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Atomic Layer Deposition of Al-doped ZnO Films: Effect of Grain Orientation on Conductivity

Neil P. Dasgupta,*[,†] Sebastian Neubert,[†] Wonyoung Lee,[†] Orlando Trejo,[†] Jung-Rok Lee,[†] and Fritz B. Prinz[†,‡]

[†]*Department of Mechanical Engineering, Stanford University, California 94305, and* [‡]*Department of Materials Science and Engineering, Stanford University, California 94305*

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Al-doped ZnO (AZO) films were deposited by atomic layer deposition (ALD) on borosilicate glass and sapphire(0001) substrates. The Al composition of the films was varied from 1% to 4% by controlling the ratio of Zn:Al pulses. Film resistivity was measured as a function of Al content and the substrate temperature used for ALD deposition. X-ray diffraction (XRD) was performed on the films, showing a reduction in lattice parameter, as a function of Al concentration, indicating that Al^{3+} ions occupy substitutional sites in the ZnO lattice. The resistivity of films deposited on sapphire substrates ($7.7 \times 10^{-4}\ \Omega$ cm) was lower than that on glass ($3.0 \times 10^{-3}\ \Omega$ cm), because of the formation of textured grains with the *c*-axis aligned with respect to the sapphire surface, as confirmed by XRD. The surface morphology of the films on glass and sapphire was compared using scanning tunneling microscopy (STM) and scanning electron microscopy (SEM), which showed similar grain sizes on each substrate, suggesting that the difference in conductivity was due to grain orientation rather than microstructural differences. Optical transparency was measured to be $>80\%$ for wavelengths of 370−1600 nm.

Introduction

Transparent conducting oxide (TCO) materials are utilized as electrode materials in a wide variety of optoelectronic devices, including photovoltaic cells,[1] flat panel displays,[2] and organic light-emitting diodes (OLEDs).[3,4] The most commonly used TCO material is indium tin oxide (ITO), because of its high conductivity and optical transparency over visible wavelengths.[5] However, there is a large amount of research into alternative TCO materials, because of the relative scarcity and high cost of indium.[6] One of the most commonly cited alternative materials is Al-doped ZnO (AZO).

AZO has been deposited by a variety of thin-film deposition techniques, including direct-current (DC) sputtering,[7] radio-frequency (RF) sputtering,[8] pulsed laser deposition,[9] chemical vapor deposition,[10] and sol−gel deposition.[11] The most common deposition techniques involve sputtering, which routinely provide resistivity values on the order of $10^{-4}\ \Omega$ cm, with an optical transparency of $>80\%$ for visible wavelengths.[8] Thus, AZO films are approaching the quality of ITO as transparent electrode materials, and they are currently being used commercially in the production of copper indium gallium diselenide (CIGS) solar cells.[12]

Recently, atomic layer deposition (ALD) has received increased attention, because of its unique ability to conformally coat high-aspect-ratio structures with pinhole-free films on a variety of surfaces.[13] Because of the self-limiting surface chemistry of ALD half-reactions, the thickness of films grown by ALD can be controlled with subnanometer precision simply by controlling the number of ALD cycles. This combination of conformality with atomic precision has allowed for the development of a variety of new nanofabrication processes and devices. AZO has been fabricated via ALD, using trimethylaluminum, diethylzinc, and water as precursors.[14−20]

*Author to whom correspondence should be addressed. Tel.: 1-773-497-9532. Fax: 1-650-723-5034. E-mail: dasgupta@stanford.edu.

