NANOCRYSTALLINE ZnO:Al THIN FILMS PREPARED BY SOL-GEL DIP COATING TECHNIQUE AND ZnO:Al/p-Si HETEROJUNCTIONS

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DECEMBER 2010
SOL-GEL DALDIRMALI KAPLAMA TEKNİĞİ İLE ÜRETİLMİŞ NANO YAPILI ZnO:Al İNCE FİLMLER VE ZnO:Al/p-Si HETEROKAVŞAKLAR

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ARALIK 2010
FOREWORD

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DECEMBER 2010

Özge KARACASU

Metallurgical and Materials Engineer
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<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>AZO</td>
<td>Aluminium Doped ZnO</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
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<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DEA</td>
<td>Diethanolamine</td>
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<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
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<tr>
<td>EL</td>
<td>Electro Luminesans</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
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<tr>
<td>HJ</td>
<td>Heterojunction</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
</tr>
<tr>
<td>LPCVD</td>
<td>Low-Pressure Chemical Vapor Deposition</td>
</tr>
<tr>
<td>MEA</td>
<td>Mono ethanolamine</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal-Organic Chemical Vapor Deposition</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light Emitting Diodes</td>
</tr>
<tr>
<td>PEM</td>
<td>Plasma Emission Monitor</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>TGA</td>
<td>Thermo Gravimetric Analysis</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent Conducting Oxide</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<td>VIS</td>
<td>Visible Range</td>
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LIST OF SYMBOLS

\( \lambda \) : Wavelength
\( \theta_\beta \) : Bragg Diffraction Angle,
\( \beta \) : FWHM (Full width half maximum of distinctive peak) of \( \theta_\beta \).
\( C \) : Capacitance
\( V \) : Applied Voltage through the Diode
\( V_{bi} \) : Built-in-potential
\( I \) : Net Current Flowing Through the Diode
\( q \) : Absolute Value of Electron Charge
\( k_B \) : Boltzmann's Constant
\( I_0 \) : SaturationCurrent
\( n \) : Ideality factor
\( E_g \) : Optical Band Gap Energy
\( (h\nu) \) : Photon Energy
\( \alpha^2 \) : Absorption coefficient
NANOCRYSTALLINE ZnO:Al THIN FILMS PREPARED BY SOL-GEL DIP COATING TECHNIQUE AND ZnO:Al/p-Si HETEROJUNCTIONS

SUMMARY

Transparent conducting oxide (TCO) films have much interest in recent years. The optical and electrical properties of the films have been improved over the years. TCO’s have been widely used in various industry areas such as optoelectronics, display industry, solar cells, with their desirable optical and electrical properties.

Zinc Oxide (ZnO) films are good candidates for TCO films with their outstanding properties such as non-toxicity, high chemical, mechanical stability, low cost and material abundance in nature. Doping of ZnO with aluminum (ZnO:Al) can increase film conductivity. ZnO films have been used as solar cell electrodes, gas sensors and optical devices. For fabrication of ZnO films various techniques have been used such as sputtering, chemical vapor deposition, spray pyrolysis, sol-gel etc.

Deposition of ZnO films on p/n type substrates provides to produce heterojunction which are generally used for fabrication of solar cells. Recently n-ZnO/p-Si heterojunctions has received much attention for electronic applications. The biggest advantage of these heterojunctions is to combine the large binding energy of ZnO thin films and the inexpensiveness of Si substrates.

In this work Al doped n-ZnO/p-Si heterojunctions were fabricated by sol-gel dip coating process. P type Si (100) wafers and glasses were used as the substrates. The structural, optical and electrical properties of ZnO:Al thin films and heterojunction properties of ZnO:Al/p-Si were investigated with respect to effects of Al doping concentration and process parameters (i.e. thermal treatment temperature and ambient). After the coating process, characterization of the ZnO:Al thin films and ZnO:Al/p-Si heterojunctions were made by X-Ray diffractometer, scanning electron microscopy, surface profilometer, UV/VIS spectrophotometer, four point resistivity probe and a semiconductor characterization system (SCS).

Structural properties investigation by X-ray diffraction method showed that the films were in the form of hexagonal wurzite structure. The XRD patterns of the ZnO:Al films on p type si substrate had (100), (002) and (101) diffraction peaks were in accordance with literature. SEM images show that ZnO:Al films had granular nanostructure. The increasing of the thermal treatment temperature caused an increase on crystalline size. The annealing ambient tended to change the crystalline size of the thin films. The thicknesses of the thin films are in the range of 150-450 nm and the certain decrease was detected while the annealing temperature was increased.

Optical properties were investigated by fabricating ZnO:Al films on glass substrates to gain transparency. As the annealing temperature increased, the transmittance of the films increased. Al doping concentration had limited influence on optical properties. All films exhibited high optical transmittance in visible ranges.
Electrical resistivity changed with respect to Al doping concentration, annealing ambient and temperature. Minimum resistivities were detected at 1.2 at. % Al concentration.

ZnO:Al/p-Si heterojunction properties were analyzed by current-voltage (I-V) measurements depend on the Al doping concentrations, annealing ambient and annealing temperatures. Most of the ZnO:Al/p-Si heterojunctions exhibited diode-like rectifying behavior. Under UV illumination the photoelectric behavior observed for the diodes. In this study the 1.2 at.% Al doping concentration, vacuum ambient and 700°C annealing temperature are the optimum process parameters to produce heterojunction.
SOL-GEL DALDIRMALI KAPLAMA TEKNİĞİ İLE ÜRETİLMİŞ NANO YAPILI ZnO:Al İNCE FILMLER VE ZnO:Al/p-Si HETEROKAVŞAKLAR

ÖZET


Çinko oksit (ZnO) filmler toksik olmayışları, yüksek kimyasal ve mekanik kararlılıkları, düşük maliyetleri ve doğada bol bulunması gibi üstün özellikleri nedeniyle geçirgen iletken oksit filmler için iyi birer adaydır. Çinko oksitin Alüminyum ile katkılanması (ZnO:Al) iletkenliği artırabilir. Çinko oksit filmler güneş pili elektrotu, gaz sensörü ve optik cihaz olarak kullanılmaktadır. ZnO filmlerin üretimi için suçratma, kimyasal buhar biririkme, sprey piroliz, sol-gel vb. birçok çeşitli tekniğin kullanılmasından yararlanmaktadır.

Al katkılı ZnO filmler p ve n tip altlıklara genellikle güneş pillerini yapımında kullanılan heterokavşakların üretimi için biriktirilmiştir. Son zamanlarda n-ZnO/p-Si heterokavşaklar elektronik uygulamalar için dikkat çekmektedir. Bu heterokavşakların en büyük avantajı geniş bağlanma enerjisi olan ZnO ince filmlerle silikon altlığın ekonomikliğini bir araya getirmesidir.

Bu çalışmada Al katkılı n-ZnO/p-Si hetrokavşaklar sol-gel daldirma prosesi ile üretilmiştir. Al katkılı ZnO filmler sol-gel daldirma prosesinde cam aaltlıklar üzerine biriktirilmiştir. Al katkılı ZnO filmler sol-gel daldirma prosesi ile üretilmiştir. P tip Si (100) waferler ve camlar aaltık olarak kullanılmıştır. ZnO:Al ince filmlerin yapısal optik ve elektriksel özellikleri ve ZnO:Al/p-Si yapılarının heterokavşak özellikleri Al katkısı konsantrasyonuna ve üretim parametrelerine (işıl işlem sıcaklığı ve ortam gibi) göre incelenmiştir. Kaplama işleminden sonra, ZnO:Al ince filmlerin X-ışınları kırınımı, XRD patenlerinde literatür uygun olarak (100), (002) ve (101) kırınım piki verildiği gözlenmiştir. SEM görüntüleri ZnO:Al ince filmlerin granüler nano-yapıda olduğu göstermiştir. ZnO:Al ince filmlerin X-ışınları kırınımı, taramalı elektron mikroskobu, yüzey profilometresi, UV/VIS spektrofotometre, dört ayaklı iletkenlik probu ve yarı iletken karakterizasyon sistemleri ile yapılmıştır.

Optik özellikler geçirgenlik sağlamak için cam aaltıklar üzerine biriktirilen ZnO:Al filmler üzerinde incelendiştir. Tavlama sıcaklığı arttıkça filmlerin geçirgenlik değerlerinin arttığı görülmüştür. Al katkısı konsantrasyonunun optik özelliklere büyük
bir etkisinin olmadığı görülmüştür. Tüm filmler görülen bölgede yüksek optik geçirgenliğe sahiptir.

Elektriksel öz direnç değişimi katkı konsantrasyonu, tavlama ortamı ve sıcaklığına bağlı olarak incelenmiştir. Minimum öz direnç değerleri %1.2 atomik katkı miktarında saptanmıştır.

Heterokavşak özellikleri Al katkı konsantrasyonu, tavlama ortamı ve sıcaklığına bağlı olarak akım-voltaj (I-V) ölçümleri ile analiz edilmiştir. Çoğu ZnO:Al/Si heterokavşaklar diyot tipi doğrultucu özellik göstermiştir. UV aydınlanma altında diyotlarda fotoelektrik özellik gözlenmiştir. Bu çalışmada heterokavşak üretmek için 1.2 at.% Al katkı konsantrasyonu, vakum ortamı ve 700°C tavlama sıcaklığı optimum işlem parametreleridir.
1. INTRODUCTION

Currently, most of the energy demand in the world is met by fossil and nuclear power plants. A small part is drawn from renewable energy technologies such as wind, solar, fuel cell, biomass and geothermal energy. Wind energy, solar energy and fuel cells have experienced a remarkably rapid growth in the past ten years because they are pollution-free sources of power. Additionally, they generate power near the load centers, which eliminates the need to run high-voltage transmission lines through rural and urban landscapes [1].

The output power of solar cells fluctuates considerably depending on solar radiation, weather conditions and temperature [1]. Not all parts of the solar spectrum are absorbed equally well by a solar cell. The light that is absorbed weakly can be trapped inside the solar cell and thereby travel a complicated optical path before being absorbed, reflected or transmitted. This makes solar cells complex optical devices [2].

One uses the solar energy in converting this energy into (a) heat, and (b) electricity. In the first case, it is used for directly heating homes or for water heating where the sun’s rays are incident on a panel containing circulating water in tubes. In the second case, it is used for generating electricity using photovoltaic panels [3].

The cost of solar photovoltaic and fuel cell electricity is still high. Nevertheless, with ongoing research, development and utilization of these technologies around the world, the costs of solar cells and fuel cell energy are expected to fall in the next few years [1]. Solar energy provides us with an alternative where there is no pollution of the environment and its use decreases the rate of depletion of energy reserve [3].

The transparent conducting film should have low resistivity, high transmittance in the visible range and high stability against heat [4]. The TCs used for solar energy and energy efficiency are normally thin films, with thicknesses between 10nm and 1mm [5]. Zinc oxide and doped zinc oxide films have received extensive attention in recent years due to their excellent optical and electrical properties. It is a good
candidate for transparent conductive oxide (TCO) films and an alternative material for tin oxide and tin-doped indium oxide (ITO) [6].

Zinc oxide (ZnO) is an inexpensive n-type semiconductor with a wide band gap of 3.3 eV which crystallizes in the hexagonal wurtzite structure [7]. It is highly resistant to chemical attack and has a good adherence to many substrates. High transparency in the visible region and refractive index value (1.7-2) enable it to act as an antireflection coating, conductive electrode and window layer in solar cells [8].

Zinc oxide is one of the few metal oxides which can be used as a transparent conducting oxide (TCO). It has some advantages over other possible materials such as In$_2$O$_3$ or SnO$_2$ due to its unique combination of interesting properties: non-toxicity, good electrical, optical and piezoelectric behavior, stability in a hydrogen plasma atmosphere [9] and together with its abundance in nature, which makes it a lower cost material when compared with the most currently used TCO materials (ITO, SnO$_2$) [10].

Zinc oxide has recently gained much interest because of its potential use in many applications, ranging from antireflection coatings, transparent electrodes in solar cells, thin film gas sensors, varistors, spintronic devices, photodetectors, surface acoustic wave devices and light emitting diodes to nanolasers, attributed to its [11] superior properties.

Reduction of resistivity of zinc oxide can be achieved either by doping with group III elements such as B, Al, In and Ga to replace zinc atoms or group IV elements, for example, F, to substitute oxygen atoms [12]. ZnO is a wide optical band gap material with wurtzite crystal structure, which exhibits a change in conductivity with the doping of Al, Ga or In. Because of their chemical stability, the ZnO films, particularly, aluminum-doped films are more useful in the fabrication of thin film solar cells compared to Sn-doped In$_2$O$_3$ (ITO) [13].

The ZnO doping is achieved by replacing Zn$^{2+}$ atoms with atoms of elements of higher valence such as indium, aluminum and gallium. The efficiency of the dopant element depends on its electronegativity and difference between its ionic radius and the ionic radius of zinc [10]. By Al-doping the electrical and optical properties of ZnO films are changed. The optical bandgap is widened in proportion to the Al-doping concentration [13]. The electrical conductivity, the charge carrier density, and
the mobility are substantially improved in Al doped films. Highest mobility values have been found at Al-doping concentrations of 2-3 at%.

