Development of AZO TCOs with ALD for HEMT and HJSC solar cell applications

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Highlights

- ❖ *Atomik Layer Deposition*
- ❖ *AZO*
- ❖ *Transparent Conductive Oxide (TCO)*
- ❖ *Ohmic Contact*

Graphical Abstract

This study focused on deposition of AZO by ALD system as thin film. Electrical, optical and chemcail properties of AZO thin films were investigated to enlighten in device performance.
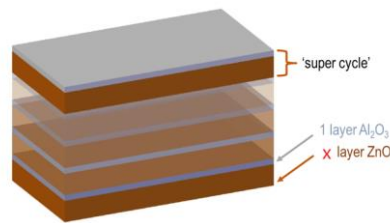

Figure 1. Cross Section of ALD of AZO

Aim

To develop AZO for device applications.

Design & Methodology

ALD growth of AZO films and their characterization electrical, optical and chemical propetires for device applications.

Originality

AZO by ALD for HEMT and HJSC solar cells.

Findings

AZ0 films with low resistivity were achieved at 225 ºC without secondary processes.

Conclusion

AZO thin films exhibited low contact resistivity and high carrier concentration which is essential for non-alloyed ohmic contact to GaN-based materials. Plasma etching conditions and post-plasma treatment should be carefully considered to have non-alloyed ohmic contact to GaN-based materials.

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

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Research Article/ Araştırma Makalesi

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ABSTRACT

Transparent Conductive Oxide (TCO) films are widely used in optoelectronic devices, such as solar cells, LEDs, and Lasers. Utilization of these contacts directly affects the device efficiencies. Purpose of this study is to produce and optimize properties of Aluminum doped Zinc Oxide (AZO) using a vapor phase technique, Atomic Layer Deposition (ALD) for (n+) a-Si:H surface of silicon Heterojunction Solar Cells (HJSCs) and High Electron Mobility Transistor (HEMT) applications. This study is focused on the effect of the deposition temperature and aluminum atomic concentration on structural, electrical and optical properties of ALD grown AZO ohmic contact films. The results show that as-deposited films have 80-90% transmittance in the visible spectra, low resistance (2.04×10^{-3} ohm.cm) and mobility value of 5.25 cm^2/V.s.

Keywords: Atomic layer deposition (ALD), aluminum doped zinc oxide (AZO), transparent conductive oxide (TCO), non-alloyed ohmic contacts, GaN HEMT contact.

AlGaN/GaN Temelli YEMT ve Heteroeklem Güneş Hücreleri Için ALD Yöntemi ile Alüminyum Katkılı Çinko Oksit(AZO) Geliştirme

ÖZ

Transparan İletken Oksit (TCO) ince filmler günümüzde güneş pilleri, LED'ler, lazerler gibi optoelektronik cihazlarda sıklıkla kullanılmaktadır. Bu kontakların kullanımı cihazların verimliliğini doğrudam etkilemektedir. Bu çalışmanın amacı heteroeklemli güneş hücrelerinin (HJSCs) (n+) a-Si:H yüzünde ve yüksek elektron hareketliliği olan tranzistörlerde (HEMT) kullanmak üzere atomik katman kaplama (ALD) tekniği kullanarak alüminyum katkılı çinko oksit (AZO) üretmek ve optimize etmektir. Bu çalışmada büyütme sıcaklığı ve alüminyum katkılama oranının ALD'de büyütülmüş AZO'nun yapısal, elektriksel ve optik özelliklerine etkisi çalışılmıştır.Sonuçlar göstermiştir ki filmler görünür bölgede %80-90 arasında ışık geçirgenliğine, düşük elektriksel rezistansa (2.04×10^{-3} ohm.cm) ve 5.25 cm^2/V.s değerinde mobiliteye sahiptir.

Anahtar Kelimeler: Atomik katman kaplama (ALD), alüminyum katkılı çinko oksit (AZO), transparan iletken oksitler (TCO), alaşımlanmamış omik kontaklar, GaN HEMT kontak.

1.INTRODUCTION

Transparent conductive oxides (TCOs) have a unique combination of properties where they have transparent window for visible light (wide band gap, $E_{gap} \geq 3.2$ eV) and low resistivity values, spontaneously. Such layers can be used in glass coatings, electrochromic mirrors, front contact windows in solar cells, light-emitting diodes, touch-sensitive screens and flat panel displays. Most used TCOs are generally ITO variations which has high transmission for visible spectra (>80%) and low sheet resistance (<10 ohm/square). However, it has some problems to its nature such as brittle structure, Post-Deposition-Annealing (PDA) dependence, slightly high production temperatures and indium content. Aluminum doped ZnO (AZO) films could achieve performance of the generic transparent conductive electrodes with lower costs [1,2].

