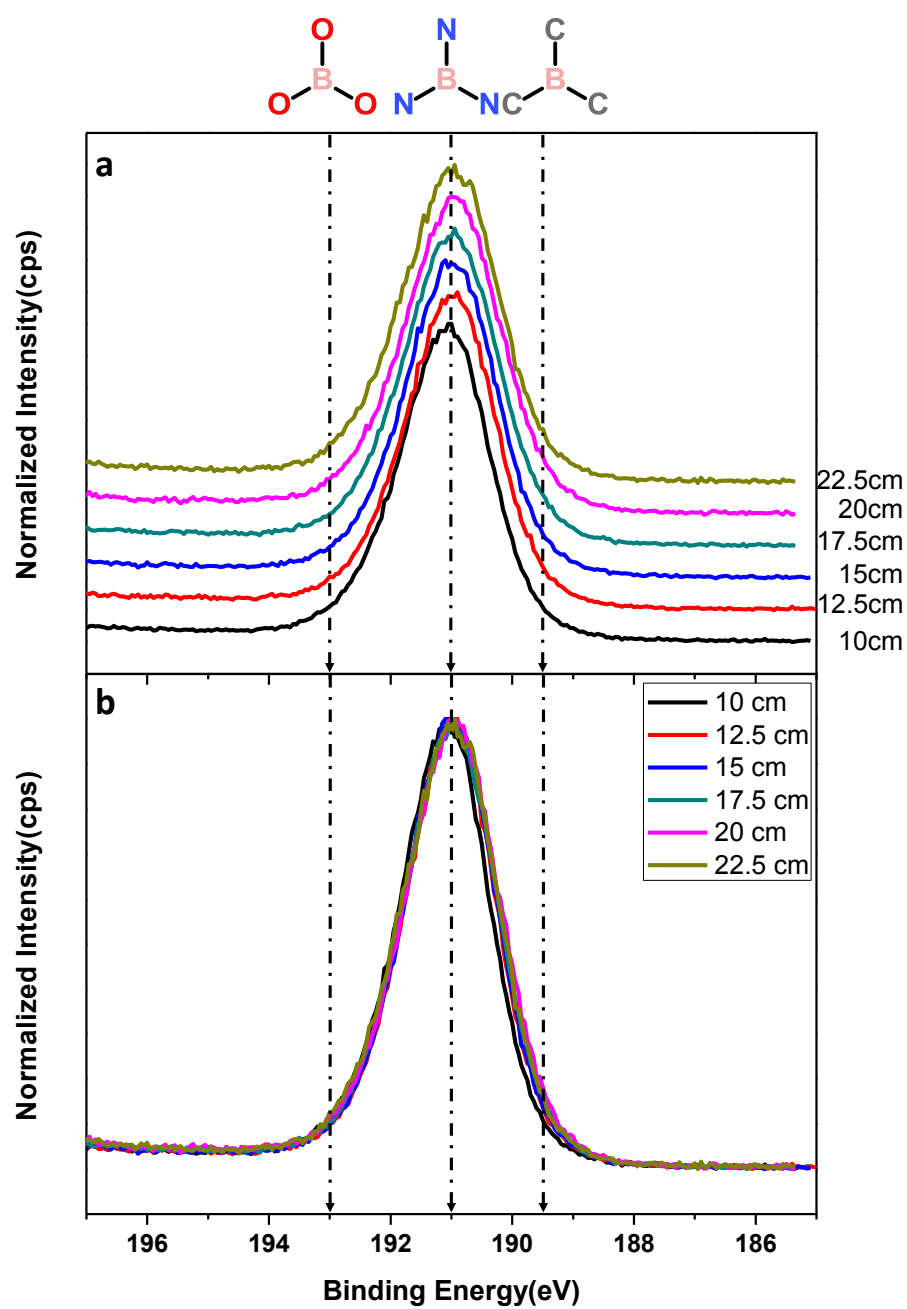


Figure 38: XPS spectra of the B 1s region of BCN films deposited on substrate located different substrate-to-target distances in BCND50 series, the substrates were -50 V p-d.c. biased. (a) waterfall representation (b) overlap representation.

This shoulder has been often identified as nitrogen atoms in a carbon rich environment such as in CN_x ¹²⁰. The decrease in the intensity of this shoulder through decreasing the substrate to target distance suggests that nitrogen atoms can find energetically more favorable arrangements under a more intense ion flux. As indicated earlier, a closer substrate location to target induces a higher ion flux which causes an increase in the total energy delivered to the growing film; in this case it is Ar^+ and N_2^+ ions providing more energy for atoms in the growing film to re-arrange themselves through diffusion. Providing support for this suggestion is the studies employing ab initio density functional theory calculations which report B-N bonding being energetically more favorable than B-C and C-N bonds^{12, 145}. Hence, N 1s data showed that C-N bonds were only observed for cases where ion-bombardment was limited.

In Figure 40 (a) and (b), the high-resolution scans of C1s region from the BCN films deposited during BCND50 series experiments are shown. The shapes of the peaks in these plots suggest a significantly complicated bonding environment for carbon atoms. In addition, a major contribution from the C-O type bonding (~289 eV) is observed in the high binding energy region. The change in the atomic composition of the BCN films obtained from the *as is* surfaces of BCN films with respect to post ion-etched BCN films suggest that the data obtained from the C 1s region of the *as is* surface mainly from the carbon atoms in the contamination layer.

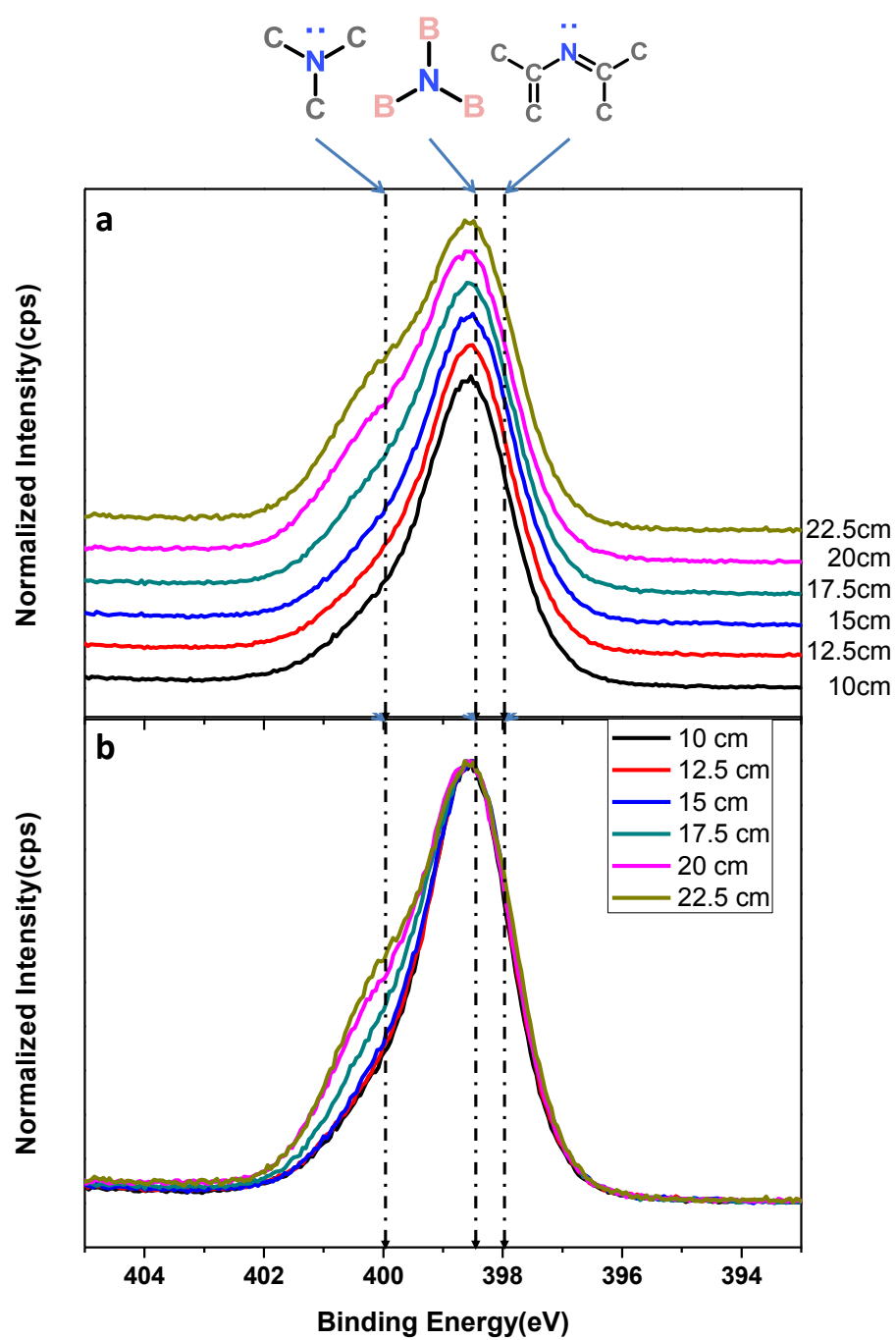


Figure 39: XPS spectra of the N 1s region of BCN films deposited on substrate located different substrate-to-target distances in BCND50 series, the substrates were -50 V p-d.c. biased. (a) waterfall representation (b) overlap representation.

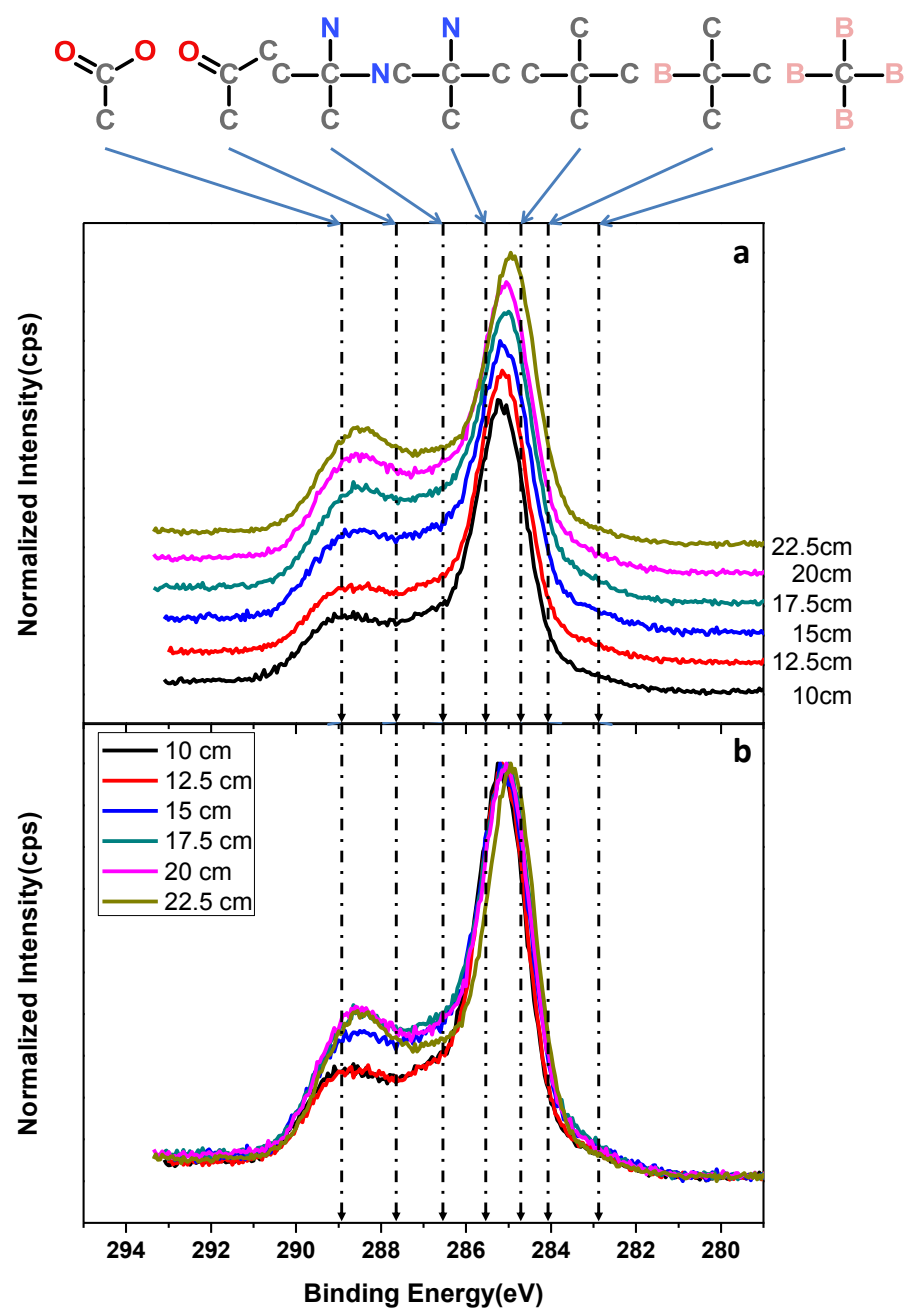
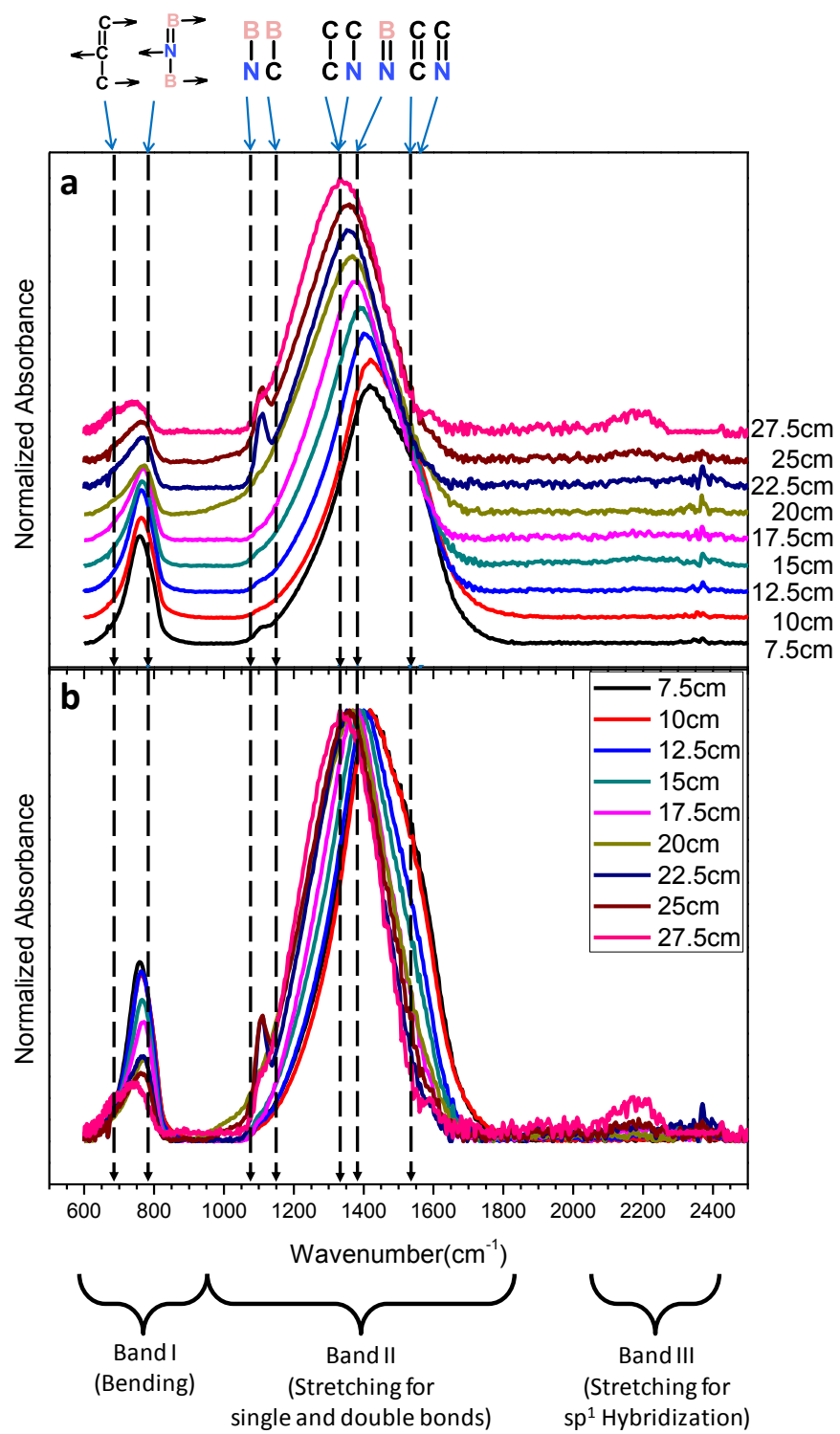


Figure 40: XPS spectra of the C 1s region of BCN films deposited on substrate located different substrate-to-target distances in BCND50 series, the substrates were -50 V p-d.c. biased. (a) Waterfall representation, (b) overlap representation.

Overall, with respect to the chemistry in the BCN films, boron atoms were found to have a strong preference toward bonding with nitrogen atoms in films grown under respectable ion-bombardment. This was also confirmed through the counter-analysis of N 1s spectra from the same films. The intensity of the high energy shoulder for N 1s indicating nitrogen atoms coordinated with carbon decreased with decreasing substrate to target distance. The increase in the supplied ion-flux to the growing film, therefore, caused adatoms to find final resting positions more thermodynamically stable, which seems to be the coordination of nitrogen with boron instead of carbon atoms. The data about the carbon atoms were not very helpful in providing useful information regarding the chemistry of BCN films deposited in BCN50 series because of the physisorbed carbonaceous impurity layer.

In addition to the XPS data, IR spectra from the BCN films were also collected. In Figure 41 (a), (b) and (c), IR spectra of the BCND50 series are shown. The bands related to stretching and bending of bonds were identified using prior studies in the literature, references were given in Table 1. Analysis of the XPS data shown in Figure 37 (c) indicated that B:N ratio of the BCN films in question remained constant which accounts for nearly the 85-90 % of the films in BCND50 series. Yet, XPS data did not present strong clues regarding changes with respect to the compositional chemistry of the films. Thus, the changes in the IR data, as shown in Figure 41, are directly related with the change in the atomic bonding and chemical environment of the atoms.