This is explained by a limited incorporation of Al into the ZnO lattice. Al acts as a donor if it is substitutionally incorporated on zinc lattice sites. Especially at high oxygen flow rates it has been suggested that Al atoms chemically bind with oxygen and form precipitates in the grains or at the grain boundaries [14].

The more pronounced electrical and optical changes were observed when the doping concentration of Al is 1 at.%. High transmittance in the visible range was achieved with 1 at.% of aluminum doped ZnO [15]. ZnO:Al thin films with high c-axis orientated crystalline structure along (002) plane can reduce the electrical resistivity due to an increase in carriers mobility by reducing the probability of the scattering of the carriers at the grain boundary [16].

The properties of ZnO thin films are much influenced by not only the growth methods but also the heat treatment parameters, especially the thermal annealing. Therefore, it is essential to investigate the effect of annealing process on the microstructure, transparent properties, and morphology of ZnO films [17]. The film exhibited a resistivity of $7.5 \times 10^{-4} \, \Omega\text{-cm}$ and an optical transmittance over 85% in the visible spectral region [18].

Al-doped ZnO (AZO) film is the Standard front electrode in CIS thin film solar cells [6]. In addition, its nanostructures can be used in various applications such as nanowire, nanolasers, bio-sensors and field emission devices [19].

Fabrication of high crystalline quality ZnO film is of great importance for practical applications, especially, for construction of nano-devices. A great number of techniques such as chemical vapor deposition, sol-gel technique, chemical solution deposition, spray pyrolysis, magnetron sputtering, pulsed laser deposition, and molecular beam epitaxy have been employed for the fabrication of ZnO films [20]. Among them, the sol-gel technique offers the possibility of preparing a small as well as large-area coating of ZnO thin films at low cost for technological applications [16]. Despite the crystalline quality being inferior to other vacuum deposition techniques, the sol-gel technique still has distinct advantages such as cost effectiveness, simplicity, excellent compositional control, homogeneity and lower
crystallization temperature. Moreover, incorporation of dopants is easier in this technique [21].

Sol-gel method is widely used to obtain various kinds of functional oxide films, including ZnO and doped ZnO thin films [22]. This method has several merits, since sol-gel processing allows low-cost deposition of AZO film in air ambient and offers excellent compositional control and film homogeneity on molecular level [18].

The main factors affecting the sol-gel film microstructure and properties are: solution chemical equilibrium (chemical composition, concentration, pH, order-time-temperature of reagents mixing), substrate–film interaction during film deposition (sol viscosity, spin/dip coating parameters) and thermal processing of the as-deposited gel film (time and temperature of preheating between each layer deposition, time-temperature-atmosphere of postheating, time-temperature, atmosphere of final annealing) [22].

In the preparation of epitaxial ZnO films with high crystallinity, sapphire substrates of the a, c and r axis have been widely employed due to its stability at growth temperatures. However, the sapphire substrates are unsatisfactory to be used as electrodes, because of its high resistivity and are also expensive. In this point of view, silicon (Si) wafers are interesting for the substrates on which optical devices are fabricated. The Si wafer is an especially suitable substrate for ZnO growth, because the thermal expansion coefficient of Si (3.57x10^-6/°C) is nearly equal to that of ZnO (4x10^-6/°C) [23].

Therefore the properties of TCO layers deposited on crystalline or amorphous (a-Si:H) Si substrates of Si based HJ solar cells is an important subject for investigation. It has been proved that the heterojunction (HJ) Si based solar cells (TCO/a-Si:H/Si) have conversion efficiency above 21%. [24].

In general, ZnO films grown without intentional doping are n-type because of donor defects such as the oxygen vacancies and zinc interstitials. With regard to applications, ZnO: p-Si heterojunctions are of particular interest because this structure can be integrated with standard Si circuits using established technologies. ZnO/p-Si structures have been prepared and their properties studied by various investigators, but they mainly focused on non-intentionally doped ZnO [25].
2. ZINC OXIDE THIN FILMS

In last years, metal oxide semiconductor films have been widely studied and have drawn much attention due to their optical and electrical properties. Some of these oxide semiconductors are suitable candidates for transparent conductive oxide (TCO) films [26]. In$_2$O$_3$, SnO$_2$ and ZnO are metal oxides [27] which widely used as transparent conductive oxide (TCO) materials.

2.1 Properties of Zinc Oxide Thin Films

Among transparent conductive oxide (TCO) materials, ZnO has raised as one of the most promising materials due to its optical and electrical properties [10], suitability to doping, non-toxicity [28], high resistivity control [29] high chemical, mechanical [10] and high thermal [16] stability together with its abundance in nature which makes it a lower cost material [10]. Due to these superior properties ZnO is a good choice for electronic or optoelectronic applications [30] such as antireflection coatings [11], transparent electrodes in solar cells [31], thin film gas sensors [32], varistors [33], light emitting diodes [34], nanolasers [35] heterojunctions etc. On the other hand, pure ZnO thin films are sensitive to oxidation and O2 absorption in the films cause a decrease in the electrical conductivity. The optical properties of ZnO are widely affected by surface morphology and optical energy band gaps [26].

ZnO crystallizes in the hexagonal wurtzite structure (c=5.205 and a=3.249) [7] and each Zn atom in the lattice is bonded tetrahedrally with four adjacent O atoms [11].

ZnO is an n-type [29] II-VI semiconductor which has a wide direct band gap of ~3.37 eV [36] and a huge exciton binding energy of ~60 meV at room temperature (300K) [37]. Its n-type electrical conductivity is due to deviations from the stoichiometry resulting from oxygen vacancies and interstitial zinc, giving rise to a shallow donor level just below the conduction band [38]. ZnO has resistivity control over the range $10^{-3}$-$10^5$ Ωcm [29], high transparency in the range of 0.4-2μm optical wavelength [21] and its transmittance is nearly 80-90% in the visible range [27].
2.2 Dopands and Their Effects on ZnO Thin Films

However, undoped ZnO films have poor electrical properties due to the low carrier concentration [39] and are not stable in air and its electrical properties are significantly affected by adsorption of O$_2$, CO$_2$, hydrocarbons, S-containing compounds, and water. ZnO can be doped with a wide variety of ions to meet the demands of several application fields. Single crystals and polycrystalline films of zinc oxide have been doped to enhance their mechanical, electrical, and optical properties with elements of the alkali metals such as Li, Ga, In, N, Al, Sn, and P from groups III B to VII B [40]. The ZnO doping is achieved by replacing Zn$^{2+}$ atoms with atoms of elements of higher valance such as In$^{3+}$, Al$^{3+}$, Sn$^{4+}$, Pb$^{4+}$ [41].

In the use for electronic components such as piezoelectric transducers and varistor, the effects of dopants are very important. Typical ZnO based varistor is a very complex chemical system containing several dopants, such as Bi, Pr, Mn, Co, Cu, Sb, V, Cr and Al. The electrical properties of ZnO are related closely to the composition and the microstructure. So it is important to understand the effects of the individual additives in a fundamental manner. There were some reports on the above doping elements in the ZnO varistor or thin film, but the effects of some doping elements on the grain and grain boundary of ZnO still remain unclear, because the doping effects have been studied in quite different systems under different experimental conditions, and the effect of individual dopant might be complicated by other dopants in ZnO with multi-components. Therefore, it is necessary to investigate the various dopants independently in a systemic way to understand the role of each dopant in the electrical properties of ZnO [42].

Doping ZnO with appropriate impurities, from III group elements such as Al, Ga, and In determined to be the most suitable elements, can increase the electrical conductivity and optical properties of ZnO thin films appreciably [39].

The electro optical properties of ZnO thin films are highly dependent on the deposition and post deposition treatment (annealing) conditions because these properties change significantly with the nature of the chosen doping element with the adsorption of oxygen that takes place during the deposition process and with the desorption during the annealing treatment in a reductive atmosphere [43].
2.2.1 Al Doped zinc oxide thin films
Comparing with undoped ZnO, Al-doped ZnO (ZnO:Al) films have lower resistivity and better stability. In most device applications, ZnO:Al films deposition was accomplished at high processing temperatures (500°C). Fabrication of high-quality ZnO:Al at lower temperature would enable the production of devices and contacts on polymer substrates and on temperature sensitive components. [44]
Also AZO thin films have been considered as suitable anodes because ZnO thin films are more stable in reducing ambient, more abundant, and less expensive in comparison with the ITO films which make them appropriate for potential use as anodes in OLEDs [45].
Al-doped ZnO (AZO) film is the Standard front electrode in CIS thin film solar cells and has been studied as a window layer for silicon thin film solar cells owning to its easily textured surface for efficient light trapping [6].

2.3 Production Techniques of ZnO:Al Thin Films
ZnO thin films have been prepared by employing various processes such as sputtering, ion-assisted deposition, spray pyrolysis, chemical vapor deposition (CVD), metal organic chemical vapor deposition (MOCVD), atomic layer deposition, and pulsed laser ablation (PLA) [46], reactive evaporation and sol-gel process [13] etc. In several studies, it was shown that the optical and electrical properties of AZO thin films could be obviously improved by optimizing deposition conditions and doping [47].
Al-doped ZnO (AZO) films prepared by the RF magnetron sputtering process exhibit the present lowest resistivity of 1-2 $10^{-4}$ Ωcm, and this has been the most commonly applied process in the preparation of AZO. However, the deposition rate of RF magnetron sputtering is relatively slow compared with other processes, making it inefficient for practical application. We believe that establishing a process for high rate deposition is one of the most important factors which will influence the expansion of AZO thin films [48].
While doped ZnO thin films with low resistivity of $10^4$ Ωcm level as well as high transmittance up to 80% at visible and near infrared range can be prepared by sputtering, as-sputtered ZnO thin films usually have a smooth surface, which is not
desirable for Si thin film solar cell application due to low haze factor [49]. PLA has been shown to yield high quality c-axis oriented ZnO films at lower substrate temperatures than many other techniques. The films deposited by PLA in vacuum are typically Zn rich due to recondensation of Zn onto the surface of the target. For this reason ZnO films are typically grown in a background pressure of oxygen [46].

Nakada et al. [49] deposited rough ZnO thin films with textured surface on glass substrate by DC magnetron sputtering in Ar–H2O mixtures. However, high deposition temperature up to 400°C was required to obtain ZnO thin films with large grain, which is too high for thin film solar cell technology. On the contrary, LP-CVD techniques can produce self formation of rough morphology, so called self-texturing, which is a significant advantage compared to sputtering method.

RF thermal plasma evaporation is a vapor-phase process using thermal plasma with high temperature and active atmosphere. This process promises a high rate of deposition and large area deposition. Moreover, RF thermal plasma evaporation also has other unique characteristics. It can use various solids, liquids or gases as raw materials because of high temperature plasma of several thousands of degrees and a relatively low gas velocity under 15.5 mys w11x, which may lead to complete evaporation of the raw materials. There is also no requirement for a high vacuum system and a contamination free reaction, thanks to the absence of electrodes. Therefore, the RF thermal plasma evaporation process is expected to be one of the candidates for practical large-scale engineering applications [48].

Among the preparation techniques of ZnO films, the sol-gel process in combination with the dip coating process is more popular because of its cheapness reliability repeatability and simplicity [37]. This technique offers the greatest possibility of preparing a small as well as large area coating of ZnO thin films for technological applications [13]. Sol-gel processing allows low-cost deposition of AZO film in air ambient and offers excellent compositional control and film homogeneity on molecular level [22]. The ZnO thin films prepared by sol-gel technique show high optical transmittance (85-90%) in the near UV, VIS and IR regions [50].
3. SOL-GEL

Sol-Gel is a coating technique which can be applied on glass, ceramic, metals and polymers to improve the optical, electrical, chemical and mechanical properties of surfaces. The fabrication and use of materials prepared by sol-gel process can be divided into three main categories, bulk glass, coatings and fibers [51].

The traditional sol-gel process drives the evolution of inorganic networks through the formation of a colloidal suspension (sol), and gelation of the sol to form a network in a continuous liquid phase (gel). [52]

3.1 Applications of Sol-Gel Process

The main factors affecting sol-gel film microstructure and properties are: solution chemical equilibrium (chemical composition, concentration, pH, order-time-temperature of reagents mixing), substrate-film interaction during film deposition (sol viscosity, spin-dip coating parameters) and thermal processing of the as-deposited gel film (time and temperature of preheating between each layer deposition, time-temperature-atmosphere of post heating, time, temperature and atmosphere of final annealing [22].

Sol-gel process can be used to fabricate almost any single or multi-component oxide coating. Such coatings have been deposited on glass to provide coloration, anti-reflection, selective reflection, electrochromism and photochromism, selective absorption, wave guiding, reduced friction, anti-soiling reduced adhesion, transparent conductors, electro-optics, Ferro-electrics, sensors, and dye lasers. [53]

The process consists of successive five stages, preparing the solution, preparing the substrates, film deposition, pre-heating and post heating. The stages are shown in Figure 3.1. In preparing the solution stage, all the required chemicals are mixed in estimated ratios to form homogeneous, clear and transparent solution. Then the prepared solution is aged for a certain time. In the second stage, the substrates are cleaned ultrasonically in acetone and alcohol then dried in air, respectively. Film
deposition stage starts with dipping the prepared substrate in the prepared solution for a certain time until the substrate is completely wetted and the film thickness reaches satisfactory levels then finished by withdrawal the substrate from the solution at a controlled rate. In pre-heating organic residuals are evaporated. The decomposing of the strong radicals and the forming of the crystal structure take place in post heating.

