

T.R.
DICLE UNIVERITY
INSTITUTE OF NATURAL AND APPLIED SCIENCE

**TEMPERATURE DEPENDENT ELECTRICAL
CHARACTERIZATION OF NiO/n-Si
HETEROJUNCTION**

Savin H. Omar

**MASTER'S THESIS
DEPARTMENT OF PHYSICS**

DIYARBAKIR

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SUPERVISED BY
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The study presented by Savin Haji OMAR titled as "Temperature Dependent Electrical Characterization of NiO/n-Si Heterojunction" has been accepted as Master of Science thesis in Physics Department.

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ÖZET

NiO/n-Si HETEROEKLEMİN SICAKLIĞA BAĞLI ELEKTRİKSEL KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ

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Bu çalışmada, NiO/n-Si heteroeklemin elde edilmesi ve sıcaklığa bağlı elektriksel özelliklerinin belirlenmesi amaçlanmıştır. Bu amaçla, n-Si yarıiletken ve cam üzerine NiO ince filmleri radio frekansı (RF) reaktif saçırma yöntemi ile biriktirilmiştir. Yüksek saflıkta Ni hedef olarak ve oksijen reaktif gaz olarak kullanılmıştır. Au metali doğrultucu kontak olarak buharlaştırılmıştır. Au/NiO/n-Si heteroeklemin sıcaklığa bağlı elektriksel parametreleri 305 ile 480 K arasında alınan akım-gerilim ölçümleri ile belirlenmiştir. İdealite faktörü, engel yüksekliği ve seri direnç gibi elektriksel parametrelerin sıcaklığa kuvvetlice bağlı olduğu görülmüştür. Ayrıca, cam üzerindeki ince filmin optik özellikleri uv-vis verileri ile analiz edilmiştir.

ABSTRACT

TEMPERATURE DEPENDENT ELECTRICAL CHARACTERIZATION OF NiO/n-Si HETEROJUNCTION

MSc THESIS

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2015

In this study, it was aimed to obtain NiO/n-Si heterojunction and determine its temperature dependent electrical properties. For this aim, NiO thin films were grown on an n-Si semiconductor and a glass by radio frequency (RF) reactive sputtering technique. High purity Ni was used as target and oxygen was used as reactive gas. Au metal was evaporated to obtain front contact. Temperature dependent electrical parameters of Au/NiO/n-Si heterojunction were executed its current-voltage (I - V) measurements between 305 and 480 K in dark. It was seen that electrical parameters such as ideality factor, barrier height and series resistance were strongly sensitive to temperature. Furthermore, optical properties of thin film on a glass were analyzed by means of uv-vis data.

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ANNOTATION AND SYMBOLS

MS	Metal-Semiconductor contacts
MIS	Metal-Insulator-Semiconductor contacts
AMOLED	Active matrix organic light emitting diode
ITO	Indium doped tin oxide
I - V	Current-voltage characteristic
C - V	Capacitance- voltage
η	Efficiency
DSSC	Dye sensitized solar cell
Nipc/p-Si	Nickel phthalocyanine p-type of Silicon
RF	Radio Frequency
SEM	Scanning electron microscopy
XRD	X-ray diffraction
K	Kelvin
LED _s	Light emitting diodes
p-Si	p-type of Silicon
n-Si	n-type of silicon
UV	Ultra violet
V	Voltage
T	Absolute Temperature
PVD	Physical vapor deposition
CVD	Chemical vapor deposition
Φ_s	Work function of semiconductor
Φ_m	Work function of metal
Φ_b	Barrier high
Φ_{be}	Barrier high of p-type
Φ_{bn}	Barrier high of n-type
E _g	Band gap

q_x	Electron affinity
q	Electron charge
x	Distance
R_s	Series resistance
R	Resistance
I	Current
K	Boltzman constant
α_s	Absorption coefficient
α_e	Emissions coefficient
E_i	Initial state of energy
E_s	Final state of energy
E_{PH}	Phonon energy
h	Plank's constant
ν	Frequency
m_e^*	Effective mass of electron
m_h^*	Effective mass of hole
T	Transmittance
A	Absorption
R	Reflection
A	Diode Area
A^*	Richardson constant
$F(V)$	Norde function
Ω	Ohm
ϵ_s	Dielectric constant of semiconductors
ϵ_s	The dielectric constant of the cavity
I	Intensity of light passing through the thin film
I_o	Intensity of incident light

1.Introduction

Semiconductor technology has an important place in our lives. Many kinds of electrical and optical applications have been discovered using semiconductor technology. A number of devices are used in high technology products including light emitting diodes, transistors, physical and chemical sensors. These applications are constructed using various junctions such as metal-semiconductor (MS) contacts, metal-insulator-semiconductor (MIS) contacts, p-n junctions, p-i-n junctions and heterojunctions.

The first semiconductor device is MS contact and it is used in all kinds of equipments. MS contacts are classified in two forms; ohmic and rectifying contacts. MS rectifying devices are also called “majority carrier” contacts. While p-n junctions have voltage drop between 0.6 and 0.7 V, MS devices have voltage drop between 0.15 and 0.45 V. This property gives higher switching speeds and possibility to use them in the heart of RF detectors and mixers.

On the other hands, p-n junctions are “minority carrier” devices and they are one of the main parts of semiconductor technology including solar cells and light emitting diodes. The p-n junctions can be analyzed in two different types; homojunctions and heterojunctions. Homojunctions are fabricated by joining different conductivity types of same semiconductor such as n-ZnO/p-ZnO and n-Ge/p-Ge and heterojunctions are fabricated using two different semiconductors such as n-GaAs/p-Si and n-ZnO/p-InPAs. When the conductivity types are same, the junctions are called isotype heterojunctions and when conductivity types are different, the junctions are called anisotype heterojunction. In general different semiconductors have different band gaps. Therefore, there is a discontinuity of energy bands at the interface. Because of this discontinuity the current-voltage (I - V) characteristics of heterojunctions are different from conventional p-n junction(Sze and Kwok 2007).

Nowadays, metal oxides are popular in the formation many a number of devices because of their electrical and optical properties. Most of the oxide semiconductors such as zinc oxide (ZnO) and indium doped tin oxide (ITO) have n-type semiconducting property. To find a suitable p-type metal-oxide-semiconductor has a great interest. Nickel oxide with NiO chemical formula is p-type conductivity with high band gap. There is a great interest on NiO thin films owing to their excellent electrical, optical and

magnetic properties as well as good chemical stability. They have been used p-type transparent conducting films for solar cells, active layer in the fabrication of chemical sensors, ultra violet light emitting diodes, photodetectors and in electrochromic devices (Gibbons and Beadle 1964; Chan, Hsu et al. 2002).

NiO thin films have been grown on different substrates using various methods including spin coating, spray pyrolysis, chemical vapor deposition and sputtering. Among all methods, magnetron sputtering technique is a unique method to obtain uniform thin films of ceramics refractory metals or ceramics.

In this study, it was aimed to obtain NiO/n-Si heterojunction and determine its temperature dependent electrical properties. For this aim, NiO thin films were grown on an n-Si semiconductor and a glass by radio frequency (RF) reactive sputtering technique. High purity Ni was used as target and oxygen was used as reactive gas. Al metal was evaporated to obtain front contact. Temperature dependent electrical parameters of Au/NiO/n-Si heterojunction were executed its current-voltage (I - V) measurements between 305 and 480 K in dark. It was seen that electrical parameters such as ideality factor, barrier height and series resistance were strongly sensitive to temperature. Furthermore, optical properties of thin film on a glass were analyzed by means of uv-vis data.

2. Literature Summary

The interest on semiconductor devices is increasing rapidly because the great improvements in modern technology. Nowadays we use electrical and optical equipments nearly in all parts of our lives. For instances, we use active matrix organic light emitting diode (AMOLED) televisions, laser printers and mobile phones which need high technology based on semiconductors. Although there is a great advancement in semiconductor devices in last several decades, the history of electronic devices started over than 100 years. Braun fabricated the first electronic device (metal-semiconductor contact) in 1874 (Braun and MacDonald 1982). He found the asymmetry in electrical conductivity of MS contacts formed using metal sulfate crystals. After him, Pierce presented the rectification behavior of MS contacts formed on the surface of the semiconductor with metal wires.

Schottky, Sörmer and Waibel performed the first principal study on rectifying properties of MS contact. They said that the rectification property can occur owing to the potential drop across all contacts when current flows in the contact. After this study, Wilson developed the theory of quantum mechanical tunneling and explained the rectification using reverse polarity (Schottky, Stormer et al. 1931).

In 1938, Schottky and Mott independently suggested that rectification mechanism can be explained electron flows and diffusion over potential barrier. According to Schottky-Mott theory, existence of potential barrier is result in differences between metal and semiconductor work functions. Thus, greatness of potential barrier can be calculated using the differences between metal work function and semiconductor electron affinity. But, the experiments showed that barrier height is approximetly independent from metal work functions and its related to preperation methods. It was conculated from experimental results that theory was insufficient because it didn't take the existance of a layer at MS interface into account. The fact that this layer is always possible in practice and preperation conditon can manipulate its thickness and chemical structure.