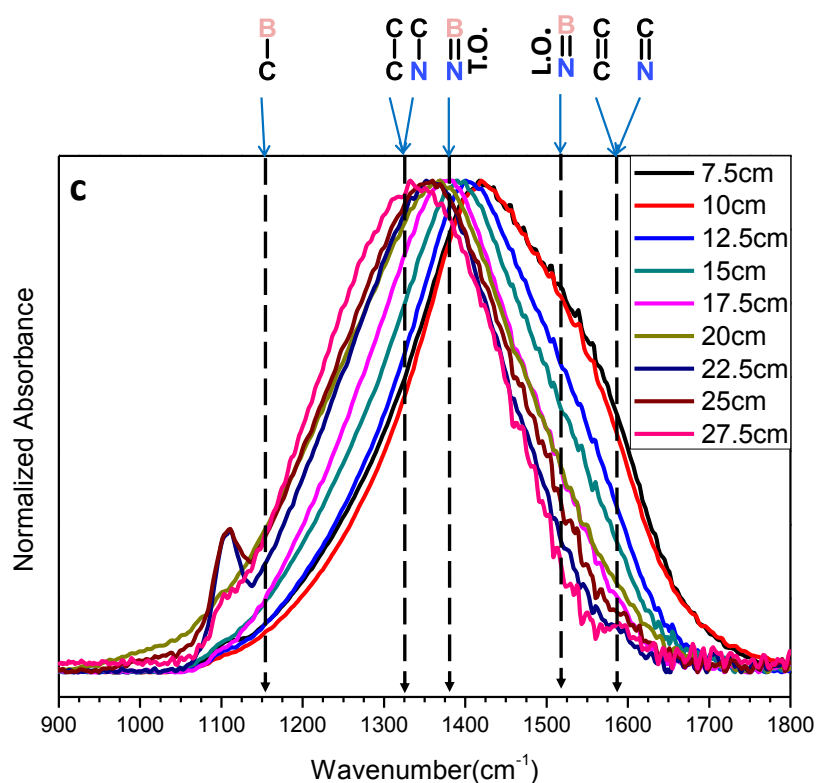


Figure 41: IR spectra of the BCN films deposited on substrate located different substrate-to-target distances in BCND50 series, the substrates were -50 V p-d.c. biased, (a) water fall representation, (b) overlap representation, (c) focused and normalized Band II region.

Upon investigation of the IR data, three main changes in the chemistry of the BCN films immediately became apparent as a response to decreasing substrate to target distance during deposition. Firstly, the intensity of the Band I was found to increase, secondly, Band II shifted to higher frequencies and the shoulder in the lower frequency side diminished, and finally, the intensity of the Band III decreased with the decreasing substrate to target distance and completely vanished below 20 cm.

As the location of the substrate approaches to the target surface, intensifying ion flux helps surface adatoms to find themselves energetically more stable regions by providing activation energy. Also, chemistry of the BCN films changes via boron, carbon and nitrogen atoms choosing themselves energetically favorable neighbors. Hence, the source for increasing intensity of the bending region in the IR data is likely that BCN films re-structure towards a layered configuration explained earlier, t-BN like, with the increasing ion-flux.

Secondly, using the clues from the XPS spectra for B 1s and N 1s regions it could be asserted that major contribution to Band II in the IR data is from the BN double bonding. Furthermore, the presence of Band I is also a supporting evidence for the dominance of BN double bond in Band II. However, upon the increase in the substrate-to-target distance, Band II is found to experience a red shift. There could be couple of reasons for this behavior. One of the reasons for such an observation could be the cumulative internal stress of the deposited films increasing, such as the case for c-BN films¹⁰¹. In c-BN case, internal stress of the films increased directly proportional to ion-flux and substrate bias which increases the density of defects in the film structure. If a chemical bond is weakened due to non-equilibrium atomic configuration, the IR bands shift to lower frequencies. However, for the BCN films increased ion-flux has an effect opposite to that observed for the c-BN films. Another explanation for the red-shift in IR spectra for the BCN films could be the increase in the abundance of single bonds appearing at lower frequency regions such as C-N, B-C and B-N, etc. This interpretation is also consistent with the explanation provided for XPS data (observation of C-N bond in N 1s spectra) which suggests domination of the kinetic limitations over thermodynamic preference during the film growth step due to increased substrate-to-target distance. While the vibration band of polarized single bonded C-C and C-N pairs can explain the change in the Band II for the range below 1380 cm^{-1} , the appearance of the shoulder in the range above 1500 cm^{-1} for Band II is likely due to polarized C-C double bonds^{131, 132},

^{138, 139, 142, 143, 178-180}. This interpretation has been discussed in detail in the section for series B, (Chapter 3.1.1). The decrease in the intensity and eventual vanishing of Band III with the decrease in substrate to target distance suggest the presence of nitrile groups, which also indicates deterioration of the layered structure as the substrate is located farther away from the target surface.

Another vibration analysis technique, Raman spectroscopy, was also used for the analysis of the bonding in the BCN films. Raman data of the BCN films in BCND50 sub series are shown in Figure 42 with assigned peak positions based on previous studies in the related literature, references were given in Table 2. The peaks observed in the respective spectra did not change their position, intensity and structure with the change in the substrate to target distance. As mentioned in Raman spectroscopy section, Chapter 1.2.2, the Raman scattering power of the C-C double bonds were significantly dominant over other bonds such as BN double and single bonds, C-C single bonds. Due to inferior character of these bonds, the increase or decrease in the intensity of related peaks were suppressed. The peak in the spectrum was a typical Raman data of carbon based materials^{131, 132, 138, 139, 142, 143, 178-180}.

As a summary, BCN films deposited in BCND50 series were characterized with XPS, IR and Raman techniques for uncovering the effect of substrate target distance on the atomic structure and chemistry of the atoms in BCN film deposited with -50 V p-d.c. substrate bias. The XPS data suggests that the atomic composition of the BCN thin films were changing with the substrate-to-target distance. However, in overall composition is B:N ~1 and B:C between six to four, in other words, the amount of boron and nitrogen atoms were always larger than the amount of carbon atoms. XPS data also suggests that the boron atoms were bonded to the nitrogen atoms, and nitrogen atoms mainly bonded to boron atoms. However, for films deposited on substrates farthest away from the target, some of the nitrogen atoms were found to be bonded with carbon.

Overall, analysis of the IR data yielded results in support of the results for XPS analysis indicating as the substrate approaches to the plasma above the target, the BCN films became more ordered and forming a layered structure similar to that of t-BN.

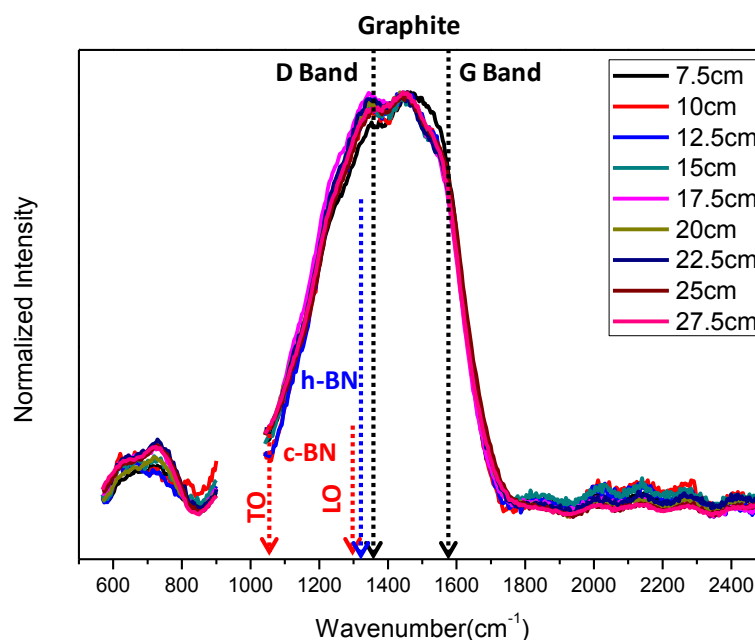


Figure 42: Raman spectra of the BCN films deposited on substrate located different substrate-to-target distances in BCND50 series, the substrates were -50 V p-d.c. biased,

BCNDGr Series

In BCNDGr series films were deposited on the substrates located on the adjustable distance substrate holder that is shown in Figure 16. In this series, BCN films were deposited on grounded substrates. As the main characterization technique for this series, XPS was used to understand the changes in atomic composition and coordination. IR and Raman were also used to understand structural change in the BCN thin films synthesized in this series.

Atomic compositions of BCN films were calculated from the XPS data collected from post ion etched surfaces of BCN films. This data are given in the Figure 43 (a) and (b). The results for atomic composition vs. substrate-to-target variation are similar to that observed for BCND50 series. While B:N ratio remained relatively constant around ~ 1 , B:C ratio changed from 3.5 to 5.5. The reasons for the increase observed in the B:C ratio was discussed in detailed in the previous sections which was related to increase in the formation of the volatile CN_x compounds due to increased N_2 flux. Therefore, even though the a substrate bias was not applied, the data presented above indicates that a significant portion of N_2 ions reached the growing film affecting the atomic composition.

The IR spectra of the BCN thin films deposited in the BCNDGr series are shown in Figure 44 (a) and (b) and in Figure 44 (c) and (d), the magnified part of the Band II and Band I are also given. The IR spectra collected from the BCN thin films deposited in BCNDGr series resemble closely the IR spectra of the BCN films of BCND50 series. As the substrates approached closer to the target, a decrease in the intensity and red shift in the position of Band I, $\sim 40\text{cm}^{-1}$ is observed. Besides, blue shift in the Band II position and a decrease in Band III intensity also were noted. The decrease in the Band I is an indication of the decrease in the layered ordering in the films, also the shift in the band II suggests a decrease in the bond strength. Therefore, the total bond order in the films decreased. The decline and vanishing in band III points out that the abundance of sp type hybridized atoms decreased.

As the location of the substrate approaches to the target surface, intensifying stray ion flux helps surface adatoms to find themselves energetically more stable regions by providing the required activation energy for surface diffusion. Also, chemistry of the BCN films changed via boron, carbon and nitrogen atoms choosing themselves *chemically* favorable neighbors, e.g. B-N and C-C

pairs. Hence, the source for increasing intensity and blue shift of the bending region in the IR data is likely that BCN films re-structuring towards a layered configuration explained earlier, t-BN like, with the increasing ion-flux.

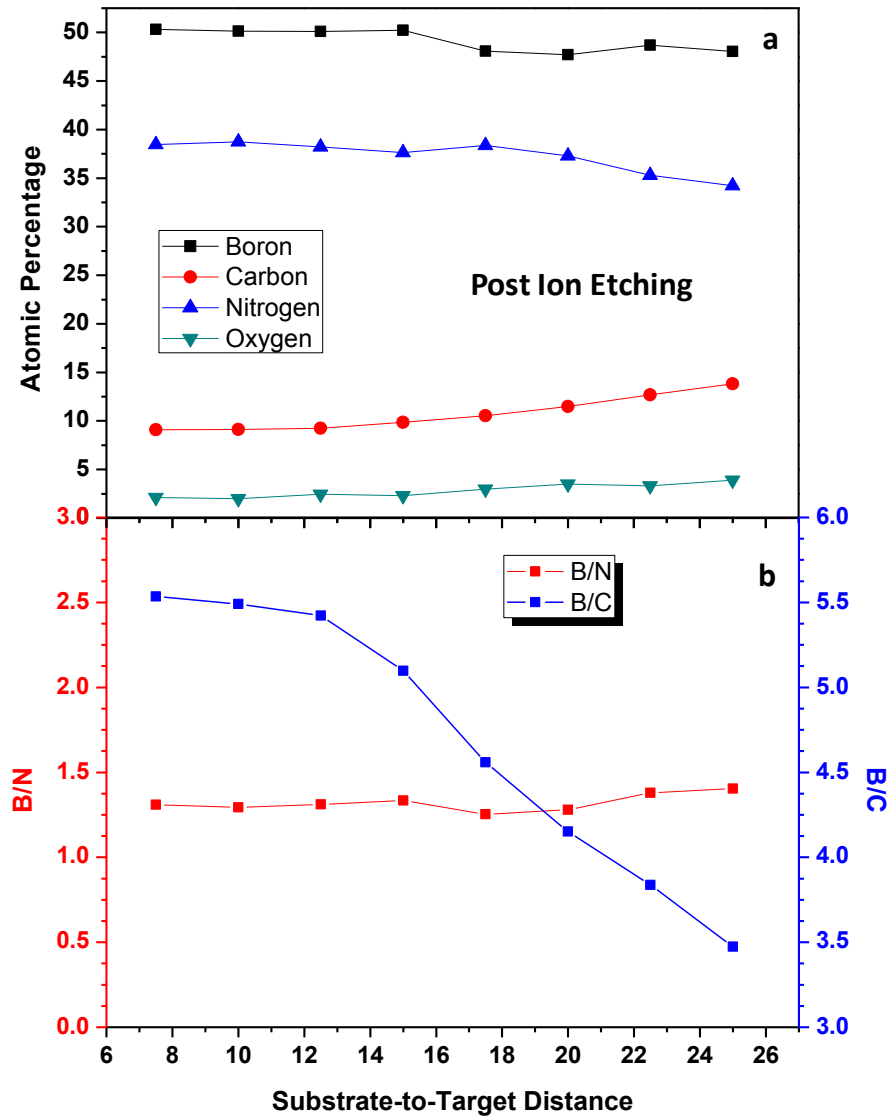


Figure 43: Atomic compositions of the BCN films deposited on substrates located at different substrate-to-target distances in the BCNDGr series. All of the substrates were grounded. The XPS data shown in (a) is obtained from post ion etched surface and, (b) displays the change in B:N and B:C ratio.

Secondly, using the clues from the atomic composition data it could be asserted that major contribution to Band II in the IR data is from the BN double bonding. Furthermore, the presence of Band I is also a supporting evidence for the dominance of BN double bond in Band II. However, upon the increase in the substrate-to-target distance, Band II is found to experience a 40 cm^{-1} red shift. This is due to domination of the kinetic limitations over thermodynamic preference during the film growth step due to increased substrate-to-target distance; torsional stress in the BN double bonding could also be the reason for the red shift. If a chemical bond is weakened due to non-equilibrium atomic configuration, the IR bands shift to lower frequencies. Another explanation for the red-shift in IR spectra for the BCN films is the vibration band of polarized single bonded C-C and C-N pairs for the range below 1380 cm^{-1} . The decrease in the intensity and eventual vanishing of Band III with the decrease in substrate to target distance suggest the presence of nitrile groups, which also indicates deterioration of the layered structure as the substrate is located farther away from the target surface.

Another vibration analysis technique, Raman spectroscopy, was also used for the analysis of the bonding in the BCN films. Raman data of the BCN films in BCNDGr sub series are shown in Figure 45 with assigned peak positions based on previous studies in the related literature, references were given in Table 2. The peaks observed in the respective spectra did not change their position, intensity and structure with the change in the substrate to target distance. As mentioned in Raman spectroscopy section, Chapter 1.2.2, the Raman scattering power of the C-C double bonds were significantly dominant over other bonds such as BN double and single bonds, C-C single bonds. Due to inferior character of these bonds, the increase or decrease in the intensity of related peaks were suppressed. The peak in the spectrum was a typical Raman data of carbon-based materials^{131, 132, 138, 139, 142, 143, 178-180}.

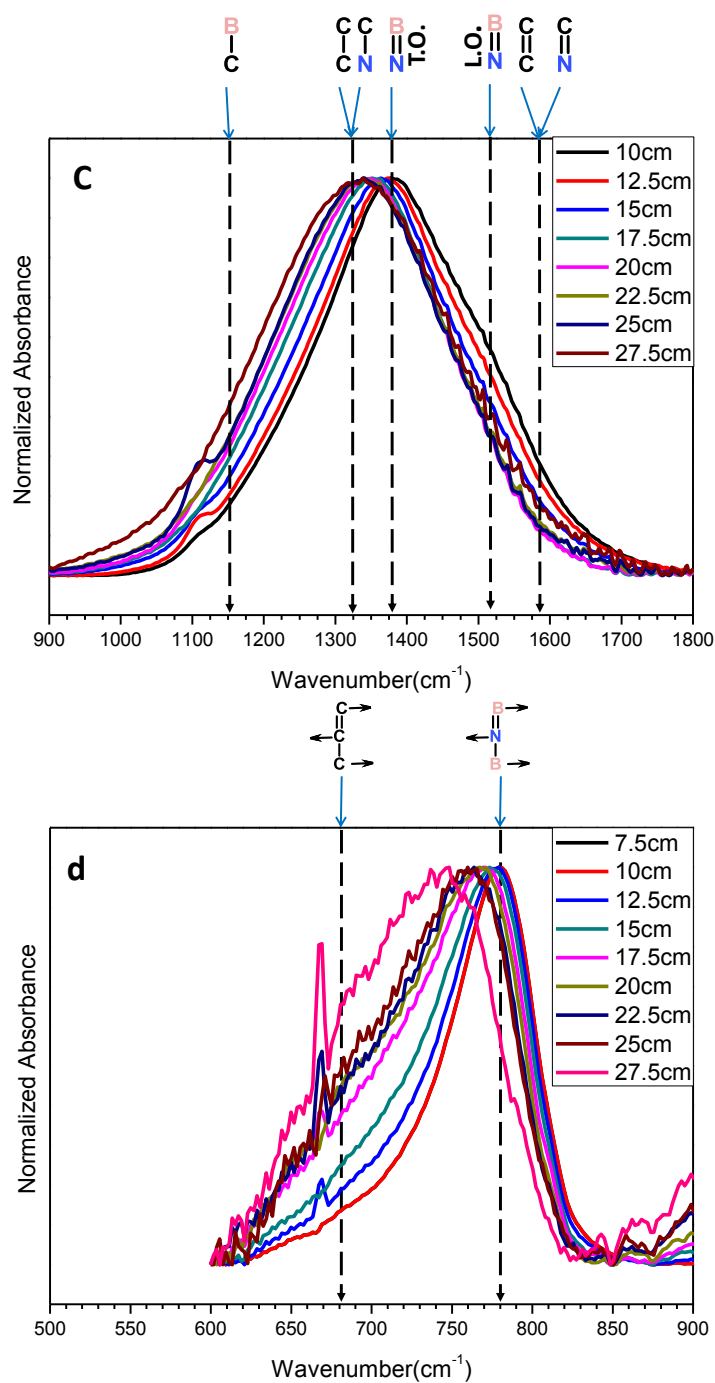


Figure 44: IR spectra of the BCN films deposited on substrate located different substrate-to-target distances in BCND50Gr series, the substrates were grounded, (a) water fall representation, (b) overlap representation. Focused and normalized (c) Band II and (d) Band I region.

