Electron transport in Al-doped ZnO nanolayers obtained by atomic layer deposition

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Abstract. Al-doped ZnO thin films with different Al content were prepared by atomic layer deposition (ALD). To carry out thermal ALD, diethyl zinc (DEZ) and tri-methyl aluminium (TMA) were used as Zn and Al precursors, respectively, and water vapor as oxidant. Various numbers \( n \) of DEZ and \( m \) TMA cycles was used to obtain different \([\text{ZnO}]_n[\text{Al}_2\text{O}_3]_m\) films, where \( n = 100 – 95, \ m = 1 – 5 \). The X-ray diffraction analysis showed a predominantly (100) oriented polycrystalline phase for the \( \text{ZnO}:\text{Al} \) films with a low Al content \( (m = 1 – 3) \) and an amorphous structure for pure \( \text{Al}_2\text{O}_3 \). In ZnO:Al with a higher Al content \( (m = 4 – 6) \) the (100) reflection disappeared and the (002) peak increased. The resistivity of the films decreased with the increase in the Al content, reaching a minimum of \( 3.3 \times 10^{-3} \ \Omega \) cm at about 1.1 % \( \text{Al}_2\text{O}_3 \) for the \([\text{ZnO}]_9[\text{Al}_2\text{O}_3]_2\) sample; for higher dopant concentrations, the resistivity increased because of the increased crystal inhomogeneity due to axis reorientation.

1. Introduction
Transparent conducting oxides (TCO) have been investigated extensively in recent years due to their applications in electronic, optoelectronic and photovoltaic devices. In this respect, zinc oxide (ZnO) is among the important TCO semiconductors because of its high transmittance in the visible range and low DC resistivity. Small additions of Al dopant in ZnO films strongly decrease their resistivity without degrading their optical properties [1-4]. Thin ZnO films have been fabricated by various chemical and physical methods, as spray pyrolysis [1], radio-frequency magnetron sputtering [3], sol–gel spin-coating [5], pulsed laser deposition [6], metal-organic chemical-vapor deposition [7], plasma enhanced chemical vapor deposition [8], molecular beam epitaxy [9], atomic layer deposition [2, 10-15], etc. Atomic layer deposition is one of the most suitable techniques for obtaining uniform ultra thin films on large areas. Dopant incorporation with atomic precision could be easily performed

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by the ALD technique. One of the most interesting applications of Al-doped ZnO thin films are as a transparent oxide conducting layer in various devices [2, 10-13]. Therefore, the theoretical and experimental studies of the electrical charge transport are of great importance.

In spite of the large number of ZnO:Al publications, no sufficient information about the electron transport is available for samples prepared by ALD. This is why in this paper we present a study of the Al dopant influence on the AC and DC electrical transport in ZnO nanolayers with different low Al dopant concentration grown by ALD. For deposition of the ZnO films and the Al addition we used the liquid precursors DEZ and TMA, respectively, alternating with H2O.

2. Experimental

Thin ZnO films doped with Al (ZnO:Al) were prepared on a Beneq TFS 200 apparatus by atomic layer deposition (ALD) on p-type Si (100) wafers (15 Ω cm) with a diameter of 10 cm. The deposition process was conducted at 200 ºC and a pressure of 2 mbar. Liquid precursors of DEZ with H2O and TMA with H2O were used for ZnO and Al2O3, respectively, at room temperature vapor pressure. A pure N2 gas flow of 600 sccm was maintained during the precursor introduction and the purging steps. The pulse and purging durations were the same for all precursors, 200 ms and 1 s, respectively. To obtain different Al concentration in the ZnO films, the number of DEZ/H2O (n) and TMA/H2O (m) pulses were varied. Five differently doped ZnO films [ZnO]n[Al2O3]m: [ZnO]100[Al2O3]; [ZnO]99[Al2O3]; [ZnO]98[Al2O3]; [ZnO]97[Al2O3]; [ZnO]95[Al2O3] were deposited. The lower right indices of the square brackets n and m here indicate the pulse repetition of DEZ/H2O and TMA/H2O, respectively. Each subcycle [ZnO]n[Al2O3]m was repeated ten times to obtain 1010 total cycles for each film.