It is accepted that main electrical parameters of semiconducting devices are barrier height and ideality factor values. They can be determined using current-voltage (I - V) plot of the device. Mönch introduced that the ideality factor a MS structure should

be 1.01 when image force lowering of Schottky potential taking into account (Mönch 1999). Another important characteristic of rectifying diodes is series resistance. Norde suggested some functions to determine series resistance and barrier height of non-ideal diodes from forward bias I - V data (Norde 1979). Cheung and Cheung proposed another method in order to examine characteristic parameters of both ideal and non-ideal diodes including barrier height, ideality factor and series resistance from forward bias I - V characteristics (Cheung and Cheung 1986).

Heterojunction formed using two semiconductors with different band gaps are one of the most desired field of semiconductor device and technology owing to their various properties. Shockley proposed abrupt heterojunction as efficient emitter. After this work, heterojunctions started to be one of the most extensively studied topics. Many kinds of devices have been fabricated using heterojunctions such as room temperature injection laser, light emitting diodes (LEDs), photodiodes and solar cells.

Muller and Zuleeg fabricated vapor deposited thin film heterojunction diodes using materials CdTe, Al_2O_3 , and SiO_x as insulating materials between semi-insulating CdS and metallic electrode. They reported the perfect rectification of these heterojunction (Muller and Zuleeg 1964).

Many studies have been performed to understand, improve and control physical properties of heterojunctions. For these purposes, a number of materials have been used in the fabrications of various kinds of devices.

Up to 1991, there had been great effort to improve silicon p-n junction solar cells. B O'regan and M Grätzel proposed organic inorganic heterojunction solar cell using optically transparent titanium dioxide particles and Ru(II) complex dye (O'regan and Grätzel 1991). They showed that formation of this heterojunction structure is also low cost and easy. They increased the surface area of inorganic semiconductor (TiO_2) to improve the photovoltaic parameters of solar cell. They called this structure as dye sensitized solar cell (DSSC). After this study, thousands of papers have been published on heterojunction solar cells.

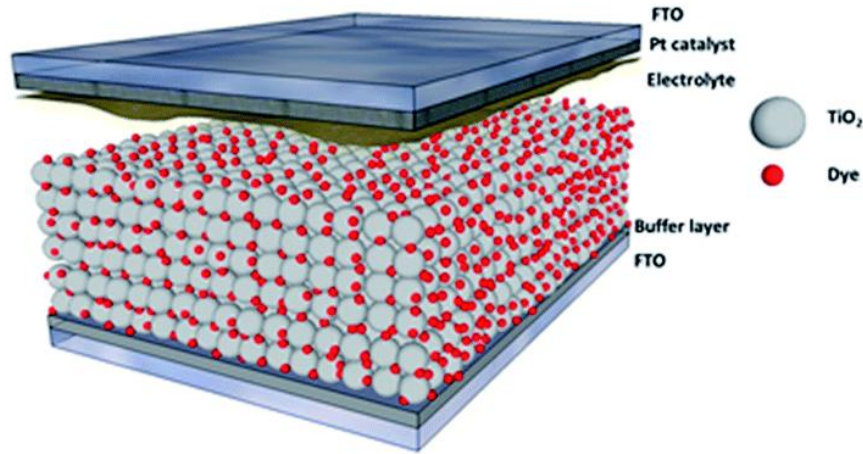


Fig 2.1. The DSSC structure

Akasaki and Amano successfully fabricated first diode emitting a bright blue light. Nakamura developed blue LED in 1988. They do many studies on GaN based LEDs. For instance, they built p-GaN/n-InGaN/n-GaN double heterojunction blue light emitting diodes in 1993. They showed that the output power as 125 mW and external quantum efficiency of the led was about 0.22 % at 20 mA at room temperature. Akasaki, Amano and Nakamura took the Nobel Prize in 2014 because of *“for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources”*(Heber 2014).

El-Nahass et al deposited nickel phthalocyanine (NiPc) thin films onto p-Si substrate to obtain organic-inorganic heterojunction (El-Nahass, Abd-El-Rahman et al. 2005). They analyzed electrical properties of the structure using Current–voltage (I – V) and capacitance–voltage (C – V) measurements. They showed that the NiPc/p-Si heterojunction had a rectification behavior and current in the forward direction obeyed diode equation and the conduction mechanism was controlled thermionic emission mechanism. They also determined the photovoltaic parameters of the junctions. They found the device had power conversion efficiency (η) of 1.11% at room temperature and under illumination of 6 mWcm^{-2} white light.

Caldiran et al formed Au/Anthraquinone/p-Si/Al junction device using electrochemical method(Çaldiran, Deniz et al. 2014). They reported that the barrier height of Au/Anthraquinone/p-Si heterojunction is larger than the conventional Au/p-Si/Al and Anthraquinone interlayer at MS interface had strong effects on electrical

properties of the diode. They carried out the current-voltage measurements of the device in the temperature range of 80–280 K. The decrease of the barrier height and an increase in the ideality factor while decreasing the temperature were reported for the device. They reported that the series resistance of the junction is also depended on temperature.

Tombak et al fabricated organic-inorganic heterojunction by deposition of Coumarin 30 thin film onto p-Si inorganic semiconductor (Tombak, Ocak et al. 2014). They showed that Coumarin 30 thin film consisted of rodlike crystallites. The device had excellent rectifying property. They analyzed the electrical properties of Coumarin 30/p-Si structure between 300-380 K. They showed that while the ideality factor and series resistance of Coumarin 30/p-Si diode decreased, its the barrier height (ϕ_b) increased with increasing temperature. They also reported that the heterojunction had photoelectrical response with 59 μ A short-circuit current and 337 mV open-circuit voltage.

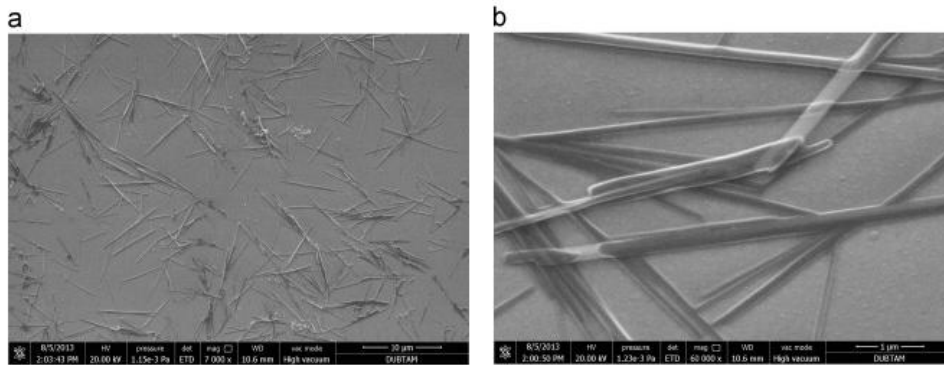


Fig. 2.2. Coumarin 30 thin film consisted of rodlike crystallites

Among all semiconductors, there is a great interest on NiO thin films and NiO based devices because of their excellent electrical, optical and magnetic properties as well as good chemical stability. So many endeavors have been done to obtain NiO thin films and devices using various methods.

Chen et al deposited NiO thin films by RF sputtering process at various RF powers and substrate temperatures (Chen, Lu et al. 2005). They analyzed structural, electrical and optical properties of thin films by the help of XRD, Hall Effect measurements and uv-visa data. They showed that the conductivity of thin films decreased as sputtering power decreased. They found the lowest resistivity for the film obtained as the sputtering power was 100 W and substrate temperature was 350 C.

Cavas et al fabricated transparent p-NiO/n-ZnO heterojunction device by spin coating technique (Cavas, Gupta et al. 2012). They showed that while ZnO thin films had fibrous structures, NiO films were very smooth. They calculated the band gaps of ZnO and NiO as 3.25 and 3.89 eV from uv-vis data. They examined the current-voltage plot of the p-NiO/n-ZnO device and calculated its ideality factor and barrier heights as 2.91 and 0.48 eV.

In this study, NiO thin films were deposited onto an n-Si and a glass by means of RF reactive sputtering method. High purity Ni was used as target and oxygen was reactive gas. Optical properties of the film were determined using uv-vis data. Au metal was evaporated as front contact to NiO/n-Si heterojunction. Temperature dependent electrical properties of NiO/n-Si heterojunction were examined using its I - V measurements between 305 and 480 K. Electrical parameters of the device were calculated using I - V data. The effect of light on photoelectrical characteristics of the device was also studied.



3. Material and Method

In this study, it was aimed to see effects of temperature on electrical properties of NiO/n-Si heterojunction. For this aim, NiO thin films were grown on n-Si and glass substrates by radio frequency (RF) reactive sputtering technique. High purity Ni metal was used as target and oxygen was used as reactive gas. The films were annealed at 500 C to increase the crystal quality. Optical properties of properties of NiO thin film on glass were analyzed using uv-vis data. The electrical properties of NiO/n-Si heterojunction were examined by their current-voltage (I - V) measurements in dark between 305 and 480 K. The characteristics electrical parameters such as ideality factor, barrier height and series resistance were calculated using its I - V data. Furthermore, the effect of the light intensity on photoelectrical parameters were also studied.

In this chapter, firstly the physics of MS structures, the conduction mechanisms in these contacts and the factors which affect physical parameters of devices will be given. Then, physical vapor deposition (PVD) systems which were used in this study will be discussed. Optical properties of materials will be also discussed in this chapter.

Finally, at the end of the chapter, all experimental parts of this study will be explained in detail.

3.1. Metal-Semiconductor Contacts

Metal semiconductor (MS) contacts have great importance because they are used in the fabrication of all kinds semiconductor based electronic devices. MS contacts can be examined in two different parts as ohmic contacts and rectifying Schottky contacts. In this part, formation of MS structures, conduction mechanisms of these structures and determination of electrical properties will be discussed.