Generally, metal contacts, TCOs or combination of metal/TCOs are used as contact layer in Heterojunction Solar Cell (HJSCs) and High Electron Mobility Transistor (HEMT) devices which are deposited by sputtering methods. Present approach cause sputter damage and inferior film qualities; therefore, post deposition treatments are necessary [3,4]. In addition to conformal coverage, atomic layer deposition (ALD) grown results suggest that it is possible to achieve preferable film qualities without post deposition treatments.

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1.1. AZO for Solar Cell

In the silicon hetero junction (SHJ) or generally photo-voltaic technology the main scope is to collect generated current from the cell by the metal contacts. The metal contacts should be optimized in dimensions (shape width height, materials etc.) generally to achieve maximum transparency, minimum recombination, and resistance. In SHJ solar cells the layer under contact conventionally used as doped amorphous layer of silicon which has significantly lower horizontal mobilities for the carrier which cause high probability of recombination. Also in order to make efficient and low cost Si based solar cells, the current approach is reducing the substrate thickness and reduce the reflection losses by surface modifications which lead to increase in surface area and consequently, increase the surface recombination further. Therefore, surface passivation is becoming one of the main subject to increase device performance for Si based solar cells. The main scope to overcome surface recombination by decreasing density of the defect imperfection or impurities [4]. Nowadays, few nano meters dielectric layer such as Al_2O_3, Si_3N_4, SiO_2 and a-Si:H is the key component to increase the efficiency of silicon based solar cells [5]. Main advantage of the dielectric passivation layer is to provide strong field-effect passivation which is caused by high density of intrinsic charge carriers. In the case of hydrogenated surface, high diffusivity of hydrogen makes the structure prone to different defects which limits the further applications [6]. Since ALD grown AZO can be produced at relatively lower temperatures, it prevents the deterioration of the solar cells or the field effect passivation layer [7].

1.2. AZO for GaN based High electron mobility transistor (HEMT) application as contact

HEMT devices based on group III-V semiconductor which has large energy bandgap ranging from 0.7eV (InN) to 6.2 eV (AlN) which are reliable in high speed operations and thermal handling. The GaN based devices are promising candidates for high-power, high-frequency application, if theoretical limits can be achieved. One of the challenges is to achieve low contact resistance which directly effects the power efficiency, frequency response and output power. Today suggested approach to obtain low contact resistance is using metallization of different metal stacks as alloyed ohmic contact [8], regrown of n+-GaN [9] and ion impantation [16] as non-alloyed ohmic contacts. Conventionally metal stacks consist of adhesion metal layer with low Schottky Barrier Height (SBT) to GaN materials, overlayer, barrier layer and cap layer. These metal stacks can be listed as Ni/Au Ti/Al, Ti/Al/Ni, Ti/Al/Pt, Ti/Al/Ni/Au and Ti/Al/Pt/Au [10]. Today commonly used metal contact is Ti/Al/Ni/Au. In GaN based HEMT with metal contact, after contact ohmic metal stacks are deposited, the structure undergoes 600 to 900 °C Rapid Thermal Annealing (RTA) which is necessity to achieve low ohmic resistance. It is known that the application causes metal to diffuse active region. Therefore, metal in the semiconductor structure result in some instabilities such as secondary phase formation, oxidized metal and clusters, contamination and most importantly distorted surface morphology and deteriorated edge acuity. Consequently, the annealing operation is reducing electrical performance and reliability of the contact as reported in various studies [11-13]. Also, further degradation of alloyed ohmic contact is inevitable due to operation temperatures [14]. In non-alloyed ohmic contacts the main challenge remains as the choosing of appropriate mask, regrowth temperature, post-annealing treatment and achieve proper surface passivation without effecting the device performance. Today mostly studied non-alloyed ohmic contact is regrowth of n+-GaN by using Moleculer Beam Epitaxy (MBE) or Metalorganic Vapor Phase Epitaxy (MOCVD) [15]. There are various studies which solve the main challenges by introducing additional pre-post treatments which creates new instabilities or increase the cost immensely.