![Figure 3.1: Stages of sol-gel process.](image)

### 3.2 Deposition Techniques of Sol-Gel

There are many types of sol-gel deposition techniques such as spin coating, dip coating, flow coating, laminar coating, roll coating and spray coating. Dip coating is the most widely used sol-gel deposition technique because of its easy application procedure and low cost.

#### 3.2.1 Dip coating technique

The sol-gel dip process is almost exclusively applied for the fabrication of transparent layers, primarily for the deposition of oxide films on float glass as a transparent substrate with a high degree of planarity and surface quality [51].

Dip coating techniques can be described as a process where the substrate to be coated is immersed in a liquid and then withdrawn with a well-defined withdrawal speed under controlled temperature and atmospheric conditions [54,55]. Schematic drawing of dip coating process is shown in Figure 3.2. The dipping-drawing cycle is continued till gain the satisfactory film thicknesses. The thickness of the coating layer is determined by the speed of withdrawal from the coating solution. The coating thickness increases with the withdrawal speed approximately at \( d \cdot v^{2/3} \) [51] where \( d \) is the thickness of the film and \( v \) is the drawing rate. The thickness also depends on the concentration of the solution, its viscosity and on the angle of the withdrawal which is normally 90°. Other parameters affecting the coating thickness are surface tension of the solution, vapor pressure and relative humidity above the coating bath [51].
The most important advantages of the dip coating technique are the high degree of uniformity obtained and simple thickness control. Since most applications fall into a thickness range comparable to the wavelength of visible light, even small thickness variations can be easily detected visually.

Another advantage is the size of the plates or the substrates that can be coated [51]. The technique requires low labor, has low cost and simplicity. Manpower and equipment requirements are minimal. The process is easily automated [57]. An additional advantage is the ability to produce multilayer coatings, permitting the fabrication of layers with widely varying optical characteristics, such as transmission and reflection [51].

Sol-gel technique also has excellent compositional control, homogeneity and lower crystallization temperature. Moreover, in cooperation of dopants is easier in this technique hence this technique is suitable for frontier researchers [21].

Nonuniformity is the biggest problem of the coatings. “Wedges” (thin films on upper surfaces, thicker on lower surfaces) tend to form on vertical surfaces. Flow lines around holes or openings can also occur. “Beads” on bottom edges are inherent defects, although proper viscosity control can minimize this effect [57]. The withdrawal speed is the most important processing parameter affecting the porosity of the films [58] the withdrawal speed should be under control during the coating process. Undesirable foam, which usually originates in the paint recirculation system, can produce voids or craters in the final finish. This problem is more prevalent with waterborne paints. Viscosity control is critical. High viscosity gives thick films and excessive consumption [57].
4. SEMICONDUCTORS

Materials can be categorized according to the way they conduct electricity when a voltage is applied across them [59]. Materials with conductivity less than $10^{-12} \Omega^{-1} \text{cm}^{-1}$ or resistivity greater than $10^{12} \Omega \text{cm}$ are considered insulating or dielectric. Materials with conductivity greater than $10^{3} \Omega^{-1} \text{cm}^{-1}$ or resistivity less than $10^{-3} \Omega \text{cm}$ are considered conductors. Materials with conductivity less than $10^{3} \Omega^{-1} \text{cm}^{-1}$ but greater than $10^{-12} \Omega^{-1} \text{cm}^{-1}$ are considered semiconductors. (These are approximate ranges of values) [60].

To understand the conductivity we need to find out which energy levels are occupied and whether specific bands are empty, partially filled or completely filled. Empty bands do not contain electrons. Therefore, they are not expected to contribute to the electrical conductivity of the material. Partially filled bands do contain electrons as well as available energy levels at slightly higher energies. These unoccupied energy levels enable carriers to gain energy when moving in an applied electric field. Electrons in a partially filled band therefore do contribute to the electrical conductivity of the material. Completely filled bands do contain plenty of electrons but do not contribute to the conductivity of the material. This is because the electrons cannot gain energy since all energy levels are already filled [61].

In order to find the filled and empty bands we must find out how many electrons can be placed in each band and how many electrons are available. Each band is formed due to the splitting of one or more atomic energy levels. Therefore, the minimum number of states in a band equals twice the number of atoms in the material. The reason for the factor of two is that every energy level can contain two electrons with opposite spin [61].

To further simplify the analysis, we assume that only the valence electrons (the electrons in the outer shell) are of interest. The core electrons are tightly bound to the atom and are not allowed to freely move in the material. Four different possible scenarios are shown in Figure 4.1 [61].
A half-filled band is shown in Figure 4.1 a). This situation occurs in materials consisting of atoms, which contain only one valence electron per atom. Most highly conducting metals including copper, gold and silver satisfy this condition. Materials consisting of atoms that contain two valence electrons can still be highly conducting if the resulting filled band overlaps with an empty band. This scenario is shown in b) No conduction is expected for scenario d) where a completely filled band is separated from the next higher empty band by a larger energy gap. Such materials behave as insulators. Finally, scenario c) depicts the situation in a semiconductor. The completely filled band is now close enough to the next higher empty band that electrons can make it into the next higher band. This yields an almost full band below an almost empty band. We will call the almost full band the valence band since it is occupied by valence electrons. The almost empty band will be called the conduction band, as electrons are free to move in this band and contribute to the conduction of the material. [61]

Semiconductor is composed of two words viz. semi and conductor. Semi means not complete; conductor refers to something which can conduct electricity. [62]. Although semiconductors have been studied for a long time—since 1920’s— they actually came into their own only after Shockley, Bardeen, and Brattain invented the transistor in the late 1940’s. Because of this invention, and because of the ensuing development of other related devices, semiconductors have become the most actively studied substrates in solid-state physics [63]. The principal reason underlying the importance of semiconductors is the fact that their electrical properties can be readily
Semiconductor devices such as diodes, transistors and integrated circuits can be found everywhere in our daily lives, in Walkman, televisions, automobiles, washing machines and computers. We have come to rely on them and increasingly have come to expect higher performance at lower cost [61]. Semiconductors have electrical resistivity in the range between those of typical metals and typical insulators, they usually have negative temperature coefficient of resistance and the electrical conductivity of semiconductors can be varied (in both sign and magnitude) widely as a function of, e.g., impurity content (e.g., doping), temperature, excess charge carrier injection and optical excitation. These factors may affect the electrical conductivity of a given semiconductor [65] Semiconductors are either elements or compounds. Si and Ge are most common elemental semiconductors. InSb, InAs, GaP, GaAs, SiC and GaN are compound semiconductors. The elemental semiconductors, Silicon and Germanium both have a crystalline structure this structure called ‘diamond lattice’ [62]. Each atom in the diamond lattice has a covalent bond with four adjacent atoms, which together form a tetrahedron. This lattice can also be formed from two face-centered-cubic lattices, which are displaced along the body diagonal of the larger cube in Figure 4.2 by one quarter of that body diagonal. The diamond lattice therefore is a face-centered-cubic lattice with a basis containing two identical atoms [61].

Compound semiconductors such as GaAs and InP have a crystal structure that is similar to that of diamond. However, the lattice contains two different types of atoms. Each atom still has four covalent bonds, but these are bonds to atoms of the other type. This structure is referred to as the zinc-blende lattice, named after zinc-

![Figure 4.2: The diamond lattice of silicon and germanium. [61]](image-url)
blende crystal (ZnS) as shown in Figure 4.3 Both the diamond lattice and the zinc-blende lattice are cubic lattices [61].

![Zinc Blende Lattice](image)

**Figure 4.3:** Unit cell structure of a zinc blende (ZnS) lattice. Zinc atoms are shown in green (small), sulfur atoms shown in red (large), and the dashed lines show the unit cell. [66]

A third common crystal structure is the hexagonal structure also referred to as the wurzite crystal structure, which is the hexagonal form of zinc sulfide (ZnS) is shown in Figure 4.4. Many semiconductor materials can have more than one crystal structure. A large number of compound semiconductors including GaAs, GaN and ZnS can be either cubic or hexagonal. SiC can be cubic or one of several different hexagonal crystal structures. The cubic crystals are characterized by a single parameter, the lattice constant a, while the hexagonal structures are characterized in the hexagonal plane by a lattice constant and by the distance between the hexagonal planes, c [61].

![Wurtzite Lattice](image)

**Figure 4.4:** Unit cell structure of a wurtzite lattice. Zinc atoms are shown in green (small spheres), sulfur atoms shown in red (large spheres), and the dashed lines show the unit cell [66]
4.1 Types of Semiconductors

Semiconductors are of two types,

a) Intrinsic
b) Extrinsic

An intrinsic semiconductor material is chemically very pure. It possesses poor conductivity. It carries same number of negative and positive charge carriers.

Extrinsic semiconductors are improved intrinsic semiconductors. Small amount of impurities are added by doping process. It alters the electrical properties of the semiconductor. It also improves conductivity. Doping process creates two groups of semiconductors.

a) Negative charge conductors or (n type)
b) Positive charge conductors or (p type) [62].

4.2 P-N Junctions

Junction is a region where the two semiconductors meet. A P-N junction is achieved by combining together P-type and N-type semiconductors closely. P-N junctions such as are manufactured from a single crystal. Different dopant concentrations are diffused across this single crystal creating a semiconductor from two different materials causes a grain boundary between them. This grain boundary severely inhibits its utility as it scatters the electrons and holes [62]. The P-N junctions are called as p-n diodes or rectifier diodes.

![Figure 4.5: Schematic diagram of p-n junction diode and depletion layer.](image)

Diodes conduct electric current just in one direction (diode's forward direction) while blocking current in the opposite direction (the reverse direction). This unidirectional
behavior is called rectification, and is used to convert alternating current to direct current, and to extract modulation from radio signals in radio receivers. Diodes are symbolized as in Figure 4.6.

![Figure 4.6: Symbol of diodes](image)

The electrical characteristics of typical diodes are shown in figure Figure 4.7. When a small voltage applied to diode in forward direction, current flows easily but when voltage applied in reverse direction, the diode shows a great resistance to current flow. Thus current flowing though a reverse biased diode varies from several mA to μA [62].

![Figure 4.7: Electrical (V-I) characteristics of ideal diodes](image)

The current through a diode as a function of voltage is expressed by the diode equation. The Ideal Diode Law, expressed as:

$$I = I_0(e^{\frac{qV}{n k_B T}} - 1)$$  \hspace{1cm} (4.1)

where, $I$ is the net current flowing through the diode; $I_0$ is the dark saturation current, (the diode leakage current density in the absence of light); $V$ is the applied voltage though the diode; $q$ is the absolute value of electron charge ($1.6 \times 10^{-19}$ C); $n$ is the ideality factor; $k_B$ is the Boltzmann's constant ($1.38 \times 10^{-23}$ J/K); $T$ is the absolute temperature in Kelvin [67].

If we take the log of both sides of the equation 4.1;

$$\ln I = \ln I_0 + \left(\frac{q}{nk_B T}\right)V$$  \hspace{1cm} (4.2)

ideality factor, $n$, is found to be;
The "dark saturation current" \( I_0 \) is an extremely important parameter which differentiates one diode from another. \( I_0 \) is a measure of the recombination in a device. A diode with a larger recombination will have a larger \( I_0 \). The value of the ideality factor of the heterojunctions can be determined from the slope of the straight line region of the forward bias log I–V characteristics [67].

### 4.2.1 ZnO/Si heterojunctions

ZnO/Si heterojunctions are of particular interest in the integration of optoelectronic devices utilizing hybrid advantages of the large binding energy of ZnO thin films and the inexpensiveness of Si substrates [67].

#### 4.2.1.1 Structural properties of ZnO/Si heterojunctions

Yang Zhang et. Al. [68] has studied on fabrication and electrical characterization of nanocrystalline ZnO/Si heterojunctions. As seen in Figure 4.8 they have investigated structural properties by XRD patterns grown on p-Si (1 0 0) substrates, which shows that the films are polycrystalline with a hexagonal wurtzite structure. It can be seen that there is not a clearly preferential orientation in the nanocrystalline ZnO thin films. The peaks at 69.58 and 33.08 correspond to the diffraction of Si (4 0 0) and (2 0 0) planes, respectively. The lattice constants of ZnO calculated from the present data are \( a = 3.249 \) Å and \( c = 5.202 \) Å, which are reasonably in agreement with \( a = 3.253 \) Å and \( c = 5.209 \) Å of ZnO (JCPDS Card No. 80–00075).

![XRD spectrum of a typical ZnO film grown on a p-Si (1 0 0) substrate.][68]
Figure 4.9 shows the AFM micrograph of a typical ZnO film grown on a p-Si substrate. It can be easily seen that the film is crack-free and quite smooth. Grains are tightly packed, and the size varies from 50 to 100 nm [68].