(1) Schulze, K.; Maennig, B.; Leo, K.; Tomita, Y.; May, C.; Hüpkes, J.; Brier, E.; Reinold, E.; Bäuerle, P. *Appl. Phys. Lett.* **2007**, *91*, 073521.
(2) Chen, M.; Pei, Z. L.; Sun, C.; Gong, J.; Huang, R. F.; Wen, L. S. *Mater. Sci. Eng. B.* **2001**, *85*, 212.
(3) Görrn, P.; Sander, M.; Meyer, J.; Kröger, M.; Becker, E.; Johannes, H.-H.; Kowalsky, W.; Riedl, T. *Adv. Mater.* **2006**, *18*, 738.
(4) Tomita, Y.; May, C.; Toerker, M.; Amelung, J.; Eritt, M.; Loeffler, F.; Luber, C.; Leo, K.; Walzer, K.; Fehse, K.; Huang, Q. *Appl. Phys. Lett.* **2007**, *91*, 063510.
(5) Kim, H.; Gilmore, C. M.; Pique, A.; Horwitz, J. S.; Mattoussi, H.; Murata, H.; Kafafi, Z. H.; Chrisey, D. B. *J. Appl. Phys.* **1999**, *86*, 6451.
(6) Coutts, T. J.; Young, D. L.; Li, X.; Mulligan, W. P.; Wu, X. *J. Vac. Sci. Technol. A* **2000**, *18*, 2646.
(7) Minami, T.; Suzuki, S.; Miyata, T. *Thin Solid Films* **2001**, *398−399*, 53.
(8) Igasaki, Y.; Kanma, H. *Appl. Surf. Sci.* **2001**, *169−170*, 508.
(9) Hiramatsu, M.; Imaeda, K.; Horo, N.; Nawata, M. *J. Vac. Sci. Technol. A* **1998**, *16*, 669.
(10) Martin, A.; Espinos, J. P.; Justo, A.; Holgado, J. P.; Yubero, F.; Gonzalez-Elipe, A. R. *Surf. Coat. Technol.* **2002**, *151−152*, 289.
(11) Ohyama, M.; Kozuka, H.; Yoko, T. *J. Am. Ceram. Soc.* **1998**, *81*, 1622.
(12) Kessler, J.; Bodegård, M.; Hedström, J.; Stolt, L. *Sol. Energy Mater. Sol. Cells* **2001**, *67*, 67.
(13) George, S. *Chem. Rev.* **2010**, *110*, 111.
(14) Lujala, V.; Skarp, J.; Tammenmaa, M.; Suntola, T. *Appl. Surf. Sci.* **1994**, *82/83*, 34.
(15) Yousfi, E. B.; Weinberger, B.; Donsanti, F.; Cowache, P.; Lincot, D. *Thin Solid Films* **2001**, *387*, 29.
(16) Kwon, S. J.; Lee, H. J.; Seo, Y. W.; Jeong, H. S. *J. Korean Phys. Soc.* **2003**, *43*, 709.

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The availability of stable, volatile liquid precursors makes this process attractive for the production of novel device architectures using ALD. For example, there is significant research in utilizing 3-D nanostructured solar cell architectures,[21,22] which could benefit from a highly conformal technique such as ALD as a transparent top electrode. However, the majority of the previously reported resistivity values of ALD AZO films have values on the order of 10^{-3} Ω cm, which is 1 order of magnitude more resistive than the best sputtered AZO films. One recent paper reported a resistivity of 4.7×10^{-4} Ω cm, which could be due to the use of rapid thermal annealing (RTA) of the film.[20] However, no explanation of the origin of this reduction in resistivity, compared to previous reports, was provided. Therefore, in this study, we perform a detailed characterization of as-deposited ALD AZO films to determine the origin of their relatively high resistivity. Sapphire(0001) substrates are used in an effort to grow oriented films and study the effect of grain orientation on film conductivity.

This report begins with an optimization of the ALD AZO process parameters, with respect to film conductivity. The film conductivity was optimized with respect to the ratio of Zn:Al ALD cycles and the substrate temperature used during deposition. Phase analysis was performed using X-ray diffraction (XRD), and the lattice parameter was calculated for different Al concentrations, to show that Al atoms substitute for Zn atoms in the ZnO lattice. Enhanced conductivity was observed in films deposited on sapphire(0001) substrates, which is explained by texturing of the grains with the *c*-axis normal to the film surface, as measured by XRD analysis. The surface morphology was studied using scanning tunneling microscopy (STM) and scanning electron microscopy (SEM), to compare the effects of the different substrates on the film microstructure. Finally, transparency of the AZO films deposited on glass substrates was measured by UV−vis spectrophotometry.

Experimental Details

Films of AZO were grown on polished silicon(100), borosilicate glass, and sapphire(0001) wafers. All of the wafers were cleaned using 5 min of sonication in toluene, followed by a rinse with deionized (DI) water. Reactions were carried out in a customized flow-type reactor[23] with an argon carrier gas at a flow rate of 10 sccm. The chamber pressure was measured at 50 mTorr. The substrate temperature during ALD was varied from 140 °C to 220 °C. The precursors used were diethylzinc (Aldrich), trimethylaluminum (Aldrich), and DI water.

(17) Park, S.-H. K.; Lee, J.-I.; Hwang, C.-S.; Chu, H. Y. *Jpn. J. Appl. Phys.* **2005**, *44*, L242.
(18) Lim, J.; Lee, C. *Thin Solid Films* **2007**, *515*, 3335.
(19) Na, J.-S.; Peng, Q.; Scarel, G.; Parsons, G. N. *Chem. Mater.* **2009**, *21*, 5585.
(20) Kong, B. H.; Choi, M. K.; Cho, H. K.; Kim, J. H.; Baek, S.; Lee, J.-H. *Electrochem. Solid-State Lett.* **2010**, *13*, K12.
(21) Martinson, A. B. F.; Elam, J. W.; Hupp, J. T.; Pellin, M. J. *Nano Lett.* **2007**, *7*, 2183.
(22) Zhu, J.; Hsu, C.-M.; Yu, Z.; Fan, S.; Cui, Y. Nano. Lett. **2010**, *10* (6), 1979−1984.
(23) Dasgupta, N. P.; Mack, J. F.; Langston, M. C.; Bousetta, A.; Prinz, F. B. *Rev. Sci. Instrum.* **2010**, *81*, 044102.