2. MATERIAL and METHOD

In this work, AZO thin films with different doping levels of Al are produced and optimized for alternative contact layers via Atomic Layer Deposition. The optimization parameters are determined as temperature, deposition sequence, pulse and purge time, capping layer thickness and total thickness. TMA, DEZ, and DI water are used as sources of aluminum, zinc, and oxygen, respectively.

AZO films were co-deposited on quartz, silicon (c-Si (100)) and sapphire wafers. All substates were cleaned before deposition with the help of acetone (≥99.9%), ethanol (≥99.9%) and deionized water in ultrasonic bath. The native oxide layer was removed with diluted HF(3-4%) deionized water solution. Films were grown in an OkyayTechALD reactor. Diethylzinc (DEZ-$Zn(C_2H_5)_2$, (Sigma-Aldrich, Inc.)), and trimethylaluminum (TMA- $Al(CH_3)_3$, (Sigma-Aldrich, Inc.), were used as metal precursors and deionized (DI) water used as oxygen source. The precursors were held at room temperature. Nitrogen (≥99.99%) gas was chosen as carrier with flow of 20 sccm. One ALD cycle consisted of DEZ or TMA pulse (15ms), N purge (10 s), water pulse (15ms), N purge (10 s). Different aluminum percents were achieved by changing DEZ to TMA cycle ratio from 18 to 35. The ALD operated at 610 μbar. The deposition temperatures were chosen as 175, 200 and 225 °C.

3. CHARACTERIZATION

Structural properties of the AZO thin films was charecterized by using X-Ray difraction (XRD) of (100) plane both in FWHM and peak positions, the XRD were caried out by using Cu Kα radiation at 40kV and 20 mA. The Aluminum zinc and oxide percentages were determined by using X-ray photoelectron spectroscopy
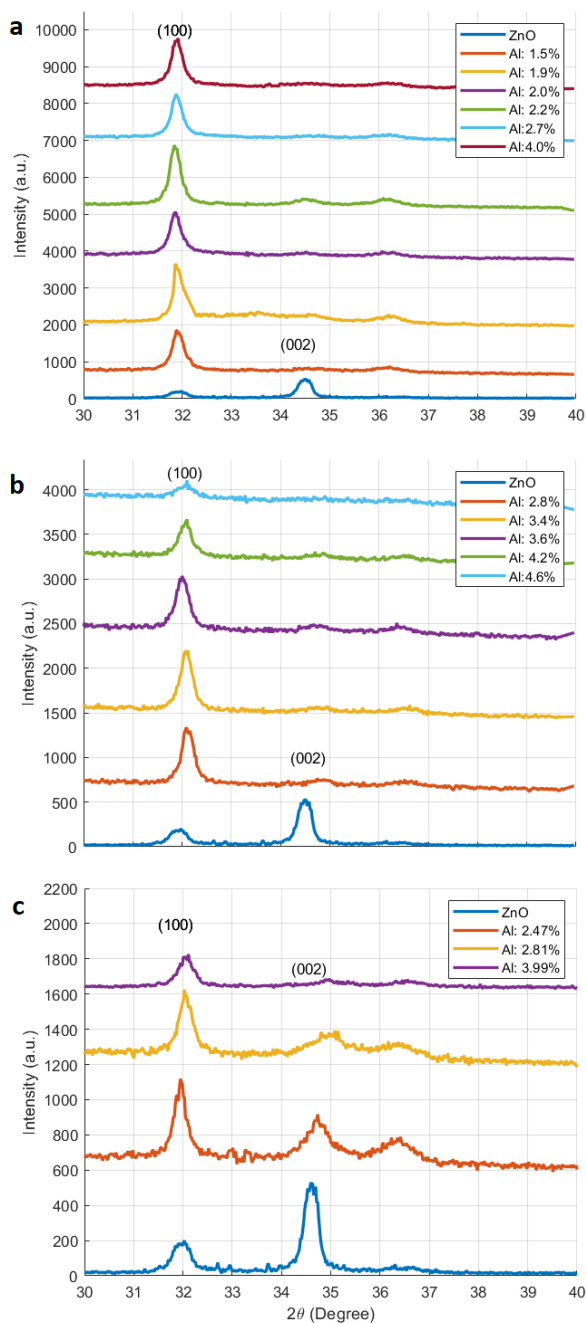
Figure 1. XRD patterns of the AZO grown at (a)225 and (b)200 and (c)175ºC. ZnO specimen grown at 200 ºC was used for comparison.