When a metal and semiconductor make a contact without any material between them it is called as MS contact. Theoretically, if the work function of semiconductor is larger than the work function of metal ($\phi_m < \phi_s$), it forms rectifying contact and if the work function of metal is larger than the work function of semiconductor ($\phi_s < \phi_m$), it forms ohmic contact for p-type semiconductors. For the n-type semiconductor it is just the opposite.

3.1.1. Rectifying Contacts

Work function of metal is expressed as ϕ_m and it is equal to $q(\chi + \phi_n)$ where $q\chi$ is electron affinity which defined as the difference between the bottom of the conduction band the vacuum level. The contact potential is defined as the difference between two work functions ($\phi_m - (\chi + \phi_n)$). When the distance between metal and semiconductor is decreased, electric field in this region increases and decreasing negative carrier occurs. A positive carrier should be created at depletion region. The potential difference is very similar to one side of p-n junction. If the distance is very small, this region becomes transparent for electrons and the situation shown in Fig. 3.1 occurs. For an ideal contact between a metal and a p-type semiconductor, barrier height is written as (Rhoderick and Williams 1988)

$$q\phi_{bn} = q(\phi_m - \chi) \quad 3.1$$

$$q\phi_{bp} = E_g - q(\phi_m - \chi) \quad 3.2$$

Therefore, sum of the barrier heights of a MS contact formed using a metal and p-type and n-type semiconductor is equal to band gap of the semiconductors.

$$E_g = q(\phi_{bp} + \phi_{bn}) \quad 3.3$$

For a MS contact formed using an n-type semiconductor, ionized donors (positive carriers) in semiconductor side of contact are space charges because they are motionless. When a reverse potential applied to contact, barrier height doesn't change for electrons which wants to pass to barrier. For this reason, current flow from semiconductor to metal becomes constant. On the other hand, for electrons pass from metal to semiconductor barrier height decreases about eV value and current flow from metal to semiconductor decreases as $\exp(eV/kT)$ factor. Therefore, the net current can be expressed as

$$I = I_0 \exp\left[\frac{q(V - IR_s)}{nkT}\right] \quad 3.4$$

Where I is the current, I_0 is the current q is the electron charge, V is the applied voltage, n is the ideality factor, k is the Boltzmann constant T is the absolute temperature. For this equation, net current is positive and this situation is called as forward bias. When a positive voltage applied to semiconductor, conduction band decreases about eV and barrier height in the semiconductor side increases about eV. This situation is called as reverse bias.

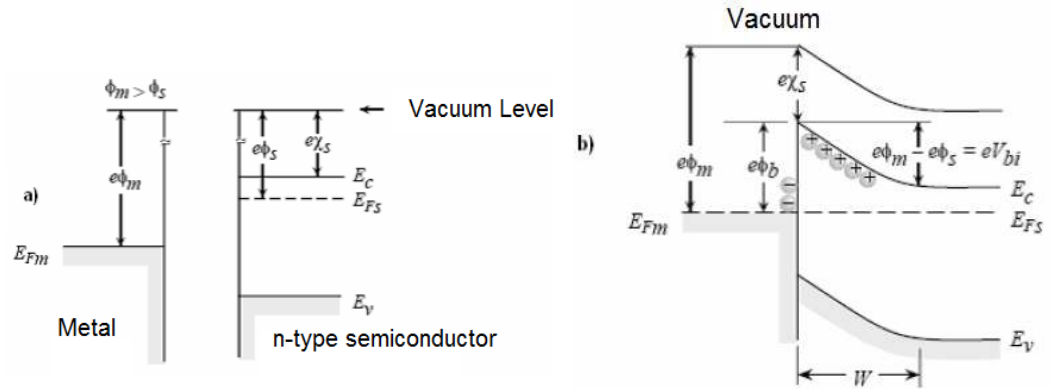


Figure 3.1 Energy band diagram of metal-n-type semiconductor a) before the formation of a contact b) after formation of a contact

3.1.2 Ohmic contacts

The main aim to use ohmic contacts is to get or give current to semiconductor with minimum resistance. Ohmic contact obeys the ohm law. The quality of the ohmic contact is related to contact resistance. This resistance is written as

$$R_C = \left(\frac{\partial I}{\partial V} \right)_{V=0}^{-1} \quad 3.5$$

The comparison of ohmic and Schottky contacts are shown in Fig. 3.1.

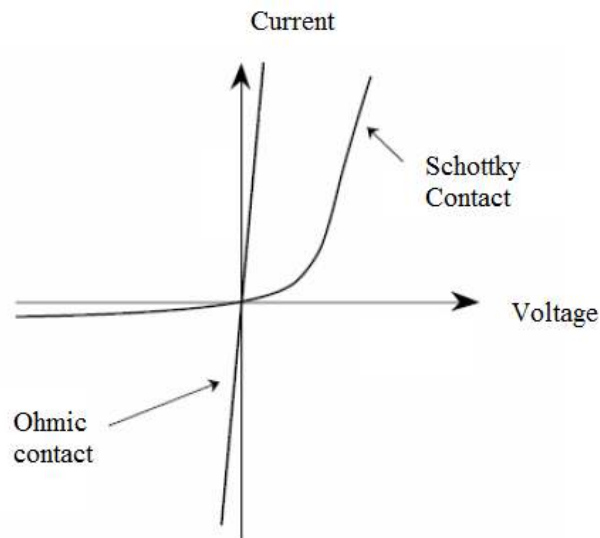


Figure 3.2. Ohmic and Schottky contact plots

3.2. Physical Vapor Deposition Methods

The main methods for depositing thin films are evaporations and sputtering, so the concentration will be on the explanation of these methods in this chapter. The aim which stands behind the process of deposition is to make a control on the transfer of atoms from the source to substrate where film consistency and outgrowth progress atomistically. During the process of evaporation, atoms are separated from the source due to thermal means but in the process of sputtering, they are expelled from solid target surface due to the effect of gaseous ions. The beginning experimentation of these kinds of deposition techniques can be obviously influence to same period of the nineteenth century. Grove in 1852 AC realize sputtering of metal deposits from cathode of an illumination discharge. Faraday after five years, testing with exploding fuse like metal in a static atmosphere, fabricated evaporated thin films. With the progress and evolution of vacuum pumping instrument and manufacturing of suitable Joule heating sources such as which made from platinum and tungsten wire, supported the progress of evaporation technology. The scientific advantage in the phenomenon of evaporation and the characteristics of thin films of metal was followed up by industrial output of optical components like beam splitters, mirrors, and antireflection coatings. Sputtering was utilized in 1877 to coat mirrors, and its usages included coating of flimsy construction with Au and deposition of metal films on record rules of phonograph records before to thickening Up to the late of 1960s, evaporation obviously exceeded sputtering as the favorite film deposition technique. Higher deposition average, superior vacuum, and cleaner environments for film consistency and outgrowth, and general usable to all categories of materials were some of the reasons for dominance of evaporation methods. Films are used for magnetic and microelectronic applications required the usage of alloys, with severe stoichiometry limits, which ought to adapt cover and abide well to substrate surfaces. These requests plus the introduction of radio frequency (RF), bias and magnetron variants that spread the power of sputtering and availability of high purity targets and working gases, assisted prefer the popularity of sputter deposition.

According to special implementations to evaporate or sputter thin films is not always clear and has encouraged a lively competition among these methods. On the other hand, characteristics of evaporate and sputter have been fabricated into mongrel operation. The basic film deposition methods treated in this thesis are physical vapor

deposition(PVD), the expression that includes evaporation and sputtering, and chemical vapor deposition (CVD) will all of variant and mongrel operations.

The following are some factors which differentiate PVD from CVD

1. Dependence on solid or molten sources.
2. Physical techniques (evaporation or collisional affect) by which source atoms get in the gas phase.
3. Reducing pressure environment through which the gaseous sort are transported.
4. Overall nonattendance of chemical reactions in the gas phase and at the substrate surface (PVD reactive processes are exclusion).

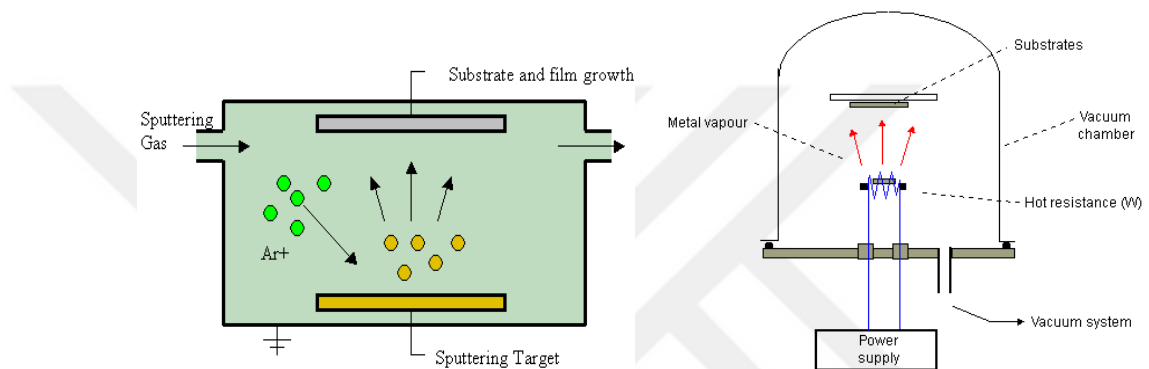


Figure 3.3. Diagrams of sputtering and thermal evaporation processes

3.3. Optical Properties of Materials

3.3.1. Absorbance

Absorption is called energy loss of an incident electromagnetic wave to a crystal plane by interacting with the electrically charged particles. The most commonly used method for determining forbidden energy band gap of semiconductors is optical absorption method. A photon coming to a semiconductor excites an electron from low energy level to a high energy level in absorption process. The correlation between incident and transmitting of beam light coming through the thin film with a thickness x is as follows

$$I = I_0 e^{-\alpha x} \quad 3.6$$

where I_0 the intensity of the incident light, I intensity of light passing through the thin film, x is thin film thickness and α is absorption coefficient of the material used (semiconductor).