Figure 4.9: AFM image of a typical ZnO film grown on a p-Si substrate [68]

In the study of Breivik at. al [24] have investigated the nano-structural properties of ZnO for si based solar cells by Transmission Electron Microscopy. They have deposited ZnO and ZnO:Al layers on p-type (100) oriented crystalline Si, a-Si:H (15 nm)/Si and Corning glass substrates by magnetron sputtering method using a HF (13.56 MHz) set up. ZnO and ZnO:Al (2 wt.% Al) sintered targets were used. The base pressure in the sputter system was about 1.33 mPa (10^{-5} Torr). The total pressure of sputtering gas mixture was adjusted to about 0.4 Pa (3·10^{-3} Torr) during the film preparation. The argon flow rate and the DC plasma power were kept constant at about 40 sccm and 100 W respectively during the deposition process. Plasma emission monitor (PEM) control was used. All depositions were done at room temperature. Nevertheless a self-heating process took place, but the temperature of the substrates did not exceed 70–80 °C during deposition.

From the TEM images in Figure 4.10. they found that TEM showed the crystal grains of the ZnO extend from the substrate interface to the top of the ZnO film in all samples [24].
The thickness of the ZnO based films is 120 nm. The width of the grains is in the order of 10–20 nm. In agreement with previous reports on ZnO growth the ZnO crystals were found to have a preference for the c-axis being perpendicular to the substrate surface and with a maximum deviation around 3° [24].

Dengyuan Song et. Al [69] have investigated structure and characteristic of ZnO:Al/n-Si wafer that produced by magnetron sputtering technique. During their experiment they have investigated the structural properties by Scanning Electron Microscopy (SEM) and X-ray diffraction patterns. The Figure 4.11 shows a SEM picture and XRD pattern (using 2θ values in the range of 30–80°) taken on the top surface of the heterojunction. The SEM picture shows that the ZnO film consists of tightly packed grains with sizes in the 50–150 nm range. The dominant peak in the XRD pattern (Figure 4.11. b) is the ZnO (002) peak (located at 2θ=34.48), while the weak peak at 2θ=72.58 is from the ZnO(004) diffraction. The peak at 2θ =69.58 is caused by the diffraction of Si (004). The XRD pattern indicates the highly oriented
crystallographic growth of ZnO:Al films with c-axes perpendicular to the substrate surface.

Figure 4.11: (a) SEM image of a ZnO:Al film (thickness 250 nm) deposited onto a n-Si wafer, using the following sputter conditions: Prfs 150 W, Tsubs 250 °C and Pws 0.5 Pa. (b) XRD pattern measured for the same ZnO:Al film. [69]

4.2.1.2 Optical Properties of ZnO/Si Heterojunctions

In the study of He Bo et al [67] have investigated of optical properties of AZO films that produced by magnetron sputtering. Optical measurements (transmission) of the ZnO and ZnO: Al thin films deposited on glass have been performed at room temperature in the wavelength range 300 to 1150 nm using a Digichrom 240 Monochromator. The transmission spectrum of the AZO film deposited on glass substrate was measured and is shown in Figure 4.12. The average transmittance of the AZO film is about 90% in the visible region and the band-edge is at 364 nm, which can be suitable for UV devices such as photo detectors.
Breivik et al. [24] have an investigation on optical properties of ZnO films. And optical measurements (transmission) of the ZnO and ZnO:Al thin films deposited on glass have been performed at room temperature in the wavelength range 300 to 1150 nm using a Digikrom 240 Monochromator. Figure 4.13 shows transmission spectra taken at room temperature for ZnO and ZnO:Al layers deposited on Corning glass substrates. These films exhibit rather good transparency (~80–90%) in the visible and near-infrared regions. The average transmittance of the ZnO:Al films is higher compared to ZnO ones in almost all measured spectral ranges. It is necessary to note that, in general, properties of ZnO based layers on glass substrate can be different from those deposited on Si substrates. Therefore, a comparative analysis of the general trends of optical and electrical properties of such layers is a subject of investigation.
Dengyuan Song et al [25] have studied heterojunction properties of ZnO:Al/p-Si prepared by RF magnetron sputtering. The optical bandgap was obtained from transmission measurements, using a Varian Cary 5G W-Vis-NIR double-beam spectrophotometer. Spectrophotometric measurements on ZnO:Al layers which were grown on glass (using the same conditions as on the Si wafer substrates) showed an average transparency of about 84% in the visible region. Figure 4.14 shows the square of the absorption coefficient ($\alpha^2$) vs. photon energy plot near the band edge. From the diagram, the optical bandgap of 3.41 eV for Zn0:Al film is deduced, which represents a blue shift compared to undoped ZnO films (3.28 - 3.30 eV).
4.2.1.3 Electrical Properties of ZnO/Si Heterojunctions

Yang Zhang et. Al. [68] have studied I–V characteristics of p-Si/n-ZnO heterostructured junctions by using an X–Y function recorder in the temperature range of 207–339 K in the dark. Un-doped nc-ZnO films were prepared on single crystalline p-Si substrates by a sol-gel method. The I–V characteristics were measured by a laboratory assembled system consisting of a function generator, an X–Y function recorder, a low-temperature cryostat, and a specially designed sampled holder. Thin films samples are mounted in a specially designed sampled holder.

Figure 4.15 shows the I–V characteristics of nc-ZnO/p-Si heterojunctions measured with temperature ranging from 270 to 339 K in a cryostat. The sample was kept in the dark condition during the measurements. It is obvious from Figure 4.15 (a) that the heterostructures are rectifying in nature with a turn-on voltage of 3.0 V, which is much larger than that of ZnO:Al/n-Si prepared by a magnetron sputtering. Under reverse voltages, the breakdown voltage for the sample is as large as 20 V (not shown in figure). Generally, the native ZnO is n-type semiconductor due to the self compensation. In the case of ZnO/Si, the work function of p-type Si is larger than that of n-type Si. The potential barrier of p-type Si is higher compared with n-type Si. Therefore, the turn-on voltage of nc-ZnO/p-Si heterojunction is larger in comparison of ZnO:Al/n-Si. Figure 4.15 (b) shows the temperature dependence of the forward current in logarithmic scale. The forward currents can be classified into two regions according to the applied voltages. In region B, above 3.8 V, the forward current deviates from linearity due to the effect of a series resistance on the system. In region A, below 3.8 V, the temperature dependence of the forward currents can be expressed by

\[ I = I_0 \exp(BV) \]  \hspace{1cm} (4.4)

where \( I \) is the current subject to an applied voltage \( V \), \( I_0 \) the saturation current, and \( B \) is a coefficient. The temperature dependence of the parameter \( B \) depends on the dominant current transport mechanism. If the current is controlled by tunneling, \( B \) is a constant independent of temperature. If the current is controlled by some other mechanisms, \( B \) is generally dependent on temperature. In the plots of log \( I \) versus \( V \) of nc-ZnO/p-Si heterojunctions, \( B \) is independent of the measurement temperature \( T \), which indicates that the current in this region is dominated by a tunneling mechanism [68].
Dengyuan Song, et. Al. [70] have investigated interfacial structure and current transport properties of sputter-deposited ZnO:Al/ c-Si heterojunction solar cells. In their studies, the Zn0:Al films were deposited by rf magnetron sputtering on (100)-oriented n-type silicon wafers with a dopant concentration of (4-6)x 10^{15} cm^{-3}. The current-voltage characteristics of the solar cells were measured with an automated measuring system consisting of a DC voltage current source monitor unit (Advantest TR 6143) and a personal computer.

Figure 4.16 (a) shows the dark I-V curve (forward and reverse bias) of one of their Zn0:Al/n-Si heterojunction solar cells. Diode-like behavior is evident, with a rectification ratio of 10^3 at ± 0.6 V. Figure 4.16 b) shows the 1-sun I-V curve of the same device (AM1.5G, 100 mW/cm^2, 298 K), giving an open-circuit voltage of 411 mV, a short circuit current density of 30.0 mA/cm^2, a fill factor of 66.7%, and an efficiency (active area) of 8.2% [70].
Figure 4.16: Measured I-V characteristics of a ZnO:Al/ n-Si cell (a) in the dark (298 K) and (b) under 1-sun illumination (AM1.5G, 100 mW/cm², 298 K) [70]

Figure 4.17 shows the temperature dependence of the dark forward I-V characteristics of one of their ZnO/n-Si cells in the range 283 to 363 K, using 10-K steps [70].

Figure 4.17: Dark forward I-V curves of one of our ZnO:Al/n-Si cells for temperatures in the range 283 - 373 K, using 10-K steps. [70]

Ibrahim et al. [71] have studied ZnO/Si solar cell fabricated by spray pyrolysis technique. Heterojunctions have been fabricated between films of ZnO prepared by
spraying technique. Studies of the junction properties of the cells were performed in order to obtain information about the current–voltage mechanism. The current through the cell was measured using a Keithely 616 electrometer and the temperature was measured by Keithely digital thermometer model 871. Illumination was carried out by a tungsten source with a power of 50 mW cm\(^{-2}\). The temperature variation of the current density (J) with voltage was measured between 295 and 375 K under dark condition. Figure 4.18 shows the dark J–V curves of the cell at different temperatures. The curves were definitely of the diode type, with the forward direction corresponding to the positive potential on ZnO. As shown in this figure, diode-like behaviour is evident, with rectification behaviour and their current leakage tends to increase with temperature.

**Figure 4.18:** The dark J–V characteristic of ZnO/Si heterojunction at different temperatures[71]

Bacaksız et al. [72] have studied the structural and electrical characterizations of ZnO-based homojunctions were grown by spray pyrolysis technique in air. Temperature dependent I–V measurements were carried out in a He cryostat in the range 150–300 K. p-ZnO/SnO2 and n-ZnO/SnO2 contacts were prepared by using Au and InGa and observed to be ohmic as indicated in Figure 4.19. Thus it was concluded that the observed rectifying effect originates purely from the p-ZnO/n-ZnO diode. It was determined from I–V measurements that the ZnO homojunction has a rectifying behavior with a turn on voltage of about 1.5V at 300 K. Chu et al. reported that the turn on voltage of p-ZnO/n-ZnO homojunction is around 6V. This value is much higher than that of our study. The turn on voltages found by several
authors scatter mostly around 2V. The reason for this variation might be attributed to the high defect concentration in the interface. A low value of the turn on voltage is critically important in device applications.

Figure 4.19: I–V characteristics of p-ZnO/SnO2 and n-ZnO/SnO2 contacts. [72]

Figure 4.20: Semilog I–V characteristics of the ZnO homojunction at various temperatures with the I–V inset showing the turn on voltage [72]
Dengyuan Song et al [25] have studied heterojunction properties of ZnO:Al/p-Si prepared by RF magnetron sputtering. The current-voltage characteristics in the dark were measured with a computer-controlled sourcelmonitor unit (Advantest, TR6143). Capacitance-voltage measurements were performed at 80 kHz using an impedance analyser (HP 4194). In C-V and I-V measurements, the devices were kept in a light-proof box shielded very carefully against light to avoid the effect from background light.

Figure 4.21 shows the forward (Figure 4.21 a) and reverse (Figure 4.21 b) current density-voltage-temperature (J-V-T) characteristics of a typical ZnO:Al/p-Si heterojunction measured in the dark in the temperature range of 298-368 K.

It can be seen that the junction exhibits a diode-like rectifying behavior. Under forward bias, the temperature dependence of the I-V curve is weak (Figure 4.21 a). The bending of the curves at higher voltages is caused by the series resistance of the device.

The ideality factor n is 3.0 at low voltages and near room temperature. Furthermore, Figure 4.22 shows a plot of log (J) versus T for ZnO:Al/pSi as a function of the forward bias voltage, suggesting that the current density in the heterojunction is exponentially proportional to the temperature. This dependence holds even for very small voltages (0.05V). The observed large ideality factor and the good linear relationship between log (J) and T in Figure 4.22 for different forward voltages seems to exclude several possible forward current transport mechanisms across the
juncture heme, namely thermionic emission, minority carrier injection, and recombination generation. The behavior shown in Figure 4.21 a, which has previously also been observed for other heterojunctions, suggests that the current transport in the junction is dominated by the multi-step tunneling process. The voltage dependence of the junction current can he expressed as

\[ J = J_0(T) \exp(\frac{AV_j}{q}) \]  

(4.5)

where \( A \) is a constant independent of temperature, \( V_j = V - R_s I \) is the voltage across the junction (i.e. the external voltage \( V \) corrected for the series resistance effect), and \( J_0(T) \) is exponentially proportional to temperature [25].

Figure 4.22: Current density versus temperature as a function of forward bias voltage. [25]

C-V curves were measured at 80 kHz as a function of reverse bias at room temperature. Figure 4.23 shows the measured 1/C²-V characteristics of a typical ZnO:Al/p-Si heterojunction. Since sputter-deposited ZnO:Al is a heavily n-doped semiconductor with a typical free electron concentration of about \( 10^{20} \) cm⁻³ at room temperature, it is reasonable to assume that the depletion region is predominantly on the Si side of the junction. The 1/C² versus V can then be expressed as

\[ \frac{A^2}{C^2} = \frac{2(V_{bi} - V - \frac{kT}{q})}{q \varepsilon_s N_A} \]  

(4.6)

where \( \varepsilon_s \) is the permittivity of Si, \( N_A \) the net acceptor concentration in the p-Si, \( A \) the junction area, \( V \) the applied voltage, and \( V_{bi} \) the built-in potential. This plot reveals a good linear relationship down to -5V, indicating that the abrupt heterojunction theory is indeed applicable to the ZnO/p-Si structure. The 1/C²–V intercept of 0.35 V (by extrapolating the straight line to the x axis) is essentially equal to the diffusion
potential within the Si. The slope of the plot gives a $N_A$ value of $1.21 \times 10^{16} \text{cm}^{-3}$ consistent with the resistivity of the p-Si used [25].