(XPS) depth profile. The band gap and transmission results were determined with UV-Vis Spectroscopy (250-700 nm). Carrier concentration, mobility and sheet resistivity of thin films were determined by Hall Effect measurements and contactless mobility measurement system. The overall aim was to understand Al, Zn and O atomic percent relations with carrier density, mobility, resistivity, transmittance and E-band gap values of the film.

4. RESULTS and DISCUSSION
4.1. Structural Properties

All of the AZO specimens shows strong peaks at around 32° which corresponds to the (100) plane of hexagonal wurtzite structure of ZnO (P63mc [186]) as seen in figure 1. The undoped ZnO thin films shows (100) and (002) peaks where the (002) peak is the strongest. This suggest that the introducing of the Al into the ZnO crystal structure changes both growth direction and the crystallinity of the thin films. As suggested in other studies this is due to both ALD growth mechanism and the Al^{3+} ion distribution during the growth [17]. The combined effect makes the thin film a-axis oriented for growth temperatures higher than the 175°C degree, the suggested effect has been seen in both 200 and 225°C degree samples, however the 175°C degree samples did not show this effect until reaching at considerable doping concentrations.
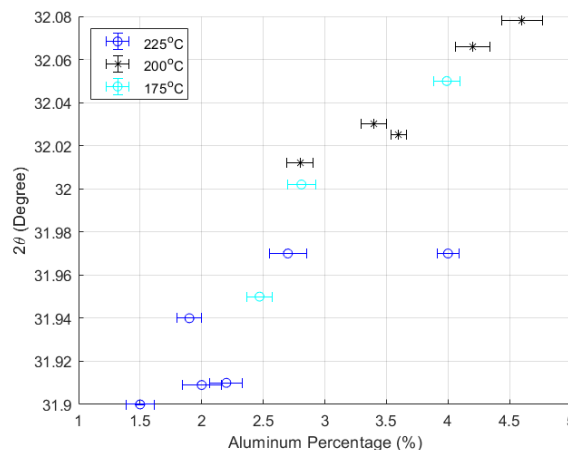

Figure 2. Peak position of the (100) plane as a function of at. % Al at different tamperatures

The doping of the Al into ZnO crystal structure with ALD technique causes a shift in the 2-theta angle toward higher degrees, which means that the lattice constant "a" decreases steadily with increasing concentration of aluminum. This is caused by aluminum replacing zinc lattice sites, i.e. substituting into Zn lattice sites. This is reported as Al^{3+} ions (53pm) being smaller than to Zn^{2+} (74pm), therefore the substitutional growth or doping makes the lattice smaller [18].

Also, the narrowing and widening in FWHM of the peaks suggest that as the at. % Al increases in the films the crystal quality increases until 2-3 at % Al for 225°C growth temperature, after this critical doping concentration reached the doping deteriorates the crystal structure and so the

FWHM. Although, growth temperature is another variable for the crystal quality, doping effect can be seen in all temperatures. Another variable was the thickness of the thin films, since the crystalline growth can be related to the thickness, the thickness of the films were adjusted to the same thicknes. Therefore, our study suggests that

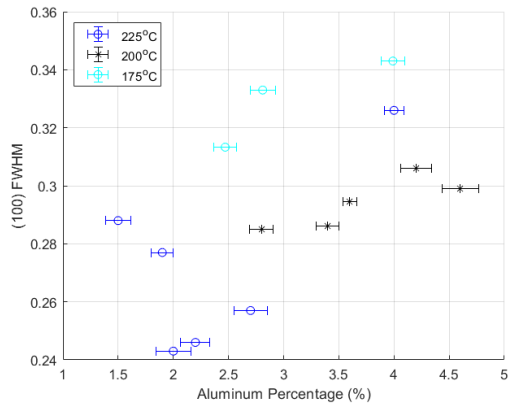suitable growth temperature for best crystalline structure is 225°C