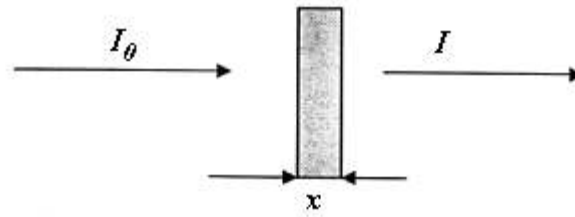


Figure 3.4 Absorption in a thin film

There are two types of band transition in crystalline and amorphous semiconductors. These are direct and indirect band transition and shown in the figure3.5. Direct transition state occurs when the momentum of minimum valance band is the same as conduction band momentum. In Figure 3.5, the electron absorbs a photon without a change in its momentum value and transmits from valence band to the conduction band with energy received from the photon.

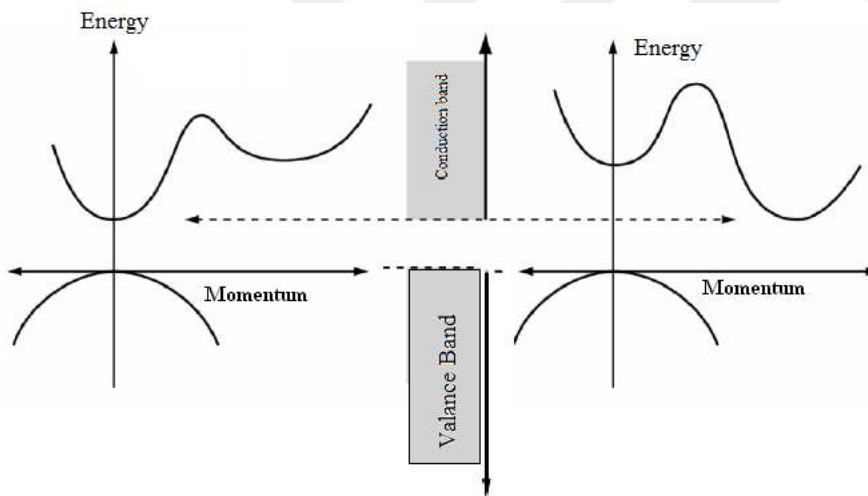


Figure 3.5 Representation of the direct and indirect transition through band gap

The minimum valance band energy is different from that of the conduction band maximum energy for the material having an indirect band gap. Electrons in the conduction band go down to the minimum band energy quickly. In the same way, holes reach the maximum of valance band. Therefore, momentum of electrons and holes is the same for a direct transition semiconductor while is not the same for

indirect transition semiconductor. This result is because of the lifetime of minority charge carriers and optical properties.

3.3.1.1. Direct band transition

When a photon with energy $h\nu$ comes to a direct band gap semiconductor, an electron jumps from the valence band to the conduction band. E_i is initial state in semiconductor, E_s is the final energy state. Therefore, the energy difference,

$$h\nu = E_s - E_i \quad 3.7$$

is given by the equation. In the parabolic band,

$$E_s - E_g = \frac{p^2}{2m_e^*} \quad 3.8$$

and

$$E_i = \frac{p^2}{2m_h^*} \quad 3.9$$

is determined by the expressions. Where m_e^* the effective mass of the electron and m_h^* is effective mass of hole. If equations 3.32, 3.33 and 3.34 are arranged

$$h\nu - E_g = \frac{p^2}{2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \quad 3.10$$

is obtained by correlation. In direct band transition relation between α and $h\nu$ is;

$$\alpha h\nu \approx K(h\nu - E_g)^m \quad 3.11$$

is given by the equation. K is constant, m is a constant, which can take 1/2 for, allowed transition or 3/2 forbidden transition values. In addition, in equation 3.8 the value making zero of the parenthesis gives the forbidden energy gap value of the semiconductor which is equal to $\alpha h\nu$.

3.3.1.2 Indirect band transition

Because the momentum of the electrons of valance band maximum and conduction band minimum, in order to conserve momentum of the electrons, photon absorption

event should contain additional particles. In this case, either emission or absorption of a photon for momentum conservation is required. The phonon absorption coefficient

$$\alpha_s(h\nu) = \frac{K(h\nu - E_g + E_{ph})^m}{\exp(E_{ph}/kT) - 1} \quad 3.12$$

and

$$\alpha_e(h\nu) = \frac{K(h\nu - E_g + E_{ph})^m}{1 - \exp(-E_{ph}/kT)} \quad 3.13$$

can be written. Here α_s is absorption coefficient and α_e is emission coefficient, E_{ph} is the phonon energy. It is also possible for both possibilities

$$\alpha(h\nu) = \alpha_s(h\nu) + \alpha_e(h\nu) \quad 3.14$$

can be written. When it is clearly written

$$\alpha(h\nu) = \frac{K(h\nu - E_g + E_{ph})^m}{\exp(E_{ph}/kT) - 1} + \frac{K(h\nu - E_g + E_{ph})^m}{1 - \exp(-E_{ph}/kT)} \quad 3.15$$

Where m is a constant, which can take 2 allowed or 3 forbidden transition values for an indirect band gap semiconductor.

3.3.2. Transmittance

Transmittance is defined as the ratio of the intensity of light incident on the sample to the intensity of light passing through a sample and expressed by the equation

$$T = \frac{I}{I_0} \quad 3.16$$

Both transmission and reflection from a medium depends on the refractive index and the absorption characteristics. Therefore, interactions are always not necessarily,

not classified as reflection and absorption. Transmittance is clearly observed by absorbance of gases (excluding reflections from the reactor wall) (Herman, 1996).

Optical transmittance or absorbance measurements are used to determine the optical absorption coefficient and specific impurities. Shallow level impurities correspond to optical measurements. Certain impurities have the characteristic absorption lines due to the vibrational mode; such as oxygen and carbon in the silicon. One of absorbed photons in semiconductor can make sudden environmental changes by producing local vibrational modes around certain impurities. During the transmittance measurements, light comes to sample and transmittance is measured as a function of wavelength. The reflection coefficient of the sample, R , absorption coefficient, α , the complex index of refraction, $n_1 - jk_1$ and thickness x are characterized. Extinction coefficient dependent absorption coefficient is as follows.

$$\alpha = 4 \frac{\pi k_1}{\lambda} \quad 3.17$$

Semiconductors band gap can be found by the measurement of absorption coefficient as a function of incoming photon energy. Light is absorbed by a larger energy from the band gap energy. However, the optical absorption $h\nu$ near the band gap (E_g) is low for the amount will be considered reasonable. Semiconductors are usually transparent to photons of lower from energy band gap energy ($\alpha \approx 0$).

Impurities may show absorption in a semiconductor sample. An example of this influence has been replaced with oxygen and silicon into silicon carbon. Their intensity is proportional to the absorption coefficient at specific wavelengths.

The relationship between transmittance and absorption is given by

$$A = -\log T \quad 3.18$$

The relationship between the absorption coefficient, reflection coefficient and transmittance ;

$$\alpha = \frac{1}{x} \ln \left\{ \frac{(1-R)^2}{2T} + \left[\frac{(1-R)^4}{4T^2} + R^2 \right]^{1/2} \right\} \quad 3.19$$

where R is reflectance. One of interactions in the semiconductor material with light is the light refraction. Refraction is to change the direction of light in the

semiconductor material while it is passing through the material. Complex refractive index for semiconductor material is (n) is given as;

$$n = n_0 - ik \quad 3.20$$

where n_0 is real part of the refractive index, k is the imaginary part of the refractive index value and is expressed as "extinction coefficient". Refractive index can be written in terms of reflection as equation 3.19.

$$n_0 = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad 3.21$$

The refractive index of a semiconductor material is a function of the wavelength of light. Semiconductor materials with a high refractive index will have the further reflection property. When the atomic number increases, due to increase in the number of electrons and increased polarization photons will be affected more and more subject to refraction. Therefore, there is a relationship between the refractive index of the semiconductor materials and dielectric constant.

Complex dielectric constant of the semiconductor material (ϵ),

$$\epsilon = \epsilon_1 + i\epsilon_2 \quad 2.22$$

is given by the equation. Semiconductor optical measurements is made as a result of the reflection coefficient of a material, refractive index and extinction coefficient, however, the dielectric constant ϵ cannot be measured directly.

The relation between dielectric constant ϵ and the refractive index n is given as

$$n = \sqrt{\epsilon} \quad 3.23$$

Real part of the dielectric constant,

$$\epsilon_1 = n^2 - k^2 \quad 3.24$$

and the imaginary part of the equation can be expressed

$$\epsilon = 2nk \quad 3.25$$

3.4 Experimental procedures

In this study, it was aimed to see the effect of temperature on electrical properties of NiO/n-Si heterojunctions. For this aim, NiO thin films were grown on n-Si and glass substrates by radio frequency (RF) reactive sputtering technique. The temperature dependent electrical properties of NiO/n-Si heterojunction were examined by their current-voltage (I - V) measurements in dark. Furthermore, the influence of light intensity on photoelectrical parameters of NiO/n-Si heterojunction was also studied.

