INFLUENCE OF ANNEALING TEMPERATURE ON THE PROPERTIES OF INDIUM TUNGSTEN OXIDE THIN FILMS

INDFLYDELSE AF ANNEALING TEMPERATURER PÅ EGENSKABERNE AF INDIUM WOLFRAMOXID TYND FILM

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Abstract

In recent times tungsten doped indium oxide, In_2O_3 :W (IWO) thin films have emerged as a promising transparent conducting oxide (TCO) material, due to the attributes of high carrier mobility and high transmittance in the visible and infra-red region. In this thesis, the influence of post-deposition annealing on the properties of two sets of IWO thin films: one having 1.6 atomic percent(at.%) W and the other having 3.6 at.% W, both deposited at room temperature by RF magnetron sputtering, are presented. The as-deposited IWO films are found to be typically highly resistive and barely optically transparent. In order to explore the beneficial effect, if any, of post-deposition annealing on the optical and the electrical properties of the IWO films, detailed investigations were carried out for a range of annealing temperatures, from 150 to 450°C. The optical properties of the films are presented in the form of total transmittance; total reflectance and optical bandgap (E_g) . The electrical properties of the films were obtained from four-probe electrical resistivity and Hall-effect measurement system. The transmittance of the films of both the sets greatly increases and reaches up to 90% in the IR-region with annealing temperatures at or above 300°C. The bandgaps were found to increase with the rise in the annealing temperature up to 300°C, but decrease with further increase in the temperature beyond 300° C. A temperature dependent variation was also observed for carrier mobility (μ), carrier concentration (*n*) and resistivity (ρ). The mobility of the IWO film with 1,6 at.% W improves by a factor of 15 through annealing up to 300°C and falls beyond that, while the carrier concentration was found to reduce with the rise in the annealing temperature. This fall in *n* is related to the reduction in the Oxygen vacancies due to the structural restructuring on annealing. Further investigations revealed a correlation between the optical and the electrical properties where E_g increases as with rising values of n due to the Burstein-Moss effect till it reaches a plateau, and with further rise in the n, the E_g decreases due to a bandgap narrowing effect. The dependence of μ with *n* can be seen as a rise in μ with decreasing values of *n*, followed by a fall with further lowering of *n*. The initial rise in μ with decreasing *n* can be related to the reduced ionized impurity scattering. However, as an increase in the annealing temperature brings about a lowered value of *n*, there are also concurrently structural changes occurring in the films. Previous studies of the structural properties of room temperature deposited IWO films indicate an amorphous structure of the films. However, we contend that in our study, at the higher annealing temperatures, the films develop small crystallite grains which enhance the grain boundary scattering effect, leading to the decrease in the mobility beyond 300°C. We conclude that post-deposition annealing is an effective method to improve the optical and electrical properties of the IWO films, but the optimum temperatures depend on the external doping in the films.

Resumé

I den seneste tid har wolframdoteret indiumoxid, In₂O₃:W (IWO) tynd-film vist sig som en lovende transparent ledende oxid (TCO), på grund af dens egenskaber, som høj mobilitet af ladningsbærer og høj transmission i det synlige og infrarøde område. I denne afhandling præsenteres indflydelsen af opvarming efter deponering på egenskaberne af to sæt IWO tyndfilm: én, der har 1,6 atomprocent (at.%) W og den anden har 3,6 at.% W, begge deponeret ved stuetemperatur af RF magnetron sputtering. De deponerede IWO film er fundet til at have meget høj resistivitet og være næppe gennemsigtig. For at udforske den gavnlige effekt, hvis der er nogen, af post-deposition varmebehandling på de optiske og elektriske egenskaber af IWO filmene blev detaljerede undersøgelser udført for en række annealing-temperaturer fra 150 til 450°C. De optiske egenskaber af filmene er præsenteret i form af total transmission; total refleksion og optisk energigab (E_g) . De elektriske egenskaber af filmene blev opnået gennem et fire-sonde-elektriskmodstand og et Hall-effekt målesystem. Transmission af filmene i begge sæt øges stærkt og når op til 90% i IR-regionen ved annealing-temperaturer på 300°C eller derover. Energigabene er fundet til at vokse med stigende annealing temperatur på op til 300°C, men aftager når temperaturen stiger over 300°C. En variation i temperatur afhængig blev også observeret for ladningsbærer mobilitet (μ), ladningsbærer koncentration (n) og resistivitet (ρ). Mobiliteten af IWO film med 1,6 på. % W forbedres med en faktor 15 gennem varmebehandling op til 300°C og falder ved temperaturer ud over dette, mens ladningsbærer koncentrationen viste sig at reduceres ved stigende temperatur. Dette fald i *n* er relateret til reduktionen af oxygen huller (vacancies) grundet omstrukturering ved annealing. Yderligere undersøgelser afslørede en sammenhæng mellem de optiske og elektriske egenskaber, hvor E_g stiger med stigende værdier af n på grund af Burstein-Moss effekten indtil den når et plateau. Med yderligere stigning i n aftager E_g på grund af en energigab indsnævrende effekt. Afhængigheden af μ på n kan ses som en stigning i μ med faldende værdier af n, efterfulgt af et fald i μ ved yderligere sænkning af *n*. Den første stigning i μ med faldende *n* kan relateres til den reducerede spredning forårsaget af ioniserede urenheder (reduced ionized impurity scattering). Eftersom en stigning i annealings temperaturen medfører en reduktion af *n*, sker der samtidigt strukturelle forandringer i filmene. Tidligere undersøgelser af de strukturelle egenskaber ved stuetemperatur deponerede IWO film indikerer en amorf struktur af filmene. Der hævdes i denne undersøgelse, at filmene ved høje annealings temperaturer udvikler små krystalline kerner som forøger korngrænse spredningseffekt (grain boundary scattering effect), hvilket fører til et fald i mobilitet ved temperaturer over 300 °C. Vi konkluderer, at post-deposition annealing er en effektiv metode til at forbedre de optiske og elektriske egenskaber af IWO tynd film, men de optimale temperaturer afhænger af den eksterne doping i filmene.