![Figure 4.23: The lip versus voltage curve of a Zn0:AVp-Si heterojunction at room temperature, measured at a frequency of 80 kHz [25]](image)

4.2.1.4 Production techniques of ZnO/Si heterojunctions

There are a few reports on the n-ZnO/p-Si heterojunction where the ZnO film is grown by different techniques. For example, Ajimsha et al. reported the electrical characteristics of n-ZnO/p-Si heterojunction diodes grown by pulsed laser deposition at different oxygen pressures. Basu prepared ZnO/p-Si junction by CVD and reported an ideality factor of 2.57. Kumar et al. studied the characterization of sol-gel derived yttrium-doped n-ZnO/ p-Si heterostructure. Sun achieved UV electroluminescence (EL) emission from ZnO nanorods with n-ZnO/p-Si heterojunction structure fabricated by the hydrothermal method [67].
5. EXPERIMENTAL PROCEDURE

This study covers production and characterization of the Al doped ZnO thin films deposited on p type silicon wafers by sol-gel dip coating method. For investigation of optical properties same n-type ZnO:Al thin films were deposited on borosilicate glasses and fused silica substrates at the same conditions. The films were deposited to produce p-n heterojunction. The heterojunction were generated between p-type silicon wafers and n-type ZnO:Al thin films by sol-gel dip coating process.

The films had been prepared by the stages of sol preparation; substrate cleaning, dip-coating, pre-heating and post heating multiprocessing. The procedure from coating to drying was repeated four times. The pre-heat treatments were performed at 400°C in oxygen ambient and post heating treatments in 550-900°C for 1 hour in oxygen, nitrogen, argon and vacuum atmosphere. Heat treatment parameters, Al doping concentration and coating process parameters effects on optical, electrical, structural properties of ZnO:Al films and ZnO:Al /p-Si heterojunctions were investigated.

Before starting the experiments, all laboratory equipments that were used for sol and substrate preparation were cleaned with detergent, than waited for 5 seconds in the solution of sulfuric acid (H$_2$SO$_4$), Potassium dichromate (K$_2$Cr$_2$O$_7$) and water. Then all the equipments were rinsed with de-ionized water. At last they were sterilized with water vapour in an autoclave furnace (Nüve OT 012 Bench Top Steam Sterilizer) then dried at 100°C in drying oven (Binder ED 53).

![Figure 5.1: (a)Nüve OT 012 Bench Top Steam Sterilizer (b) Binder ED 53](image-url)
5.1 Production Process of ZnO:Al Thin Films and ZnO:Al/p-Si Heterojunctions

5.1.1 Preparation of solutions

The first stage of the dip coating process is sol preparation. A 50 ml aqueous solution was prepared. The solution consists of absolute ethanol as a solvent material, zinc acetate dihydrate Zn(CH$_3$COO)$_2$·2H$_2$O, 99.5% purity) is added as a starting material and the molar concentration of the zinc is 0.5M. The diethanolamin DEA(CH$_2$CH$_2$OH)$_2$ is added as a stabilizer and a measured amount of Al nitrate nano hydrate Al(NO$_3$)$_3$·9H$_2$O (extra purity) is added as dopand sources to obtain 0.8-1.0-1.2-1.6 at % Al ratio (Rm = Al/Zn).

The molar ratio of DEA to Zincacetat-dihydrat was maintained at 1.0. Then the resulting mixture was stirred with Magnetic stirrer (Heidolph MR 3001K) at 60°C for 1 h to form clear, transparent and homogeneous solution. After cooling the solutions, they are aged at room temperature for 1 day, then the colloidal suspensions are ready to use. The humidity level of the ambient was fixed at 43 % by dehumidifier to protect the solution quality during the preparation of the solution and the dip coating processes. The solutions were kept in refrigerator to prevent the precipitation and to extend the life of the solution.

![Figure 5.2](image)

**Figure 5.2**: TG/DT Analyses of dried ZnO:Al gel with 10°C/min heating and cooling rate [73,74]
Differential thermal and thermo gravimetric analyses (DTA/TGA) were performed by using Perkin Elmer Diamond TG-DTA thermal analyses equipment to investigate thermal behaviours of the ZnO:Al thin films, the result analysis is shown in Figure 5.2.[73,74]. Thermal analyses were performed in air atmosphere with 10°C/min heating and cooling rate from room temperature to 900°C and 900°C to room temperature, respectively. The analysis in Figure 5.2 was used to settle on heat treatment conditions for annealing of the films.

TG-DT analyses of ZnO:Al indicated an endothermic peak between 290°C and 420°C which shows solvent and organic residuals started to evaporate between these temperatures. A noticeable mass loss (~70 %) was seen at ~520°C which meant the crystallization starts at ~520°C and the increasing lasts till 900°C then started to decrease again. According to these results, the pre-heating temperature which is made to evaporate the organic residuals were defined as 400°C and the annealing temperature which is made for crystallization deposited films were defined as above 520°C till 900°C; 550°C, 600°C, 700°C, 800°C and 900°C.

5.1.2 Pre-treatments of substrates

P type silicon wafers (100), fused silica and borosilicate glasses were used as substrates which are in the dimensions of 10x30 mm, 30x30 mm and 35x35 mm respectively.

A three-step pretreatment to wafers and four-step pretreatment to glasses were applied to clean and dry them just before ZnO film deposition. At first, silicon wafers were ultrasonically cleaned in acetone than in alcohol solution for 10 minutes, respectively. Finally, the wafers were dried in air. Glasses were ultrasonically cleaned in acetone than in alcohol solution than in rinsed water for 10 minutes, respectively. Finally, the glasses were dried in air. Ultrasonic cleaning was performed by Bondelin Sonorex Ultrasonic Bath. After pretreatment, the wafers and the glasses were ready for subsequent sol-gel film deposition.

5.1.3 Deposition of films

The readily-prepared ZnO:Al solutions were deposited on cleaned substrates by sol-gel dip coating technique by a cycle of dipping and drawing the substrates into the solution with 200 mm/min dipping drawing rate and the samples are kept in solution for 5 sec then pre-heated at 400°C for 10 minutes in oxygen ambient. The dipping-
drawing cycle with pre-heating was repeated for four times. A computer controlled dip coater (KSV dip coater LMX2) showed in Figure 5.3 was used during film deposition.

![Figure 5.3: KSV Dip coater equipment](image)

The four layered prepared films were post-heated at a range of 550-900°C temperatures for 1 hour in oxygen, nitrogen, argon and vacuum ambient. The pressure was 0.003 mbar in vacuum and 1013.25 mbar in nitrogen and argon ambient and the flow rate of argon and nitrogen gases were 30L/h.

5.2 Characterization of ZnO:Al Thin Films

Sol-gel technique has some difficulties and limitations among to other coating techniques. In sol-gel process the properties of the films depend on many different variables such as temperature, humidity and cleanliness of the samples, solutions and ambient. The production also has poor reproducibility and reliability. In this study the structural, optical and electrical behaviors of the ZnO:Al films were investigated.

5.2.1 Structural properties

X-Ray diffraction patterns and SEM images of the ZnO:Al thin films were investigated to determine the structural properties. The X-Ray diffraction patterns of the thin films were taken at room temperature and the humidity level of the ambient
was fixed at 43 % by a dehumidifier. GBC-MMA X-Ray diffractometer in Figure 5.4 with Cu Kα radiation of wavelength 1.54 Å was used to record XRD patterns. Diffractometer was operated at 35 kV and 28.5 mA with the energy of 1 kWatt and a 2 deg/min constant scan rate was used to collect 20 data from 20° to 60°.

![Figure 5.4: GBC-MMA X-Ray diffractometer](image)

JEOL JSM 7000F Field Emission Scanning Electron Microscope (Figure 5.5 a) with 5.0 and 10.0 kv accelerating voltages and JEOL 6335F Scanning Electron Microscope (Figure 5.5 b) with 20.0 kv accelerating voltage were used to take SEM images from the surface of the thin films.

![Figure 5.5: (a) JEOL JSM 7000F Field Emission Scanning Electron Microscope (b) JEOL 6335F Scanning Electron Microscope](image)

The thickness measurements were performed by using a surface profilometer (Veeco Dektak- 6M surface profilometer shown in Figure 5.6) with 3mg load at different parts of the films. The 3mg load moves for 2000 nm. which includes coated and
uncoated parts. The measurement depends on the thickness difference between coated and uncoated parts of the films.

![Figure 5.6](image)

(a) Veeco Dektak- 6M surface profilometer (b) zoom to probe

5.2.2 Optical properties

Optical properties of the films were investigated by optical transmittance and reflectance measurements also optical band gap energies were calculated. Measurements were performed in the wavelength range from 192.5 to 900 nm by using T80 UV/VIS Spectrophotometer (Figure 5.7).

![Figure 5.7](image)

Figure 5.7: T80 UV/VIS Spectrophotometer
5.2.3 Electrical properties

The electrical resistivity of ZnO:Al thin films were measured by using a Four Point Resistivity Probe with Mounting Stand (SIGNATONE). The resistivity values calculated with measured thickness values.

5.3 Characterization of ZnO:Al/Si Heterojunctions

The current-voltage characteristics of the p-n junctions produced by sol-gel dip coating were investigated to examine junction existence. Heterojunctions were fabricated using the configuration of Cu/ZnO:Al/Si/Al. Univex 450 Thermal Evaporator (shown in Figure 5.8 a and b) was used to prepare the samples for current voltage characteristic investigation.

![Univex 450 Thermal Evaporator](image)

Figure 5.8: a) Univex 450 Thermal Evaporator b) Vacuum chamber of the Univex 450 Thermal Evaporator

After the ZnO:Al film deposition, the ohmic back contact of Si wafer was fabricated by thermal evaporation of Al (~0.8 µm-thick), while the other ohmic contact was fabricated with Cu-grid (~0.8 µm-thick) through a mask on the front side. During the thermal evaporation the vacuum level was ~ 6.5x10^-6 Pa. The areas of Al and Cu electrots were 0.25 cm², 0.07cm². Figure 5.9 shows schematic diagram of ZnO:Al/Si heterojunctions.
The current voltage characteristic analyses were made with direct current voltage (DC) in the range between -20 and +20 at room temperature, under dark and light (xenon lamp 100mW/cm²) conditions by Keithley 4200 Semiconductor characterization system (SCS) are shown in Figure 5.10.
6. RESULT AND DISCUSSION

Al doped ZnO thin films were produced by sol-gel dip coating technique on to borosilicate glass, fused silica and p type silicon wafer substrates at different concentrations. Thin film structure has been characterized by X-ray diffraction, UV-Visible spectrophotometer, Scanning electron microscopy (SEM), Field emission electron microscopy (FESEM). All the films are polycrystalline with wurtzite structure. The thicknesses of the thin films were determined by using surface profilometer and measured in the range of 150-400 nm. The four-point probe technique was used to evaluate the electrical resistivity of thin films. The heterojunction properties of ZnO:Al/ p-Si structures were investigated by I-V measurements evaluated with Keithley 4200 Semiconductor characterization system.

6.1 Structural Properties of ZnO:Al Thin Films

Structural properties were analyzed by X-ray diffraction patterns and SEM images of the ZnO:Al thin films. According to X-ray diffraction patterns the average crystallite sizes were calculated by application of Scherrer-Warren formula in (Eq. 6.1).

\[ D = \frac{0.9\lambda}{\beta \cos \theta_{B}} \]  

(6.1)

Where \( \lambda \) is the wavelength X-ray of 1.54 Å, \( \theta_{B} \) is Bragg diffraction angle, \( \beta \) is the FWHM (Full width half maximum of distinctive peak) of \( \theta_{B} \).

6.1.1 Effects of Al Concentration

X-ray diffraction patterns of the films doped with 0.8-1.0-1.2-1.6 at. % Al were determined nanosize hexagonal Bravais flock in Figure 6.1. and exhibited the wurtzite structure with all XRD peaks identified in the 20-60 2θ range. According to these patterns, the films with all Al dop concentration were polycrystalline and showed three orientation peak as (100), (002) and (101). The dominant orientation peak was (101) for all. According to these patterns, the films with all Al dop concentration were polycrystalline and showed peaks correspond to the diffraction
(100), (002) and (101) planes. According to calculation of the crystallite sizes from the XRD patterns, it is suggested that the ZnO films are nanocrystalline and the average crystallite sizes are in the range of 21-43 nm. The calculated average crystallite sizes at (100), (002) and (101) orientation showed in Appendix A.1.

![X-Ray diffraction patterns of ZnO:Al thin films](image)

**Figure 6.1:** X-Ray diffraction patterns of ZnO:Al thin films depends on Al concentration annealed at 700°C in nitrogen ambient

There is an increasing on the average crystallite size by decreasing of the dopant concentration due to film crystalline distortion. The decrease in the calculated average crystallite sizes depend on Al concentration is shown in Figure 6.2. The reason of increasing on the average crystallite size could be the difference between ionic radius of the Zn and the dopant element Al ($r_{\text{Zn}^{2+}}=0.074\text{ nm}$, $r_{\text{Al}^{3+}}=0.054\text{ nm}$). The difference between ionic radiiuses of Zn and Al might cause a drag on grain growth by compression stress [75].