3.4.1. Formation of ohmic contact

An n-Si wafer with (100) orientation and 1-10 Ωcm resistivity is used. The wafer firstly degreased by boiling in trichloroethylene and cleaned by ultrasonically vibrating in acetone and methanol for 5 min. After each step, the wafer was washed with deionized water. After cleaning procedures, the wafer is dried under nitrogen ambient. The n-Si semiconductor was put into the vacuum chamber. Au metal was evaporated at 10^{-6} Torr and n-Si/Au structure was annealed under nitrogen ambient for 3 min at 420 C to make high quality ohmic contact. The annealing furnace is shown in Fig 3.6.



Figure 3.6 The annealing furnace used in the study

3.4.2. Deposition of NiO thin film

NiO thin films were growth on n-Si semiconductor and glasses by reactive sputtering technique using Nanovak NVTs 400 vacuum system. Ni metal was used as target and O₂ was used as reactive gas. Pressure of the vaccum system was decreased at 10⁻⁶ Torr. Argon gas was send to system and the pressure was increased to 20 mTorr. The flow of the Argon gas was about 4 ccm. 80 W power was applied to high purity Ni target and 0,4 ccm oxygen was send to vacuum system to make reactive sputtering process. This process continued 10 minutes. The substrate temperatures were kept at 40 C during sputtering process. To increase crystallianity, NiO thin films were annealed at 500 C for 30 minutes in air ambient.



Figure 3.7. Nanovak NVTs 400 vacuum system

3.4.3. Formation of front contact and measurements

Au metal was evaporated to obtain front contact. The circular diameters of the Au contacts were about 1.5 mm. To make circular front contacts a shadow mask is used. The schematic diagram of Au/NiO/n-Si devices is given in Fig. 3.8.

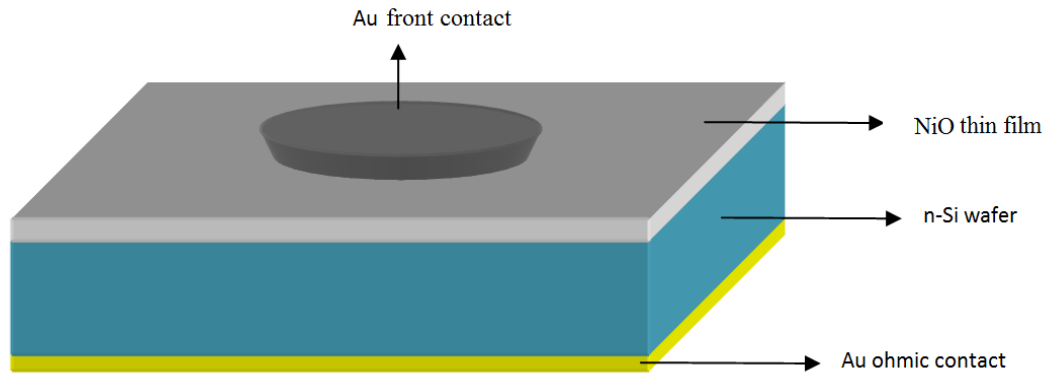


Figure 3.8. The cross section illustration of Au/NiO/n-Si diode

Temperature dependent electrical characteristics of Au/NiO/n-Si structure were analyzed using its current-voltage (I - V) measurements between 305 and 480 K by the help of Keithley 2400 sourcemeter.



Figure 3.9a. Current-voltage measurement system with Keithley 2400 sourcemeter and Oriel solar simulator

Optical properties of the thin film on a glass were analyzed using Shimadzu 3600 Uv-vis-nir spectrophotometer. The system is presented in figure 3.10.



Figure 3.10. Shimadzu 3600 Uv-vis-nir spectrophotometer

4. Findings and discussion

4.1. Introduction

In this chapter, firstly optical properties of the NiO thin film on a glass will be analyzed. After that, temperature dependent electrical characterization of NiO/n-Si heterojunction will be examined. Finally, the effect of light intensity on photoelectrical parameters of the diode will be studied.

4.2. Optical properties of NiO thin film on a glass

UV-Vis spectra were used to determine the optical properties of the reactively sputtered NiO thin film. The film was deposited on a glass and its absorbance and transmittance properties were determined. Fig. 4.1 shows the both absorbance vs. wavelength and transmittance vs. wavelength plots. As seen from the figure, the transmittance value of the NiO thin film has a sharp increase between 300 and 500 nm. The transmittance value is NiO thin film at 300 nm is 59 % and this value reaches 88 % at 530 nm. The increase continues till 1000 nm. At 1000 nm the transmission value of the film is 98 %. After 1000 nm the transmittance of the film is nearly constant. It means that the NiO thin film is very transparent visible region and nearly full transparent in infrared region.

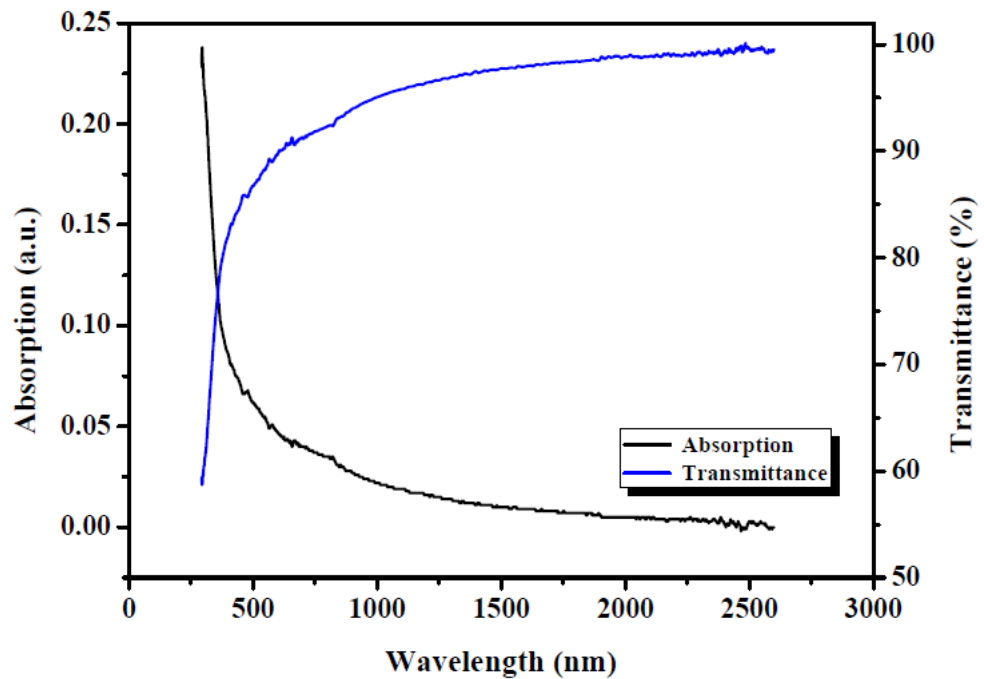


Figure 4.1. Absorbance vs. wavelength and transmittance vs. wavelength plots of NiO thin film on a glass

Furthermore, the absorbance of the film decreases sharply between 300 and 500 nm. The decrease continues till 1000 nm. After 1000 nm, the film has nearly no absorbance.

The optical band gaps (E_g) of the NiO can be calculated through the equation

$$\alpha h\nu = B(h\nu - E_g)^m \quad 4.1$$

where α is the absorption coefficient, B is a constant, h is the Plank constant, m is $\frac{1}{2}$ for direct band gap and 2 for indirect band gap. NiO has direct band gap. Therefore, the direct band gap of reactive sputtered NiO thin film was determined by using absorption vs. wavelength data with the help of equation 4.1 using $(Ah\nu)^2-h\nu$ plot. Figure 4.2 shows the $(Ah\nu)^2-h\nu$ thin film. The E_g of the NiO thin film was determined as 3.02 eV by extrapolating the straight line of the graph to intercept the photon energy.