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Chapter 1

Introduction

Transparent conductive materials are used in many electronic technical devices. They are used in field-effect transistor (FET) and optoelectronic devices like LED, Touchscreens, Smart Windows, LCD TV's and solar cells. They are known for their high optical transmittance in the visible range and high electrical conductivity.

Today the mostly used type of transparent conducting materials are transparent con-



Figure 1.1: an example of application for transparent conducting material, solar cells. Picture taken from ref [33]

ducting oxides (TCOs), which took over the market from silicon. TCOs are n-type semiconductors with bandgaps bigger then 3eV, which are doped intrinsic (defects and vacancies) or extrinsic (external dopant). Examples of TCOs are ITO, SnO, ZnO and InO. Indium tin oxide (ITO) was widely used, but because of the high cost of indium the usage is been narrowed. ITO is stil the dominant material in flat-panel displays [16]. While other TCOs are used in the manufacturing e.g ZnO and SnO in the manufacturing of thin-film solar cells. Transparent conductive materials is a large research area, trying to optimize the already known materials and to develop new ones, e.g. are Graphene and nanowires upcoming transparent conducting materials. However, until now the first choice Transparent conducting material is indium oxide, because of its great electrical and optical properties in combination with its chemical stability [2]. A subgroup of TCOs

are high mobility TCOs, which have carrier mobility above $65 \text{ cm}^2/\text{Vs}$. This group is important for increasing the electrical conductivity. The conductivity is given by electron charge times the mobility times the carrier concentration $\sigma = e\mu n$. There are two ways to increase the conductivity, by increasing the carrier concentration or the carrier mobility. Carrier mobility depends on carrier concentration, if increasing the carrier concentration to far electron scattering will become a big factor and mobility will decrease. The challenge is to find the state where μn has the highest possible value. High mobility improves electrical conductivity without the cost of optical transparency in the visible light region, and simultaneously it provides high operation speed in transparent electronic devices [1]. Tungsten doped indium oxide (IWO) is a promising candidate for high mobility. Indium oxide (In_2O_3) has a direct bandgap of 3,7eV, is fairly transparent in the visible region and has high electron concentration. When it is doped with transition metals like tungsten (W), Titanium (Ti), Molybdenum (Mo) or other (extrinsic doping) the carrier concentration can be raised further up. The electrons can come from impurities, oxygen vacancies (intrinsic doping) [2] and from activating W^{6+} during heat treatment (annealing). Doped indium oxide has high electron concentration, to get a high conductivity the mobility must be increased. That can be done by post deposition treatment like annealing. IWO is an amorphous material, which becomes crystalline during annealing. There are different deposition techniques, the samples in this project are deposited at room temperature by magnetron sputtering. Deposition at room temperature is of great interest due to the application of IWO thin films. IWO thin films are often developed on heat sensitive substrate e.g. the a-Si films on the heterojunction solar cell [1]. An other benefit of room temperature is the reduce of energy input. The aim of thesis is to study the impact of post deposition annealing on the optical and electrical properties of (highly doped) IWO thin films. The samples are deposit on borosilicate glass at room temperature with 1,6 atmospheric percent tungsten(at.%W) and 3,6 atmospheric percent tungsten. After deposition the samples were annealed at different temperatures from 150° C - 450° C, one sample of each deposition series stayed unannealed, further mentioned as non annealed or room temperature sample.

The experimental setup and theory can be found in kapitel 2 and the results in kapitel 3. The discussion can be found in kapitel 4

Chapter 2

Experimental details

This chapter will give an insight in the thin film fabrication of 1,6 and 3,6 atmospheric percent tungsten(at.%W) doped indium oxide (IWO). Furthermore the optical and electrical experimental set-up and theory are processed.

2.1 Thin film fabrication

Before developing the samples, the substrate, which is borosilicate glass, must be cleaned. After cleaning the glass, the thin films are developed by magnetron sputtering.