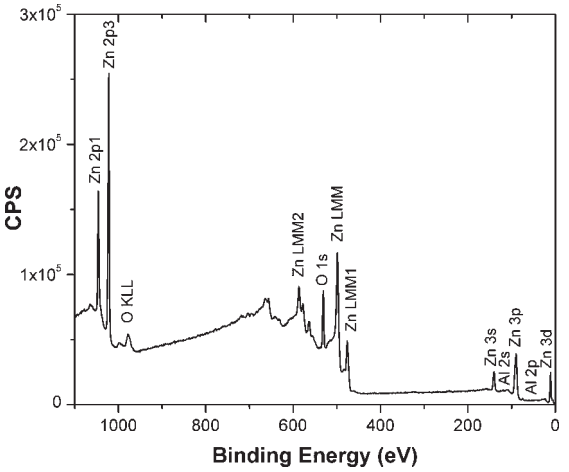

Figure 1. X-ray photoelectron spectroscopy (XPS) analysis of Al-doped ZnO (AZO) film deposited on a glass substrate with a Zn:Al cycle ratio of 15:1. The Al concentration was measured to be 3.0%.

X-ray photoelectron spectroscopy (XPS) analysis was performed with a Phi VersaProbe XPS microprobe. Film thicknesses were measured on silicon substrates using a Rudolph AutoELLIII Ellipsometer (single wavelength of 6328 Å). Sheet resistances were measured with a Prometrix OmniMap Model RS35e resistivity mapping system. XRD measurements were performed with a PANalytical X'Pert PRO XRD system. STM and atomic force microscopy (AFM) measurements were taken with a JEOL Model JSPM-5200 system in air. Pt/Ir tips (Veeco Instruments) were used for the STM measurements, after a mechanical cut to sharpen the tip apex and remove contamination. SEM images were taken with a FEI XL30 Sirion SEM system with a field-emission gun (FEG) source. Optical absorption measurements were performed on a Varian Cary Model 6000i UV−vis−NIR spectrophotometer.

Results and Discussion

Optimization of ALD Conditions. XPS analysis was performed on AZO films after varying the ratio of Zn cycles to Al cycles. The Al cycles were performed in the middle of the sequence of Zn cycles, so that the surface of the film was terminated by ZnO rather than Al_2O_3. The film composition was analyzed using the Al 2p, Zn 3p, and O 1s peaks. An example spectrum is shown for a ratio of 15:1 Zn:Al cycles at a substrate temperature of 160 °C in Figure 1. The composition was measured to be 3.0% Al, 45.7% Zn, and 51.3% O. A brief argon etch was performed on the surface to remove contamination, which adsorbed onto the surface from exposure to air. Within the film, no carbon contamination was observed, suggesting that the removal of ligands from the metallorganic precursors during the reaction was complete.

To study the effect of Zn:Al pulse ratio on aluminum content, the substrate temperature was maintained constant at 160 °C, and the pulse ratio was varied from 13:1 to 27:1. The aluminum content was measured by XPS for each sample, and the results are plotted in Figure 2. As the figure shows, for this range of cycle ratios, the aluminum content can be precisely controlled in the range of 1%−4% Al.

To study the effect of aluminum content on film resistivity, ALD AZO films were deposited on insulating

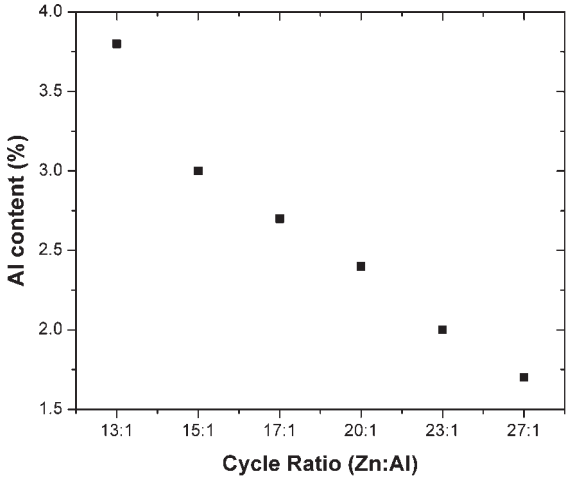

Figure 2. Al content of AZO films, as a function of Zn:Al cycle ratio, as measured by XPS.