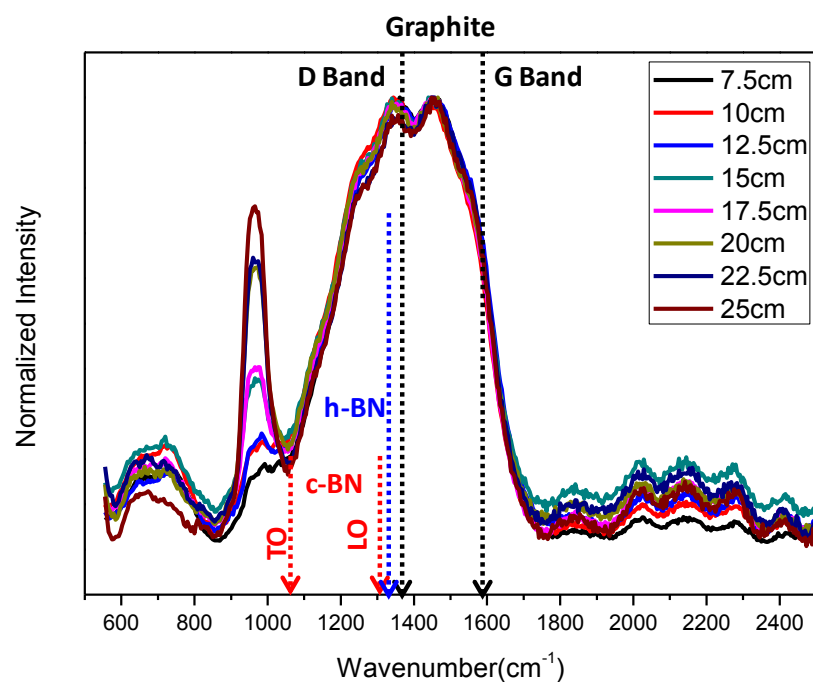


Figure 45: Raman spectra of films deposited in BCNDGr series experiments. Substrates were grounded

Overall, B:N ratio of this films remained stable with respect to changing substrate-to-bias ratio, but B:C ratio increased as the substrate moved away effectively limiting the flux of N₂ ions reaching the growing film surface. The IR and Raman data indicate that the atomic structure was influenced from the position of the substrate. The portion of the sp³ and sp hybridized atoms declined as the substrate gets closer to the target surface. This suggests that, stray ion bombardment was sufficient to derive the chemistry on the growing films toward a thermodynamically more stable state favoring B-N and C-C pairs.

BCND50DC series

In the BCND50DC series, BCN films were deposited on the substrates that were biased at -50 V d.c. using a d.c. power supply placed on the adjustable target-to-substrate distance substrate holder. The aim of this series was to understand the effect of the type of bias by comparing the results from BCN films deposited with same parameters in series BCND50. In BCND50 series, bias applied on the substrates was of p-d.c. type. The resulting BCN films were characterized by using IR spectroscopy.

The results of the previous series, BCND50 and BCNDGr, indicated several changes taking place in the atomic structure and composition of the thin films with the change in the substrate-to-target distance. In addition, the change in the atomic compositions in both cases varied the same way with respect to distance from the target. Furthermore, the results from IR spectra from the BCN films tracked parallel with the results from XPS analysis. Therefore, in series BCND50DC, analysis of the films mainly relied on IR spectroscopy. In Figure 46 (a) and (b), the IR spectra of the BCN film deposited in BCN50DC series are shown with assigned peak positions that were obtained from the BN, B₄C and CN_x studies in the literature, references were given in Table 2.

The IR data of the BCND50DC series BCN films resembles the IR data of BCND50 and BCNDGr series very closely, no significant discerning changes were observed. The results from the analysis of the IR spectra could be summarized as follows; first, the intensity of the Band I was found to increase and Band I shifted to higher frequencies as the substrate location was moved further away from the surface of the target. Secondly, Band II shifted to higher frequencies and the shoulder in the lower frequency side diminished and a shoulder on the higher frequency side become apparent. Finally, the intensity of the Band III decreased with the decreasing substrate to target distance that completely vanished.

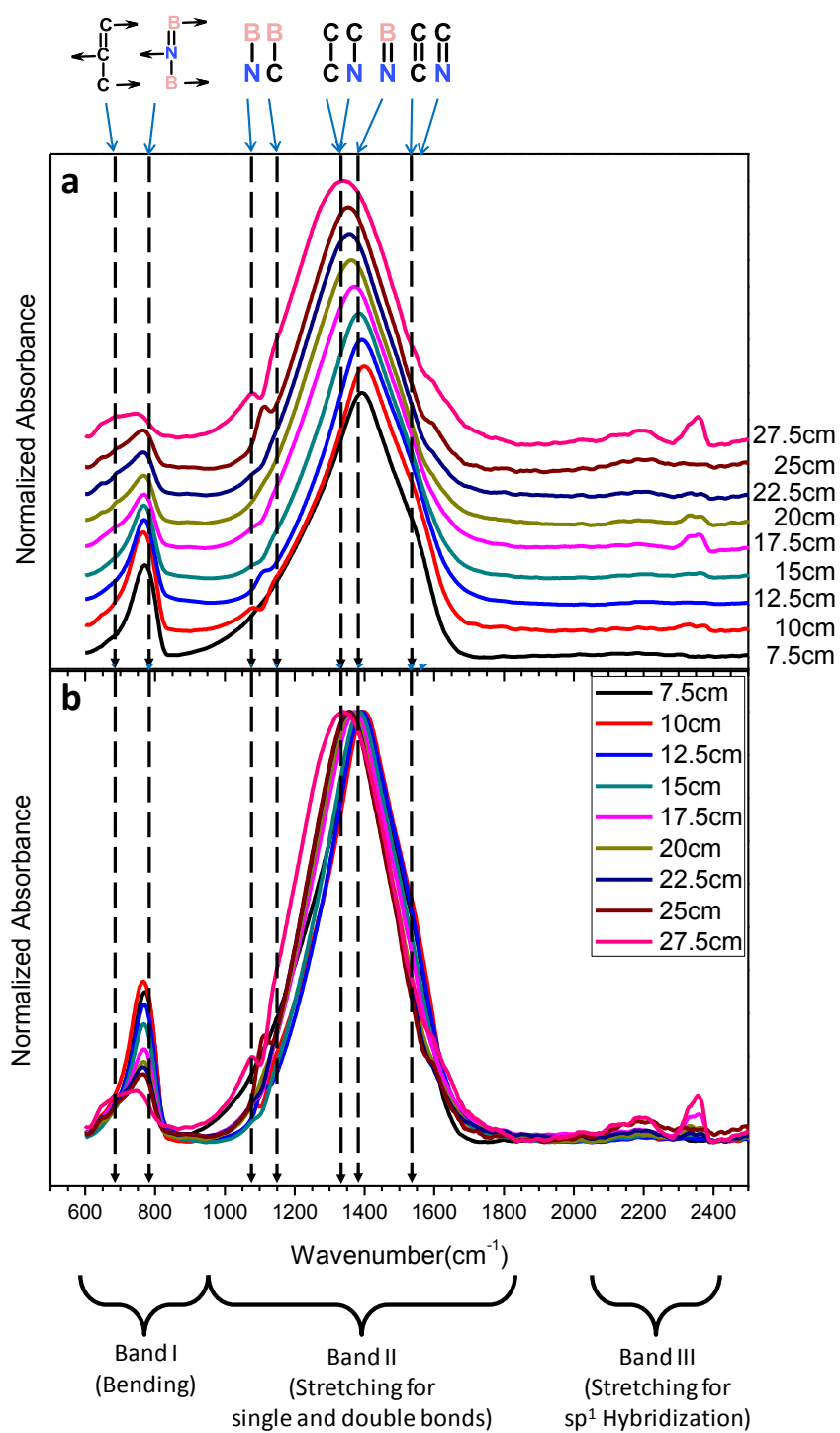


Figure 46: IR spectra of the BCN films deposited on substrate located different substrate-to-target distances in BCND50DC series, the substrates were -50 V d.c. biased, (a) waterfall representation, (b) overlap representation,

As the location of the substrate approaches to the target surface, intensifying ion flux helps increase the mobility of surface adatoms allowing them to find more stable regions. Also, local chemistry of the BCN films changes via boron, carbon and nitrogen atoms choosing themselves energetically favorable neighbors. Hence, the source for increasing intensity of the bending region in the IR data is likely that BCN films re-structure towards a layered configuration as explained earlier, t-BN like, with the increasing ion-bombardment. Furthermore, using the clues from the atomic composition data of BCND50 and BCNDGr, it could be asserted that major contribution to Band II in the IR data is from the BN double bonding.

There could be several reasons behind the shift observed for Band II. One could be that the cumulative internal stress of the deposited films increases with increasing ion-bombardment, such as the case for c-BN films¹⁶⁰. In c-BN case, internal stress of the films increased directly proportional to ion-flux and substrate bias which leads an increase in the density of defects in the film structure. Hence, under such conditions chemical bonds between atoms adjacent to point defects will be under significant stress causing bond strength to get weaker. If a chemical bond is weakened due to non-equilibrium atomic configuration, the IR bands shift to lower frequencies. However, for the BCN films increased ion-flux has an effect opposite to that observed for the c-BN films. Therefore, red-shift in Band II can be explained using such an assertion suggesting ordering of the films decreasing overall stress of in the films.

Another explanation for the red-shift in IR spectra for the BCN films could be a result of the increase in the abundance of single bonds appearing at lower frequency regions such as C-N, B-C and B-N, etc. This interpretation is also consistent with the explanation provided for XPS data where evidence of C-N bond in N 1s spectra is observed for BCN50 series in Figure 39. This finding suggests the kinetic limitations become dominant over thermodynamic

preference during the film growth step due increased substrate-to-target distance. While the vibrational band dipole induced single bonded C-C and C-N pairs can explain the change in the Band II for the range below 1380 cm^{-1} , the appearance of the shoulder in the range above 1500 cm^{-1} for Band II can be due to dipole induced C-C double bonds^{131, 132, 138, 139, 142, 143, 178-180}. This interpretation has been discussed in detail in the section for series B, see Chapter 3.1.1.

The decrease in the intensity and eventual vanishing of Band III with the decrease in substrate to target distance suggest the presence of nitrile groups, which also indicates deterioration of the layered structure as the substrate is located farther away from the target surface. In summary, the atomic structure of the film were changed with the substrate-to-target distance changed, the portion of sp and sp^3 type hybridized atoms were incline as the substrates approached the target surface.

BND Series

BN films in BND series were deposited to provide comparative data for the IR information gathered from the BCND series. Similar atomic compositions (approximately B_4CN_4) of the BCN films and the turbostratic nature of the sputter deposited BN films allow for the BN thin films to be the most suitable candidate for comparison of the IR data from BCN films. In BND series, films were deposited from a BN target using an r.f. power supply. Similar to the one used in BCND series, BN films were also deposited using the substrate holder with the adjustable substrate-to-target distance. During film deposition a negative 50 V p-d.c. bias was applied on the substrates. The effect of the location of the substrate with respect to target on the atomic composition of BN films was investigated by analyzing the XPS data of three BN films located at the closest, the middle and the farthest position with respect to target surface.

The XPS data from the post ion-etched film surfaces were used for calculating the compositional and data is given in Figure 47. This data shows that the films were mainly consisting of boron and nitrogen with small amounts of impurities like carbon, oxygen and buried argon. Thus, the compositional data also indicates that the changes in the IR data of the BN films in BND series will only depend on the structural changes due to substrate position- thus, varying dose of ion-flux. The IR data of the BND series are shown in the Figure 48 (a), (b), (c) and (d).

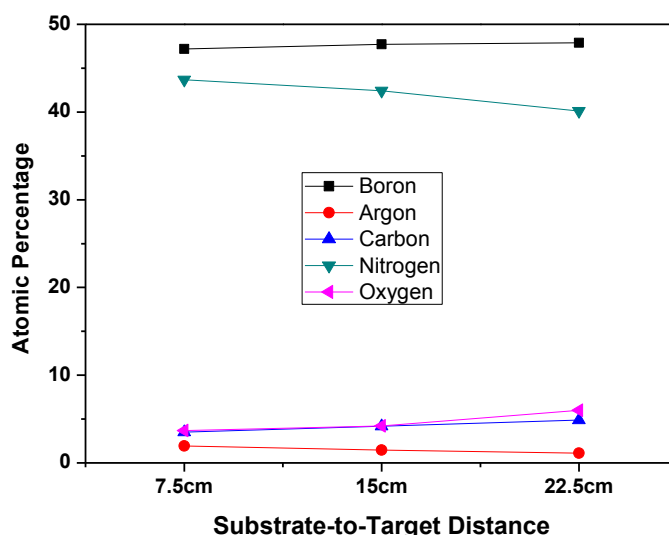
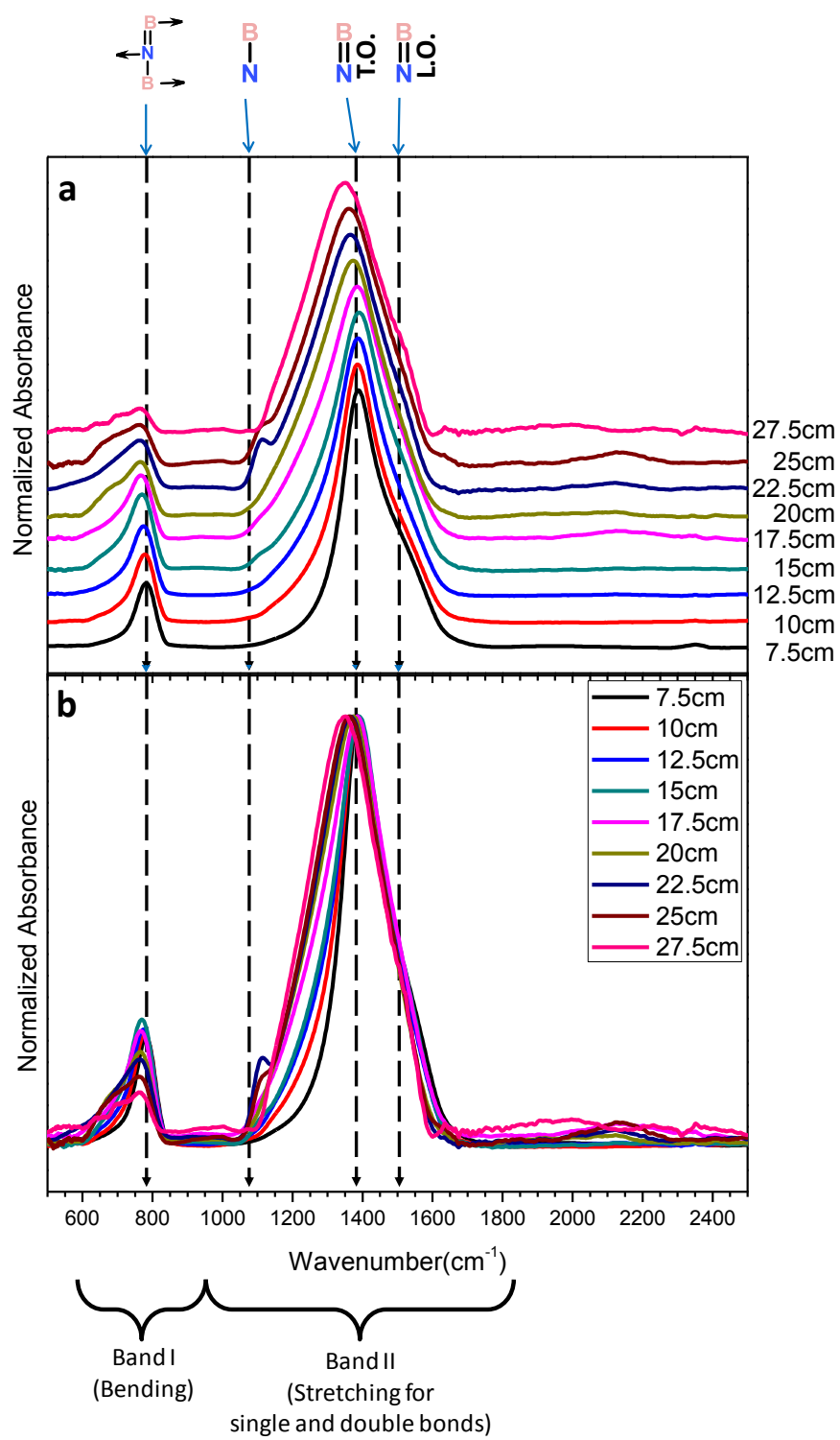


Figure 47: Atomic compositions of the BN films deposited in BND series obtained from the XPS data of post ion-etched surface (at 750 eV, 5 min).

Upon careful analysis, the following changes are observed from the IR data of the BN films in this series. First, increase in the intensity, decrease in the width and a blue shift in the frequency of the Band I. Secondly, sharpening of the Band II- loss of low frequency components, and formation of a shoulder in the higher frequency side of the Band II as the substrate-to-target distance

decreases. Increasing intensity of Band I for BND films indicate that ordering is improving and a conversion from an amorphous structure toward a layered one is taking place. Thus, the interpretation of this observation could be that as the ion-flux - non-thermal energy provided to the substrate- increases, the microstructure of the films transform in to a more ordered and layered one. For further analysis, the IR spectrum acquired from powdered h-BN (Aldrich %99.5) is provided in comparison with data from two films of the BND series in Figure 48, namely the closest and the farthest substrates.