Usually, a few DEZ cycles followed by only one TMA cycle [2, 11] are used for Al doping of ZnO films. In this work we gradually increased the number of TMA cycles to investigate the change in the resistivity.

The ellipsometric data were taken using a Woollam M2000D rotating compensator spectroscopic ellipsometer with a wavelength range from 193 to 1000 nm. The film thickness was determined by fitting the experimental Psi and Delta data using a three layer model which includes the Si substrate, the ZnO layer and a roughness layer. For the ZnO layer we used the general oscillator model consisting of two Tauc-Laurentz oscillators.

The X-ray diffraction patterns were collected within the 2θ range from 10 to 80º with a constant step of 0.02º on a Bruker D8 Advance diffractometer with Cu Kα radiation and a LynxEye detector. The phase identification was performed with the Diffractionplus EVA using ICDD-PDF2 Database.

The sheet resistance was obtained by the standard four-probe technique on a Veeco EPP-100 apparatus at room temperature and the resistivity was calculated using the thickness data taken from the ellipsometric measurements.

An electrochemical impedance spectroscopy (EIS) analyzer with a low-current probe (Bio-Logic SP-200 potenti-/galvano-stat) was used for measuring the frequency response of the samples. The reference voltage range was from 0.1 to 500 mV. The electrochemical impedance spectroscopy measurement was preformed in the frequency range from 1 Hz to 3 MHz. The data were processed with the software package EC-Lab.

3. Results and discussion

Thin ZnO:Al films were prepared by the ALD technique described above. The doped (ZnO:Al) films were with an average thickness of about 190 nm. The films were moderately uniform and smooth across the entire 4" Si wafers with a standard thickness deviation of 1-2 nm. The thickness reported was taken from the mean value of 54 uniformly distributed points on the Si wafer surface extracted from the ellipsometric data. The roughness was taken from AFM analysis (not presented here) and was between 1 and 2 nm. The volume percentage of the Al2O3 layer content α in [ZnO]n[Al2O3]m was calculated from the formula: \( \alpha[\%] = \frac{mA}{mA + nB} \times 100 \) [2], where m and n are the TMA and DEZ...
number of pulses, respectively, $A$ and $B$ are the growth rates for pure $\text{Al}_2\text{O}_3$ (1.14 Å/cycle) and pure $\text{ZnO}$ (2.05 Å/cycle) films, respectively. The total growth rates for the Al-doped $\text{ZnO}$ films were slower than that for pure $\text{ZnO}$ film and decreased with the increase in the $\text{Al}_2\text{O}_3$ content (table 1). This result, namely, a decreased $\text{ZnO}$ growth rate after TMA exposure, is in accordance with the work of Na et al. [14]. In contrast, Oh et al. [2] and Elam et al. [15] reported an increase in the $\text{ZnO}$ growth rate after TMA exposure due to a nucleation process. The sheet resistance deviation across the whole 4" Si surface for all films was less than 2 %. All films presented possessed a low resistivity in the range of $\sim10^{-3}$ Ω cm, which is in agreement with the properties of other $\text{ZnO}$ and Al-doped $\text{ZnO}$ films obtained by ALD [2, 10-13]. The resistivity of the Al-doped $\text{ZnO}$ films was lower than that of pure $\text{ZnO}$ films and reached a minimum of $\sim3.3\times10^{-3}$ Ω cm for $[\text{ZnO}]_{99}[\text{Al}_2\text{O}_3]_2$ sample with 1.1 % $\text{Al}_2\text{O}_3$ content (table 1 and figure 2).