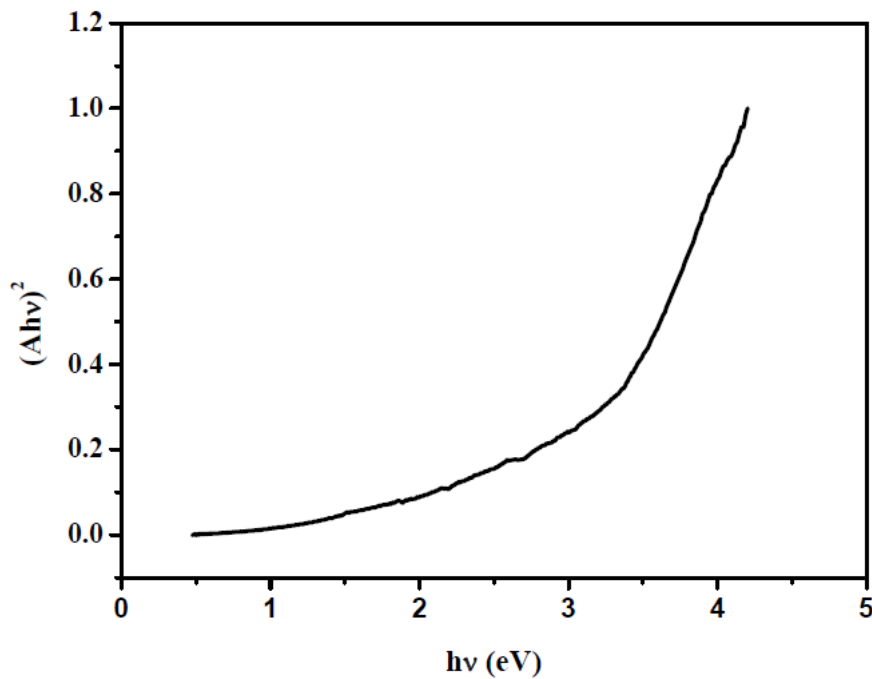


Figure 4.2. $(Ah\nu)^2-h\nu$ plot of NiO thin film on a glass

4.3. Temperature dependent current-voltage properties of NiO/n-Si heterojunction

Current-voltage measurements of NiO/n-Si heterojunction showed that the device had an excellent rectification. When the series resistance of a diode is taken into account, the relationship between current and voltage is given as (Rhoderick and Williams 1988)

$$I = I_0 \exp\left(\frac{q(V - IR_s)}{nkT}\right) \quad 4.2$$

where, q is the electron charge, V is the applied voltage, R_s is the series resistance, n is dimensionless ideality factor, k is the Boltzmann constant, T is the absolute temperature and I_0 is the saturation current which can be written

$$I_0 = AA^* T^2 \exp\left(-\frac{q\Phi_b}{kT}\right) \quad 4.3$$

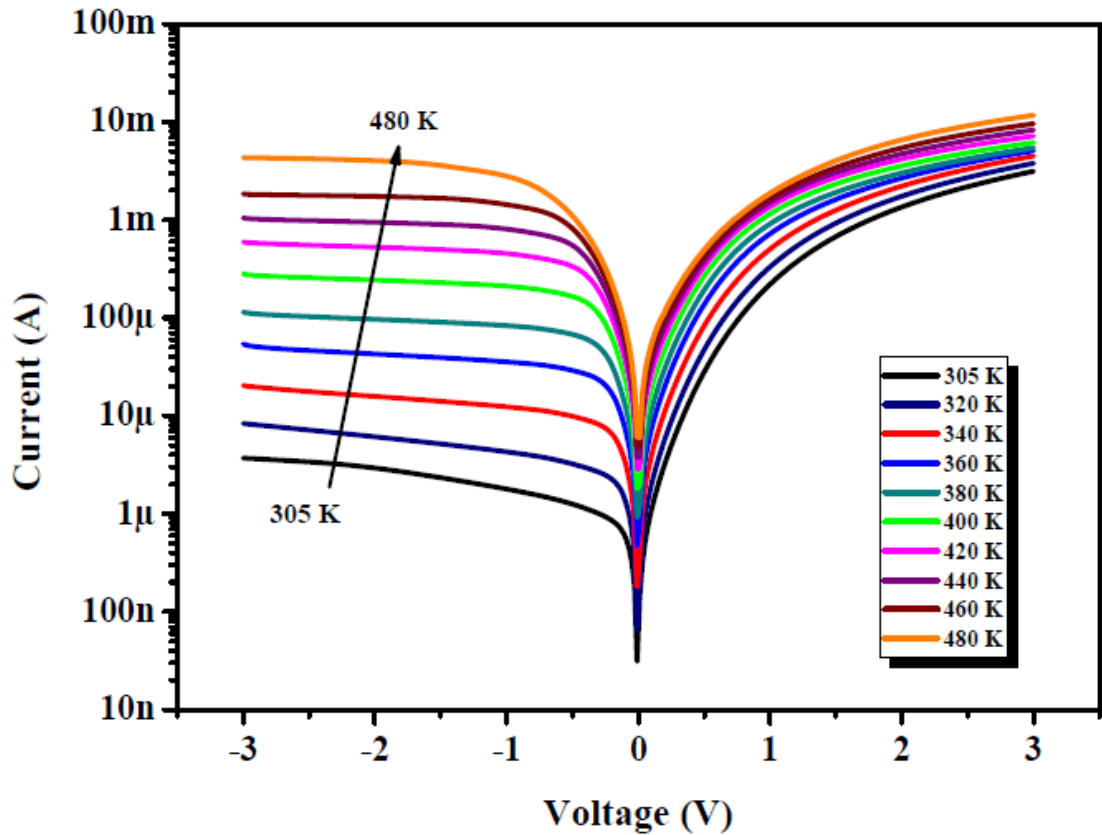


Figure 4.3. $\ln I$ - V plots of Au/NiO/n-Si structure between 305 and 480 K

Where A is the diode area, A^* Richardson constant, Φ_b is the barrier height. The ideality factor of a diode can be calculated from the slope of the linear region of the $\ln I$ - V plot of the diode using the equation

$$n = \frac{q}{kT} \frac{dV}{d \ln(I)} \quad 4.4$$

The $\ln I$ - V plots of Au/NiO/n-Si structure measured between 305 and 480 K are given in Figure 4.3. The ideality factor at 305 K calculated as 2.472. The ideality factor of for an ideal diode is should be unity. The deviation from 1 shows non-ideal diode behaviour. This deviation can be because of the effects of native insulator layer on n-Si surface, interface states and the effect of series resistance. The electrical parameters of the Au/NiO/n-Si diode are given in table 4.1. As seen from the table, the ideality factor of the structure decreases by increasing temperature. The ideality factor decreased from 2.472 (305 K) to 1.704 (480 K). Similar results have been reported for various heterojunctions. Tombak et al (2014) formed Coumarin 30/p-Si heterojunction device and determined its basic electrical parameters in the range from 300 and 380 K. They reported that the ideality factor decreased from 2.2 to 1.77. Furthermore, the decrease of ideality factors of Au/Pyronine-B/n-InP and Sn/MnHA/n-Si were also reported (Ocak, Kulakci et al. 2009; Soylu, Abay et al. 2010).

Table1. Some electrical parameters of NiO/p-Si heterojunction

Temperature (K)	$\ln I$ - V			Norde		
	n	Φ_b (eV)	$F(V_0)$ (V)	V_0 (V)	Φ_b (eV)	R_s (Ω)
305	2.472	0.725	0.7126	0.1114	0.723	9279
320	2.372	0.747	0.7321	0.1115	0.742	7136
340	2.245	0.777	0.7593	0.1116	0.767	4863
360	2.121	0.807	0.7860	0.1117	0.792	3222
380	2.013	0.841	0.8163	0.1314	0.827	1951
400	1.946	0.871	0.8598	0.0711	0.861	499
420	1.887	0.905	0.8911	0.0713	0.890	481
440	1.828	0.941	0.9280	0.0516	0.916	369
460	1.784	0.978	0.9602	0.0711	0.956	275
480	1.704	1.014	0.9942	0.0916	0.999	243

The barrier height of the junction can be calculated using I_0 value obtained from interception of $\ln I$ - V plot to I axis by the help of the equation

$$\phi_b = \frac{kT}{q} \ln \left(\frac{AA^*T^2}{I_0} \right) \quad 4.5$$

The barrier heights of the device were calculated using saturation current values by the help of the equation 4.5. Barrier height value of Au/NiO/n-Si device determined as 0.725 eV at 305 K. Table 1 and Figure 4.4 also show the increases of barrier height from 0.725 to 1.014 eV with increasing the temperature in the range between 305 and 480 K. As seen from both table and figure, the increase in barrier height linearly depend on temperature.

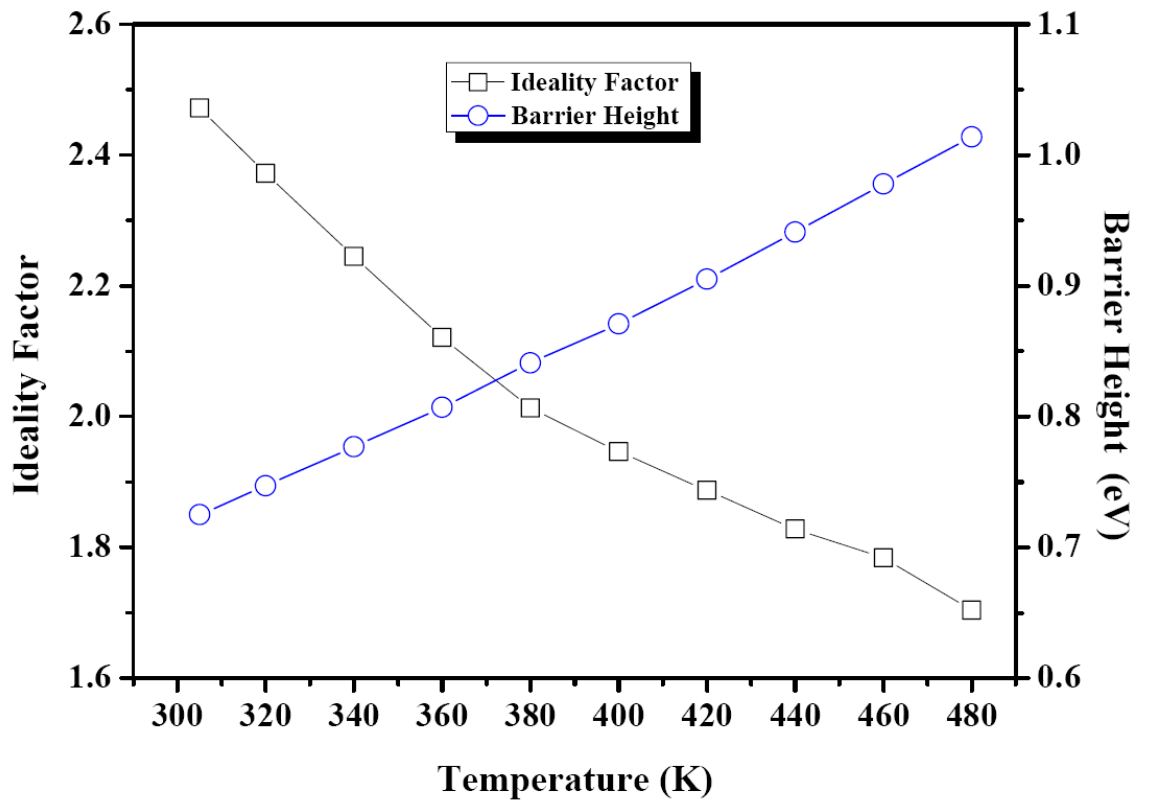


Figure 4.4. Temperature dependence of ideality factor and barrier height values obtained from $\ln I$ - V plot