2.1.1 Substrate cleaning

The borosilicate glass were cleaned chemically with Acetone, ISO-Propanol and deionized water in a ultrasonic bath. The glass is first placed in Acetone, then in deionized water and finally in ISO-propanol each time it is place in the ultrasonic bath for five minutes. When the last step is finished the glass is carefully blown dry and sat in a heating cabinet for at least half an hour.

2.1.2 Radio frequency magnetron Sputtering

Although there are many other physical and chemical deposition techniques as molecular beam epitaxy and pulsed laser ablation [3], which partially gives give better results, magnetron sputtering is chosen because of its low cost and scalability. The rf-magnetron sputtering is a form of physical vapour deposition. Sputtering is a process where material is ejected from a target (source) onto a substrate (destination), sketched in figur 2.1. The ejection of atoms occurs by bombarding the surface of the target with argon carrier gas ions (Ar⁺) figur 2.1 [3]. For producing the samples in this project AJA ATC Orion sputtering system was used with parameters as shown in tabel 2.1, with borosilicate glass as substrate.



Figure 2.1: Deposition of substrate in UHV chamber via. Magnetron sputtering. The yellow atoms are Indium Oxide doped with Tungsten that has been knocked of the target with Ar-ions. The blue atom is the electron which is trapped in magnetic field. The pink cloud is the plasma created from collision of an electron and a neutral Ar. This figure is taken from Ref[4].

Table 2.1: Parameters of the	sputtering process	at room tem	ıperature
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Parameter	Value [unit]
Deposition time	36 [min]
Magnetron power	40 [W]
Working pressure	2,2 [mT]
Tungsten doping level	3.6[at.%] and 1.6 [at.%]
Gas composition	Ar:20, <i>O</i> ₂ : 0, Ar+ <i>O</i> ₂ :0

2.2 Post deposition annealing

After the deposition the samples were annealed for an hour at different temperatures. The annealing took place in an air furnace with Nitrogen flow. Nitrogen is not as reactive as Oxygen. The temperature is measured in the middle of the furnace, close to the samples, a sketch of the furnace is seen on figur 2.2. The samples are placed in the furnace, when the temperature has stabilized. The annealing temperatures were set to 150°C, 200°C, 350°C

and 400°C for the 1,6at.%W series and to 250°C, 300°C, 350°C, 400°C and 450°C for the 3,6 at.%W. The temperatures are different for the samples series. The 1,6at.%W series were annealed and it was seen, that there were not much difference between non annealed and annealed at 150°C, but there were a big difference between annealing temperatures of 200°C and 300°C. For get a better idea of what there is happening at higher temperatures, the 3,6at.% series were annealed at different temperatures. Both series have one non annealed sample, referred to as RT.



Figure 2.2: A sketch of the furnace used for annealing. Around the sample, the temperature is almost constant and there is a constant Nitrogen flow. The blue line presents the thermometer, the temperature is measured close to the sample.

2.3 Optical characterisation

This section is about the optical measurements and calculations. The total transmittance and total reflectance are measured by spectrophotometry. From the out comes the absorption can be calculated by subtracting the total transmittance and total reflection from 100%. The optical bandgap can be calculated through the absorption coefficient, which can be found from the total transmittance and total reflectance measurement.

2.3.1 UV-VIS-IR- optical spectrophotometry

The optical measurements are exerted on a Perkin Elmer Lambda 1050 spectrophotometer with a 150 nm integration sphere for wavelength from 300nm to 2500nm. A sketch of the set up can be seen onfigur 2.3, it is a sketch for Lambda 950, but it is the same principle for Lambda 1050. There is a hole for incoming light, for transmittance measurement the sample is placed between the incoming light beam and the sphere, marked red on the figur 2.3. For the reflection measurement there is a hole on the back at the sphere, marked green on figur 2.3. The sample is angled by 8° to the incident light so the mirrored light do not escape through the entrance hole. For the reflection calibration a calibrated mirror is used, which spreads the reflected light like the sample.



Figure 2.3: Picture of the 150 mm integrating sphere installed in a Lambda 950 with a top down view of the diagram of the sphere below. The red marked area is where transmission of the material is done, and the green area the reflectance of the material. Figure taken from ref[5]

2.3.2 Optical bandgap calculation

The relation between the absorption coefficient (α) and optical bandgap (E_g) is given by [6]

$$(\alpha h\nu)^2 = C(h\nu E_g) \tag{2.1}$$

Where C is a constant. So the optical bandgap is the intercept with the x axis of the $(\alpha h\nu)^2$ vs $h\nu$ graph where $h\nu$ is the photon energy and α the absorption coefficient. The absorption coefficient for direct bandgaps is given by

$$\alpha = -\frac{ln(\frac{T}{1-R})}{d} \tag{2.2}$$

where d=55nm=5, $5 * 10^{-6}$ cm is the thickness of the samples. The energy of the photon is given by $hv = \frac{1240}{wavelength[nm]} [eV]$, where v is the photon frequency and h is plancks constant. In the calculations the reflectance corrected transmission T/1-R is used, to avoid most of the optical interference effect [6]. When plotting $(\alpha hv)^2$ as function of the photon energy, the bandgap can be found through the intercept and slope of the a tangential fit to the most linear region, demonstrated on figur 2.4. The bandgap is then given by dividing the

intercept with the y-axis by the slope, times -1 to remove the minus sign, which gives the intercept with the x-axis.