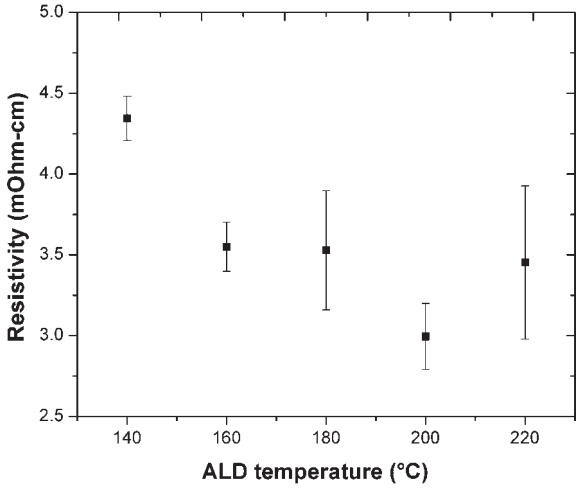

Figure 3. AZO film resistivity, as a function of Zn:Al cycle ratio used during ALD growth.

borosilicate glass wafers, and the sheet resistance was measured using a four-point probe technique. The total number of cycles varied slightly among the different samples, because of the requirement of maintaining the correct pulse ratio throughout the film. Each sample was deposited with as close as possible to 480 total cycles, while maintaining the correct pulse ratio. In addition, because the growth rate of Al_2O_3 is different from that of ZnO, the total thickness per cycle will be slightly different for different pulse ratios. Therefore, the thickness was measured by ellipsometry for each film condition to precisely calculate resistivity from sheet resistance values.

The results of the resistivity measurements on glass substrates, as a function of pulse ratio, are shown in Figure 3. As the figure shows, in the range of ratios studied, the conductivity varies from 3.6×10^{-3} Ω cm to 5.7×10^{-3} Ω cm. The optimal condition was measured to be a ratio of 15:1 Zn:Al cycles, with a resistivity of 3.6×10^{-3} Ω cm. Therefore, in subsequent experiments, this ratio was maintained.

Next, the effect of substrate temperature on conductivity was measured for the optimal pulse ratio. The substrate

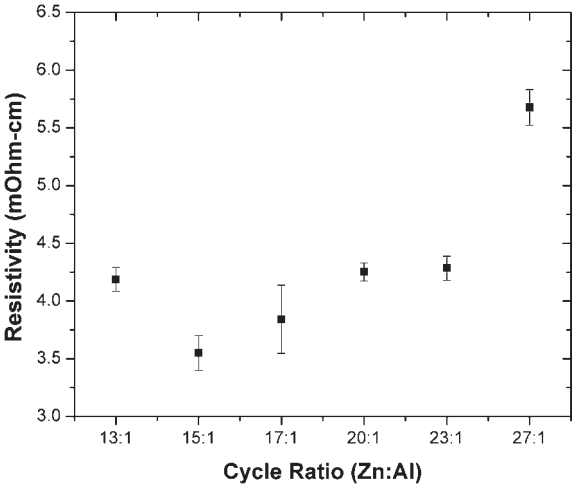

Figure 4. AZO film resistivity, as a function of substrate temperature.

temperature was varied from 140 °C to 220 °C. The overall film thickness was measured by ellipsometery at each temperature for the resistivity calculations and has been seen to decrease with increasing temperature. The results are shown in Figure 4. Resistivity did not change much in the range of 160−200 °C, with the best performance observed at a substrate temperature of 200 °C.

From these measurements, the optimal pulse ratio of 15:1 and a substrate temperature of 200 °C yielded films with a resistivity of 3.0×10^{-3} Ω cm, as deposited on borosilicate glass substrates. This value is ∼1 order of magnitude higher than typical values for sputtered ITO, indicating that the ALD AZO deposited on glass would require a thickness at least 10 times greater than that of ITO to obtain the same sheet resistance.

There are several possible reasons why the resisitivity of ALD AZO is higher than values reported from other techniques. Since the aluminum is deposited in a nonhomogeneous manner, there will be a variation in aluminum content throughout the thickness of the film, causing an uneven dopant distribution.[19] Furthermore, the crystallization of a solid solution of AZO from a nonhomogeneous composition will be different than that for techniques in which the aluminum is distributed evenly throughout the film. Also, the morphology of AZO will vary among different deposition techniques, and the presence of defects such as grain boundaries can contribute to an increase in film resistivity. To further characterize the ALD AZO films, and gain an understanding of their relatively high resistivity, XRD, STM, and SEM measurements were performed.

XRD Analysis on Glass Substrates. Phase analysis on the films was performed by XRD. A spectrum obtained from a symmetrical $\theta/2\theta$ scan on a sample with a 15:1 ratio and substrate temperature of 200 °C is shown in Figure 5. The hexagonal phase of ZnO is confirmed, with the (100), (002), (101), and (200) peaks visible. No crystalline Al_2O_3 or $ZnAl_2O_4$ peaks were visible in the spectrum, suggesting that phase segregation could not explain an increase in film resistivity.