The thicknesses of the films annealed at 700°C in vacuum, oxygen, nitrogen and argon atmospheres for four different Al concentrations were investigated and showed in Figure 6.3. As seen in the figure the increase of Al concentration had limited effect on the thickness.
Figure 6.2: Average crystallite sizes of ZnO:Al thin films oriented in (101) depends on Al concentration annealed at 700°C in nitrogen ambient.

Figure 6.3: Thickness of ZnO:Al thin films depends on Al concentration annealed at 700°C in argon, vacuum, nitrogen, oxygen ambient.
6.1.2 Effects of Annealing Temperature

The X-ray diffraction patterns of the films 1.2 at. % doped and annealed at the temperature range of 550-900°C in oxygen ambient are shown in Figure 6.4.

![X-ray diffraction patterns of 1.2 at. % Al doped ZnO:Al thin films annealed in oxygen ambient depends on annealing temperature.](image)

**Figure 6.4:** X-ray diffraction patterns of 1.2 at. % Al doped ZnO:Al thin films annealed in oxygen ambient depends on annealing temperature.

![Average Crystallite Size 1.2 at. % Al doped ZnO:Al thin films oriented in (101) annealed in oxygen ambient depend on annealing temperature.](image)

**Figure 6.5:** Average Crystallite Size 1.2 at. % Al doped ZnO:Al thin films oriented in (101) annealed in oxygen ambient depend on annealing temperature.
Figure 6.6: FESEM images of 1.2 at. % Al doped ZnO:Al thin films annealed in the oxygen ambient at (a) 550°C (b) 600°C (c) 700°C (d) 800°C (e) 900°C (20,000X and 30,000X magnifications)
The intensity of the films are higher at the higher temperatures at the orientation of (101) plane as showed in Appendix A.2. The films annealed at each temperature showed peaks correspond to the diffraction (100), (002) and (101) planes. According to XRD results, increasing in the annealing temperature increased the average crystal size. This increasing is shown in average crystallite size calculations in Appendix A.2. and FESEM images in Figure 6.6.

The grain sizes of ZnO:Al nanocrystallites were in average value range from ~ 22 nm to 66 nm in diameter when the annealing temperature increased from 550 to 900°C in oxygen ambient in Appendix A.2.

The structural changes of ZnO:Al nanocrystallites were investigated due to the annealing temperature. The surface of ZnO:Al structure has some voids. FESEM images for ZnO:Al in different annealing temperatures showed the formation of spherical grains on the surface in 20.000X and 30.000X magnification for all annealing temperatures.

![Graph](image)

**Figure 6.7**: The changes on the thickness of the ZnO:Al thin films with the increase of the annealing temperature at 1.2 at.% Al concentration.

Effects of different annealing temperature, ambient and dopant concentration on the film thickness were investigated. 1.2 at. % Al doped films annealed at the temperature range of 600°C-900°C in vacuum and oxygen atmospheres showed in
Figure 6.7. According to the graph a decrease in the thickness is obviously seen by the increase of annealing temperature. The thicknesses of the films annealed in oxygen and vacuum ambient are in the range of 150-400 nm.

6.1.3 Effects of Annealing Ambient

Figure 6.8 shows X-ray diffractions for the 1.2 at. % Al doped films annealed at 700°C in different ambient such as argon, nitrogen, vacuum, and oxygen. The crystallization was taken place in each ambient. The ZnO:Al thin films when annealed in oxygen, argon, and nitrogen environments showed peaks correspond to the diffraction (100), (002) and (101) planes. Appendix A.3. shows the intensity of the peaks for 1.2 at. % Al doped ZnO:Al films, annealed at 700°C in different annealing ambient and the calculated average crystalline sizes. Finest crystallite size is seen in vacuum ambient. The crystallite sizes of the films are affected by the change of annealing ambient.

![X-ray diffraction patterns of 1.2 at. % Al doped ZnO:Al films annealed at 700°C depends on annealing ambient](image)

**Figure 6.8:** X-ray diffraction patterns of 1.2 at. % Al doped ZnO:Al films annealed at 700°C depends on annealing ambient
Figure 6.9: Average Crystallite Sizes of 1.2 at. % Al doped ZnO:Al films annealed at 700°C depends on annealing ambient

Change in average crystallite sizes of the films annealed in all ambient are shown in Figure 6.9. SEM images in Figure 6.10, Figure 6.11 and Figure 6.12 also support these results.

The effect of the different annealing atmosphere on grain size of ZnO:Al films annealed in nitrogen, oxygen and vacuum atmospheres were investigated also with SEM and showed in Figure 6.10, Figure 6.11 and Figure 6.12. Relative intensity and the crystallite sizes of the films annealed in nitrogen atmosphere have higher values than that of the films annealed in argon atmosphere therefore the investigation of nitrogen ambient preferred.

SEM images of 1.2 at. % Al doped ZnO:Al films annealed at 700°C in nitrogen ambient with 50,000X and 100,000X magnification were shown in Figure 6.10 (a) and (b) respectively. Noncluster nano spherical particles were seen on the surface of ZnO:Al film after annealing process in nitrogen ambient. The maximum sizes of nanospheres were in range of ~35-48 nm in SEM image with 100,000X magnification.
Figure 6.10: SEM images of 1.2 at. % Al doped ZnO:Al thin films annealed in nitrogen ambient at 700°C (a) 50,000X magnification (b) 100,000X magnification

SEM images of 1.2 at. % Al doped ZnO:Al films annealed at 700°C in Oxygen atmosphere with 50,000X and 100,000X magnification were shown in Figure 6.11 (a) and (b) respectively. Films show the similar surface morphology with the surface of the annealed film in Nitrogen atmosphere at the same temperature. The size of nano spheres were about 28.5 nm in SEM image with 100,000X magnification.
Figure 6.11: SEM images of 1.2 at. % Al doped ZnO:Al thin films annealed in oxygen ambient at 700°C. (a) 50.000X magnification (b) 100.000X magnification

The nanospherical structure of ZnO:Al for the annealed film in vacuum atmosphere at 700 °C in Figure 6.12 have the similar surface morphology with the surface of the annealed film in nitrogen and oxygen atmosphere at the same temperature. The size of nano spheres were about 30 nm in SEM image with 100.000X magnification.
The grain size of ZnO:Al raised when ZnO:Al thin film was annealed in nitrogen ambient at 700°C. The pressure in vacuum ambient was 0.003 mbar, where the pressure in nitrogen ambient was 1013.25 mbar and the flow rate was 30 L/h. The application of the inert gas to the annealing ambient can be a reason of big grain size and granularity growth of ZnO:Al. As seen in Figure 6.3 the annealing ambient has little influence on the thickness, the thicknesses of the films at 700°C are in the range...
of 250-350 nm and the thickness of annealed films increased due to vacuum, oxygen, nitrogen and argon ambient respectively.

6.2 Optical Properties of ZnO:Al Thin Films

6.2.1 Effects of Al Concentration

The optical properties of ZnO:Al thin films annealed at 700°C in nitrogen ambient were investigated with the increase of aluminum concentration. Figure 6.13 shows the transmittance spectrum of ZnO:Al thin films with different Al concentration. For each ZnO film, sharp absorption edges at ~370 nm wavelength were observed in ultraviolet (UV) range (Figure 6.13).

![Optical transmittance spectra of ZnO:Al thin films with different dopant concentrations at 700°C in nitrogen ambient](image)

**Figure 6.13:** Optical transmittance spectra of ZnO:Al thin films with different dopant concentrations at 700°C in nitrogen ambient

In section 6.4.2., Figure 6.32 indicates a considerable photocurrent in reverse bias under UV illumination for junctions annealed in nitrogen ambient when compared to other annealing ambient. Hence the films annealed in nitrogen ambient were preferred for the investigation of the optical band gap. It is obviously seen in Figure 6.14 the energy band gap is widening with the increasing of the Al concentration from 0.8 to 1.6 at. % for the films annealed in nitrogen ambient at 700°C. The widening of 1.6 at. % doped zinc oxide is higher than that of 0.8 at. % doped zinc.
oxide films. The widening in these band gaps depending on the increase of Al concentration could be explained by Moss-Burstein shift [76]. According to the Moss–Burstein theory, the donor electrons occupy bottom states of the conduction band in highly doped zinc oxide films [77]. The optical gap is defined as the minimum energy needed to excite an electron from the valance band to the conduction band [78]. In general the blue shift of the absorption onset of Al doped nano crystalline films is associated with the increase of the carrier concentration blocking the lowest states in the conduction band, well known as the Burstein–Moss effect [16]. Plots of \((\alpha h\nu)^2\) versus \(h\nu\) was drawn for ZnO:Al thin films in Figure 6.14 by calculating \(\alpha\) and \(h\nu\) values from the equations given below;

\[
an_0\eta\omega \sim (\eta\omega - E_0)^n
\]  

\[
\alpha = A(h\gamma - E_0)^{1/2}
\]

where, \(E_0\) is the optical gap and \(n_0\) refractive index in Eq. (6.2) [79-80]. In an allowed direct transition, \(\alpha\) is given in Eq. (6.3). A is a constant [81-82]. For this study, \(n\) value is determined as 1/2 for \((\alpha h\nu)^{1/n}\). From the plot, the band gap energy was determined by extrapolating the linear portion of the graph to \(h\nu = 0\). It is determined that there is an allowed direct transition as \((\alpha h\nu)^2\) for ZnO:Al film.

![Figure 6.14: The changes on the energy band gap of the ZnO:Al films with different dopant concentrations at 700°C in Nitrogen ambient.](image)

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As clearly seen in Table 6.1 the optical band gap is blue shifted with increasing Al doping concentration band gap (E_{opt}). From the transmittance spectra, E_{opt} is computed as 3.29, 3.32, 3.34 and 3.38 eV for the ZnO:Al thin films with the Al doping concentration of 0.8, 1.0, 1.2 and 1.6 at.% respectively.

Table 6.1: Optical band gaps of ZnO films with different dopand concentrations.

<table>
<thead>
<tr>
<th>Al concentration (at. %)</th>
<th>Optical band-gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>3.29</td>
</tr>
<tr>
<td>1.0</td>
<td>3.32</td>
</tr>
<tr>
<td>1.2</td>
<td>3.34</td>
</tr>
<tr>
<td>1.6</td>
<td>3.38</td>
</tr>
</tbody>
</table>

6.2.2 Effects of Annealing Temperature

Figure 6.15 shows that the annealing temperature effect on optical transmittance of the films with 1.2 at. % Al doped and annealed in vacuum ambient. The optical transmittances of the films are in the range of 85-90 % after 500nm wavelength.

![Optical transmittance spectra of 1.2 at. % Al doped ZnO:Al thin films at different annealing temperatures in vacuum ambient.](image)

**Figure 6.15:** Optical transmittance spectra of 1.2 at. % Al doped ZnO:Al thin films at different annealing temperatures in vacuum ambient.
A decreasing on the optical transmittance was investigated by the increasing of the annealing temperature. The films annealed at 900°C showed highest transmittance after the wavelength of 500 nm, where the film annealed at 600°C showed the lowest transmittance. It is seen the increase of transmittance occurred with the decrease of annealing temperature from 900°C to 600°C in Figure 6.15. The absorption edge of ZnO:Al thin film exhibited over 300 nm after the film annealed at 600°C. However, the increase of annealing temperature caused to shift the absorption edge. When the annealing temperature reached to 900°C, the absorption edge settled below 200 nm. This event led to a blue shift with the increase of annealing temperature.

6.2.3 Effects of Annealing Ambient

The effect of different annealing ambient on transmittance, T (%) of the ZnO:Al films was determined for four different annealing ambient such as vacuum, nitrogen, argon, and oxygen in Figure 6.16. The transmittance was investigated for 1.2 at.% doped films after the films were annealed at 700°C. It was seen from the results that the annealing ambient has a huge effect on transmittance. The films have showed the lowest transmittance in the nitrogen atmosphere when compare with the other films that annealed in argon, oxygen, and vacuum ambient.

![Figure 6.16: Optical transmittance spectra of 1.2 at % Al doped ZnO:Al thin films annealed at 700°C in different ambient](image-url)
6.3 Electrical Properties of ZnO:Al Thin Films

6.3.1 Effects of Al Concentration

The resistivity of Al doped ZnO films with different doping concentrations annealed at 700°C in nitrogen, argon and oxygen ambient showed in Figure 6.17 and in vacuum ambient in Figure 6.18. The resistivity decreased with increasing of Al concentration from 0.8 to 1.2 at. % Al concentration. The minimum resistivity of $9.966 \times 10^{-3}$ Ω.cm in argon, $9.366 \times 10^{-3}$ Ω.cm in nitrogen, $7.364 \times 10^{-3}$ Ω.cm in oxygen and $0.737 \times 10^{-4}$ Ω.cm in vacuum ambient were obtained at a doping concentration 1.2 (at. %). The resistivity has increased from 1.2 to 1.6 at. % Al concentration for all the annealing atmospheres in Figure 6.17 and Figure 6.18. Decrease in the resistivity with increased Al concentration till 1.2% can be interpreted as a result of electrons come from the donor Al$^{3+}$ ions incorporate as substitutional Zn$^{2+}$ cation sites or in interstitial position [73]. The lowest resistivity is seen in vacuum ambient.