Figure 2.4: Band gap fitting for 1,6 at.%W (a) and 3,6 at.%W (b) respectively.

2.4 Electrical characterisation

This section is about the electrical measurement, the Hall effect measurement, which out come is the resistivity, carrier concentration and carrier mobility of the samples.

2.4.1 Four-point probe technique

The Hall effect is measured by four point probe technique in the Van-der-Pauw configuration [7, 8] on a self made instrument presented in ref[9]. The samples are attached on holders schematic shown in figur 2.5. The edges of the samples are attached to the contacts of the holder by silver paste, this are the four probes, they can be located arbitrarily around the edges. In the past it was necessary to know the distance between the contacts to determine the in-plane geometric factor. Through the four-point probe method the geometric factor is determines by switching the probes, which are used for current and voltage, no distance measurement necessary. Further description can be found in ref [7, 9].





2.4.2 Hall effect

The Hall coefficient is given by

$$R_H = \frac{V \cdot d}{B \cdot I} \tag{2.3}$$

where *V* and *I* are the voltage and current across the sample respectively, *d* is the thickness of the conducting layer (the thin film), and B is the strength of the magnetic field. From the Hall coefficient the mobility (μ) and the carrier concentration (n) can be calculated.

$$\mu = \frac{R_H}{\rho}, \quad n = \frac{1}{e \cdot R_H} \tag{2.4}$$

 ρ is the resistivity of the sample and *e* the electron charge [9]. The relation between resistivity (ρ), mobility (μ) and carrier concentration (*n*) is given by

$$\rho = \frac{1}{n\mu e} \tag{2.5}$$

The Hall measurements provide information for not only the Hall coefficient, but also the resistivity, mobility, carrier concentration and the related errors For each sample the measurement has been run five times to get a collection of data. For the data evaluation the average of these 5 measurements are used. Except for the samples annealed at 300°C, 350°C and 450°C doped with 3,6 at.%W, for those samples, maybe because of high resistivity, there where large variation between the data values, so for those samples the three-four closets measurement results were taken, to improve the results.

2.5 Error analysis

To calculate the errors of the electrical measurement, hence the error og the resistivity, mobility and carrier concentration, the sample standard deviation for n measurements is used;

$$\sqrt{\sum \frac{(x_i - \bar{x})^2}{n - 1}} \tag{2.6}$$

where x_i is the result of one measurement and \bar{x} is the average. An experimental error for the Hall measurement occurs in relation to the contact, where the Ag paste is placed figur 2.5. The errors for horizontal and vertical dimension of the silver blob respectively are given by

$$\delta \rho_x = \rho \frac{-l^2}{16D^2 ln(2)}$$
 and $\delta \rho_y = \rho \frac{-l^2}{4D^2 ln(2)}$ (2.7)

where ρ is the resistivity value, l is the horizontal and vertical length of the blob respectively and D is the diagonal of the sample [7]. For the sample in this thesis the error is so low, that it can be neglected.

The error for the bandgap (E_g), is found from the intercept and slope deviation of the fit 2.3.2. It can be calculated by Gaussian Error distribution, as the errors are assumed to be uncorrelated:

$$\langle E_g \rangle \sqrt{\left(\frac{Err\ intercept}{intercept}\right)^2 + \left(\frac{Err\ slope}{slope}\right)^2}$$
 (2.8)

Chapter 3

Results

This chapter presents the results of the optical and electrical measurements and calculation for samples deposited with 1,6 atmospheric percent tungsten (at.%W) and 3,6 at.%W and annealed with the annealing temperatures (Ta) from non annealed (RT) to 450°C. Starting out with presentation of the optical transmittance, reflectance and absorption for wavelength from 300 to 2500nm and moving on to the optical band gap. Round of with results for the electrical properties as the resistivity, mobility and carrier concentration.

3.1 Optical properties

This section presents the optical results for 1,6 atmospheric percent tungsten (at.%W) and 3,6 at.%W deposited and annealed samples, the total transmittance, total reflection and the resulting absorption, given by 100-T-R, and the band gap for varying annealing temperature.

Figur 3.1 presents the development of the total transmittance and total reflection for varying annealing temperature. figur 3.1a show the transmission for the 1,6 at.%W deposit series. The transmittance for the non annealed sample, labelled as RT, is very low a little over 40%. The transmittance increases not much, when the annealing temperature is raised up to 150°C. At the annealing temperature of 200°C the transmittance is improved in the inferred range up to 60%. For 300°C Ta the transmittance is improved in the visible range at further improved in the IR-range above 80 %. The transmittance for 300°C Ta temperatures for the other annealing temperatures. For Ta of 350°C and 400°C the transmittance stays above 80%.