Doping of ZnO films with Al can lead to either substitution of Al^{3+} ions for Zn^{2+} ions in the ZnO lattice or

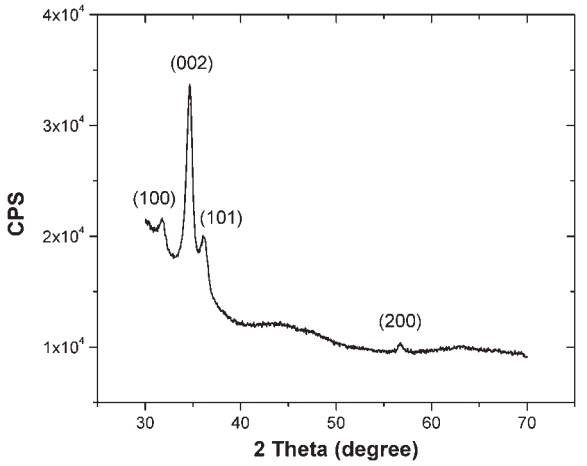

Figure 5. XRD spectrum of an AZO film deposited on glass.

interstitial Al defects in the crystal structure. In the case of substitution, Al acts as an electron donor, contributing to the *n*-type conductivity of the ZnO films. Furthermore, formation of the gahnite ($ZnAl_2O_4$) phase can lead to decreased conductivity of the film. The substitutional defect mechanism can be observed through a measurement of the lattice parameter of the film, as a function of dopant concentration. Because the ionic radius of the Al^{3+} cation (0.53 Å) is smaller than that of the Zn^{2+} cation (0.74 Å), substitutional Al^{3+} defects will lead to a reduction of the lattice parameter in the ZnO phase.[24] This leads to a shift in diffraction angles from the wurtzite structure to higher values, because of a reduction in *d*-spacings between the atomic planes. In the case of interstitial Al incorporation, the lattice parameter has been shown to increase with Al concentration,[25] which was not observed here, suggesting that the majority of Al exists as substitutional defects.

In the ALD AZO films, a shift to larger diffraction angles was observed in all crystalline ZnO peaks with increasing Al incorporation. From this diffraction data, a shift in the hexagonal lattice parameters *a* and *c* were calculated. First, the *d*-spacings were calculated using Bragg's law:

$$d = \frac{n\lambda}{2 \sin \theta} \tag{1}$$

Here, $\lambda = 1.541874$ nm (Cu $K\alpha_1$ radiation) is the X-ray wavelength, $n = 1$, and θ is the scattering angle. From the *d*-spacings, the lattice parameters *a* and *c* can be calculated using eq 2 for hexagonal structures:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \tag{2}$$

The lattice parameter *a* was calculated using the (100) diffraction peak. Lattice parameter *c* was calculated using the shift of the (002) peak. The results are shown in Figure 6. An almost-linear trend in the decrease of lattice parameter, as a function of Al content in the films, can be observed in both plots. This is consistent with Vegard's law, which predicts an empirical linear relationship between lattice parameter and solid solution concentration. This supports the hypothesis that Al^{3+} ions are occupying Zn^{2+} lattice sites, causing a contraction of the lattice. These substitutional Al ions act as electron donors in the AZO film, increasing the *n*-type conductivity.

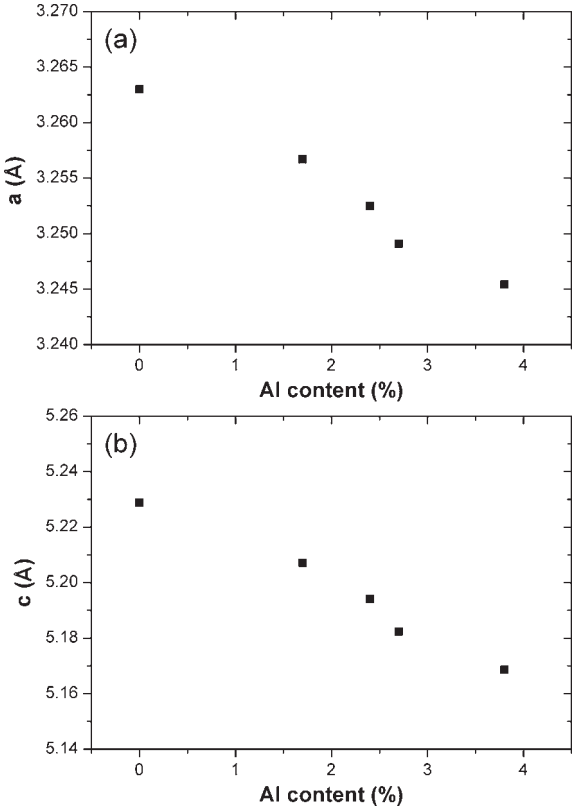

Figure 6. Lattice parameters of AZO films deposited on glass, as a function of Al content, as calculated from XRD data.