A close inspection of the three IR spectra, given in Figure 48, reveals striking differences in Band II and Band I regions. Band II of the films were broader than the h-BN reference. Secondly, the peak position of the Band II for h-BN reference and BN film deposited on the substrate 7.5 cm away from the target surface (BND7.5) are found to be same and matching perfectly with the transverse optical (T.O.) BN stretching position given in the literature, references were given in Table1. On the other hand, the peak position of the Band II for BN film deposited on the substrate located 25 cm away from the target (BND25), shifted toward lower frequencies. Another peculiar finding was that the Band II of BND25 and h-BN reference are symmetric, whereas the Band II of BND7.5 indicated a shoulder on the higher frequency side. This shoulder is likely to be due to the L.O. stretching mode of BN bond in the layer. As the c-planes (basal planes) for the BN films are aligned perpendicular to the substrate during deposition (t-BN films), the phonon-lattice interaction giving rise to the L.O. mode of BN stretching signal is getting stronger. The schematic representation of the t-BN and the phonon interaction is shown in Figure 50. Due to the anisotropy in the t-BN structure, L.O. mode of BN stretching signal is more apparent in IR spectrum for t-BN than for the h-BN reference, where the c-planes are randomly oriented with respect to incoming photons.



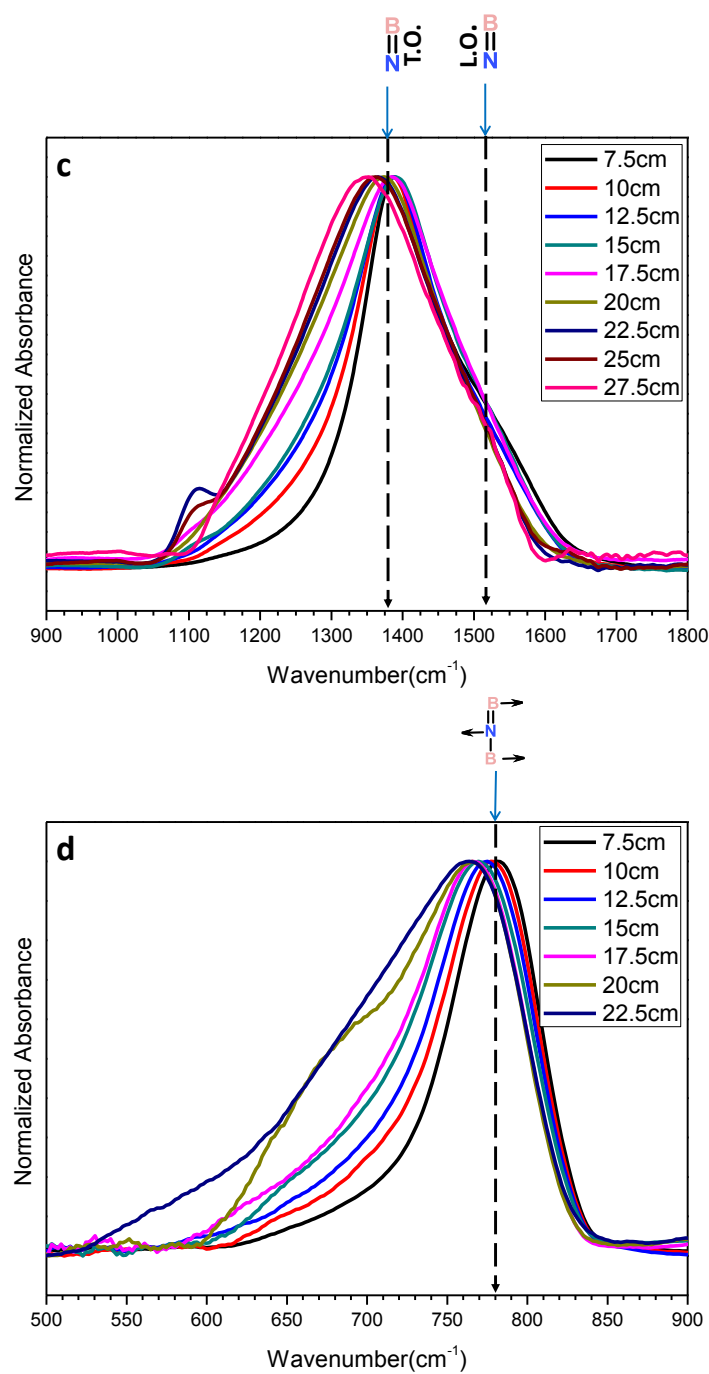


Figure 48: IR spectra of the BN films deposited on substrates located at different substrate-to-target distances in BND50 series. All of the substrates were -50 V p-d.c. biased; (a) water fall representation, (b) overlap representation, (c) Band II region and (d) Band I region in focus.

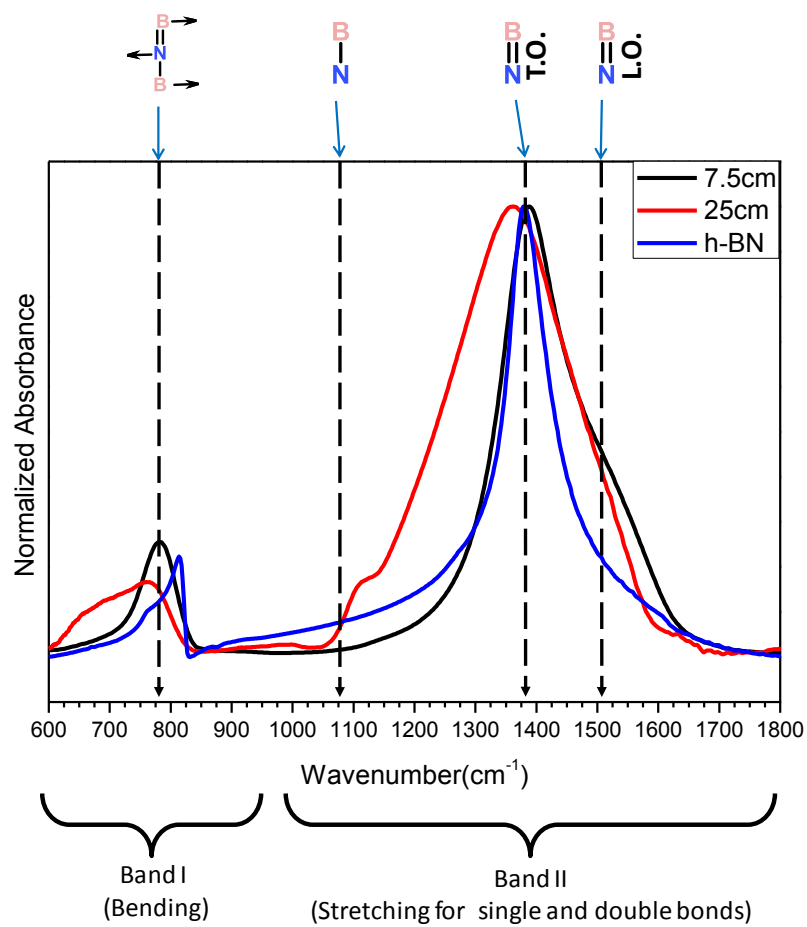


Figure 49: A comparison of the reference IR spectrum from powered h-BN and BN films deposited on the substrates located 7.5 cm and 25 cm away from the target surface.

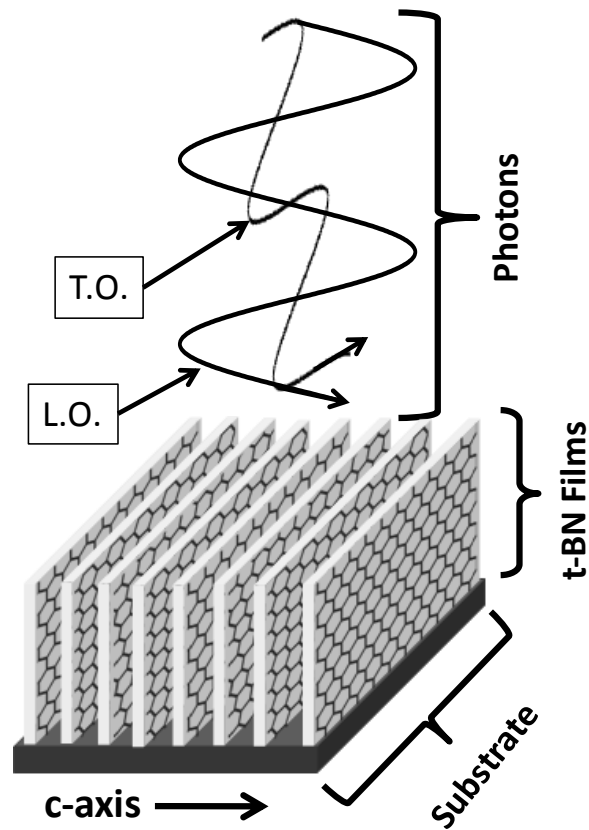


Figure 50: Schematic representation of the interaction between alignment of basal planes in t-BN and the incoming photons.

Summary of D Series

The data gathered from the characterization of the films generated in D series can be summarized as follows. One of the most important results is that the atomic compositions in the films were not affected by the changes in the distance from target and/or applied bias to the substrate. This indicates that the rate of atom incorporation to films is not preferentially a factor of ion energy or flux. Re-sputtering from the surface is also not related to the type of the atoms. Another observation relates to the atomic structure of the films. IR results suggested formation of ordered films on substrates positioned closer to the target surface – under more intense ion-flux. A microstructure similar to t-BN

films observed for c-BN growth studies were encountered where basal planes grew perpendicular to the substrate surface as mentioned earlier in section 3.1.1. This was indicated by the intensity increase in Band I for these films. On the other hand, films farthest away from the target surface had a significant low frequency component in their Band II and also formation of Band III. These suggest presence of sp^3 and sp type hybridized atoms. Results of XPS also showed strong evidence for the dominance of B-N bonding in these films, and the decreasing amount of nitrogen atoms in carbon environment with decreasing substrate-to-target distance.

3.1.4. Summary of B, P and D Series

In the experiments covered in series B, P and D, the N_2 flow rate during depositions were kept constant while the ion flux and the energy of the ions reaching the growing BCN films were manipulated through the substrate bias, bias type, and also target to substrate distance. The final chemical composition, atomic structure and chemical environment of atoms in BCN films were investigated as a function of energy provided to the growing film. XPS, IR, Raman, XRD and TEM equipment were used to scrutinize these films.

The results of the studies immediately pointed out that substrate biasing was played an important role only if the substrate was positioned close to the ion source which is the plasma on the surface of the target. This effect is displayed by the ordering in the films in a way that basal planes orienting themselves perpendicular to the substrate surface. The experimental evidence for this is the Band I in the IR spectra and the cross-sectional TEM images from the films. Furthermore, at the same time XPS data indicates the formation of a dominant BN network and diminishing amount of carbon atoms in coordination with boron and nitrogen. These findings indicate that a layered B-N networking is

energetically more stable for BCN films. Therefore, when sufficient energy is supplied to the growing BCN films, the chemistry and atomic structure of is driven toward the thermodynamically most suitable configuration, hence a layered and sp^2 bonded film.

In addition to this, evidence for phase segregation was observed in these layered structures irrespective of the substrate bias, bias type, and also target to substrate distance. The dominant phase seems to be made up of hexagonal networks of BN, whereas the minor phase changes with respect to the amount of energy provided to the growing films. If the surface diffusion of the adsorbed species were low enough, while the layered structure was still observed, sp^3 and sp type bonding was encountered in IR and N 1s provided evidence of C-N coordination. Thus, minor phase is likely to be CN_x . In the case of intense ion-bombardment, and sufficiently high substrate bias, IR spectra shows a shoulder appearing in the high frequency side of the Band II suggesting C-C signal from isolated C islands forming in the BN network. Hence, the minor phase is more likely to be graphitic carbon in this case.

3.2. Investigation of the effect of nitrogen amount on the atomic structure and chemistry of BCN thin films

In the previous part of this chapter, effects of growth mechanisms on atomic structure of deposited BCN films were investigated. In the second part of this chapter, the effect of the relative arrival rates of film forming components on the surface are manipulated to understand the bonding preference of atoms. For this reason, atomic composition of the deposited films was changed by changing the N₂ gas flow during deposition of BCN films synthesized by r.f. plasma sputtering the B₄C target.

3.2.1. G series

In the G series experiments, the effect of relative nitrogen gas flow with respect to argon gas flow to the chamber was investigated. By using a B₄C target, the amount of B:C ratio was kept constant. The amount of N₂ gas flow to the chamber was controlled by manipulating the mass flow controller for nitrogen. Deposited BCN films in G series were characterized by XPS, IR and Raman techniques. The N₂ flow in the following text is expressed by the percentage of N₂, $[N_2/(Ar+N_2) \times 100]$, in the process gas entering to the deposition chamber. The total pressure in the chamber has been kept constant with the help of a butterfly valve in front of the turbo-molecular pump.

In the previous parts of this chapter, it was argued that kinetically limited growth processes induced formation of amorphous BCN films and the bonding chemistry was relatively difficult to understand. For this reason, effect of chemistry on BCN films deposited in a thermodynamically limited growth

regime and a kinetically limited regime were comparatively examined in this section. In literature, there are a number of studies about the BCN films synthesized with different atomic compositions. Generally, these studies used CVD methods where flow rate of the reactant gases were changed to influence the final film compositions³⁰⁻⁴¹. In addition, there were some studies using sputter deposition^{102, 104, 124, 126, 127, 183, 184}. As mentioned earlier in the literature review Chapter 1.1.4, these studies following the sputter deposition route can be grouped into two: reactive single source (target) sputtering and reactive co-sputtering using composite or separate targets. Hence, a large range of atomic compositions in BCN ternary phase diagram was examined. However, due to the inadequate interpretation induced by the shortcomings of the XPS and IR techniques mentioned earlier, mostly confusing and contradictory conclusions were reached.^{109, 115, 127, 184-186}. Therefore, in this section, the experiments in the respective series are designed in a manner to better understand factors leading to possible phase segregation and how it proceeds. In order to achieve this task, BCN films were deposited using N₂ flows that are 0, 1, 2, 3, 5, 8 and 10 % of the total gas flow to the chamber. Furthermore, in the GT sub-series BCN films were deposited on -50V p-d.c. biased substrates located 8 cm away from the target, for examining thermodynamically preferred growth mechanisms. BCN films for GK sub-series films were deposited on the electrically grounded substrates located 18 cm away from the target for investigating the effect of chemistry on the kinetically limited growth regime.

GT series

In the following section of the chapter, the characterization and interpretation of data provided from BCN films deposited on the -50 V p-d.c. substrate that was located 8 cm away from the target were discussed. Firstly, atomic composition of the films are analyzed. In Figure 51 (a), (b) and (c), the changes in the atomic compositions of the films are showed with increasing N₂ flow.

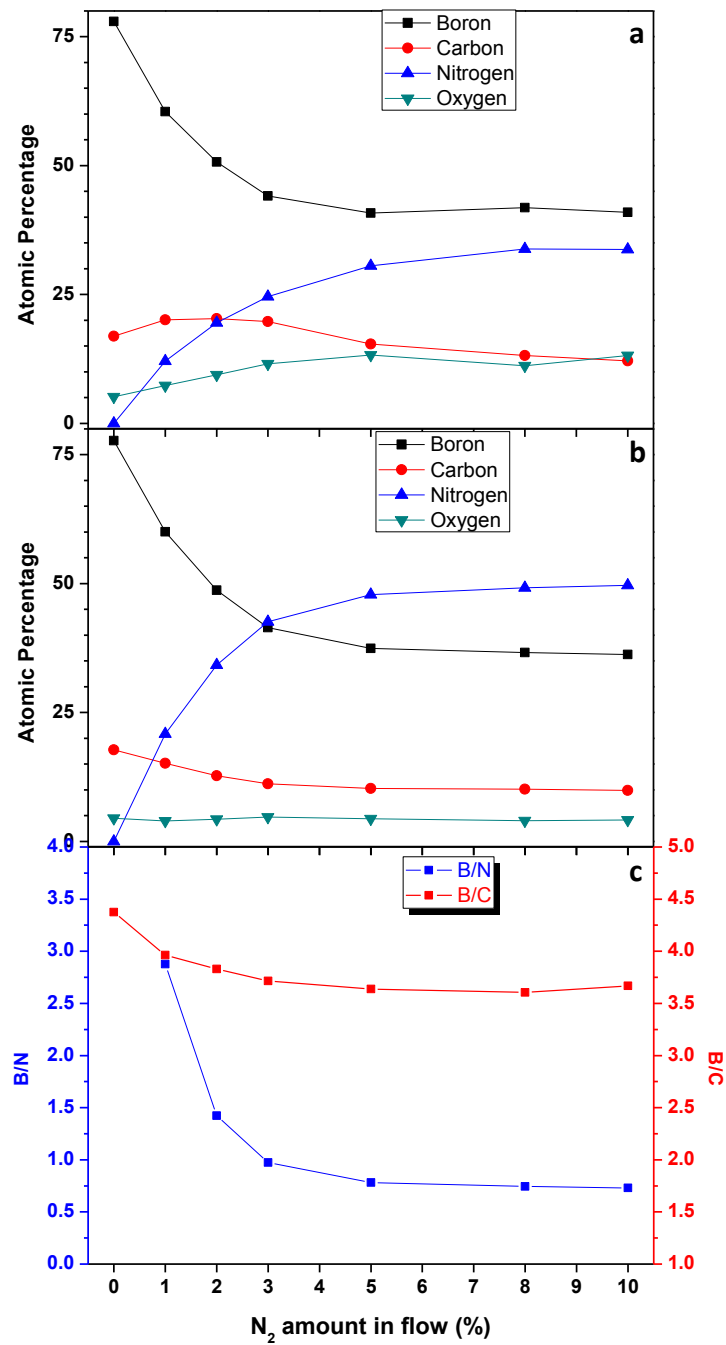


Figure 51: The change in the atomic composition with the increasing in N_2 amount in flowing gas, (a) pre-ion etched data, (b) post-ion etched data, (c) comparison of the atomic ratios obtained from post ion etched surface.