Current-voltage measurements of the plots presented in Figure 4.4 have deviation from linearity for high voltages. This deviation implies the effect of series resistance. The series resistance results from the contact wires or bulk resistance of the NiO and n-Si semiconductors. The series resistances of the Au/NiO/n-Si structure were calculated by means of Norde functions given below as (Norde 1979)

$$F(V) = \frac{V}{\gamma} - \frac{kT}{q} \left(\frac{I(V)}{AA^*T^2} \right) \quad 4.6$$

where γ is the first integer greater than ideality factor and $I(V)$ is the current obtained from I - V measurements. The barrier height of device can be calculated using the minimum value of F vs. V plot using the equation

$$\phi_b = F(V_0) + \frac{V_0}{\gamma} - \frac{kT}{q} \quad 4.7$$

where $F(V_0)$ is the minimum $F(V)$ value and V_0 is the corresponding voltage value.

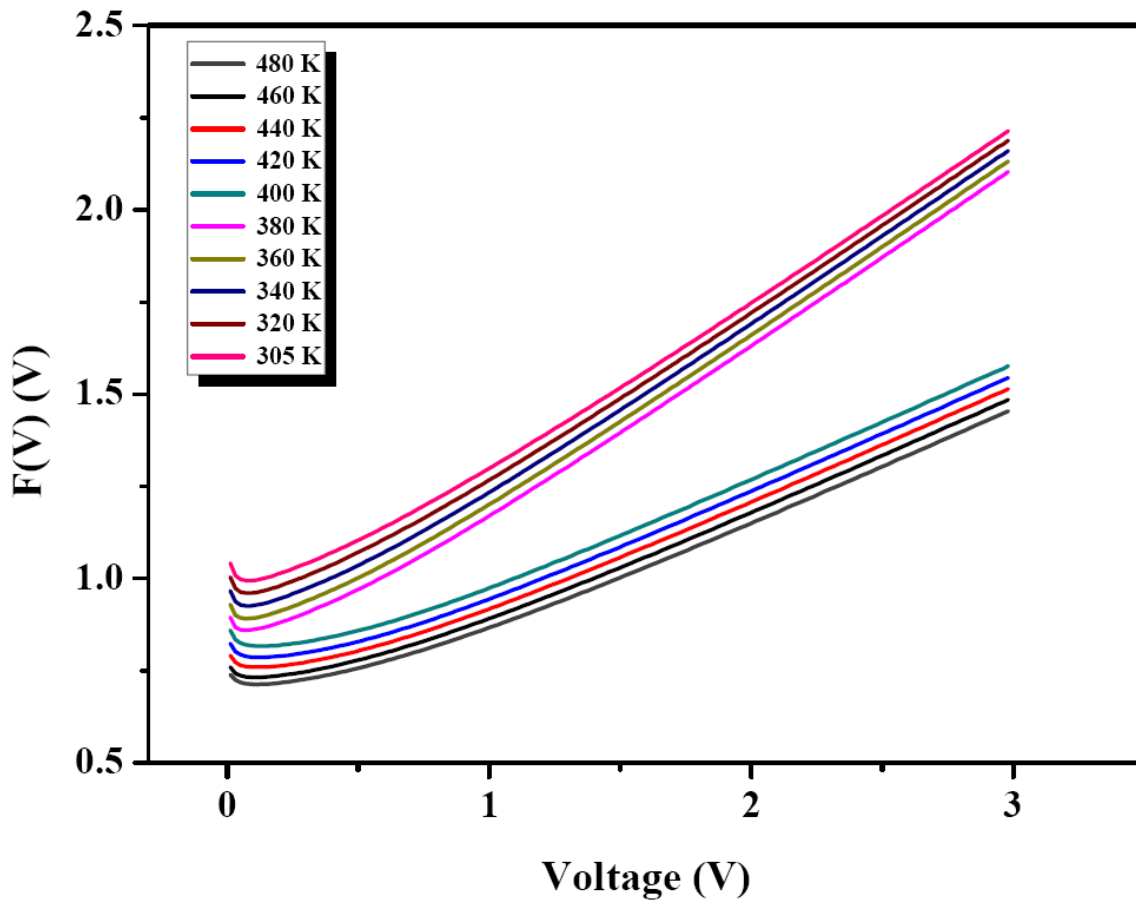


Figure 4.5. Norde plots of NiO/n-Si heterojunction between 305-480 K

$F(V)-V$ curves of Au/NiO/n-Si heterojunction structure with respect to temperature is shown in Figure 4.4. The series resistance of the device is executed through the relation

$$R_s = \frac{kT(\gamma - n)}{qI_{\min}} \quad 4.8$$

where $I_{\min}$ the corresponding current value at V_0 .

The barrier height and the series resistance values of the heterojunction are also depicted in table 1 and Fig. 4.5. As it is seen from the table and figure, the series resistance of the diode calculated as 9279 Ω at 305 K. This value decreased with the increase in temperature. The series resistance value of the device calculated as 243 Ω at

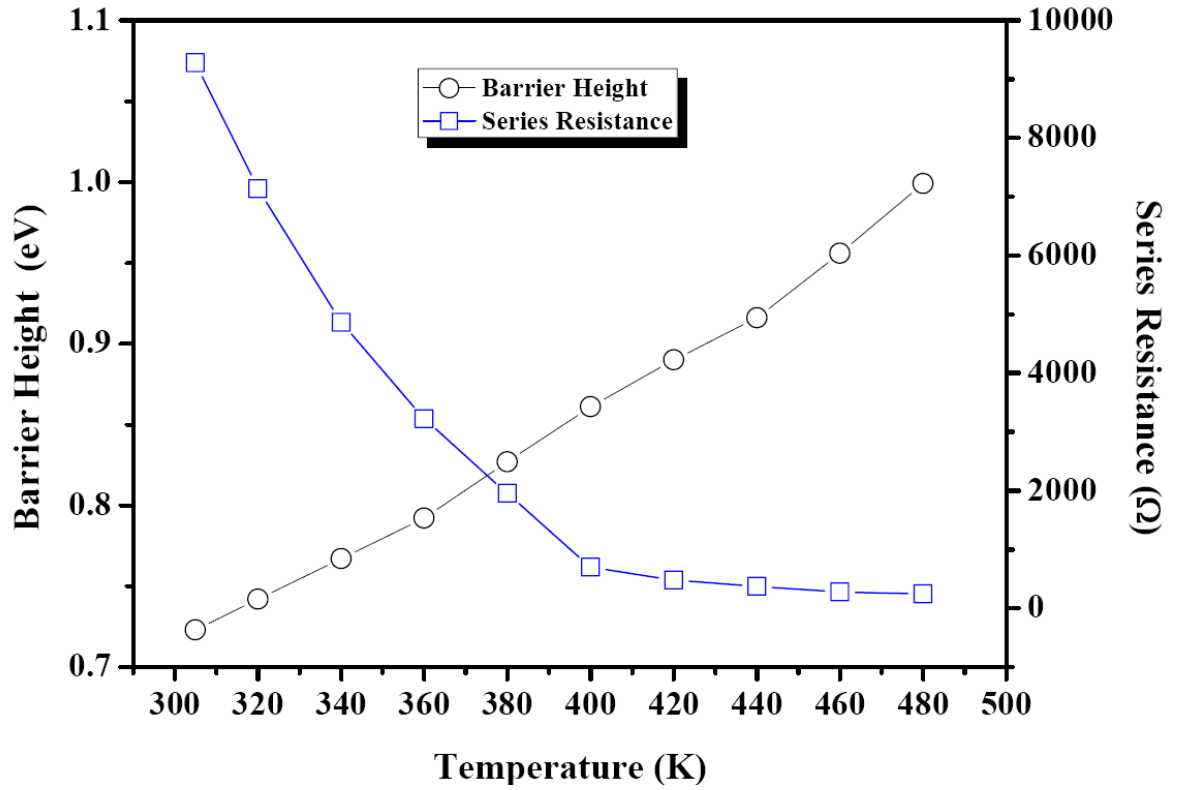


Figure 4.6. Temperature dependence of barrier height and series resistance values obtained from Norde plots

480 K. These results show the strong effect of the temperature on series resistance of the diode. Furthermore, the barrier height values of the heterojunction increased from 0.723 (at 305 K) to 0.999 eV (at 400 K) with the increase in temperature. These results proved that the thermionic emission theory has a strong dependence to the temperature as seen in equation 4.2. At lower temperatures, electrons are able to pass over the lower barriers and the current transport will be dominated by current flow through the patches of lower Schottky barrier height and a larger ideality factor. When the temperature increases, more electrons can get sufficient energy to pass over the higher barrier. Tecimer et al fabricated Au/(Zn-doped)PVA/n-GaAs Schottky barrier diodes by electrospinning technique (Tecimer, Türüt et al. 2013). They reported the the barrier height of diode as 0.145 eV at 80 K and 0.606 eV at 350 K. Deniz et al formed Au/Fe₃O₄/p-Si Schottky diodes using Fe₃O₄ nanoparticles (Deniz, Çaldıran et al. 2013). They made current-voltage measurements in a wide temperature range. They showed that series resistance of Schottky diode increased with the fall in temperature and it was because of the factors responsible for the increase of ideality factor or lack of free carrier concentration at low temperature.

