

# Study of the properties of Al:ZnO thin films grown by plasma-enhanced atomic layer deposition

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**Abstract:** The deposition of Al-doped ZnO (AZO) thin films grown by plasma-enhanced atomic layer deposited (PE-ALD) was studied. Doping was achieved by alternating cycles with a Zn-precursor and cycles with an Al-precursor. The results show that changing the ratio of cycles containing one precursor or the other allows to control the aluminium-content. The films with 1 at.% Al showed low resistivity as well as a change in the inter-planar distance and of the crystallite size, compared to pure ZnO.

**Keywords:** zinc oxide, plasma enhanced atomic layer deposition, doping, AZO.

## 1. Introduction

ZnO is a direct band gap semiconductor with attractive piezoelectrical, optical, and electrical properties, particularly appealing for a variety of functional devices (e.g., gas, bio, and UV sensors, piezoelectric nanogenerators and actuators). Being able to tailor these material properties to meet specific technological requirements is crucial for enhancing the device efficiency or sensitivity. Engineered material properties can be obtained only with advanced growth methods that are highly controllable. To date, high quality ZnO has been produced by a variety of techniques, including RF-sputtering, chemical vapor deposition (CVD) and atomic layer deposition (ALD).[1] The ALD methods are attractive for electronic applications, especially for devices with ultra-thin film and 3D architectures.

This work focuses on the properties of ZnO thin films obtained by a variety of ALD, called plasma enhanced ALD (PEALD). The main difference between conventional thermal-ALD and PEALD is in the first activation step. In thermal-ALD, a high substrate temperature ( $>300^{\circ}\text{C}$ ) is used to induce the water vapor to react with the surface. In PEALD, on the other hand, the oxidant is an oxygen plasma, therefore the process can be run at temperatures below  $100^{\circ}\text{C}$ .

In these processes, the surface is first activated either by thermal energy or by plasma with concurrent flow of water vapors or oxygen in the first half-cycle.[2] This results in the formation of OH groups on the substrate surface. The subsequent step consists in purging the chamber from the oxidizer vapors and exposing the surface to the precursor vapors (second half-cycle). The latter react only with the OH groups present on the surface. The surface is exposed to the precursor vapors until saturation, i.e. until all the OH groups have reacted. Another purging step follows to remove the unreacted precursor molecules, and the cycle restarts from the oxidant exposure. Purging time is a very important factor. It is the time that separates the introduction of the first precursor and the second (e.g. the oxidant) to the reactor. If precursors are introduced simultaneously, a CVD-like process takes place. In such case, growth rates are significantly higher from those in the ALD process but

films are rougher. The ALD mechanism of growth limits growth rate up to maximum 1 monolayer/ cycle. The self-limiting surface reactions of the ALD processes result in very high conformality and uniformity. [3]

The ZnO thin films deposited by ALD showed n-type conductivity with carrier concentration between  $10^{16}$  and  $10^{20} \text{ cm}^{-3}$  depending on the deposition temperature.[4] Low carrier concentration and low conductivity (high resistivity) were observed for samples grown at lower temperature, and they increased with increasing the temperature up to  $200^{\circ}\text{C}$ . An electron mobility of  $\sim 13.6 \text{ cm}^2/\text{V/s}$  was measured on ZnO deposited by ALD at  $200^{\circ}\text{C}$ , resulting in a high conductivity:  $169 \text{ S/cm}$  without intentional doping.[5] Plasma-ALD has already been demonstrated to produce higher semiconducting properties than thermal-ALD as method of deposition of ZnO because  $\text{O}_2$  plasma is a much stronger oxidizer than  $\text{H}_2\text{O}$ , therefore the film is more stoichiometric and it has higher resistivity and smaller crystallites.[6] One way to increase the conductivity of the ZnO films without using high deposition temperatures is by adding a dopant, like Al. The carrier concentration of the Al:ZnO (also called AZO) films increased 2–3 times with increasing Al doping content. A resistivity as low as  $4.4 \times 10^{-3} \Omega\text{cm}$  was obtained for AZO films grown by conventional ALD at  $150^{\circ}$  with 3.0 at. % Al.[7] Beside conventional-ALD-AZO, PEALD-AZO deposited at low temperature has never been extensively investigated for its electrical transport properties.