Both pre- and post ion-etching data indicate similar trends in atomic composition with the increase in the percentage of N₂ gas flow. In both graphs, i) boron and carbon contents of the films decrease, ii) nitrogen content of the films increased, iii) for N₂ gas flows reaches 5% and above in the total gas flow during deposition, it was found that the BCN films were saturated with nitrogen atom and the atomic compositions stabilized. The difference in the atomic percentage of carbon and oxygen between the pre- and post -ion etched data suggest that the main contamination on the films were from carbon and oxygen. Hence, the effect of contamination is obvious from C 1s data, as the also indicated from the XPS data of previous series. The atomic ratio between the boron-to-nitrogen and boron-to-carbon atoms, given in Figure 51 (c), indicate that the B:C ratio in the films were relatively stable with the increase in the N₂ flow. On the other hand, the change in the B:N ratio is apparent, and stabilizes above 5% N₂ flow Figure 51 (c).

For chemical environment analysis, shifts in the binding energy of the 1s electrons of the boron, carbon and nitrogen atoms were investigated. Firstly, 1s region of boron atoms in XPS data is analyzed. In Figure 52 (a) and (b) XPS of B1s region are shown with the assigned peak positions in the literature.

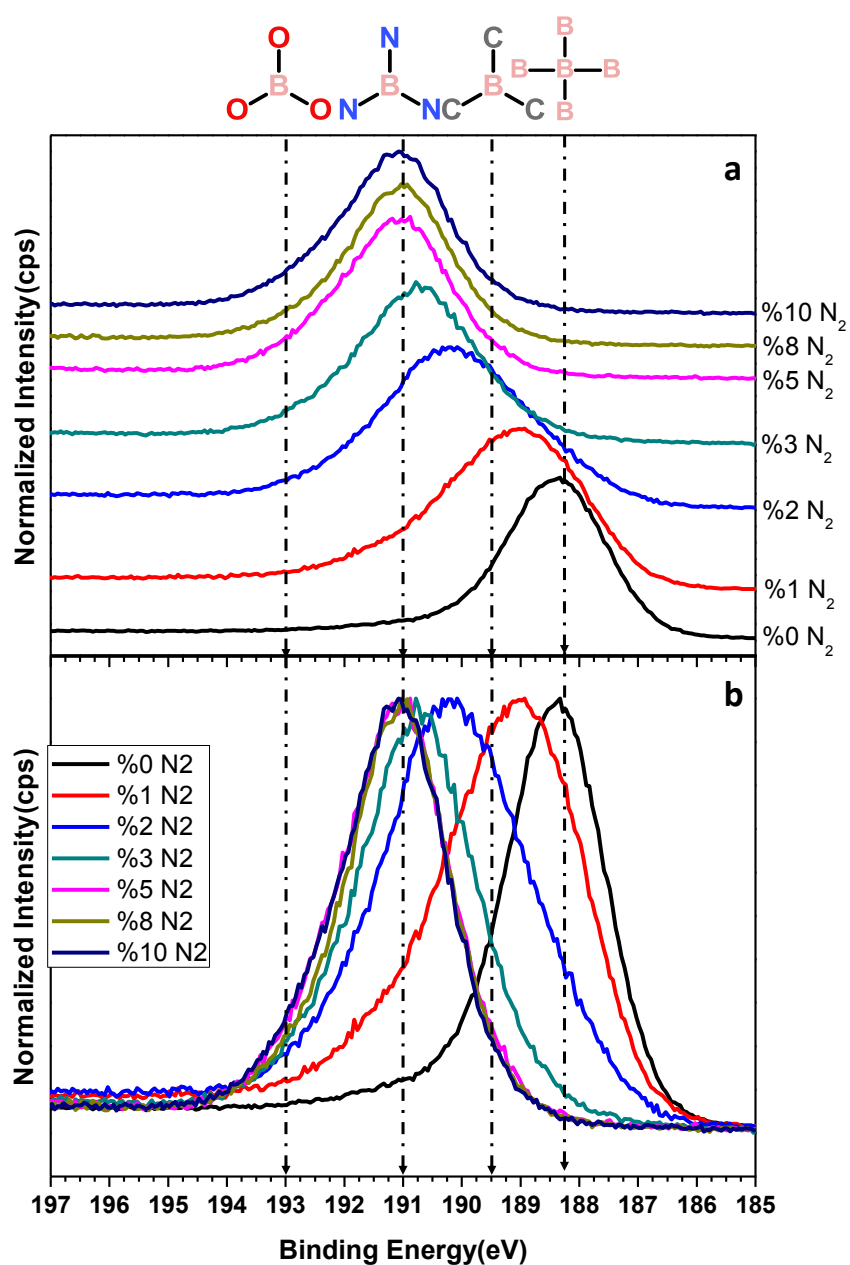


Figure 52: XPS spectra of the B 1s region of BCN films deposited with varying N₂ flow rate in GT series. During depositions substrates were -50 V p-d.c. biased and substrates were located 8 cm away from target surface. (a) Waterfall representation (b) overlap representation.

The XPS data indicates that as the nitrogen concentration increases due to increased N₂ flow, the B 1s peak position shifted from 188.3 eV to 191 eV. The increase in the binding energy of the 1s electrons of an atom is an indication for the change in the chemical environment of B atoms towards more electronegative environment. Hence, nearest neighbors of the boron atoms change from mainly other boron atoms to more electronegative nitrogen atoms until the binding energy of the boron 1s electrons reach the 191 eV, which is B 1s binding energy obtained for the boron atoms in a BN network. The B1s peak in the sample 5 %, 8 % and 10 % N₂ gas flow overlap which means suggests boron atoms existing in a dominant BN environment starting at 5% N₂ gas flow. A similar observation is also encountered for the atomic composition representation in Figure 54 c.

The chemical environment of the nitrogen atoms was also changed with the inclusion of more nitrogen in the films, as shown in Figure 53 (a) and (b) with assigned peak positions using literature values, references were given in Table 3. N 1s peak shifted from 398 eV to 398.4 eV. N 1s binding energy at 398.4 eV matches those for nitrogen atoms in BN network. The counter effect was mentioned for B 1s data. The main N 1s peak position from BCN films deposited with 5% and over N₂ gas flow did not change but a shoulder becomes apparent on the high-energy side. This may imply that the excess N started to bond with C when B reached saturation at around 5 % N₂ gas flow in GT series. Furthermore, this shoulder gains more intensity on the higher binding site of the N 1s as 5%, 8% and 10% is analyzed. This may indicate that as the nitrogen concentration was increased the amount of the nitrogen atoms in the carbon environment increases.

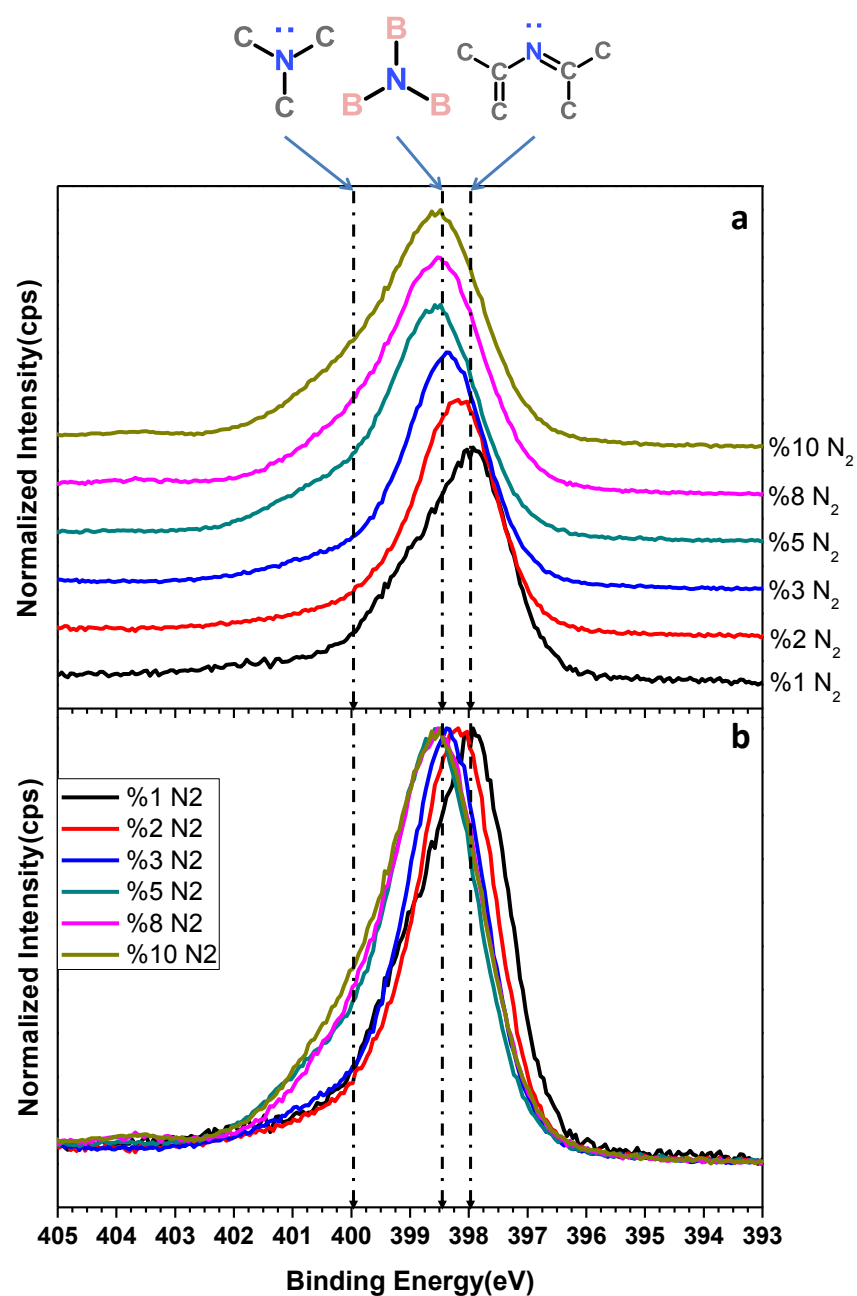


Figure 53: XPS spectra of the N 1s region of BCN films deposited with different N₂ flow rate in GT series. During depositions substrates were -50 V p-d.c. biased and substrates were located 8 cm away from target surface. (a) Waterfall representation, (b) overlap representation

In the Figure 54 (a) and (b), XPS data of the C 1s region of the films deposited in GT series experiments are shown with the assigned peak positions from the literature. The graphs show that as the percentage of N₂ increase in process gas C 1s peak shifted to higher binding energy, in addition, shape of the peak changes and full width at half maximum (FWHM) of the peak increased. The shift in the binding energy is an indication of the change in the coordination of carbon atoms from one environment to more electronegative environment. In GT series, added nitrogen atoms to the BCN films provide an electronegative environment. Hence, the nearest neighbors coordinating to carbon atoms exchanged from boron to nitrogen atoms as the amount of nitrogen was increased.

The XPS data collected from C 1s region from each sample is analyzed separately instead of examination for general review. XPS data of nitrogen free BCN film shows a peak suggesting majority of carbons to be in a boron-rich environment such as ones in B₄C indicated by a C 1s peak around 284.7 eV. The XPS data of 1 % N₂ flow shows two C 1s peaks; first one is from carbon atoms in a boron-rich environment and second one is from carbon atoms in a mainly carbon-rich environment which are also nitrogen coordinated. The XPS data of 2 % and 3 % N₂ flow samples shows similar peak shapes and peak positions as in BCN films deposited with 1 % N₂ flow.

The relative intensities of the two peaks in the C 1s region for BCN films change as the N₂ flow increases. The amount of carbon mainly in carbon environment with nitrogen coordination increases with respect to amount of carbon atom in boron environment as more nitrogen is introduced to the BCN films. On the other hand, the shape of the C 1s peaks from BCN films deposited with 5 % to 10 % N₂ flow are similar to each abut are different from the C 1s peaks of previous samples. The component originating from the carbon atoms in the boron environment vanished gradually. Furthermore, a shoulder on the

higher binding energy side starts appearing with an increasing intensity following the amount of nitrogen in the BCN films. This shoulder component is assigned to C bonded to N with different ratios.

The changes in the C 1s peak of the GT series samples indicate two important points. i) the amount of boron atoms coordinating to carbon atoms decreases due to preference of nitrogen atoms by boron atoms, ii) hence some of the carbon atoms bond with other carbon which are also nitrogen coordinated which is increasing the intensity of the shoulder on higher binding energy region, assigned to C bonded to N with different ratios increase.

As a summary for the XPS data of GT series, the XPS data collected from ion etched surface indicated that the nitrogen content in the film was increased until B:N ratio reached ~ 1 , which means the nitrogen content of the film saturated at 5% N₂ flow. On the other hand, boron and carbon content of the films decreased. However, the B:C ration was not affected from the change in the gas composition in the process chamber. The detailed scans of the regions B 1s and N 1s regions indicated that at 5 % and over N₂ flow, boron and nitrogen atoms in the films preferred each other for bonding. Secondly, the boron atoms were mainly coordinated with nitrogen atoms for all N₂ contents. Nitrogen atoms first preferred boron atoms for bonding establishing a BN network, and then the excess nitrogen bonded to carbon atoms. Finally, C 1s region of XPS data suggests that as the nitrogen content in the film increased the bonding preference of the carbons atom turned from bonding with carbon or boron to bonding with nitrogen.

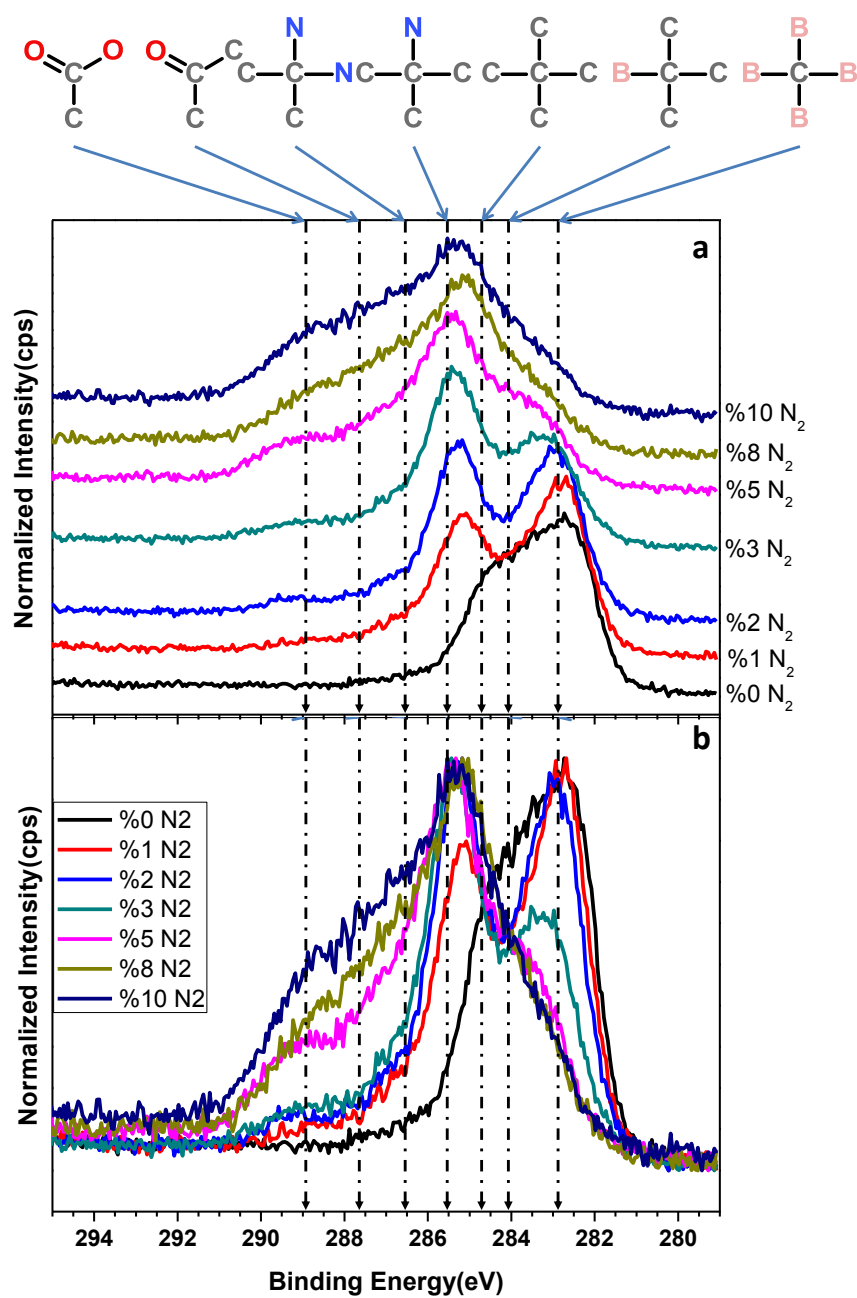


Figure 54: XPS spectra of the C 1s region of BCN films deposited with different N₂ flow rate in GT series. During depositions substrates were -50 V p.d.c. biased and substrates were located 8 cm away from target surface. (a) Waterfall representation, (b) overlap representation.

In addition to XPS data, BCN films deposited in GT series were also characterized using IR spectroscopy. In Figure 55 (a) and (b), the IR data of the BCN films deposited in GT series are given. The IR Spectra of the films gradually change with the increase of the N₂ flow is observed. As the N₂ content increases in the film, the main band in the IR experiences a blue shift which stops 8 % N₂ flow. In the films, with N₂ flow equal and above , bending mode of layered BN structure at about 780 cm⁻¹ becomes apparent. The blue shift in Band II and the formation of Band I indicate that a layered and ordered structure started appearing in the BCN films deposited with N₂ flow exceeds 3 % in progress gas. The assigned bands in conjunction with XPS data suggest that as the nitrogen amount in the films were increased the bonding preference found in the BCN film turn from B-B and/or B-C to B-N double bonding, and furthermore a layered structure is appearing.

Raman spectroscopy technique was also used for the characterization of the BCN films deposited in GT series. First of all, as a reminder, the Raman scattering efficiency of C-C bonds are significantly stronger than the Raman scattering efficiency of other possible combinations of bonds in BCN films. Thus, using this property an analysis of the C-C bonding in BCN films will be provided. More information on Raman scattering is provided in Chapter 1.2.2.