4.4. Photoelectrical properties of NiO/n-Si heterojunction

Figure 4.6 shows the current-voltage plots of NiO/n-Si junction for various light intensities. As seen from the figure, light intensity has a strong effect on photoelectrical performance of the device. Some photoelectrical parameters including sensitivity to light at -2V (illuminated current/dark current), open circuit voltage and short circuit current values are given in table 4.2. As seen from the table, all photoelectrical parameters increase with the increase in light intensity. This property showed that the device had photodiode characteristics which are attributable to the formation of electron-hole pairs following optical absorption. Similar results have been reported for various metal oxide/silicon heterojunctions. For instance, Lee et al (2002) optimized n-ZnO/p-Si heterojunctions for photodiode applications. They deposited n-ZnO thin films onto p-Si semiconductor at various temperatures in Ar/O₂ ambient. They reported that all structures had typical rectifying properties and maximum amount of photocurrent observed for n-ZnO/p-Si heterojunction when the ZnO film was deposited at 480 °C.

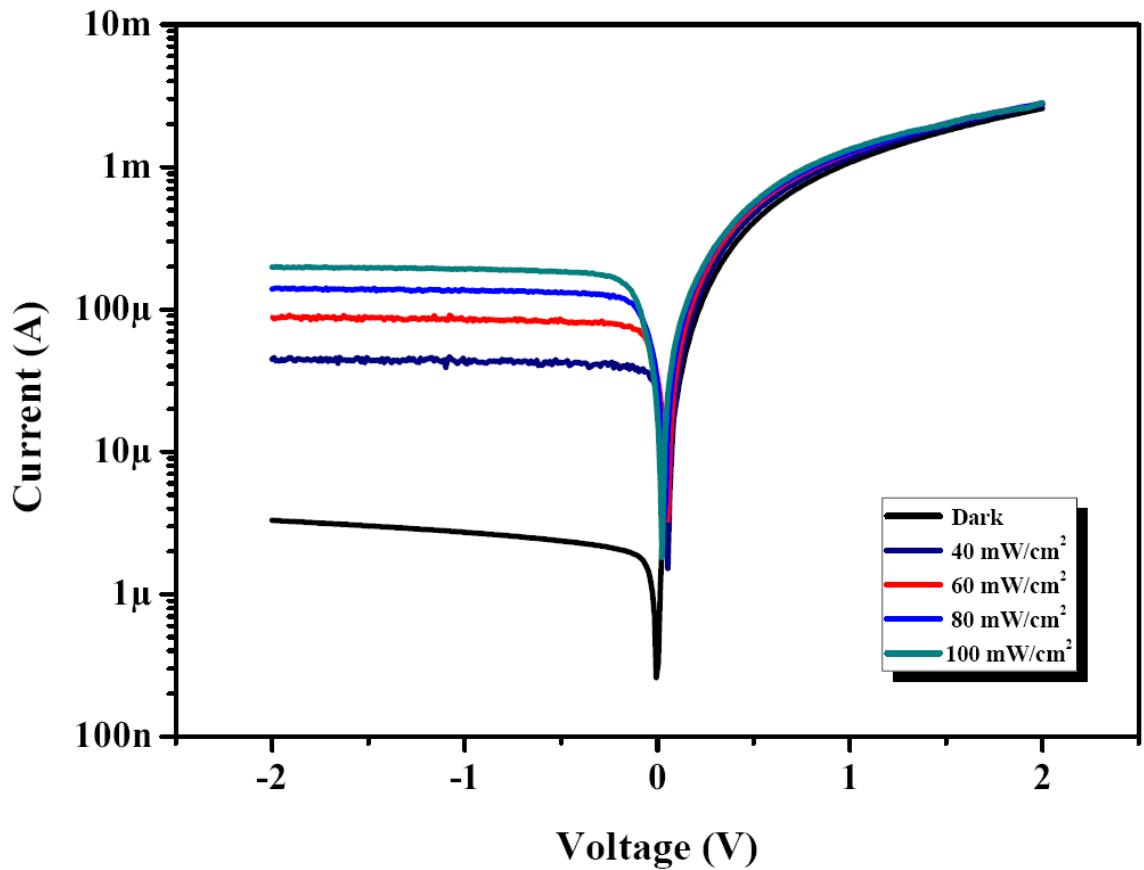


Figure 4.7 $\ln I$ - V plots of NiO/n-Si heterojunction in dark and various illumination conditions at room temperature

The results showed that film growing conditions had strong effects on photoelectrical characteristics. Similarly, Alsayed et al prepared CuNiO₂ thin film by sol gel method onto p-Si substrate (Elsayed, Çavaş et al. 2015). They determined the size of CuNiO₂ nanoparticles as 115 nm and the band gap of the film as 2.4 eV. They showed that the Al/p-Si/CuNiO₂/Al heterojunction good rectification property in dark and high photosensitivity value of 1.02×10^3 under 100 mW/cm².

Table 2. Some photoelectrical properties of NiO/n-Si heterojunction

Light intensity (mW/cm ²)	Sensitivity (times)	V_{OC} (mV)	I_{SC} (μA)
40	15.11	55	22.38
60	28.92	55	26.97
80	45.56	55	35.26
100	63.95	55	36.41



5. Results and suggestions

The effect of temperature on electrical properties of NiO/n-Si heterojunction was studied. For this purpose, NiO thin films were grown on n-Si and glass substrates by radio frequency (RF) reactive sputtering technique. High purity Ni metal was used as target and oxygen was used as reactive gas. The films were annealed at 500 C to increase the crystal quality.

UV-Vis spectra were used to determine the optical properties of the reactively sputtered NiO thin film. The film was deposited on a glass and its absorbance and transmittance properties were determined. Fig. 4.1 shows the both absorbance vs. wavelength and transmittance vs. wavelength plots. As seen from the figure, the transmittance value of the NiO thin film has a sharp increase between 300 and 500 nm. The transmittance value is NiO thin film at 300 nm is 59 % and this value reaches 88 % at 530 nm. The increase continues till 1000 nm. At 1000 nm the transmission value of the film is 98 %. After 1000 nm the transmittance of the film is nearly constant. It means that the NiO thin film is very transparent visible region and nearly full transparent in infrared region. The optical direct band gap of reactive sputtered NiO thin film was determined by using absorption vs. wavelength data with the help of equation 4.1 using $(Ah\nu)^2 - h\nu$ plot. Figure 4.2 shows the $(Ah\nu)^2 - h\nu$ thin film. The E_g of the NiO thin film was determined as 3.02 eV by extrapolating the straight line of the graph to intercept the photon energy.

Current-voltage measurements of NiO/n-Si heterojunction showed that the device had an excellent rectification. The electrical properties of the junction were characterized by means of thermoionic emission theory. The electrical parameters of the Au/NiO/n-Si diode are given in table 4.1. As seen from the table, the ideality factor of the structure decreases by increasing temperature. The ideality factor decreased from 2.472 (305 K) to 1.704 (480 K). The barrier height of the junction calculated using I_0 value obtained from interception of $\ln I - V$ plot to I axis by the help of the equation 4.5. Barrier height value of Au/NiO/n-Si device was determined as 0.725 eV at 305 K. Table 1 and Figure 4.4 also show the increases of barrier height from 0.725 to 1.014 eV with increasing the temperature in the range between 305 and 480 K. As seen from both table and figure, the increase in barrier height linearly depend on temperature.

The barrier height and the series resistance of the junction were also calculated using Norde method. The series resistance of the diode calculated as $9279\ \Omega$ at 305 K. This value decreased with the increase in temperature. The series resistance value of the device calculated as $243\ \Omega$ at 480 K. These results show the strong effect of the temperature on series resistance of the diode. Furthermore, the barrier height values of the heterojunction increased from 0.723 (at 305 K) to 0.999 eV (at 400 K) with the increase in temperature. These results proved that the thermionic emission theory has a strong dependence to the temperature as seen in equation 4.2.

Finally, the influence of light intensity on electrical properties of NiO/n-Si heterojunction was studied. It was seen that light intensity had a strong effect on photoelectrical performance of the device. Some photoelectrical parameters including sensitivity to light at -2V (illuminated current/dark current), open circuit voltage and short circuit current values are given in table 4.2. As seen from the table, all photoelectrical parameters increase with the increase in light intensity. This property showed that the device had photodiode characteristics which are attributable to the formation of electron–hole pairs following optical absorption.

The results showed that NiO thin films can be used in the fabrication of temperature and light sensors.

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