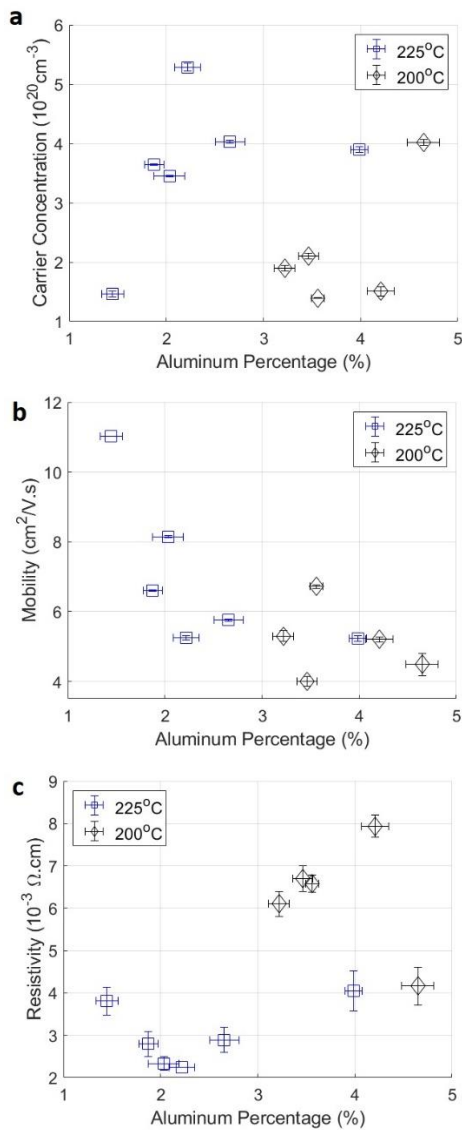**Figure 3.** FWHM of the (100) plane and at. % Al of the samples with different growth temperatures

Figure 4. (a) Carrier Concentration (10^{20}cm^{-3}) (b) Hall Mobility (cm^2/V.s) (c) Resistivity (x10^{-3} Ω cm) measurements with varying aluminum atomic percentages.

In figure 3 the doping concentrations of the samples coupled with the FWHM of the (100) peaks suggests an increasing trend with increasing doping concentrations. However, this increasing trend is interrupted with low sample resistivity as mentioned in electrical properties below in the figure 4 (c). The electrical resistivity values of the thin films are mostly crystalline quality dependent.

4.2. Electrical Properties

The electrical properties of the thin films are matched with aluminum percent since the percent difference of aluminum changes the doping effect. Studies suggest that the aluminum atoms replace the zinc positions in wurtzite structure while it creates zinc interstitials along the crystal structure and causing degenerate doping therefore one of the aim was to keep Al % between 2-4 atomic percent to achieve minimum resistivity.

What is demonstrated in figure 4 is the effect of temperature on electrical properties for the same Al atomic percentages obtained at different growth temperatures, specifically 200 and 220°C. The 175°C results are not shared as the mobility and carrier density values were much lower and resistivity values were much higher.

The Hall mobility, carrier concentration and resistivity are demonstrated in figure 4. The Al atomic percentages are gathered from XPS depth analysis. The vertical error bars in figure 5(a)-(b) are showing a slight difference for each sample while the resistivity error bars in figure 4(c) are in the range of ±0.5x10^{-3} Ω cm and shows great uniformity along the samples. As expected, the Hall mobility of the films decreases with the increasing doping concentration while the carrier concentration for 200°C does not show certain trend. In figure 4(c), the resistivity for samples deposited at 225°C decreases until the it has lowest value of 2.04 x10^{-3} Ω cm at 2.2 aluminum atomic percent. As suggested in many studies, the resistivity values decreases until 2.2 aluminium atomic percent and then starts increasing again as the doping concentration increases. The samples deposited at 200°C, on the other hand, do not show such behaviour most likely due to Al doping level 3.2% and up being over critical doping level of 2-3%.

Increasing deposition temperatures resulted in lower GPCs for ZnO layers and corresponding Al contents were increased for the AZO films. Increasing Al doping results in the formation of Al$_2$O$_3$ clusters which acts as carrier traps and increase the resistivity however such clusters were not seen in XRD curves.
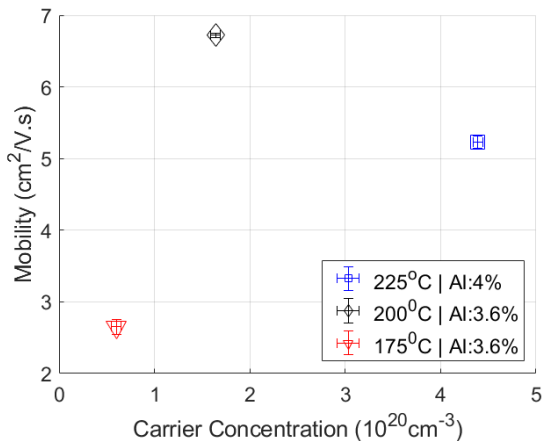
Figure 5. Carrier Concentration ($10^{20}cm^{-3}$) vs Hall Mobility (cm2/V.s) of AZO with different deposition temperature