Because of the nonhomogeneous manner in which dopants are deposited in the ALD process, it is possible that not all of the Al atoms act as substitutional donors in the film. The presence of residual Al atoms, especially near the layers where the Al pulse was performed, could lead to the presence of other localized metastable phases at the nanoscale. While no other crystalline phases were detected in the XRD measurements, there could be regions of amorphous insulating material (such as Al_2O_3) present in the regions of high Al concentration, which could lead to a reduction in film conductivity. Therefore, while the linear relationship between Al concentration and lattice parameter suggests that a consistent increase in substitutional Al defects in the ZnO lattice occurs with increasing Al concentration, we speculate that there could be additional effects from residual Al present in the film that may act to decrease the overall film conductivity. Further research is required to identify such compositional and structural features with nanoscale resolution.

(24) Bahşi, Z. B.; Aslan, M. H.; Ozer, M.; Oral, A. Y. *Cryst. Res. Technol.* **2009**, *44*, 961.
(25) Shukla, R. K.; Srivastava, A.; Srivastava, A.; Dubey, K. C. *J. Cryst. Growth* **2006**, *294*, 427.

Analysis of ALD AZO on Sapphire Substrates. One hypothesis on the higher resistivity of ALD AZO films, relative to other deposition techniques, is that there is a large contribution from randomly oriented grains in the polycrystalline film. In an effort to grow oriented films, ALD AZO films were grown on sapphire(0001) substrates. Epitaxial growth of ZnO on sapphire substrates has been studied using other thin-film fabrication techniques.[26,27] A coincident site lattice is enabled by parallel orientation of the *c*-axis of hexagonal ZnO with the *c*-axis of sapphire(0001). A reduction in the lattice mismatch occurs with a 30° in-plane rotation of the ZnO, relative to the sapphire substrate.[28]

ALD AZO films were grown on commercially available sapphire (0001) substrates. A substrate temperature of 200 °C was used with a Zn:Al pulse ratio of 15:1. To study the orientation of the films, symmetrical $\theta/2\theta$ XRD scans were performed. Figure 7a shows the resulting XRD scan, as well as a scan on the sapphire substrate. These scans were plotted on a semilogarithmic scale, because of the sharpness of the peaks.

A sharp peak is observed for the ZnO(002) reflection, while other peaks are suppressed, compared to XRD scans of AZO on glass substrates, as shown in Figure 5. This suggests a texturing of the film with the *c*-axis of the ZnO parallel to the sapphire(0001) surface. To quantify this texturing, a rocking curve was measured on the ω-axis around the ZnO(002) peak, as shown in Figure 7b. This rocking curve produced a sharp peak with a full width at half maximum (fwhm) value of 1.54°. This indicates a strong out-of-plane orientation with the (002) planes parallel to the substrate surface. On the other hand, the rocking curve around the ZnO(002) peak performed on an AZO film deposited with the same conditions on the glass substrate exhibited a flat profile, indicating a lack of preferred grain orientation.

Interestingly, the resistivity of the film deposited on sapphire was measured to be 7.7×10^{-4} Ω cm. This is substantially lower than the resistivity of all of the AZO films grown on glass, which had resistivity values on the order of 10^{-3} Ω cm. The films were still polycrystalline, because of the relatively low temperatures used and the steric hindrance of the ligands in the ALD reaction. However, this demonstrates that the nucleation direction of crystalline grains during the initial ALD cycles can be influenced through the use of an appropriate substrate. It also indicates that the nonhomogeneous distribution of Al throughout the film cannot completely explain the higher resistivity values of ALD AZO films, compared to those deposited by other techniques, because the textured films on sapphire substrates were still deposited in a nonhomogeneous manner.

Highly oriented AZO films with the *c*-axis perpendicular to the surface have been observed to improve the conductivity in films deposited by other techniques, including sol−gel deposition.[11] Lee et al. demonstrated that the film resistivity was inversely proportional to the degree of (002) orientation of doped ZnO films.[29] One possible hypothesis on the origin of this enhanced conductivity is due to the anisotropic nature of the hexagonal crystal structure of ZnO. If the mobility of charge carriers in the *c*-plane is higher than that along the *c*-axis, films oriented with the *c*-axis normal to the substrate will show a lower sheet resistance than those with randomly oriented grains. In addition, the type of grain boundary formed in films with grains oriented in the same crystallographic direction may scatter carriers less effectively than grain boundaries between randomly oriented grains.[11] Thus, the improved conductivity of ALD AZO films with oriented grains provides valuable insight into the origin of the relatively high resistivity of ALD AZO films, compared to those deposited by other techniques.