Figure 3.1: The total transmittance and total reflection spectra for brought wavelength range 300-2500nm for varying annealing temperatures from non annealed (RT) to 450° C. Graph a and b show the total transmittance and graph c and d show the total reflectance for In₂W₃ thin films deposited with 1,6 at.%W and 3,6 at.%W respectively.

Figur 3.1brepresents the transmittance for the 3,6 at.%W deposited series. The transmittance for the non annealed sample stays below 40%. The transmittance increases, when the annealing temperature is raised to 250°C, the highest improvement takes place in the IR-region, raising the annealing temperature further the transmittance increases further in the IR and also in the visible range. There is not much difference between 300°C, 350°C and 450°C Ta, for those temperatures the transmittance reaches slightly over 90% about a wavelength of 2000nm. The non annealed samples labelled as RT for both 1,6at.%W and 3,6at.%W deposited IWO have the lowest transmittance, the samples themselves appeared darker than the annealed ones. The transmittance for 3,6at.%W RT is below 40%, it is even lower then equivalent of the 1,6 at.%W series, which reaches a little over 40%. The sample annealed at 150°C appeared slightly lighter than the non annealed and has a little higher transmittance compared to 1,6at.%W RT. There is a bigger difference between the sample annealed at 150°C and at 200°C, both from the 1,6at.%W series and seen on figur 3.1a. the next higher transmittance reaching above 70% in the IR-range occurred by the sample annealed at 250°C. The transmittance for samples annealed at 300°C, 350°C and 400°C, and for 3,6at.%W also 450°C, are close to each other, with some deviation. For those samples the highest transmittance is reached, which is slightly above 90% at a wavelength around 2000nm for both 1,6at.%W and 3,6at.%W doped IWO. In the visible range, which occurs from 380nm to 760nm, the transmittance reaches above 80%. For both deposition series the increasing of the annealing temperature gives rise to the total transmittance.

The total reflection for the 1,6at.%W deposition series is presented in figur 3.1c. The non annealed sample shows a high reflection, the reflection for 150°C is a little lower, most in the IR-region. Increasing the annealing temperature to 200°C decreases the reflection further especially in the IR-region. There happens also a little right shift of the peak in the visible region. For higher annealing temperatures, above 300°C the peak is shifted to the left below the wavelength of 500nm. The reflection of 300°C Ta lays a little beneath the ones of 350°C and 400°C between the wavelength of about 500nm to around 1700nm. Above about the wavelength of 2200nm the reflection for 300°C Ta lays above the ones of 350°C and 400°C. There is not much improvement in the visible range, the reflection lays around 27% fro RT and all Ta except the one for 300°C Ta, it lays a little below about 26%, and the one for 200°C Ta, which lays about 25%. In the infra red region the reflection for the higher annealing temperatures 300°C, 350°C and 400°C reaches beneath 10%. The transmittance increases and the reflection decreases with increasing annealing temperature.

Figur 3.1d presents the reflection for the 3,6at.%W deposition series. The reflection for the non annealed sample is high, the peak in the visible range lays above 30%, near 34%. The reflection for 200°C Ta is much lower then the one for RT, in the IR range it lays beneath 20% and in the visible it lays just a little above 22%. The peak in the visible range is shifted to the right, whereas for Ta above 300% it is shifted to the left, below 500nm. The peak for 300°C lays around 24%, whereas the peaks of 350°C, 400°C and 450°C lay about 26-27%. The reflection of 300°C, 350°C, 400°C and 450°C Ta at wavelength above 1500nm reaches values beneath 10%. Like for the 1,6at.%W series the absorption will decrease with increasing annealing temperature. The highest reflections occurs in the

visible range and the highest is seen for the non annealed sample in the 3,6at.%W series, which is slightly below 34%. The lowest reflections under 10% are reached by the samples annealed by 300°C-450°C on both series. As in the transmittance the curves for the higher annealing temperature are close at least for the 3,6at.%W series. For the 1,6at.%W series there are small difference, especially for the sample annealed at 300°C. The curves for RT and 150°C in the 1,6at.%W series are close too, the curve for 150°C is slightly beneath the one for RT. The curves at small wavelength for low temperatures are broader then the curves for higher temperature for both deposition series. Overall the transmittance increase and the reflection decrease with increasing annealing temperature. The resulting absorption, given by 100% - total reflection- total transmittance, is seen in figur 3.2.



Figure 3.2: Resulting absorption, graph a displays the absorption for 1,6 at.%W for varying annealing temperatures and graph b displays the absorption for 3,6 at.%W for varying annealing temperatures. The annealing temperature is variating from non annealed (RT) to 450°C.

The absorption for the 1,6 at.%W deposition series is presented in figur 3.2a. The absorption for the non annealed sample is high compared to the absorption of the other samples, the absorption for 150°C Ta lays close by about 30%. There is a bigger difference to 200°C Ta then between RT ans 150°C Ta. The decrease in absorption takes especially place in the IR range, where the absorption comes close to 22%. For higher annealing temperature the absorption comes close to zero in the visible and part of the IR-region. The absorption for 300°C Ta increases at wavelength above 1000nm. For the 3,6 at.%W series almost the same behaviour can be obtained, the highest absorption is occurred from the non annealed sample. The absorption improves with increasing the annealing temperature, for 200°C highest improvement is reached in the IR-range. For high Ta as

300°C and higher the absorption comes close to zero.