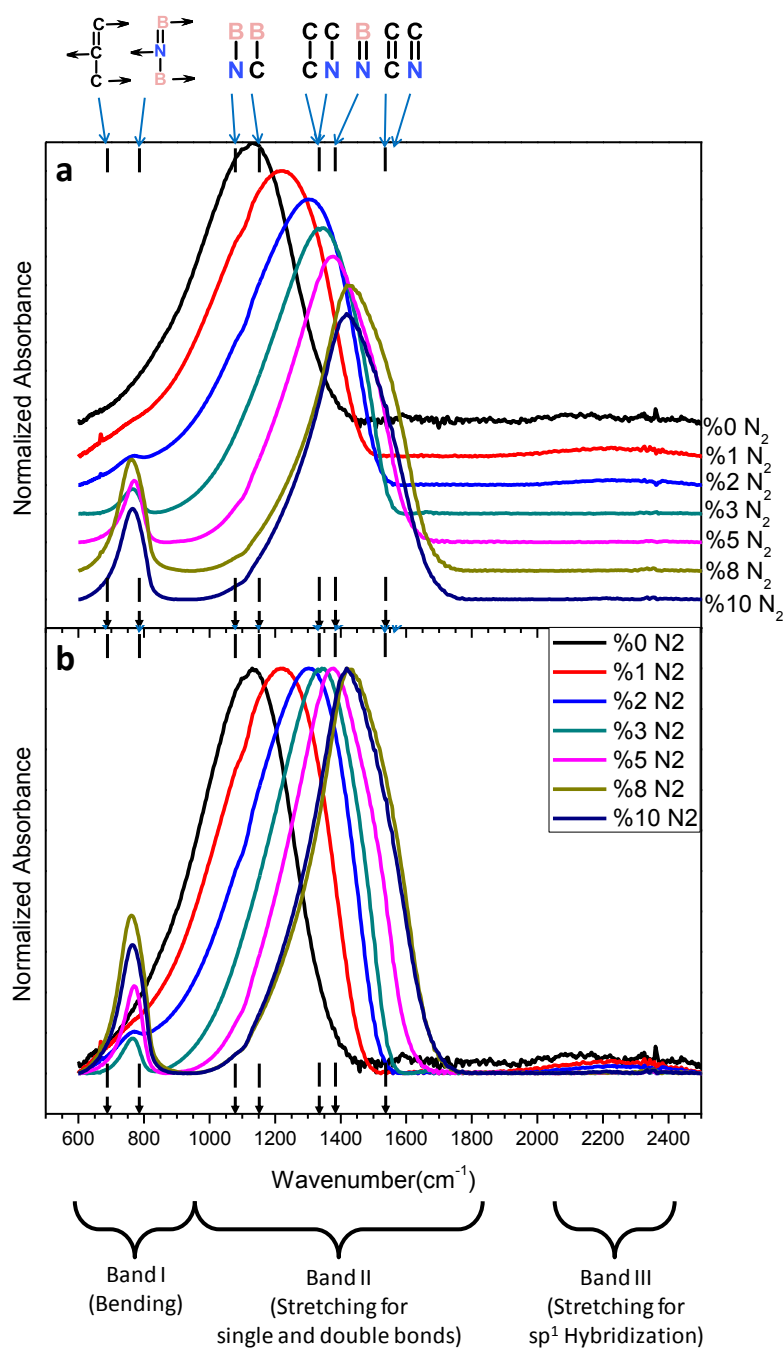


Figure 55: IR spectra of the BCN films deposited with different N_2 flow rate in GT series. During depositions substrates were -50 V p-d.c. biased and substrates were located 8 cm away from target surface, (a) waterfall representation, (b) overlap representation.

In Figure 56 normalized Raman spectra from BCN thin films in GT series are given. The data in Figure 56 is analyzed in two groups as shown in Figure 57 (a) and (b). In Figure 57 (a), the Raman spectra of the GT series is presented in comparison with Raman scattering spectrum from bulk B₄C as a reference. Bulk B₄C has a well-known Raman spectrum. In Figure 57 (a), no Raman peaks are observed in the Raman spectra for BCN films deposited with 0%, 1%, and 2% N₂ flows. Also, nearly no features are present for these spectra. On the other hand, a wide band between 1000 cm⁻¹ and 1600 cm⁻¹ is observed for the Raman spectra of the BCN thin film deposited with 3% N₂ flow.

In Figure 57 (b), the thickness of the BCN films were close to each other, as the deposition times were kept constant. Nevertheless, the intensity change in the Raman scattering of the well-known Si peak from the Si (100) substrate, at 521 cm⁻¹ shown, suggests that the optical transparency of BCN films increases with the amount of added nitrogen for the wavelength of the laser used. For a better review, the normalized Raman spectra from the BCN films shown in are given in Figure 58 with assigned peak positions in literature. As mentioned before in Chapter 1.2.2, the Raman scattering ability of the C-C double bond is dominant over the other possible bonding combinations in the BCN films. The observed peak in the Raman spectrum of the BCN films deposited with 5 %, 8 % and 10 % N₂ flow indicates a wide band over the region where well known D and G band of carbonaceous materials are observed. There is a large literature about the relation between atomic structure of carbonaceous materials and the position and the relative intensity about the D and G peaks in Raman spectra from these materials. Thus, the observation from the earlier XPS data suggesting formation of carbon rich domains together with the formation of a band in the D and G peak region for BCN films with increasing nitrogen support each other. Hence, the Raman spectra is confirming the formation of carbon rich domains or “islands of carbon networks” in the BCN films as the nitrogen content of the films are increasing. Therefore, it can be concluded that carbon atoms start to

agglomerate and precipitate hexagonal carbon networks in a predominantly hexagonal BN network which is also heralded by the gaining strength of the Band I in IR spectra. In conclusion, both XPS and IR, and now Raman data provide a strong evidence for the phase segregation in BCN thin films due to increased nitrogen content.

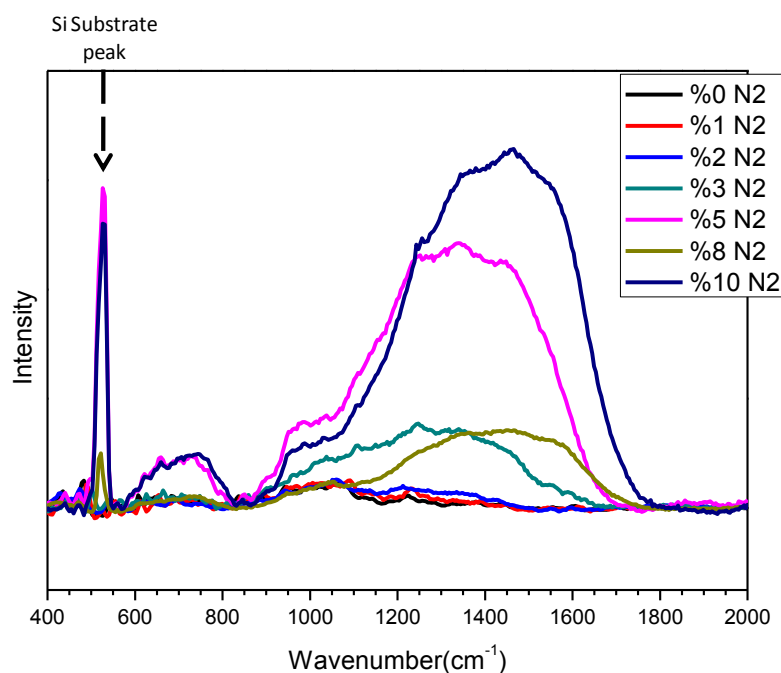


Figure 56: Raman spectra of the BCN films deposited with different N₂ flow rate in GT series. During depositions, substrates were biased using -50 V p-d.c. and they were located 8 cm away from target surface raw data.

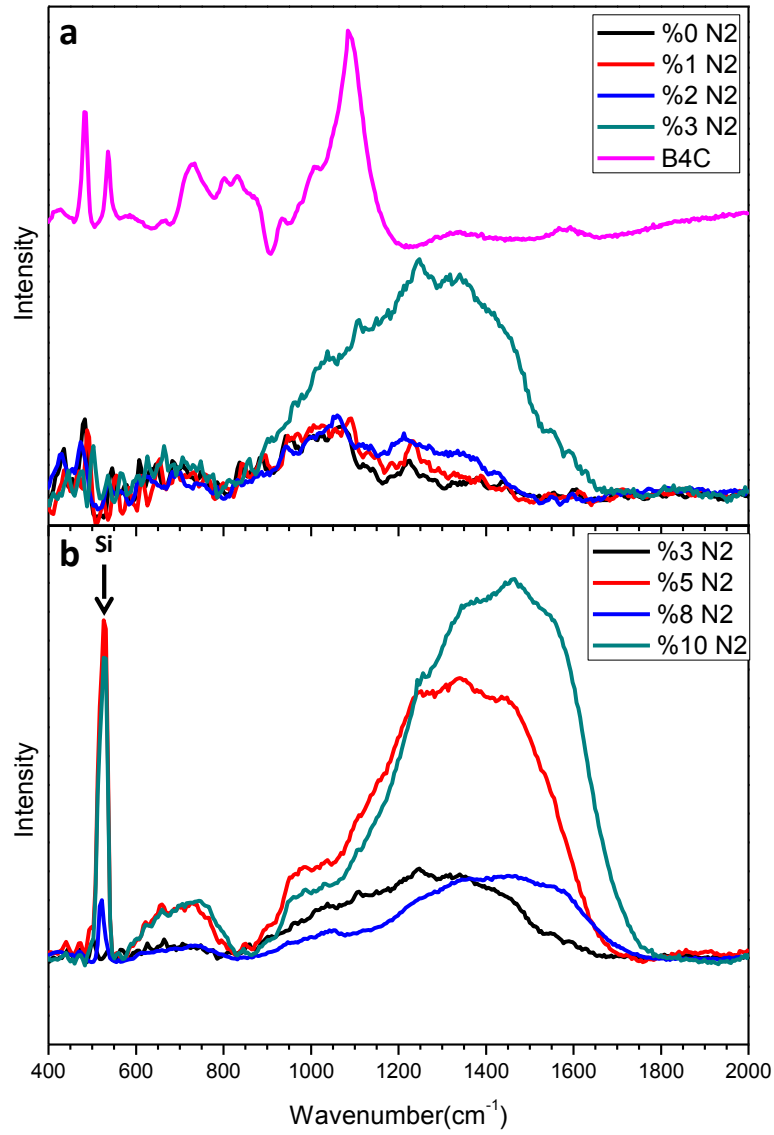


Figure 57: Raman spectra of the BCN films deposited with N₂ flows up to 3% in GT series in comparison with bulk B₄C spectrum are shown in (a). Raw Raman spectra of the BCN films deposited with N₂ flows 3% and above in GT series are given in (b) with increasing intensity in the 1000-1600cm⁻¹ region.

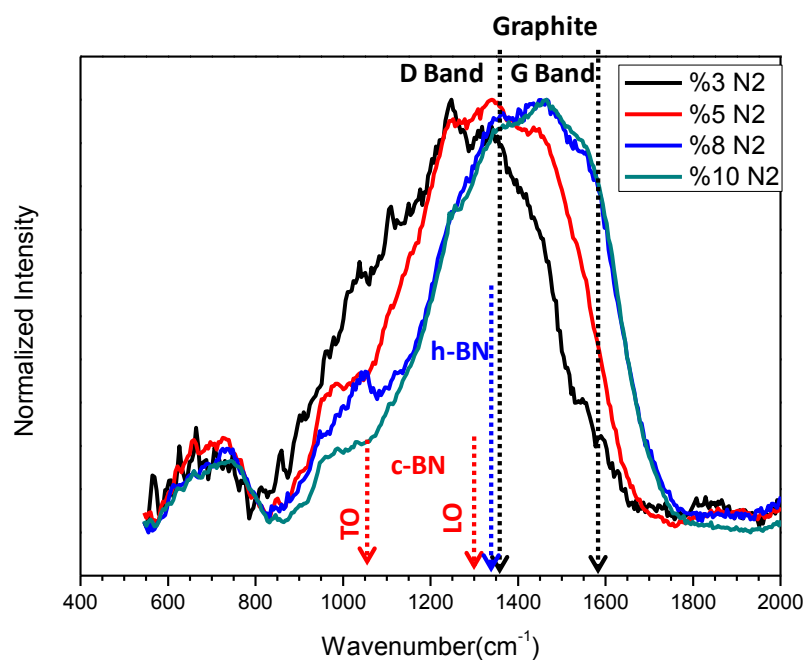


Figure 58: Raman spectra of the BCN films deposited with different N_2 flow rate in GT series. During depositions, substrates were biased using -50 V p-d.c. and they were located 8 cm away from target surface; assigned peak positions for the D and G peak positions for carbon-based materials and c-BN and h-BN are shown.

GK series

In this series of experiments, BCN films were deposited on grounded substrates located 18 cm away from target surface. In other words, for this particular series films were deposited under conditions favoring kinetic limitations. The IR spectra of the BCN films deposited in GK series are shown in Figure 59 (a) and (b). Overall, the IR spectra of the films in GK series are similar to those in GT series; as the N_2 flows during depositions are increased the IR spectra displays a gradual change. The major change is observed to be the blue shift in Band II until 8% N_2 flow as shown in Figure 59 (a) and (b). Another change observed is

the formation of the bending band for h-BN, Band I, around 780 cm^{-1} as the N_2 flow exceeded 3%. The blue shift in Band II and the formation of the Band I indicate that a layered and ordered structure in the BCN film starts dominating the overall microstructure. In terms of chemistry in the films, assigned peak positions listed in literature, references were given in Table 1, suggest that as the nitrogen amount in the films were increased the bonding preference of the films turn from B-B or B-C to B-N double bonding.

In the following section, a comparison of the IR spectra from GT and GK series will be presented. In the earlier sections of this chapter, in B and D series, it was shown that the atomic compositions of the BCN films were not affected by the change in bias and/or substrate-to-target distances. Therefore, the atomic composition of the films in GT and GK series are assumed to be the same. Hence, in Figure 60 (a)-(g) IR spectrum from BCN films deposited using the same N_2 flow but with different substrate-to-target distances are shown.

The IR spectra comparisons shows that as the amount of nitrogen atoms increase, the differences between the IR spectrum of the corresponding GT series films and GK series films are getting more apparent. In the low N_2 flow region, 0 %, 1 % and 2 % N_2 flows, the overlap between the spectra are remarkable. This indicates that the films have a very similar chemistry and microstructure. Above 3% N_2 flow, Band I formation observed for the GT series is getting more prominent indicating the formation of the layered structure. However, for the GK series Band I stays relatively underdeveloped. On the other hand, there is also a shift in the Band II between the corresponding films in GK and GT series which becomes significant above 3% N_2 flow concurrent with the formation of Band I, as well. These two observations demonstrate the fact that the effect of bias and substrate-to-target distance becomes only significant after the N_2 flow exceeds 3%. It can be said that before a certain amount of nitrogen in the films, the structure of the films are

rather disordered. In this regime, by itself the non-thermal energy component could not trigger any ordering and phase segregation in the films. Therefore, it can be said that phase-segregation is also related to chemistry also. Beyond, this critical chemistry, excess ion-bombardment and nitrogen activates the formation of a layered BN network, which is evident from the Band I formation. Yet, in the GK films the extend of this ordering remains limited even at 10% N₂ flow. In conclusion, nitrogen content seems to be a key factor initially in the BCN films for the onset of ordering, and thus, ordering then becomes a driving factor for the phase segregation.

In conclusion, BCN films in G series were deposited with different N₂ flows for each deposition experiment in order to probe the effect of chemistry on the final structure. The vibrational spectroscopy techniques (IR and Raman) and XPS were combined for the examination of the films. The nitrogen content of the BCN system that reactive deposited from r.f. sputtered B₄C target were nitrogen saturated when the N₂ flow exceeded 3%. The results also indicated that, boron atoms preferred for bonding to nitrogen atoms, whereas nitrogen atoms bonded to carbon atoms only after saturating boron atoms. Carbon atoms were found to prefer carbon atoms unless there are boron atoms which are not bonded to nitrogen. As the nitrogen amount is in the films increased, the dominant BN bonding induces the formation of large BN networks that in turn results in the formation of a layered microstructure.