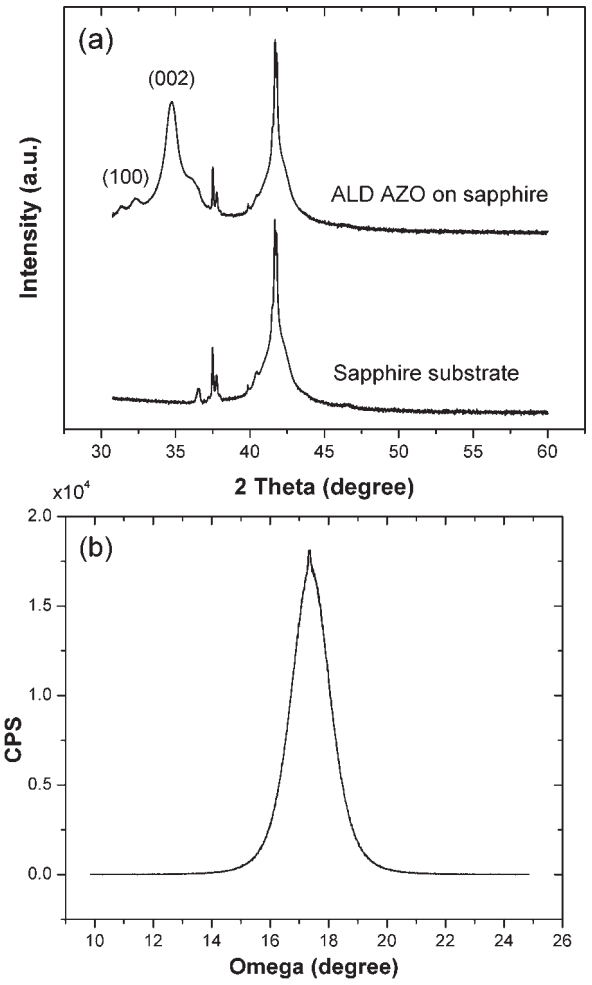

Figure 7. (a) XRD spectra of a sapphire(0001) substrate (bottom trace) and AZO film (top trace) deposited on an identical substrate; (b) ω-axis rocking curve around the ZnO(002) peak.

Surface Morphology Measurements. To study the impact of the substrate on film morphology, the surface grain structure was analyzed using STM and SEM. These complementary techniques allowed for high- and low-magnification

(26) Sun, X. W.; Kwok, H. S. *J. Appl. Phys.* **1999**, *86*, 408.
(27) Akiyama, S.; Minegishi, K.; Tanaka, T.; Ogawa, H.; Kasuga, M. *Jpn. J. Appl. Phys.* **2007**, *46*, 342.
(28) Chen, Y.; Bagnall, D. M.; Koh, H.-J.; Park, K.-T.; Hiraga, K.; Zhu, Z.; Yao, T. *J. Appl. Phys.* **1998**, *84*, 3912.
(29) Lee, J.-H.; Park, B.-O. *Thin Solid Films* **2003**, *426*, 94.

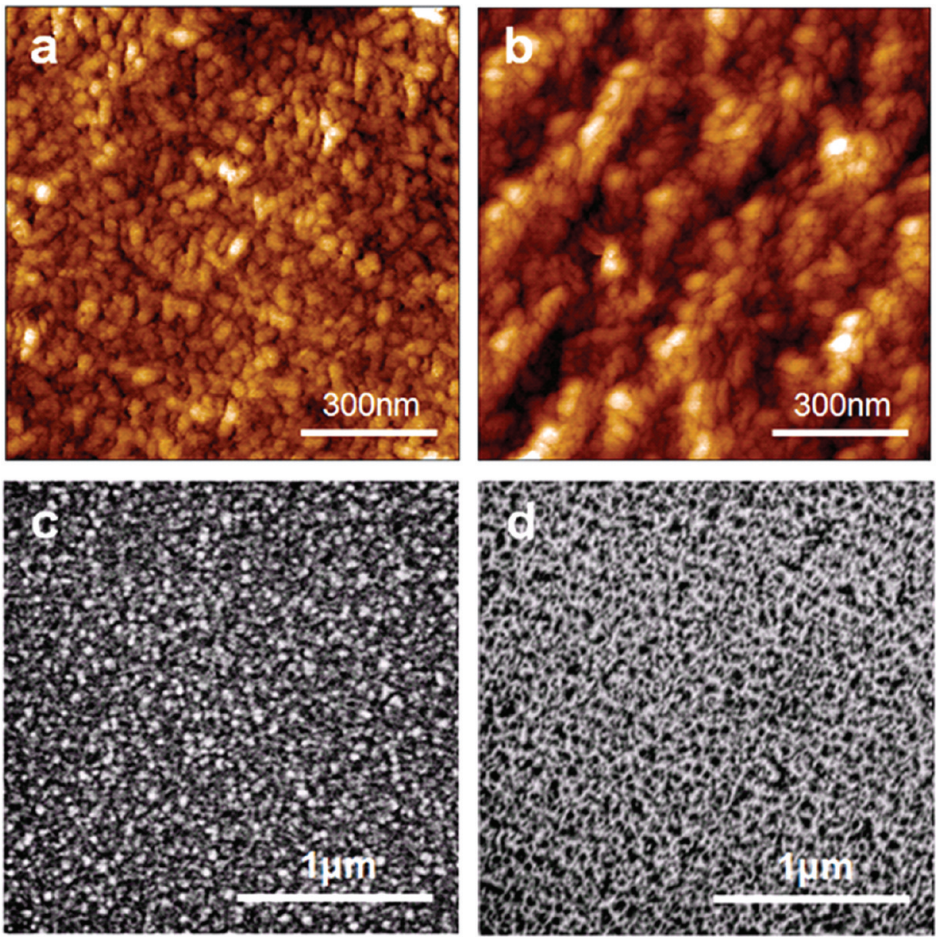

Figure 8. (a) STM image of AZO film on glass; (b) STM image of AZO film on sapphire; (c) SEM image of AZO film on glass; and (d) SEM image of AZO film on sapphire.