The absorption is significantly deduced by increasing the annealing temperature. The lowest absorptions, below 10% occurs for samples annealed at temperatures above 300°C for the series of 1,6 at.%W and 3,6 at.%W respectively. The highest absorptions is seen for the non annealed samples.



Figure 3.3: The calculated band gap for variating annealing temperatures from non annealed (RT) to 450°C. Graph a and b present the results of the band gap calculation for 1,6 at.%W and 3,6 at.%W respectively.

Annealing Temp. (Ta)	Band gap [eV] 1,6at.%	Band gap [eV] 3,6at.%
RT	3,27	2,46
150°C	3,44	-
200°C	3,66	-
250°C	-	3,74
300°C	3,92	3,82
350°C	3,88	3,81
400°C	3,83	3,85
450°C	-	3,82

Table 3.1: The Band gap values for the 1,6 at.%W and the 3,6 at.%W deposit series

The band gaps calculated from the absorption coefficient, review afsnit 2.3.2, are presented in figur 3.3. figur 3.3a shows the band gaps for the series deposited with 1,6 at.%W as function of the annealing temperature. For the 1,6 at.%W series the band gap is lowest at 3,27eV for the non annealed sample. The band gap increases up to 3,44eV for 150°C Ta and further up to 3,92eV for 300°C Ta, which is the biggest band gap. For annealing temperatures above 300°C the band gap slightly decreases down to 3,83eV. The band gap for the 3,6 at.%W series is presented in figur 3.3b, it starts at 2,46eV for the

non annealed sample and increases to 3,7eV for 200°C. The graph flattens out around 3,82eV fro high annealing temperature. There is a greatly difference, more then 0,5eV, between the band gap for the non annealed samples in the 1,6 at.%W and 3,6 at.%W series. So the band gap value for the non annealed sample for the 3,6 at.%W series is much lower, then for the non annealed sample of the 1,6 at.%W series, whereas the values for annealing temperatures above 250°C, are almost similar, varying between 3,8eV and 3,9eV, for both series. Neglecting the band gap for 3,6 at.%W RT, the average band gap lays around 3,8eV. For both series the value of the band gap increases with increasing annealing temperatures.

3.2 Electrical properties

The electrical results of the Hall measurement as function of the annealing temperature (Ta) are presented in this section. The Hall measurement gives the resistivity (ρ), carrier mobility (μ) and carrier concentration (n) they are presented in tabeller 3.2 og 3.3 and figur 3.4. For visual comparative the scale bar are chosen to be the same for the properties respectively.

Annealing Temp. (Ta)	$\mu [\mathrm{cm}^2/\mathrm{Vs}]$	n [$\cdot 10^{20}$ cm ⁻³]	$\rho \left[\cdot 10^{-3}\Omega \cdot \mathrm{cm}\right]$
RT	1,61	2,61	3,05
150°C	2,01	9,23	3,36
200°C	6,13	4,74	2,15
300°C	24,36	2,995	0,86
350°C	19,85	0,94	3,35
400°C	13,66	0,63	7,26

Table 3.2: Electrical results for 1,6at%W deposit series

Table 3.3: Electrical results for 3,6at%W deposit series

Annealing Temp. (Ta)	μ [cm ² /Vs]	n [$\cdot 10^{20}$ cm ⁻³]	$\rho \left[\cdot 10^{-3}\Omega \cdot \text{cm}\right]$
RT	0,03	4,77	32,73
250°C	2,13	1,13	25,96
300°C	2,38	0,19	137,28
350°C	1,38	0,29	182,02
400°C	2,16	0,27	108,35
450°C	2,73	0,27	84,62

Figur 3.4a shows the resistivity of the 1,6at%W series as function of annealing temper-



Figure 3.4: The electrical properties of IWO for different annealing temperatures from the Hall measurement. Graph a and b show the resistivity for 1,6at%W and 3,6at%W respectively. Graph c and d show the carrier mobility (μ) and graph e and f show the carrier concentration (n) for 1,6at%W and 3,6at%W respectively. The annealing temperatures differs from non annealed (RT) to 450°C.

ature. For the non annealed sample the resistivity is about $3 \cdot 10^{-3}\Omega$ cm there happens not much on to 150° C Ta. At annealing temperature above 150° C the resistivity decreases to a minimum at $0, 8 \cdot 10^{-3}\Omega$ cm for 300° C, then the resistivity increases up to $7 \cdot 10^{-3}\Omega$ cm for 400° C. The resistivity for the 3,6at%W series is shown in figur 3.4b. The resistivity for

the non annealed $(33 \cdot 10^{-3}\Omega \cdot \text{cm})$ and the sample annealed at 250°C ($26 \cdot 10^{-3}\Omega \cdot \text{cm}$) do not show much difference. For higher annealing temperatures the resistivity increases and peaks at $182 \cdot 10^{-3}\Omega \cdot \text{cm}$ for 350°C , then the resistivity decreases foe even higher annealing temperatures. The resistivity for the 3,6at%W series is much higher then for the 1,6at%W series and shows almost the opposite behaviour.