![Figure 6.17: The changes on the resistivity of Al doped ZnO thin films annealed at 700°C in nitrogen, argon and oxygen ambient as a function of dopant concentration](image-url)
The changes on the resistivity of Al doped ZnO thin film annealed at 700°C in vacuum ambient as a function of dopant concentration

6.3.2 Effects of Annealing Temperature

The electrical resistivity values of the films with different doping concentrations were plotted in Figure 6.19 after the films were annealed at four different annealing temperatures in vacuum ambient. The resistivity has decreased from 0.8 to 1.2 at. % Al concentration. The lowest resistivity is ~0.2x10^{-4} \, \text{Ω.cm} and the lowest resistivity was obtained at 900°C at vacuum ambient. The resistivity decreased by the increase of the annealing temperature both in Figure 6.19 and Figure 6.20. The reason of this decreasing could be crystallinity enhances and big grain size in high temperatures. There is not a considerable change on resistivity values while the temperature increased from 800 to 900°C. This small shift could be explained by the saturation on the decrease of the resistivity with the increase of annealing temperature over 800°C.
The changes on the resistivity of Al doped ZnO thin films with different annealing temperatures in vacuum ambient as a function of dopant concentration were investigated at the dopant concentration of 1.2 at. % after the thin film was annealed in vacuum and oxygen ambient in Figure 6.20 and Figure 6.21. Decrease on the resistivity was determined with increase of the annealing temperature from 600 to 900°C. There was a rapid decrease on resistivity from 600 to 700 °C in Figure 6.20 and Figure 6.21, where there is not a big change on resistivity values while the temperature increased from 800 to 900°C. This small change could be explained by the saturation on the decrease of the resistivity with the increase of annealing temperature over 800°C.

Resistivity of the film decreased from ~ 1.8x10^{-4} to ~ 0.2x10^{-4} Ω.cm in vacuum ambient. However there was a decrease on resistivity from ~15x10^{-3} to ~ 5x10^{-3} Ω.cm in oxygen ambient, this decrease was slower with respect to resistivity decrease in vacuum ambient. ZnO:Al thin films have excess metal ions, while the pure ZnO have oxygen vacancies which cause oxygen adsorption [83]. When the annealing temperature increased the oxidation of ZnO films increased [83]. Because of that the slow decrease in resistivity can be explained with the oxidation rising of...
ZnO:Al texture depending on the increase of the annealing temperature at oxygen ambient.

**Figure 6.20:** The changes on the resistivity of 1.2 at % Al doped ZnO thin films annealed in vacuum ambient as a function of annealing temperature.

**Figure 6.21:** The changes on the resistivity of 1.2 at % Al doped ZnO thin films annealed in oxygen ambient as a function of annealing temperature.
6.3.3 Effects of Annealing Ambient

The resistivity of Al doped ZnO films annealed with different doping concentrations at 700°C in nitrogen, argon and oxygen ambient showed in Figure 6.17 and in vacuum ambient in Figure 6.18. The minimum resistivity of 9.966x10^{-3} (Ω.cm) in argon, 9.366x10^{-3} (Ω.cm) in nitrogen, 7.364x10^{-3} (Ω.cm) in oxygen and 0.737x10^{-4} (Ω.cm) in vacuum ambient were obtained. The lowest resistivity is determined in vacuum ambient.

6.4 Heterojunction Properties of ZnO:Al/ p-Si

6.4.1 Effects of Al Concentration

Figure 6.22 showed the current–voltage characteristic of the ZnO:Al/p-Si heterojunctions measured at room temperature in the dark. The ZnO:Al heterojunctions annealed at 700°C in nitrogen ambient had different Al concentrations ranging from 0.8 to 1.6 at. %. In forward bias the current though the heterojunctions change with the applied voltage where in reverse bias the current though the heterojunctions does not change substantially with voltage change. These I-V characteristics of the ZnO:Al/ p-Si heterojunctions prepared by sol- gel dip coating technique are similar with I-V characteristic of typical diode. The similarity of I-V characteristics indicates the formation of a diode between sol-gel prepared ZnO:Al thin films and p-Si. The diodes show rectifying behavior with rectification ratio, $I_F/I_R$ ($I_F$ and $I_R$ are forward and reverse current respectively) values at a ±20 V bias voltage showed in Table 6.2. The most conductive and rectifier heterojunction is determined as ZnO:Al/p-Si with 1.0 at.% Al concentration. I-V curve of ZnO:Al/p-Si heterjunction with 0.8 at.% Al concentration takes place in the positive side of the reverse bias, states in the second quadrant. This leads to the deviation of a diode characteristics from those of the ideal diode.
Figure 6.22: Measured current-voltage characteristics of ZnO:Al/p-Si Heterojunctions at different Al dop concentrations annealed at 700°C in nitrogen ambient under dark condition.

Figure 6.23 shows dependence of the forward current in logarithmic scale with the change of the Al concentration. The value of the ideality factor of the ZnO:Al / p-Si heterojunction is determined from the slope of the straight line region of the forward bias log I–V characteristics.

Figure 6.23: Semilog I-V characteristics of the ZnO:Al/p-Si heterojunctions with different Al dop concentrations annealed at 700°C in nitrogen ambient under dark condition.
When the semi-logarithmic forward-biased curves in Figure 6.23 are fitted to the standard diode equation given in (4.1), the ideality factors of the diodes fabricated in nitrogen ambient at 700°C are shown in Table 6.2. It is determined that heterojunctions with 1.0 and 1.2 at.% Al concentration declare lower ideality factors (n) than that of with 0.8 and 1.6 at.% Al concentration. There is a consistency between the changes on the ZnO:Al thin film resistivity (ohm.cm) and ideality factor of heterojunctions according to Al concentration. There is an increase in $I_0$ as well as an increase in ideality factor in Table 6.2.

**Table 6.2:** $I_0$, $n$ and $I_F/I_R$ values of ZnO:Al/ p-Si heterojunctions with different Al concentrations.

<table>
<thead>
<tr>
<th>Al Concentration %</th>
<th>$I_0$ (A)</th>
<th>$n$</th>
<th>$I_F/I_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>3.5x10^{-6}</td>
<td>38.5</td>
<td>26.80</td>
</tr>
<tr>
<td>1.0</td>
<td>3.0x10^{-7}</td>
<td>23.4</td>
<td>100.06</td>
</tr>
<tr>
<td>1.2</td>
<td>2.0x10^{-6}</td>
<td>28.1</td>
<td>18.59</td>
</tr>
<tr>
<td>1.6</td>
<td>3.2x10^{-6}</td>
<td>38.0</td>
<td>14.21</td>
</tr>
</tbody>
</table>

Figure 6.24 shows current-voltage characteristics of the ZnO:Al/p-Si heterojunction measured at room temperature under illumination by UV light source (xenon lamp 100mW/cm²). The ZnO:Al/p-Si heterojunctions annealed at 700°C in nitrogen ambient were at different Al concentrations ranging from 0.8 to 1.6 at. %. Hence, photoelectric behaviors were observed for the heterojunctions. UV illumination improved the current though the ZnO:Al/p-Si heterojunctions in forward bias. In reverse bias the photocurrent caused by xenon lamp (100 mW/cm²) is obviously much larger than the current under dark conditions. Since, the ZnO:Al films are highly transparent as ~80 T (%) in the visible region, visible light passes through the ZnO:Al films. UV light is absorbed mainly in the subjacent p-Si wafers generating electron–hole pairs depending on the ionizing radiation effect of light source. The creation of new electron-hole pairs is responsible for the observed photocurrent under reverse bias conditions.
Figure 6.24: Measured current-voltage characteristics of ZnO:Al/p-Si Heterojunctions at different Al dop concentrations annealed at 700°C in nitrogen ambient under light condition.

In Table 6.3 the values of the current flow through the ZnO:Al/p-Si heterojunctions under dark and UV illumination in reverse bias are shown. The current flows have risen in each Al concentration with the UV illumination. High photocurrent is obtained under reverse bias due to the crystalline quality of ZnO:Al thin films (obtained in XRD results) is good enough to transmit light into p-Si.

Table 6.3: Measured current values at -10V in the dark and light for heterojunctions with different Al concentrations.

<table>
<thead>
<tr>
<th>Al Concentration (at.%)</th>
<th>I_{dark}</th>
<th>I_{light}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>-48,9026x10^{-6}</td>
<td>-2,7206x10^{-3}</td>
</tr>
<tr>
<td>1.0</td>
<td>-14,5837x10^{-6}</td>
<td>-2,1496x10^{-3}</td>
</tr>
<tr>
<td>1.2</td>
<td>-65,3068x10^{-6}</td>
<td>-1,9634x10^{-3}</td>
</tr>
<tr>
<td>1.6</td>
<td>-50,0536x10^{-6}</td>
<td>-2,1689x10^{-3}</td>
</tr>
</tbody>
</table>

Figure 6.25 shows the current density–voltage characteristics of ZnO:Al/p-Si heterojunction were measured at room temperature in dark condition and under illumination by UV light source (xenon lamp 100mW/cm²). The heterojunctions with different Al concentrations were annealed at 700°C in nitrogen ambient. The results
show that the current–voltage characteristics of ZnO:Al/p-Si heterojunction measured in the dark demonstrating fairly good rectifying behavior and indicating formation of a diode between ZnO:Al and p-Si [67, 69].

**Figure 6.25:** Measured current density-voltage characteristics of ZnO:Al/p-Si Heterojunctions at different Al dop concentrations annealed at 700°C in nitrogen ambient. (a) 0.8 at. % (b) 1.0 at. % (c) 1.2 at. % (d) 1.6 at. %

### 6.4.2 Effects of Annealing Temperature

Figure 6.26 shows the current-voltage characteristic of the ZnO:Al/p-Si heterojunctions measured at room temperature in the dark. The heterojunctions were with 1.2 at. % Al concentration annealed at different temperatures in vacuum ambient. The junctions annealed at 700 and 800°C exhibit a diode like behavior where the junction annealed at 600°C does not exhibit a diode like behavior. The diodes show rectifying behavior with rectification ratio ($I_F/I_R$) values at a ±20 V bias voltage showed in Table 6.4. The highest conductivity is observed when the heterojunction is annealed at 800°C. However, the current flow though the junction does not change considerably over 15V applied potential and current value stays at 0.1 A.
Figure 6.26: Measured current density-voltage characteristics of ZnO:Al/p-Si Heterojunctions with 1.2% Al dop concentration, annealed in vacuum ambient at different annealing temperatures under dark condition.

Figure 6.27 shows the changes on semi logarithmic current- voltage curves of heterojunctions annealed in vacuum ambient at 700 and 800 °C. As the junction annealed at 600°C does not exhibit a diode like behavior, the change on semi logarithmic current- voltage curve of this heterojunction does not plotted in this figure. If I-V and log I-V characteristics of the junctions were evaluated together, the diode formation improved with the increase of annealing temperature. This behavior almost depend on the annealing temperature while the heterojunctions prepared by sol-gel process. The ideality factors also support this suggestion by decreasing from 26.5 to 18.5 with increasing of the annealing temperature from 700 to 800°C. In addition I₀ values of these heterojunctions were given in Table 6.4. It is determined that the I₀ values decrease with the decrease of ideality factor. The ideality factors that we found are in our research are similar with the ideality factors found in various works in literature [84-86]. It is suggested there is a relation between ideality factor of the diodes and resistivity of the ZnO:Al thin films anneled in vacuum ambient. Because of the lowest resistivity values are seen in ZnO:Al thin films anneled in vacuum ambient (details in Figure 6.20) and the ideality factors are given in Table 6.4.
Figure 6.27: Semilog IV characteristics of the ZnO:Al/p-Si heterojunctions with 1.2 at.% Al annealed at 700°C and 800°C in vacuum ambient measure under dark condition.

Table 6.4: $I_0$, $n$ and $I_F/I_R$ values for ZnO:Al/ p-Si heterojunctions annealed at 700°C and 800°C

<table>
<thead>
<tr>
<th>Annealing Temperature (°C)</th>
<th>$I_0$ (A)</th>
<th>$n$</th>
<th>$I_F/I_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>$2 \times 10^{-6}$</td>
<td>26.6</td>
<td>550.17</td>
</tr>
<tr>
<td>800</td>
<td>$5 \times 10^{-8}$</td>
<td>18.5</td>
<td>578.48</td>
</tr>
</tbody>
</table>

Figure 6.28 shows current-voltage characteristics of ZnO:Al/p-Si heterojunctions measure under light condition. The heterojunctions with 1.2% Al dop concentration were annealed in vacuum ambient at different annealing temperatures. By the affect of UV light source, the current flow of the heterojunction annealed at 800°C improves where the junction annealed at 700°C does not change considerably in reverse bias. This indicates the junction annealed at 800°C has photoelectric behavior. In forward bias till 15V the current flow though the junction improved where the current flow does not change considerably over 15V and current value stays at 0.1 A similar under dark condition.
Figure 6.28: Measured current -voltage characteristics of ZnO:Al/p-Si Heterojunctions with 1.2% Al dop concentration, annealed in vacuum ambient at 700 and 800 °C under light condition.