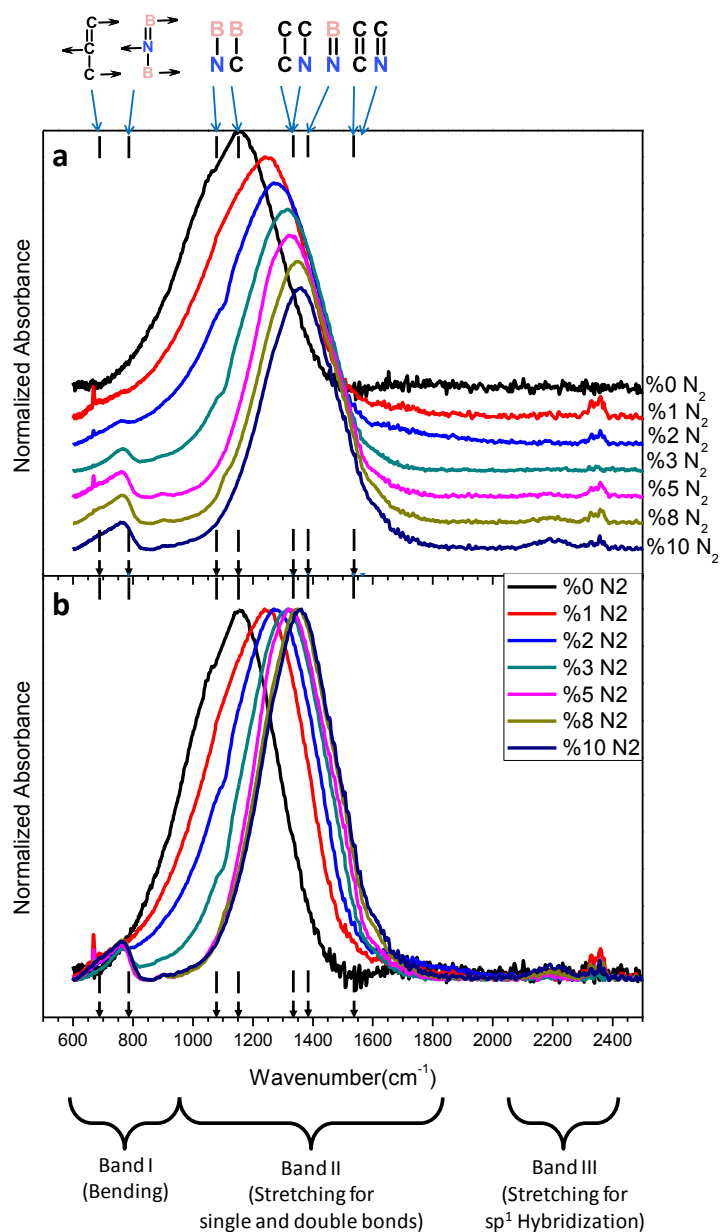


Figure 59: IR spectra of the BCN films deposited with different N_2 flow rate in GK series. During depositions substrates were grounded and substrates were located 18 cm away from target surface, (a) waterfall representation, (b) overlap representation, focused and normalized

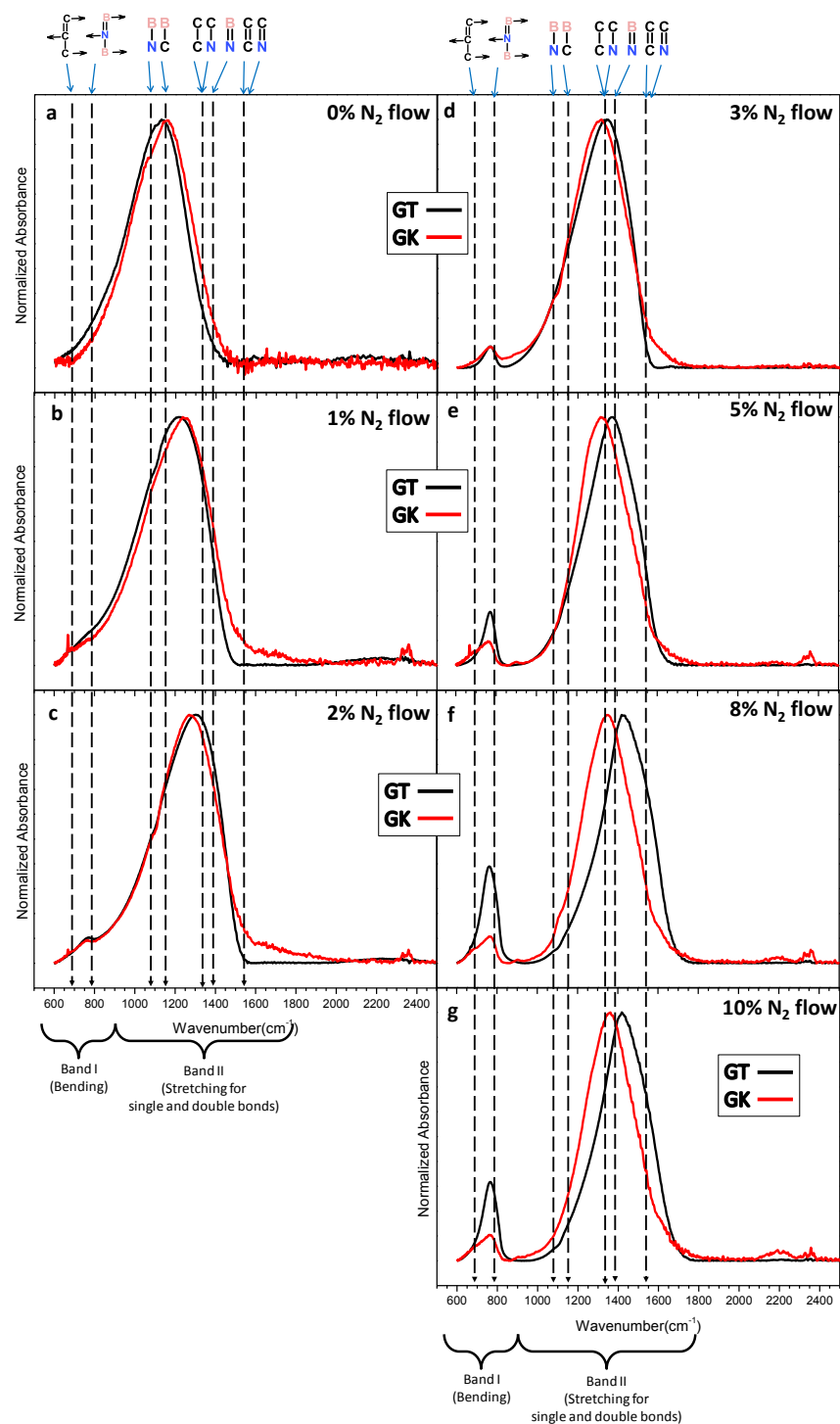


Figure 60: Comparison of the IR data of the BCN films between GK (8 cm) and GT (18 cm) series for corresponding N₂ flows; (a) % 0, (b) % 1, (c) % 2, (d) % 3, (e) % 5, (f) % 8, (g) % 10 N₂ flow rate.

4. CONCLUSION

In this thesis, the effect of deposition parameters on the atomic structure and chemical environment of the atoms in the BCN thin films were investigated. In order to achieve this aim, several sets of BCN films were synthesized using carefully considered combinations of process parameters to drive the synthesis into two extremes region where in one thermodynamic constraint prevail, and in the other kinetics dominate.

First, the changes in the atomic structure of the BCN films in these two regimes are investigated. Ion-bombardment is a well-known process variable capable of providing non-thermal activation energy for mechanisms favoring thermodynamics. The amount of energy supplied to the substrate by ion bombardment was controlled by the type of biasing applied, magnitude of the bias on the substrate and the ion flux. Hence, the effect of energy provided to the growing film during the deposition procedure was investigated thoroughly using HR-TEM, EELS, XPS, IR and Raman spectroscopy. The results of investigations showed that as the amount of energy provided to the system increased, an order is induced in the films through the re-structuring of the atomic configuration forming a layered organization where layers grow perpendicular to substrate surface. Within the layers, atoms were dominantly sp^2 hybridized. The overall atomic structure of the films could be called turbostratic, which has been observed for BN and DLC type films. Depending on the amount of energy, sp^3 and sp type atoms were also observed, however declining in abundance as the energy is increased. In conclusion, in the parameter ranges used in this work increasing the amount of non-thermal energy (increasing the bias and decreasing substrate-to-target distance) caused the formation of turbostratic-BCN films. In the case of films grown on

substrates, which were placed significantly far away from energetic ion-flux, due to the limitation of the kinetics (i.e. surface diffusion of adatoms) the BCN film, structures were disordered and amorphous.

Competition between the thermodynamics and kinetics due to non-thermal energy provided to growing films had also implications on the chemistry of the BCN films. Although, spectroscopic analysis clearly indicated strong evidence for a phase-segregation between B-N (majority) and C-C or C-N (minority) domains, thermodynamic and kinetics determines whether the minority domain will be consisting of C-C or C-N based pairs. Under conditions favoring kinetic limitations, XPS and IR data strongly suggests a segregation behavior where separate disordered B-N rich and C-N rich domains exist in BCN films. On the other hand, upon the increase in the average ion-energy or flux phase segregation is observed. Well-ordered h-BN and graphitic C regions are observed. Hence, in this work evidence suggesting fully hybridized BCN structures were not encountered.

Secondly, the data presented regarding the ion-bombardment effect also indicated that not only the ion-flux, related to substrate-to-target distance, but also the average ion-energy, controlled by substrate bias, were equally important in defining the regime for the synthesis of BCN film. Furthermore, depending on the conductivity of the growing film type of bias applied were shown to have an importance. It was demonstrated that pulsed-d.c. and r.f. biasing were more effective for conductivity-limited cases, where charge gathered on the growing BCN film was easily leaked due to periodic reversal of the polarity. Excessive charge accumulation on the film due to ion-bombardment could easily diminish the number and average energy of ions reaching the film surface, and thus will shift the growth conditions toward a kinetically limited regime.

Another factor investigated in this regard is the effect of N_2 flow in the synthesis environment. As the N_2 amount in the process gas increased during r.f. sputtering of the B_4C target, it was observed that nitrogen atoms incorporating to the growing BCN film preferred bonding to boron atoms. Both the XPS and IR spectroscopy results showed that only after near saturation of boron atoms, an evidence for carbon-nitrogen bonding was observed. However, as mentioned above depending on the non-thermal energy either C-C or C-N pairs were observed only under nitrogen rich growth conditions. In contrast, carbon atoms were found to be markedly different in the sense that regardless of the bias or substrate distance, in nitrogen deficient growth regime carbon atoms have no tendency to make C-C pair domains in the BC_x film that is sputter deposited from a B_4C . This means, the carbon atoms prefer boron atoms for bonding until the B:C ratio is ~ 4 . If the B:C ratio is lower than four, carbon atoms prefer to carbon atoms for bonding because of excess carbons atoms. Possible bonding between carbon and nitrogen was found to depend on the effective growth mechanisms as mentioned before. Furthermore, it is also shown that infrared spectroscopy to be a very powerful tool in the indirect characterization of atomic structure and also indirect identification of bonding chemistry BCN films.

Finally, the data and its analysis presented in this work lay down a framework for the control of structure and chemistry of BCN films for future studies dealing with the development of materials with controllable optical and electrical band gap. These materials can be used for various optical and electrical applications such as sensors. Especially, such materials can carry significant potential for the engineering of the band gap for graphene based field-effect transistors.

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APPENDIX

A.1 Thin Film Technology

The scope of the thesis was to understand the chemical environment of the atoms and the atomic structure of BCN thin films. For this, some elementary information regarding thin film deposition techniques will be provided in the following sections. There are numerous books and other reference materials and interested readers can easily find them through library or even over internet.¹⁻⁵

Thin films are a thin layer of materials that are coated on the surfaces of bulk materials. Properties that cannot be attained or hard to obtain by a bulk material can be imparted to the surfaces the material with the application of a suitable thin film on the bulk material in question. In addition, in some cases, it is easier or cheaper to synthesize thin films rather than processing the bulk material to attain required properties. Briefly, owing to its numerous advantages, in science and technology the importance of thin film deposition technology ever increases with time.

A.2 Physical Vapor Deposition (PVD)

In PVD techniques, the thin films are deposited from the vapors of the materials. For example metals can be evaporated thermally, refractory materials are generally evaporated using e-beam evaporation, or sometimes glow discharge plasma sputtering is employed as well. As the scope of the thesis covers mainly sputtering, the emphasis will be kept on sputter deposition.

A.2.1 Plasma

Plasma is the partially ionized gas medium. Degree of ionization in the plasmas, which is of interest to us, is $\sim 10^{-5}$, so the mentioned medium consists of mainly neutrals. Although the coulomb interaction between the charged particles is strong and long range, these charged particles move around like free particles.

On the other hand, as the ionized particles will eventually be annihilated via association reactions or adsorbed on surfaces of the chamber over time, population of ions and free electrons will decrease and plasma will quickly extinguish. Hence, ions and electrons must be constantly generated to sustain a plasma. New ion-electron pair generation can be achieved with an applied external electric field. In an electric field, negatively charged particles are directed towards to the positive side, on the other hand, positively charged particles directed towards to negative side. On their way, charged particles moving in an electrical field gain speed thus increase their kinetic energy. Fast moving, energized charged particles also have a non-zero probability for colliding with neutral gas atoms or molecules which make-up the majority of atoms in the medium. During these collisions, new ion-electron pairs can be generated through dissociative reactions will occur. So, plasma is actually a non-equilibrium phase, where the energy of the electrons and ions are greatly differing than the “colder” neutral and excited species. In order to sustain plasma, the rate of generation of new ion-electron pairs should be equal to the loss rate. There are several ways of inducing an electrical field to sustain plasmas. In the following sections, these are covered briefly.

Direct Current (d.c.) Plasma

In this type of plasma, the applied electric field poles are essentially the cathode and the anode of a simple system. In Figure A-1 schematic representation is shown with the potential change in the chamber.

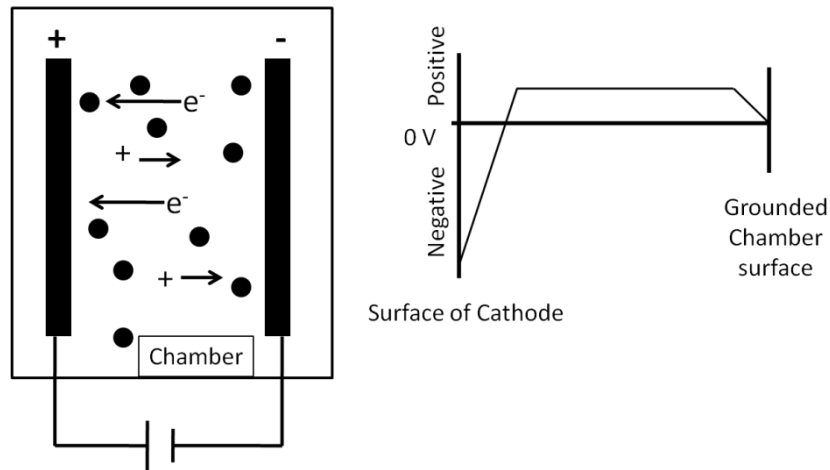


Figure A-1: Schematic representation of a dc plasma system and the voltage distribution between the cathode and anode.

Pulse- d.c. Plasma

In this type of plasma, the applied electrical field on the cathode and anode is not continuous but it is varying over time; pulsed. A sample for the applied voltage differential between the anode and the cathode versus time is shown in the Figure A-2 (a). This kind of pulsation of the electrical field can be used on the insulating cathode and anode materials in order to overcome charge accumulation problem. A reverse bias can be applied to poles to obtain better results again the charge accumulation problem. A sample voltage vs. time graph for a bipolar-pulsed d.c. cathode is shown in Figure A-2 (b).

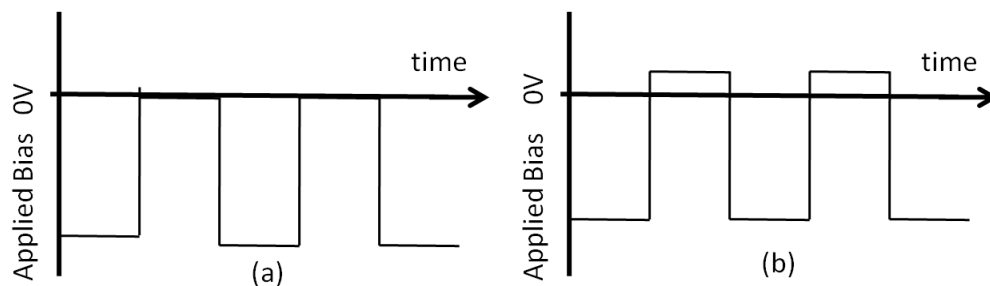


Figure A-2: Sample time vs. applied bias graph (a) pulsed dc and (b) bipolar-pulsed dc

Radio Frequency (r.f) Plasma

Here, a cyclic voltage variation, which has a cycle frequency at or multiples of 13.56 MHz, is applied to the cathode and/or anode. This number is not a magic number or has any special scientific reason behind it. 13.56 MHz is selected, because this frequency or harmonics of this frequency are out of the common radio or mass communication frequencies. Therefore, these devices do not interfere with the communication systems.

In a plasma/glow discharge, most of the negative charge carriers are electrons, and positive charge carriers are ions. The mass difference between ions and electrons are significant. The mass of an ion is $\sim 10^4$ times larger than that of an electron. Hence, under the influence of an electric field because of the mass difference, the electrons will be moving faster than the ions. When the electric field changes direction due to polarity change in the applied bias, electrons can easily react to the change in the direction of the electrical field. On the other hand, because of their relatively larger mass, ions cannot accelerate or decelerate that quickly. Before a polarity change can occur on an electrode, electrons can quickly reach the surface of the electrode, and cause a buildup of negative charge on it. Hence, due to this accumulation, an electrode even a dielectric one can assume a permanent negative charge on itself. In Figure A-3 schematic representation of r.f. bias vs. Time graph on an r.f. powered cathode (a) just at the start of biasing and (b) after equilibrium reached can be seen.

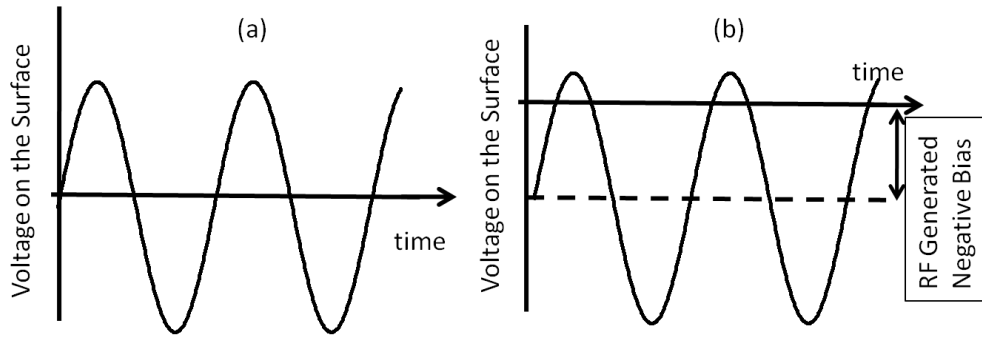


Figure A-3: Applied r.f. bias on the cathode; (a) the negative electron accumulation with time and affect of that accumulation, generated negative bias (b)

A.2.2 Particles- Surface Interaction and Sputtering

Due to the as mentioned mass difference between an electron and an ion, ion-surface interactions and electron-surface interactions display different characteristics. For a binary elastic collision, using the principles of conservation of momentum and energy, one can easily obtain the amount of kinetic energy transferred (T_m) from initial energized particle to the target particle by using following equation:

$$T_M = \frac{4m_i m_t}{(m_i + m_t)^2} E_i \quad (1)$$

In equation (1) m_i is mass of the impinging particle and m_t is the mass of the target particle and E_i is the initial kinetic energy of the impinging particle. From this equation one can see that if the mass of the colliding particles are close to each others, the energy transfer is much more effective. For example, if an electron ($m_e = 9.1 \times 10^{-31}$ kg) hit a Fe atom ($m_{Fe} = 9.3 \times 10^{-26}$ kg) with initial energy of 10keV then T_m is 0.38 eV, this much of energy can only heat up the Fe atom, not able to change its position. On the other hand, if the mass of the impinging

particles within the range of double of each other, the T_m is about $0.9 E_i$. Thus, ions with small energy can change the position of the target material, in other words, ions with few energy has a significant effect on the target material. On the other hand, electrons can only heat up the sample.