The goal of this study is to relate the properties of the material such as composition, carrier concentration, crystalline order, density of defects to the deposition conditions.

## 2. Experimental section

The films were grown by direct PE-ALD using diethylzinc (DEZ), trimethylaluminium (TMA) and  $\text{O}_2$ -plasma as reactants. The reactor was custom-built for direct plasma in an asymmetric plate configuration. DEZ (optoelectronic grade, Dockweiler Chemicals) and TMA (Aldrich) were pulsed into the reactor using ALD-valves (Swagelok ALD3) without additional heating or bubbling system. An RF-power generator (Advanced Energy Cesar

13.56MHz) combined with a matching network (Advanced Energy Navio) served as the power source for the  $O_2$ -plasma. The pumping system consisted of a turbomolecular pump (Pfeiffer vacuum TMH071P) and a rotary vane pump (Pfeiffer vacuum DUO5M). The pressure in the reactor was  $\sim 75$  mTorr during plasma exposure. The flow rates of  $O_2$  and Ar were set to 20 sccm during the plasma and purging step, respectively, using a multi gas controller (MKS 647C) and mass flow controllers (MKS MF1-C). Prior to the deposition, the samples were exposed to 8 s  $O_2$ -plasma to activate the surface. The RF-power for the plasma dose was fixed at 60 W for all depositions. The films were grown on single side polished Si (100) substrates with a native oxide layer for spectroscopic ellipsometry and X-ray reflectivity, on quartz substrates (Esco Optics) for UV-Vis spectroscopy, and on glass substrates for X-ray diffraction and four-point probing. The films were prepared at substrate temperatures of 25°C and 150 °C. The growth per cycle (GPC) for each deposition was obtained by dividing the mean value of the film thickness of three samples, put on different positions on the substrate heater, by the number of cycles.

Spectroscopic ellipsometry was used to characterize the thickness and optical constants of the thin films. The model consisted in three layers: the silicon substrate, native silicon dioxide and a Cauchy function to model the AZO. The chemical composition was evaluated by x-ray fluorescence (Epsilon 1 of PANalytical) and x-ray photoelectron spectroscopy. The crystal-structure was evaluated by x-ray diffraction (Panalytical Empyrean diffractometer) and the resistivity via 4-point probe. A source meter (KEITHLEY 2614B SourceMeter), was used to set the fixed injection current and the chosen voltage range (-20 V to +20 V).

### 3. Results and discussion

AZO thin films with different Al-contents were obtained alternating varying  $n$ , the number of DEZ- $O_2$  plasma cycles inserted for every TMA- $O_2$  plasma cycle. The Al content of the films is shown in Table 1.

Table 1. Al-content measured by XPS for the AZO films deposited at 25°C and 150°C.

$n$	Al-content @ 25°C (at%)	Al-content @ 150°C (at%)
40	2.08	0.69
30	2.72	0.91
20	3.95	1.35
10	7.19	2.61

The Al-content changes with the deposition temperature even if the ratio among cycles,  $n$ , is the same, as a

consequence of the different growth per cycle of ZnO and  $Al_2O_3$  at the different temperatures.

Next, the structural properties of the films were analyzed. Figure 1 shows the XRD-pattern of several AZO films deposited at different cycle ratios, compared to a pure ZnO. The red lines indicate the reference peak positions of a ZnO powder.