imaging of the film surface. All images were taken with the optimized 15:1 Zn:Al ratio and a substrate temperature of 200 °C, after a total of 480 ALD cycles. The results are shown in Figure 8.

It can be seen that the average grain size is approximately the same on both substrates. Therefore, the hypothesis that the decreased film resistivity on sapphire, compared to glass, is due to a lower concentration of grain boundaries cannot be validated. This provides further evidence that the origin of the decreased resistivity on sapphire is due to the formation of highly oriented grains with the *c*-axis normal to the film surface, as shown by the XRD analysis, rather than a surface morphology effect.

While the average grain size does not show a strong difference on glass and sapphire substrates, a more macroscopic texture can be observed on the sapphire, compared to a more homogeneous grain distribution on glass. This difference in the film surface can be seen at a lower magnification in the SEM images. The STM images show that smaller grains tend to coalesce into larger features, leading to a rougher surface on sapphire, compared to glass. The root-mean-square (rms) surface roughness of the AZO films measured by STM was 0.82 nm on glass and 2.38 nm on sapphire over an area of 1 μm × 1 μm. This rougher surface could be a result of the growth of more-oriented

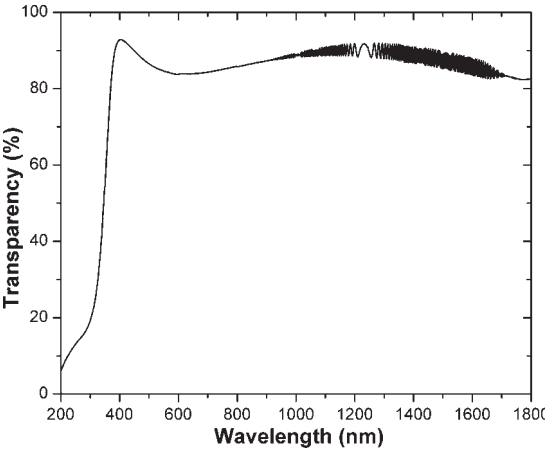

Figure 9. Transparency spectrum of an AZO film deposited on glass measured by UV−vis spectrophotometry.

grains on the sapphire surface, compared to more randomly oriented grains on glass. To confirm that this was not due to the roughness of the original surface, AFM scans were performed on the bare glass and sapphire substrates. The rms roughness values of the bare substrates were measured to be 0.43 nm for glass and 0.15 nm for sapphire over an area of 1 μm × 1 μm.

Transparency Measurements. Besides conductivity, transparency is an important parameter of TCO material

quality. Optical transparency measurements were performed on the ALD AZO films using UV−vis spectrophotometry. Transmission spectra were similar for the various conditions presented in this study. Figure 9 shows a transmission spectrum for an AZO film deposited with the optimized conditions of a 15:1 Zn:Al ratio for a total of 480 cycles and a substrate temperature of 200 °C. Transparency of >80% was measured over a range of wavelengths of 370−1600 nm. This suggests that its use as a transparent electrode material for devices such as solar cells and other optoelectronic applications is feasible.

Conclusions

Atomic layer deposition (ALD) Al-doped ZnO (AZO) films have been deposited on sapphire and glass substrates, to study the effects of deposition parameters on film conductivity. Films deposited on glass wafers after optimizing the Zn:Al pulse ratio and substrate temperature had resistivity values of $3.0 \times 10^{-3}\ \Omega$ cm. XRD measurements showed that the films were hexagonal, with no measurable insulating phases. The lattice parameter was shown to decrease with increasing Al concentration, suggesting the incorporation of Al atoms into substitutional Zn lattice sites. Films grown on sapphire(0001) wafers showed a decrease in resistivity to $7.7 \times 10^{-4}\ \Omega$ cm. This was explained by an increased grain orientation in films grown on sapphire, with the *c*-axis aligned normal to the substrate, while films grown on glass showed no preferential orientation. Scanning tunneling microscopy (STM) and scanning electron microscopy (SEM) images showed a grain size similar to that in films grown on glass and sapphire, indicating that orientation of the grains was responsible for the decreased resistivity, rather than a difference in grain-boundary density. Film transparency was measured to be >80% for visible and near-infrared (near-IR) wavelengths.

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