The X-ray diffraction analyses showed that the $\text{Al}_2\text{O}_3$ film was amorphous, while the $\text{ZnO}:\text{Al}$ films consisted of a polycrystalline hexagonal phase with wurtzite-type structure (figure 1). The unit cell parameters and the mean crystallite size for films with different Al concentrations are presented in table 2. In the table one can see that the $\text{ZnO}$ films with low Al doping have lower unit cell parameters and a higher mean crystallite size than the undoped $\text{ZnO}$. Moreover, the preferred orientation of <100> is observed for these films. As the level of Al doping increases, the unit cell parameters of the wurtzite phase increase and the mean crystallite size decreases. The preferred orientation changes its direction from <100> to <002> (see figure 1). There is a weak peak of $\text{ZnO}$ (110) at 2θ ~ 56.8º (not shown in figure 1), whose intensity also decreases with increasing the Al content. For the highest level Al-doped $\text{ZnO}$ film, $[\text{ZnO}]_{95}[\text{Al}_2\text{O}_3]_6$, the (100) and (110) peaks disappear completely and only the (002) peak is seen. It can be concluded that Al doping affects strongly the morphologic parameters (crystallite size and shape) of the $\text{ZnO}$ films.

### Table 1. Growth rate, volume percentage of $\text{Al}_2\text{O}_3$ layer content calculated from the growth rates of pure $\text{Al}_2\text{O}_3$ and $\text{ZnO}$ and the number of TMA and DEZ cycles, thickness and resistivity of Al-doped $\text{ZnO}$ films.

| $[\text{ZnO}]_n[\text{Al}_2\text{O}_3]_m$ | Growth rate, Å/cycle | $\text{Al}_2\text{O}_3$ layer content, % | Thickness, nm | Resistivity, Ω cm |
|----------------------------------|-----------------------|----------------------------------------|----------------|------------------|
| $[\text{ZnO}]_{100}[\text{Al}_2\text{O}_3]_0$ | 2.05                  | 0                                       | 207.00         | 9.0×10^{-3}      |
| $[\text{ZnO}]_{100}[\text{Al}_2\text{O}_3]_1$ | 1.94                  | 0.55                                    | 196.14         | 4.2×10^{-3}      |
| $[\text{ZnO}]_{99}[\text{Al}_2\text{O}_3]_2$ | 1.87                  | 1.11                                    | 188.69         | 3.3×10^{-3}      |
| $[\text{ZnO}]_{98}[\text{Al}_2\text{O}_3]_3$ | 1.84                  | 1.67                                    | 186.33         | 3.9×10^{-3}      |
| $[\text{ZnO}]_{97}[\text{Al}_2\text{O}_3]_4$ | 1.81                  | 2.24                                    | 182.57         | 4.2×10^{-3}      |
| $[\text{ZnO}]_{95}[\text{Al}_2\text{O}_3]_6$ | 1.77                  | 3.39                                    | 178.51         | 4.6×10^{-3}      |

**Figure 1.** X-ray diffraction spectrum of $\text{ZnO}:\text{Al}$ films obtained by ALD. The Si substrate reflexes are denoted with an asterisk (*).

**Figure 2.** DC resistivity and crystallite size for different pulse ratios of DEZ and TMA precursors.
Table 2. Unit cell parameters and mean crystallite size for the ZnO films with different degree of Al-doping. The space group is SG P63mc.

| Composition         | \(a\) [Å] | \(c\) [Å] | Crystallite size [nm] |
|---------------------|------------|------------|-----------------------|
| ZnO                 | 3.259(3)   | 5.192(7)   | 41±3                  |
| [ZnO]_{100}[Al_{2}O_{3}]_{1} | 3.249(2)   | 5.181(8)   | 54±6                  |
| [ZnO]_{99}[Al_{2}O_{3}]_{2} | 3.246(1)   | 5.184(6)   | 46±3                  |
| [ZnO]_{99}[Al_{2}O_{3}]_{3} | 3.255(3)   | 5.21(1)    | 23±2                  |
| [ZnO]_{97}[Al_{2}O_{3}]_{4} | 3.269(5)   | 5.24(1)    | 15±1                  |
| [ZnO]_{95}[Al_{2}O_{3}]_{6} | 3.289(7)   | 5.28(1)    | 15±1                  |

The resistivity of Al-doped ZnO films decreased with increasing the Al content, which acts as an electron donor. Above 1.1% Al_{2}O_{3} in the [ZnO]_{99}[Al_{2}O_{3}]_{2} sample, the crystallinity worsened because of the crystal axes reorientation and the formation of new domains and grain boundaries due to the lower grain dimensions (figure 2). The crystal structure degradation suppressed the electron mobility and the resistivity started to increase slightly (figure 2), so that a local minimum of resistivity at 3.3×10^{-3} Ω cm was observed.