This efficient energy transfer of impinged particle is the main reason that ion bombardment usage in the science. If the m_i is close to m_t , an particle with few eV E_i can move a target atom on the surface or can move the surface atom into the bulk or can remove an atom from the surface to vapor phase. In Figure A-4, the possible effects of impinging ions on the target are shown. The impinged ion has different effect on the target material with respect to initial energy. The effect of ion on the target material can be analyzed in two parts:

Surface Effect

If the impacted ion has small energy, a few eV to a few thousand eV, the surface of the target material mainly affected from that energy conversion by fallowing ways:

- the impact of the ion will ionized the target material so the material will eject electron, is called secondary electron. [FigureA-4 (a)]
- some structural rearrangement can be occur on the surface; (i) ad-atom creation [Figure A-4 (b)], (ii) removal of the ad-atom deep inside the bulk [Figure A-4 (c)] (iii) mobility enhancement of the ad-atoms through the surface, surface diffusion [Figure A-4 (d)],
- removal of the atoms to the vapor phase, sputtering [Figure A-4 (e)]
- if the impacted ions are molecular reactive molecules they will dissociate or adsorbed molecules will dissociated with the collision of another ion, reactive magnetron sputtering (RMS).[Figure A-4 (f) and (g)]

Sub-Surface Effects

If particle energy exceed over a few tens of eV, the ions start to penetrate into the bulk. The ion bombardment has variety of influence over the sub surface of the target material. These influences are either beneficial or damages the bulk structure. These effects can be list as follows:

- a surface atom will take that energy to penetrate deep inside the bulk and this will create; (i) Frenkel-pair creation [Figure A-4 (h)], (ii) defects in crystal structure, (iii) ion mixing
- the kinetic energy of the ions will so high that the ion can penetrate deep inside the bulk structure before it loses kinetic energy with sequent collision, ion implantation [Figure A-4 (i)]
- escape of atoms to the gas phase, sputtering.

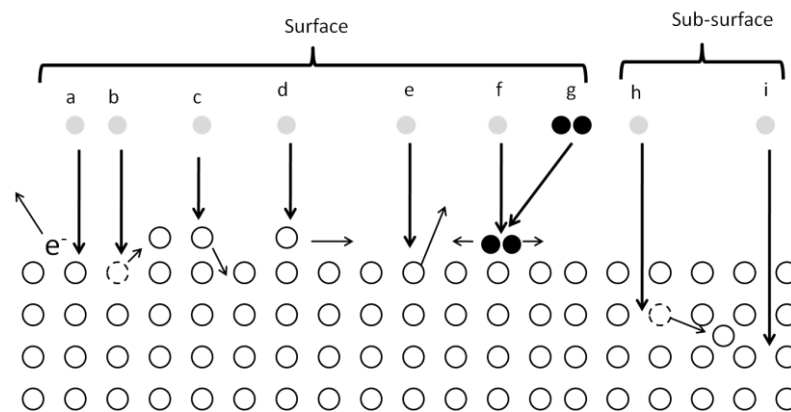


Figure A-4: Schematic representation ion bombardment effect on the surface and subsurface

However, a small portion of the energy was transferred for displacement of the atoms or sputtering process, most of the energy was transferred to vibrational motion in atoms those are not displaced their initial lattice point. This vibrational energy turns into the heat and propagate into the bulk as phonons.

In summary, to vaporized particles with glow discharge/plasma first a plasma must be generated and sustained with different methods and then the generated energetic, positively charged ions are impacted to surface of the target material and beside the other process some of the atoms removed from the target material.

A.2.3 Thin Film Growth and Deposition

Deposition process is important part of the thin film technology most of the properties, like hardness, conductivity, topology, crystallinity can be controlled in that step. Because this part of the thin film production processes affect the atomic structure of the deposited material.

Deposition process consists of 5 subsequent process:

- (i) First atoms that evaporate from target material and arriving the substrate adsorbed on the surface of the substrate
- (ii) Movement of the atom or molecule on the surface of the substrate, surface diffusion of the particles
- (iii) Reaction of the adsorbed material between each other and substrate material
- (iv) Early agglomeration of film materials, nucleation,
- (v) The bulk film structure grow.

Adsorption

When the atomized target material or gas molecule approached the surface of the substrate, they attracted to the surface because of van der Waals force or London dispersion forces. These weakly adsorbed states are known as

physisorption. Due to these weak bonds, physisorbed atoms or molecules are mobile on the surface so they can diffuse easily on the substrate surface.

Surface diffusion

Mobility of the adsorbed species on the substrate surface is very important on the film structure. The reason is that this diffusion allows atoms or molecules, to find thermodynamically more stable sites, to find most active sites or to find each other. Mathematically surface diffusion can be calculated by using the following equation.

$$R_s = n_s v_{os} e^{-E_s/RT} \quad (4)$$

In equation (2), the R_s value is the surface diffusion of the adsorbate, n_s is concentration of the atoms or molecules on the adsorption sides, v_{os} is the vibrational frequency of adsorbate on the surface, and finally E_s is the activation energy for surface movement, the energy barrier to overcome for moving one active side to other one. From the equation, one can see that all of the variables, which affect the surface diffusion except temperature, is constant and depends on adsorbate and substrate properties, one can increase or decrease the surface diffusion of the adsorbate by only change substrate temperature or energy of the ad-atoms.

The relation between surface temperature and surface diffusion was drawn in Figure A-5. Graph shows that up to some extend the surface diffusion of the molecules or atoms increase with substrate temperature. Further increase in the substrate temperature will cause desorption of weakly bounded molecules or atoms.

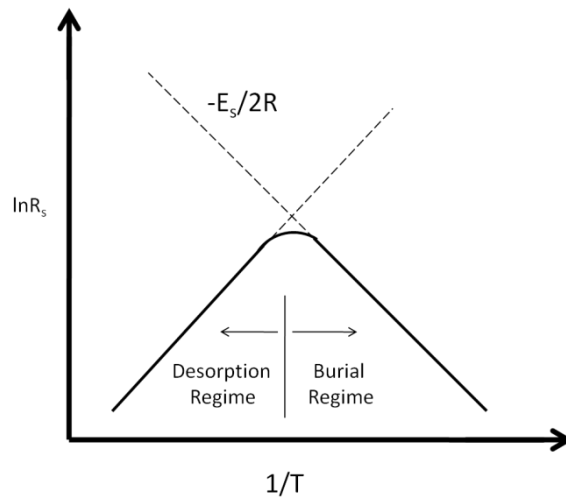


Figure A-5: Behaviors of surface diffusion rate with substrate T

Chemisorptions and Reactive Sputtering

In that step of the deposition the physisorbed species will undergo further and stronger interaction with the substrate and a chemical bonds start to established with substrate or the other atoms which are also adsorbed on the substrate's surface. Chemical bonds' potential well is much deeper than the physical interactions potential well, so the mobility of the adsorbed species stops.

In addition to these, if the sputtering gas contains a non-noble gas, this step of deposition is important very important. Because the inclusion of reactive atoms into the deposited film is take place in this step. If non-noble gas molecules exist in the process gas this kind of process is called reactive sputtering. It is obvious that this kind of sputtering open a wide range of deposition compounds from simple targets.

Nucleation

Further step in deposition process is nucleation. When the number of the adsorbed species reaches the number of possible side on substrate surface, there are two possibilities it will cover the surface with a mono layer adsorbed molecule or it will start to make island on the surface with 2 or more layered structure. Competition between surface energy (γ) of possible surface and interfaces will determine path.

By definition, surface energy (γ) is the needed energy per area to create new surface or interface. If the diffusion rate is enough and diffusion length is much longer than the active side of the substrate, minimum energy gain phenomena determine the nucleation type during new surface formation.

Three models are developed about this phenomena and their schematic representation is shown in the Figure A-6. First model is Frank- van der Merwe model in that growth the surface energy of the film (γ_f), surface energy of the substrate (γ_s) and surface energy of the interface between film and substrate (γ_i) has a relationship as fallowing equation.

$$\gamma_f + \gamma_i < \gamma_s \quad (5)$$

This equation indicates that if the sum of the energy gain of the new film surface and creation of new interface between deposited atoms on substrate is less than the energy gain for substrate surface energy, system tends to wet the surface until the surface is fully occupied with adsorbed species. In this model, there are strong bonds between the film and substrate so the interface surface energy became smaller. In Figure A-6 (a), schematic representation of model was shown.

In the second model the interface surface energy is not so small or

$$\gamma_i = \gamma_f + \gamma_s \quad (6)$$

This equality means that there is no interaction between the substrate and film. So to decrease the energy gain, system tends to decrease surface area so instead of wetting the surface the species that build up the film agglomerate in some part of the substrate surface and make islands this model is called Volmer-Weber model, Figure A-6 (b).

Actually third model is discussed one step further it is about development of bulk film. Third model, Stranski-Krasktanov model, is related with the second or above layers of the deposited film. After fully coverage of substrate surface the situation is changed, the interaction between atoms, compose the film, start to control growing path, so to decrease the surface energy, island of film atoms seed on the layer of the film covered surface. The schematic representation of Stranski-Krasktanov model is shown in the Figure A-6 (c). However, with this step development of bulk film structure starts and discussed as another part.

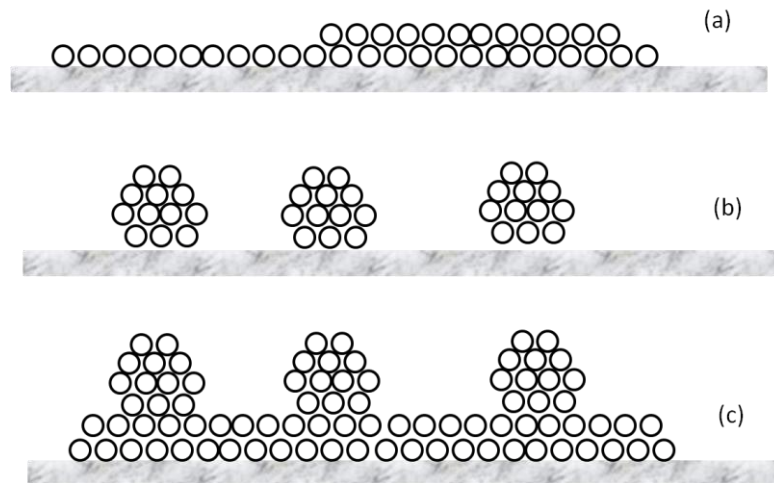


Figure A-6: Schematic representation of nucleation models (a) Frank- van der Merwe (b) Volmer-Weber (c) Stranski-Krasktanov

These models depend on the assumption that substrate temperature is high enough that diffusion rate of the atoms and species are high that they can move long distance on substrate surface until they find thermodynamically stable sites. If the energy of the species not enough which causes to stick adsorbed species on a place where they landed or near to landed place. In that case, kinetic limitations determine nucleation procedure.

Structure Development

After nucleation step, the substrate surface covered with the film, development of bulk structure of the film starts. The main basis that influences the bulk structure of the film is thermal mobility of the atoms on the surface. Therefore, the comparison between the substrate temperature (T_s) and melting temperature of the film material (T_m) will give us a clue about the structure of the film.

If T_s approaches to T_m , by additional energy supply to the growth surface, the atoms would have enough energy for diffusion on the surface so they can find a sitting point where their energy is minimized. In this condition, the film growth on the nucleation sides, no new nucleation sides will be created so the microstructure of the film shows bigger, stress free grains. Therefore, thermodynamical preferences dominate the film growth mechanism.

If T_s far lower than T_m the atoms landed to film surface does not have enough thermal energy to be mobile, most of the case they stay the place where they landed. Under those circumstances, kinetic limitations determine the structure of the bulk by controlling the film growth mechanism. Size of the grains are small and grains has lots of voids and defects. Moreover, If the $T_s \ll T_m$ and if the bonds are directional as in covalent bonds an amorphous film can be growth. This two examples show us the two opposite face of the conditions. Therefore, film structure can be altered by changing the substrate temperature or

energy of the ad-atoms. Because of the physical property and structure has strong relation, physical property effected profoundly from the structure development of the thin films.

A.3 Magnetrons

In sputtering process, increasing the number of atoms sputtered from the target material is important for deposition rate that effects time and money. To achieve this or in other word to increase the amount of sputtered atom, the number of ion in the plasma or energy of the ion must be increased. Firstly, let us consider increasing the number of ion in the plasma, with same gas content, number of the ion in the plasma can be increased by the increase the number of collision in the gas medium. To achieve this one must increase the number of particle in unit volume, which means that to increase in the pressure of the chamber. This method has limit for other part of the deposition and this parts will be mentioned later, in mean free path phenomena. Secondly, the energy of the ion that hit the surface can be increased in order to increase sputtering but also this method has limitations in some extend. Over a value, the sputter yield does not change so much because of the domination of the implantation procedure. Furthermore, more energy means, more energy turn into heat so the cooling will be problem. Thus, increasing the applied bias is a temporary solution.

To increase sputter yield scientist use the cyclic motion of charged particle in the magnetic field. This applied magnetic field is perpendicular to movement direction of the charged particle, in other words, electric field. A schematic representation of magnetron can be seen in Figure A-7 (a). In magnetrons, magnetic field must be perpendicular to electric field..Charged particles, for example electrons, have special motion in the magnetic field so the path length of an electron can be increased before it quenched on the wall of chamber. The

movement of electrons in magnetrons is shown in Figure A-7 (b). Because of the huge mass of the ions, ions are affected less from that magnetic field.

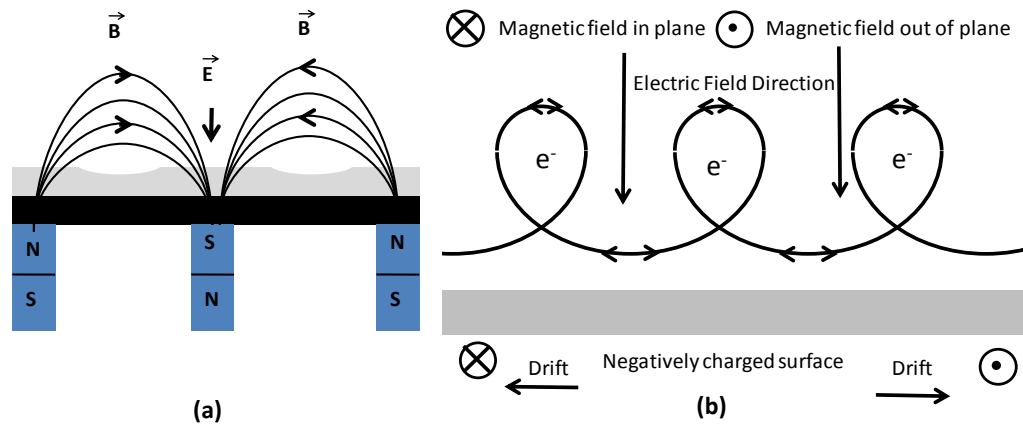


Figure A-6: Schematic representation of a magnetron (a), Movement of the electron in the magnetic field of cathode (b)

This type of path increase the path length of the electron so much that the number of ion generated in the plasma increase significantly. Hence, plasma can sustain at much lower pressure, 20 times less than non-magnetron one, and with the same energy application, bias voltage decrease so the energy that converted to heat decrease. The disadvantage of magnetrons is that because of longer electron paths the ion generation in magnetic field regions are much more than other place. So the sputtering action happen much more than other place so an erosion pattern arise on the target material, Figure A-7 (a)

If the magnetic field intensities of the inner and outer magnets used in the magnetron are the same, this type of magnetron will be called balanced. Otherwise, generally the outer magnets has stronger magnetic power, the magnetron will be called unbalanced. The magnetic fields lines in the unbalanced magnets are extend inside the chamber, so ions generated in the confinement region can escape easily toward the target. Then, substrate is

subjected to a higher ion-bombardment which increases the quality of the growing films.

A.4 Vacuum Environment and Mean Free Path Phenomena

The PVD sputtering techniques need low-pressure environments, it has two main reasons;

- (i) To get rid of reactive sputter deposition action,
- (ii) For directional motion of the sputtered atoms.

Firstly, air consists of mainly nitrogen and oxygen molecules. These molecules contain atoms that can give reactions with other atoms that reaction will produce undesired compounds. In order to get rid of these undesired compounds, air molecules must be removed from the reaction chamber. Cleaning up the system from these molecules, N_2 and O_2 , is an easy process. The main contamination will come from water vapor. Although the amount of the water vapor in the air is small, removing water vapor from the reaction chamber is not easy, because water vapor can stick to wall of reaction chamber. In that stage, one can curious about what would be the base pressure of the reaction chamber. The higher vacuum, the better chamber but keeping the base pressure level of the chamber before deposition less than 1% of deposition pressure is not good but enough for most of the application.

Secondly, to deposit sputtered atoms on the surface of the substrate, sputtered atom pass through a long distance, with respect to their size. During that journey, if they make elastic collision with other molecules or ions, they will

change their directions because of the conservation of momentum and energy law. Hence, instead of deposition on substrate, the wall of the chamber will be deposited. The mean distance that a molecule can travel without any collision is called as mean free path. The mean free path of the Ar molecule in room temperature in environment with pressure 1 mbar is 6.6 cm. This distance is directly proportional with pressure of the chamber. However, if the pressure is decreased too much, sustaining the plasma became impossible. Because the ions and electrons get pair or quenched at surfaces without creating new ion particles. Therefore, the plasma will be diminished as mentioned in plasma section.

References of Appendix

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