Figur 3.4c presents the mobility for the 1,6at%W series. The mobility starts low at almost zero cm²/Vs. At annealing temperatures above 150°C the mobility increases rapidly onto $24\text{cm}^2/\text{Vs}$ for the annealing temperature of 300°C, further above the mobility decreases. The increase of the mobility is about a factor 15. The mobilities for the 3,6at%W series are shown in figur 3.4d. For the non annealed sample the mobility is around 1,6 cm²/Vs, increases slightly to 2,4cm²/Vs for 300°C Ta. There is a little dip in the mobility at 350°C to 1,4cm²/Vs at higher annealing temperature the mobility increases again. The highest mobility for the 3,6at%W series is much lower then for the 1,6at%W series.

Figur 3.4e shows the carrier concentration for the series deposited with 1,6at%W. From non annealed to annealed at 150° C *n* from 2,6 $\cdot 10^{20}$ cm⁻³ to $9 \cdot 10^{20}$ cm⁻³. From annealing temperature of 150° C to 400° C the carrier concentration decreases almost linear with a little out blow for 300°C Ta. The carrier concentration of the 3,6at%W is shown in figur 3.4f. For the 3,6at%W series *n* decreases from 4,8 $\cdot 10^{20}$ cm⁻³ to 0,2 $\cdot 10^{20}$ cm⁻³ for non annealed and 300°C Ta respectively. For annealing temperature above 300°C the graph flattens out in a kind of tail about 0,3 $\cdot 10^{20}$ cm⁻³.

The resistivity for the 1,6at%W series has a minima looking at ligning (2.4) and figur 3.4c, it is clear that the minimum for resistivity occurs because of the high mobility. When looking on figurer 3.4a og 3.4c, the resistivity (ρ) decreases when the mobility (μ) increases and vice versa. The corresponding extrema occur at the same annealing temperature of 300°C. In a way that can be seen for the 3,6at%W series too, figurer 3.4b og 3.4d. The top point for resistivity lays at 350°C like the minima of the mobility. The resistivity of the 3,6at%W is higher than the resistivity of the 1,6at%W, while the mobility shows the opposite relation. Comparing each data point of the carrier concentration for both deposition series the carrier concentration for the 1,6at%W series is all in all higher then for the 3,6at%W series, except the non annealed sample. The behaviour of the mobility for ITO [10].

Chapter 4

Discussion

In the previous chapter the results for indium tungsten oxide (IWO) were presented. For both deposition series the optical properties transmittance and bandgap increased with annealing temperature, while the absorption decreases. The bandgap for 1,6at.%W first increases and decreases as the annealing temperature exceeds 300°C. The electrical properties for the 1,6 atmospheric percent tungsten(at.%W) show a adverse connection between the resistivity and mobility. When the mobility increases, the resistivity decreases and vice versa, both curves peaks at 300°C Ta. For the 3,6at.%W series the electrical properties show a different behaviour. The resistivity increases together with the mobility, while the carrier concentration decreases. After the reaching the extrema the resistivity decreases while the mobility and carrier concentration increases. The partly high resistivity makes the electrical measurement difficult, what can explain the large errors e.g 4.3b. To sum up for the 1,6at.%W series the bandgap starts decreasing at 300°C Ta at the same temperature resistivity and mobility have extrema and the carrier concentration has a little fluctuation. For the 3,6at.%W series the bandgap is almost the same for high annealing temperatures, while there is development in the electrical results. The resistivity and mobility peaks at 350°C Ta, while the carrier concentration peaks at 300°C Ta.

4.1 Optical bandgap - carrier concentration relationship

The results of the 1,6at.% series indicates a relation between optical and electrical properties besides that both depend on the crystalline structure. When plotting the bandgap as function of the carrier concentration (figur 4.1a) it can be seen that when increasing



Figure 4.1: Band gap mobility as function of carrier concentration presented by graph a for 1,6at%W and graph b for 3,6at%W respectively

the carrier concentration the bandgap increases to a certain point, after that by further increasing the carrier concentration the band gab decreases. The same behaviour can be seen for the 3,6at.% series, when zooming in on figur 4.1b, there is a raise between the two first points and from point two to five there is a decrease. This are the typical observed behaviours of TCOs. There are observed two kinds of dependence for the bandgap on carrier concentration. The first one is when carrier concentration is raised the bandgap will raise too, this is described by the Burstein-Moss effect. The second dependence is when further raising the carrier concentration the bandgap will decrease, this is described by the bandgap anarowing effect.