Figure 3 presents the real and imaginary parts of the complex impedance of Al-doped ZnO thin films vs. the frequency at an amplitude of 50 mV at room temperature. The impedance measurements of pure ZnO, [ZnO]_{100}[Al_{2}O_{3}]_{1}, [ZnO]_{99}[Al_{2}O_{3}]_{2}, and [ZnO]_{97}[Al_{2}O_{3}]_{4} films at the high-frequency region 0.5 – 3 MHz are also presented. For all samples measured, the impedances decreases as the frequency is increased.

Figure 3. Impedance measurements of Al-doped ZnO films: the real (in the left figure - a) and the imaginary (in the right figure - b) parts of the impedance versus the frequency. The insets of both figures show an enlarged region of Al-doped ZnO films with a lower Al content, \(m = 1, 2\).

The real and imaginary parts of the impedance of the low Al content samples, \(m = 1, 2\) (see the insets of figure 3) possessed the lowest values corresponding to the minimum of DC resistivity (see figure 2), while the pure ZnO and [ZnO]_{97}[Al_{2}O_{3}]_{4} films showed values that were several times higher. As previously mentioned, the pure ZnO has a lower concentration of mobile electrons, while the films with a higher Al content (\(m > 3\)) have strong crystal distortion and inhomogeneity. In spite of the large differences in the impedance values, all samples showed the same behavior in the above frequency range. The real part of the impedance starts at a higher value and decreases smoothly to a lower value. The imaginary part at this frequency range has the same behavior, but with a negative sign. Such behavior is characteristic of a resistance and a capacitance connected in series, where the real part is attributed to the resistance and the imaginary part corresponds to the capacitance. Therefore, the resistance decreases with the increase of the electron donors (the Al content, respectively), and the capacity increases with the increase of crystal inhomogeneity as the Al content increases. In fact, not all of Al^{3+} cations of the deposited Al_{2}O_{3} layer substitute the Zn^{2+}. The Zn substitution by Al depends on the growth temperature and the pulse duration of the TMA precursor.
Moreover, the increased number of TMA cycles ($m > 3$) could lead to a relative decrease of the Al substitution on Zn sites in the neighboring ZnO layers due to the longer distance which will lead to an increase in the resistivity. Therefore, a more detailed investigation, such as cross-section EDAX analysis, is needed to properly define the Al content.

To obtain a deeper understanding on the electrical transport, we plan to perform additional impedance measurements.

4. Conclusions

Thin ZnO:Al films with different content of Al were prepared by atomic layer deposition on 4" Si. Various number $n$ of DEZ and $m$ of TMA ALD cycles was used to obtain different $[\text{ZnO}]_n[\text{Al}_2\text{O}_3]_m$ films, where $n = 100 – 95$, $m = 1 – 5$. The films were relatively uniform and smooth with a uniform DC resistivity distribution. The films with lower Al content ($m < 3$) showed a predominantly (100) crystal orientation, while increasing the Al content ($m > 3$) caused a reorientation to (002). It was found that the DC and AC resistance decreased with the doping due to an increase of mobile electrons and reached a minimum of $3.3 \times 10^{-3} \ \Omega \ \text{cm}$ at about 1.1% Al$_2$O$_3$ for $[\text{ZnO}]_99[\text{Al}_2\text{O}_3]_2$, and then increased slowly because the crystallinity worsened due to the axis reorientation and because of the relative decrease of Al substitution on Zn sites in the neighboring ZnO layers, which suppressed the electron mobility.

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