In Table 6.5 the values of the current flow thought the ZnO:Al/p-Si heterojunctions under dark and UV illumination at 10V reverse bias are shown. The current flows have risen slightly in each temperature with the UV illumination.

Table 6.5: Measured current values at -10V in the dark and light for heterojunctions annealed at 700 and 800 °C

<table>
<thead>
<tr>
<th>Annealing Temperature (°C)</th>
<th>$I_{dark}$</th>
<th>$I_{light}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>-1.13452x10^{-5}</td>
<td>-2.09992x10^{-4}</td>
</tr>
<tr>
<td>800</td>
<td>-4.73645x10^{-3}</td>
<td>-1.68518x10^{-3}</td>
</tr>
</tbody>
</table>

Figure 6.29 shows the current–voltage characteristics of a ZnO:Al/p-Si heterojunctions measured at room temperature in the dark and light. The investigated heterojunctions in this figure were with 1.2 at. % Al concentration annealed at different temperatures in vacuum ambient. The curves in forward-bias plotted according to measurements under the dark and light conditions are higher than the curves plotted in reverse bias which indicates that the junctions exhibit diode-like rectifying behavior at 700 and 800°C. However the curve in forward-bias is lower than the curve in reverse bias at 600°C under dark condition which explains the nonformation of a diode. The junction fabricated at 800°C shows highest current conduction under dark and light.
Figure 6.29: Measured current density-voltage characteristics of ZnO:Al/p-Si Heterojunctions with 1.2% Al dop concentration, annealed in vacuum ambient at different annealing temperatures (a) 600°C (b) 700°C (c) 800°C

6.4.3 Effects of Annealing Ambient

Figure 6.30 shows the current–voltage characteristic of the ZnO:Al/p-Si heterojunction measured at room temperature in the dark. The heterojunctions with 1.2 at. % Al concentration were annealed at 700°C in different ambient such as nitrogen, vacuum, argon and oxygen. The heterojunctions annealed in different annealing ambient exhibit similar I-V characteristic with typical rectifier diodes with the rectification ratio ($I_F/I_R$) at a ±20 V bias voltage showed in Table 6.6. The similarity of I-V characteristics indicates the formation of a diode between ZnO:Al thin films and p-Si in different annealing ambient. The junction annealed in vacuum ambient shows the highest current conduction in the dark.
Figure 6.30: Measured current-voltage characteristics of ZnO:Al/p-Si Heterojunctions with 1.2 at.% Al dop concentration annealed at 700°C in different ambient under dark condition.

Figure 6.31 explains the semi logarithmic current-voltage characteristics for different annealing ambient. The slope of the straight line region of the log I–V curves are used to determine the ideality factor of the ZnO:Al/p-Si heterojunctions. When these slope values are fitted to the standard diode equation given in (4.1), the results declare that the ideality factor varieties due to the change of annealing ambient.

Figure 6.31: Semilog I-V characteristics of the ZnO:Al/p-Si heterojunctions with 1.2 at.% Al annealed at 700°C in different ambient measured under dark condition.
The calculated ideality factor (n) and saturation current (I₀) values of heterojunctions are shown in Table 6.6. It is determined the ZnO:Al/p-Si heterojunction annealed in vacuum ambient has the lowest ideality factors and highest rectification behavior.

Table 6.6: I₀, n and Iₚ/Iₚ values for ZnO:Al/p-Si heterojunctions annealed in different ambient.

<table>
<thead>
<tr>
<th>Annealing Ambient</th>
<th>Io (A)</th>
<th>n</th>
<th>Iₚ/Iₚ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>2.0x10⁻⁶</td>
<td>26.6</td>
<td>550.17</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.5x10⁻⁶</td>
<td>28.1</td>
<td>100.06</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5.0x10⁻⁶</td>
<td>38.8</td>
<td>7.82</td>
</tr>
<tr>
<td>Argon</td>
<td>3.0x10⁻⁶</td>
<td>42.5</td>
<td>9.11</td>
</tr>
</tbody>
</table>

There is not a considerable change on current-voltage characteristics of heterojunctions annealed in vacuum and oxygen ambient in Figure 6.27. However conductivity of p-n heterojunction annealed in nitrogen and argon ambient under UV light source increased in comparison to conductivity under dark conditions. This raise in the connectivity indicates the photoelectric behavior occurred dominantly after the heterojunction was annealed in nitrogen ambient.

Figure 6.32: Measured current-voltage characteristics of ZnO:Al/p-Si Heterojunctions with 1.2 at. % Al dop concentration annealed at 700°C in different ambient under light condition.
In Table 6.7 the values of the current flow through the ZnO:Al/p-Si heterojunctions under dark and UV illumination at 10V reverse bias are shown. The current flows have risen considerably in nitrogen and argon ambient but risen slightly in oxygen and vacuum ambient with the UV illumination. These indicate the photoelectric behavior of the diodes.

Table 6.7: Measured current values at -10V in the dark and light for heterojunctions annealed at different ambient.

<table>
<thead>
<tr>
<th>Annealing Ambient</th>
<th>( I_{\text{dark}} )</th>
<th>( I_{\text{light}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>-1.13452x10(^{-5})</td>
<td>-2.09992x10(^{-4})</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-6.53068x10(^{-5})</td>
<td>-1.96335x10(^{-3})</td>
</tr>
<tr>
<td>Argon</td>
<td>-5.78947x10(^{-5})</td>
<td>-8.94059x10(^{-4})</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-4.71414x10(^{-5})</td>
<td>-9.29450x10(^{-5})</td>
</tr>
</tbody>
</table>

Figure 6.33: Measured current density-voltage characteristics of ZnO:Al/p-Si Heterojunctions with 1.2 at. % Al dop concentration annealed at 700°C in (a) nitrogen (b) vacuum (c) argon (d) oxygen ambient.
Figure 6.33 shows the current–voltage characteristics of ZnO:Al/p-Si heterojunctions measured at room temperature in the dark and light. The heterojunctions with 1.2 at. % Al concentration were annealed at 700°C in different ambient such as nitrogen, vacuum, argon and oxygen. J-V curves explain that the junctions exhibit diode-like rectifying behavior due to higher current density in forward bias than in reverse bias.
7. CONCLUSIONS

In this study the ZnO:Al films with 0.8, 1.0, 1.2 and 1.6 at. % Al concentrations were fabricated on p type silicon substrates by sol-gel dip coating technique. After immersing the p type Si wafer substrates into the colloidal suspension, the samples were preheated at 400°C for 10 minutes. This procedure was repeated for four times. After the final preheating, the samples were then annealed at 550°C, 600°C, 700°C, 800°C and 900°C annealing temperatures for 1 hour. The annealing ambients were argon, nitrogen, oxygen and vacuum. After the coating process, structural, optical, electrical and heterojunction properties were examined.

Following conclusions can be drawn according to the results of this study:

1. ZnO:Al thin films were in hexagonal wurtzite crystal structure. The average crystallite sizes had a tendency to decrease with increase in Al doping concentration. The increase in annealing temperature caused an increase in grain size. Thicknesses of the films varied in between 150-450nm. The increase in Al concentration and change in the annealing ambient had nearly no influence on thickness where the increase in annealing temperature caused a decrease in the thickness of the films.

2. For the Al concentration ranging from 0.8 at.% to 1.6 at.%, the optical transmittance of the films varied in between 40-80% in visible range. Optical transmittance of 1.2 at. % Al doped ZnO:Al thin films annealed in vacuum ambient was over 85 % in visible range. Rising of Al concentration led to increase in optical band gap. Broadening of the optical band gap was detected upon increasing Al concentration of the films. The increase of annealing temperature led to a blue shift of ZnO:Al thin film.

3. The minimum resistivity values were obtained from the film containing 1.2 at. % Al concentration which was annealed in vacuum ambient at 900°C. As a general
trend the resistivity of ZnO:Al thin films decreased with the increase of annealing temperature.

4. In forward bias the current though the ZnO:Al/p-Si heterojunctions changed with the applied voltage where in reverse bias the current though the heterojunctions had inconsiderable change in the dark. These I-V characteristics of the ZnO:Al/p-Si heterojunctions are similar with I-V characteristic of typical diode. The photoelectric behaviors were observed for the heterojunctions under light conditions. UV illumination improved the current though the ZnO:Al/p-Si heterojunctions in forward bias. In reverse bias the photocurrent caused by illumination was obviously much larger than the current under dark condition.

5. Consequently, deposition of the 1.2 at. % Al doped ZnO:Al thin film on p type Si substrate by annealing at 700°C in vacuum ambient, is the best candidate for the ZnO:Al/p-Si heterojunction to utilize in electronic devices.
REFERENCES


[67] He Bo, Ma Zhong Quan, Xu Jing, Zhao Lei, Zhang Nan Sheng, Li Feng, Shen Cheng, Shen Ling, Zhou Cheng Yue, Yu Zheng Shan, Yin Yan Ting, 2009, Characterization of AZO/p-Si heterojunction prepared by DC magnetron sputtering, *Materials Science in Semiconductor Processing*, 12, 248-252


APPENDICES

APPENDIX A.1: Average crystallite sizes and relative intensities changing of the peak diffractions depend on Al concentration in nitrogen ambient.

APPENDIX A.2: Average crystallite sizes and relative intensities changing of the peak diffractions at 1.2 at. % Al dop concentration in oxygen ambient depend on annealing temperature.

APPENDIX A.3: Average crystallite sizes and relative intensities changing of the peak diffractions at 1.2 at. % Al dop concentration at 700°C depends on annealing ambient.
APPENDIX A.1:

Table A.1: Average crystallite sizes and relative intensities changing of the peak diffractions depend on Al concentration in nitrogen ambient

<table>
<thead>
<tr>
<th>Dopant Concentration</th>
<th>Relative Intensity (100)</th>
<th>Crystallite Size (nm) (100)</th>
<th>Relative Intensity (002)</th>
<th>Crystallite Size (nm) (002)</th>
<th>Relative Intensity (101)</th>
<th>Crystallite Size (nm) (101)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>74</td>
<td>41.12</td>
<td>98</td>
<td>42.21</td>
<td>100</td>
<td>43.10</td>
</tr>
<tr>
<td>1.0</td>
<td>73</td>
<td>30.22</td>
<td>84</td>
<td>30.54</td>
<td>100</td>
<td>31.45</td>
</tr>
<tr>
<td>1.2</td>
<td>95</td>
<td>28.45</td>
<td>86</td>
<td>27.52</td>
<td>100</td>
<td>29.04</td>
</tr>
<tr>
<td>1.6</td>
<td>67</td>
<td>19.32</td>
<td>79</td>
<td>20.15</td>
<td>100</td>
<td>21.07</td>
</tr>
</tbody>
</table>

APPENDIX A.2:

Table A.2: Average crystallite sizes and relative intensities changing of the peak diffractions at 1.2 at. % Al dop concentration in oxygen ambient depend on annealing temperature

<table>
<thead>
<tr>
<th>Annealing Temperature (°C)</th>
<th>Relative Intensity (100)</th>
<th>Crystallite Size (nm) (100)</th>
<th>Relative Intensity (002)</th>
<th>Crystallite Size (nm) (002)</th>
<th>Relative Intensity (101)</th>
<th>Crystallite Size (nm) (101)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>55</td>
<td>17.90</td>
<td>100</td>
<td>22.80</td>
<td>71</td>
<td>21.84</td>
</tr>
<tr>
<td>600</td>
<td>70</td>
<td>22.14</td>
<td>94</td>
<td>25.58</td>
<td>100</td>
<td>29.00</td>
</tr>
<tr>
<td>700</td>
<td>61</td>
<td>29.80</td>
<td>97</td>
<td>28.36</td>
<td>100</td>
<td>43.00</td>
</tr>
<tr>
<td>800</td>
<td>72</td>
<td>33.22</td>
<td>96</td>
<td>39.47</td>
<td>100</td>
<td>58.00</td>
</tr>
<tr>
<td>900</td>
<td>57</td>
<td>36.01</td>
<td>84</td>
<td>43.42</td>
<td>100</td>
<td>66.00</td>
</tr>
</tbody>
</table>

APPENDIX A.3:

Table A.3: Average crystallite sizes and relative intensities changing of the peak diffractions at 1.2 at. % Al dop concentration at 700°C depends on annealing ambient

<table>
<thead>
<tr>
<th>Dopant Annealing Ambient</th>
<th>Relative Intensity (100)</th>
<th>Crystallite Size (nm) (100)</th>
<th>Relative Intensity (002)</th>
<th>Crystallite Size (nm) (002)</th>
<th>Relative Intensity (101)</th>
<th>Crystallite Size (nm) (101)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>61</td>
<td>29.80</td>
<td>97</td>
<td>28.36</td>
<td>100</td>
<td>43.00</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>95</td>
<td>28.45</td>
<td>86</td>
<td>27.52</td>
<td>100</td>
<td>29.04</td>
</tr>
<tr>
<td>Argon</td>
<td>70</td>
<td>26.73</td>
<td>56</td>
<td>24.14</td>
<td>100</td>
<td>28.01</td>
</tr>
<tr>
<td>Vacuum</td>
<td>90</td>
<td>23.08</td>
<td>100</td>
<td>24.00</td>
<td>90</td>
<td>23.05</td>
</tr>
</tbody>
</table>
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