The Burstein-Moss effect seen as segment (b) on figur 4.2 occur when doping rises above the Mott critical density [11] and thus a moderately doping is reached. Thus the conduction band is filled partial, leading to a blocking of the lowest states and thereby widening the optical bandgap. In other words when increasing the carrier concentration by doping the material, the lowest state of the conducting band are filled, which increases the bandgap. When decreasing the free carrier concentration, the energy will decrease in the higher occupied state in the conduction band, which leads to a decrease in the bandgap. When further increasing the doping, reaching a heavy doping the valence and conduction band are shifted in energy, because of many-body interactions and other exchange forces between the electrons. Electron-impurity scattering increases this shift further. This interactions causes a downward shift for the conduction band and a up ward shift in the valence band. Which compensates for the Burstein-Moss effect and the bandgap is been narrowed, see figur 4.2 (c). The narrowing leads to an increase in the electron affinity.



Figure 4.2: Schematic band structure of IWO, (a) showing parabolic conduction and valence band separated by the bandgap, (b) after moderately doping and (c) narrowing of the bandgap from many body interactions from heavily doping..Figure taken from ref[4]

The values for the room temperature (RT) samples do not fit in, maybe because they are high absorbent and highly amorphous. It could be that RT has metallic components. Another reason could be that the samples are deposited without oxygen at RT. Other studies of IWO shows the same offset for samples deposited with out oxygen at room temperature see ref [2] chapter 4.

4.2 Carrier mobility - carrier concentration relationship

The carrier concentration and mobility are close related, the relation can be seen in figur 4.3.

Figur 4.3a presents the mobility as function of carrier concentration on a log-log graph. Looking on the graph from the right, then the mobility increases to a certain point as the carrier concentration decreases after this when the carrier concentration decreases further the mobility decreases. The mobility as function of carrier concentration for the 3,6at.% series is shown in figur 4.3b. It is hard to see something, again looking on it from the right,

Figure 4.3: mobility as function of carrier concentration presented by graph c for 1,6at%W and graph d for 3,6at%W respectively

overall first there is a decrease of mobility and then a increase . As in figur 3.4d the values of mobility lay close to together. That could be explained by the microscopic structure, as a result of the sputtering the material composition gets amorphous. For high doped material the amorphization gets high, so the temperature to get a crystalline structure must be even higher then the used temperatures. So the applied annealing temperature was to low to crystallize the samples. The crystalline structure can maybe be reached at higher annealing temperatures or never.

The behaviour of the mobility for the 1,6at.%W can be described by different scattering effects. When the mobility increases while the carrier concentration decreases, it could be because the ionised impurity scattering is reduced. When the mobility decreases together with the carrier concentration it could be due to the grain boundary trapping effect. Grain boundary scattering is scattering at the boundaries of the crystals and at the boundaries of crystal and amorphous grains[10]. When increasing the grain size, the electron mobility will increase, due to higher mean free path of the electrons. The grain boundary scattering occur because the electrons must overcome a potential barrier caused by the space charge occurred at the grain boundary. This potential barrier occur from the trapped carriers. When carriers are trapped they are immobilized and the traps becomes charged. The trapping states occur from defects caused by incomplete atomic bonding [12]. Ionised impurity scattering is dominant when the material is crystallized. Ionised impurity scattering is based on carriers deflection or trapping[10] by long-range electrostatic fields induced by dopants and defects[13]. Non-ionised impurities also contributes to scattering by neutral impurity scattering, at low annealing temperature the structure of the IWO

films might still be amorphous and in the presence of high carrier concentration, the grain boundary trapping related scattering mechanism is unlikely to occur. In fact the initial rise in mobility with decreasing n can be related to the reduced ionized impurity scattering. However, as an increase in the annealing temperature brings about a lowered value of n, there are also concurrently structural changes occurring in the films. We contend that in our study, at the higher annealing temperatures, the films develop small crystallite grains which enhance the grain boundary scattering effect, leading to the decrease in the mobility beyond 300°C. The reduced value of carrier concentration with a possibility of rise in trapped charges making the grain boundary barrier voltage to play its role in the carrier transport. This barrier will reduce the carrier mobility.

With increasing temperature the degree of crystallization increases and the optical and electrical properties changes. From the results it can be seen that the properties of IWO can be improved by annealing. Especially seen for the 1,6at.%W series, where the mobility is improved by a factor of 15 for the annealing temperature of 300°C.

Chapter 5

Conclusion

In this project i have investigated, the influence of post-deposition annealing on the properties of two sets of IWO thin films: one having 1.6 atomic percent(at.%) W and the other having 3.6 at.% W, both deposited at room temperature by RF magnetron sputtering. Based on the experiments, I have found that by annealing the deposited samples, their optical and electrical properties could be improved. In case of the 1,6at.%W doped samples, the mobility could be improved by a factor of 15, together with decreasing the resistivity and increasing the transmittance by annealing at 300°C for one hour. From the results, it is seen that the electrical and optical properties of IWO depend strongly on annealing temperature. The properties of IWO are also sensitive to the oxygen partial pressure under preparing[2, 14]. A suggestions for the future could be to prove if already good samples can be improver further by annealing. A combination of improvement by oxygen vacancies [2] and the through this thesis found improvement of annealing. Another suggestion would be to deposit the samples during heating to avoid that tungsten do place at the boundaries.

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