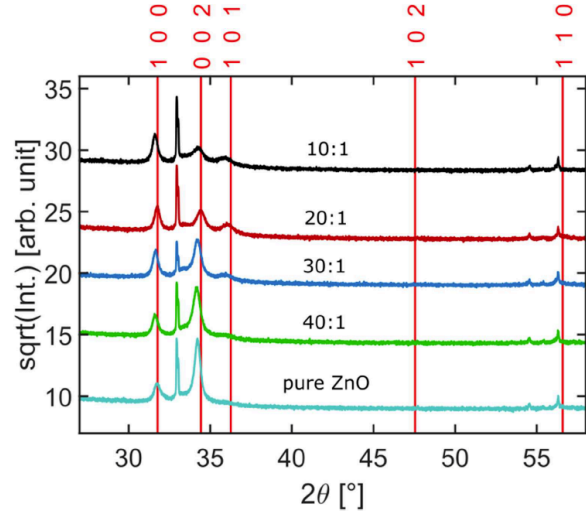


Fig. 1.  $\theta/2\theta$  – scan of aluminium doped zinc oxide thin films deposited at different cycle ratio and at substrate temperature of 150 °C.

The ZnO thin film showed a polycrystalline wurtzite-structure with a preferential orientation along the (002)-direction. By adding Al, the (002) peak intensity decreased, leading to a change of the preferential orientation from the (002)- to the (100)-direction. Banerjee et al. [7] attributed the change in orientation of the AZO films with increasing Al content with an exchange reaction at the surface between  $Zn^{2+}$  and  $Al^{3+}$  ions. We calculated the crystallite size from the (002) peak width by using the Scherrer formula for spherical crystallites. The crystallite size decreased with the Al-content: pure ZnO had crystallite size of 299 Å, while the AZO thin film with a cycle ratio of 10:1 (2.61 at% Al-content) had smaller crystallites of 111 Å.

The ZnO thin film deposited at room temperature were characterized by a preferential (100) orientation. Adding Al, in this case did not result in a preferential orientation change but in a peak shift towards higher  $2\theta$  angles. This implies that Al addition into ZnO film reduces the d-spacing along the (100) direction as a consequence again of the exchange between  $Zn^{2+}$  and  $Al^{3+}$  at random sites.

Four-point probe measurements were carried out at room temperature to investigate the electrical properties of AZO thin films deposited at 150°C. A minimum in the resistivity was measured for Al-content of 0.91 at% corresponding to a cycle ratio of 30:1. At higher Al content, the resistivity increased probably as a consequence of the too small crystallite size, which could

lead to high carrier scattering and therefore lower mobility and conductivity.

#### 4. Conclusions

In a nutshell, the results of this work show how the growth and material properties of ZnO films deposited by PE-ALD are affected by doping concentration and deposition temperature. AZO thin films were prepared by systematically changing the number of DEZ cycles inserted between two TMA cycles at 150 °C and 25°C. Whereas, pure ZnO films deposited at 150°C showed a preferential (002) orientation, the AZO films crystallized preferentially along the (100) direction as a result of doping with Al. It was found that at low at. % Al doping, the AZO films were characterized by a high degree of crystallinity and consequently low resistivity.

#### 5. References

- [1] Janotti, A.; Van de Walle, C. G. Fundamentals of Zinc Oxide as a Semiconductor. Reports Prog. Phys., **72**, 126501 (2009).
- [2] S. George, Chem. Rev., **110**, 111–131 (2010)
- [3] S.M. Sultan et al., Microelectronic Engineering, **97** 162–165 (2012)
- [4] Fortunato, E. M. C.; Barquinha, P. M. C.; Pimentel, A. C. M. B. G.; Gonçalves, A. M. F.; Marques, A. J. S.; Pereira, L. M. N.; Martins, R. F. P. Adv. Mater., **17** (5), 590–594 (2005).
- [5] Zhang, J.; Yang, H.; Zhang, Q.; Dong, S.; Luo, J. K. Appl. Surf. Sci., **282**, 390–395, (2013).
- [6] Hoffman, R. L.; Norris, B. J.; Wager, J. F. Appl. Phys. Lett., **82** (5), 733–735, (2003)
- [7] Banerjee, P.; Lee, W.-J.; Bae, K.-R.; Lee, S. B.; Rubloff, G. W. J. Appl. Phys., **108** (4), 43504 (2010)