4.3. Optical Properties

The transmittance spectra as a function of wavelength for the different aluminum content of 200°C (a) and 225°C (b) deposited samples are shown in figure 6. The data taken from AZO on sapphire substrate and the substrate contribution is taken off. As deposited samples clearly shows that the films have over 80 % transmittance in visible range. The data suggest that the transmittance dependent to deposition temperature rather than the aluminum content.
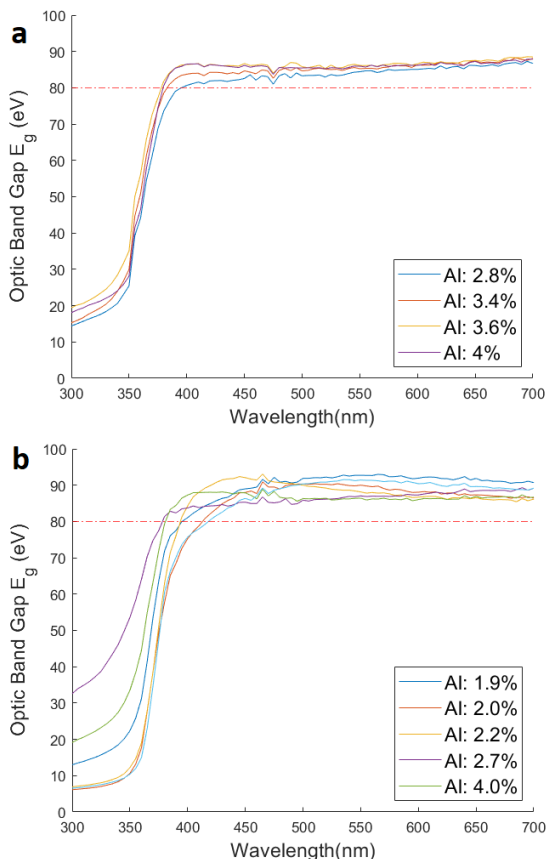

Figure 6. Optical Band Gap of AZO with varying aluminum content grown at (a)200 and (b)225°C
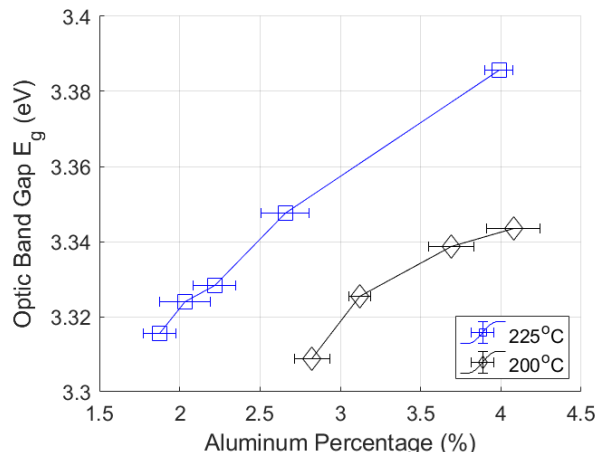

Figure 7. Optical Band Gap of AZO with varying aluminum content grown at 200 and 225°C

Also, as shown figure 7 the bandgap of the ALD grown AZO thin films are sensitive to change of aluminum atomic percentage as expected. Theoretically optical band gap depends on crystallinity and doping concentration. Therefore, the same Al doping content but different growth temperature results suggest that the change in crystallinity of the films with change in temperature is also a factor in change in optical bandgap.

5. CONCLUSION

In conclusion, transparent conductive AZO thin films deposited on sapphire, silicon and quartz wafer with different aluminum content and deposition temperatures. So far, the best values achieved at 225 °C with resistivity as 2.04×10^{-3} (ohm.cm), carrier density as 5.84×10^{20}(cm^{-3}) , mobility with 5.25 (cm^2/V.s). It was also seen that fine-tune of bandgap values of AZO films within the range 3.30 eV and 3.40 eV was successfully demonstrated by optimizing both deposition temperatures and cycle ratio of growth conditions. These results are promising for integration of AZO thin films to suggested devices.

DECLARATION OF ETHICAL STANDARDS

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS' CONTRIBUTIONS

Deniz TUGRUL: Performed the experiments, analyzed the results and wrote the manuscript.

Huseyin CAKMAK: Performed the experiments and analyzed the results.

Ekmel OZBAY: Advised the experiments.

Bilge IMER: Adivsed the experiments, analyzed the results and wrote the manuscript.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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