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High Rate Deposition of High Quality ZnO:Al by Filtered Cathodic Arc

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ABSTRACT

High quality ZnO:Al (AZO) thin films were prepared on glass substrates by direct current filtered cathodic arc deposition. Substrate temperature was varied from room temperature to 425°C, and samples were grown with and without the assistance of low power oxygen plasma (75W). For each growth condition, at least 3 samples were grown to give a statistical look at the effect of the growth environment on the film properties and to explore the reproducibility of the technique. Growth rate was in the 100-400 nm/min range but was apparently random and could not be easily traced to the growth conditions explored. For optimized growth conditions, 300-600 nm AZO films had resistivities of 3-6 x 10^{-4} Ωcm, carrier concentrations in the range of 2-4 x 10^{20} cm^3, Hall mobility as high as 55 cm^2/Vs, and optical transmittance greater than 90%. These films are also highly oriented with the c-axis perpendicular to the substrate and a surface roughness of 2-4 nm.

INTRODUCTION

Transparent conducting oxides (TCOs) are an important part of many emerging technologies, including energy saving windows with dynamic optical properties. Window applications as well as TCOs for solar cells or displays require high rate growth processes which are capable of depositing uniform coatings over several square meters. The current industry standard for oxides is reactive magnetron sputtering, with several companies supplying sputtering equipment for in-line coating systems up to 3.5 m wide. However, standard reactive sputtering typically produces inferior AZO compared to other techniques, such as pulsed laser deposition (PLD) (1) (2) or cathodic arc deposition (3) (4) where the material condensing on the substrate is highly ionized plasma. Increasing the ionization by sputtering in a high power impulse mode (5) typically reduces the deposition rate and has the disadvantage of producing highly energetic negative oxygen ions (10). These ions are even a problem for standard sputtering in oxygen since they damage the growing film, leading to strong spatial variations in the electrical properties (6).

In this work, high quality AZO films were deposited by direct current filtered cathodic arc deposition at growth rates over 10 times faster than magnetron sputtering. The resistivity of the films is nearly as low as that obtained by optimized PLD growth, which typically produces very high quality material but only over small areas and at low growth rates. Unlike PLD, cathodic arc doesn't require an expensive high-power laser which means scaling up to large area coatings may be as simple as arranging multiple cathodes in a suitable geometry.

EXPERIMENT

For a statistical study of DC cathodic arc growth of AZO, a large number of samples were grown and characterized. Samples were deposited at room temperature, 200°C, and 425°C both with and without the assistance of a 75 W oxygen plasma from a constricted hollow cathode plasma source (7). For each growth condition, three samples were prepared (giving 18 total) in order to observe the reproducibility of the films and to provide an accurate estimate of the overall uncertainty of the growths. Samples were grown in a random order to minimize the effect of any systematic uncertainties.

All samples were prepared in an oxygen ambient of around 5 mTorr with the oxygen partial pressure set before growth using a differentially pumped residual gas analyzer. Base pressure in the chamber was typically around $1\text{-}2\times10^{-5}$ Torr once the substrates were at growth temperature. Arc current was set at 70 A. The cathode was a low cost Zn:Al (<4% Al) alloy which gives Al concentrations in the films of (1.0 ± 0.3) at.% as measured by Rutherford Backscattering (to be reported elsewhere). Once ignited, the arc consumed enough oxygen to drop the pressure to 2.5-3.5 mTorr. An open particle filter in a 90° bend was used to filter the arc plasma, which travelled a distance of approximately 30 cm from cathode to substrate.

Borosilicate microscope slides were used as substrates and were gently cleaned using commercial glass cleaner (Liquinox) and thoroughly rinsed before loading into the chamber. Prior to deposition, the substrates were exposed to a 75 W oxygen plasma for two minutes to burn off any hydrocarbons on the glass surface. This procedure was chosen since it does not produce waste solvents and could be easily integrated into an inline coating system. Films grown on these substrates are very adherent and do not typically delaminate from the surface, even up to several microns thick.

Structural, electrical, and optical characterization was performed on all the samples after growth. Thickness was measured with a Dektak 150 profilometer. Simultaneous transmission and reflection was measured at normal incidence over the visible range using an Ocean Optics CCD system. Sheet resistance was measured by a 4-point probe, and Hall measurements at room temperature were carried out in the Van Der Paw geometry in an Ecopia HMS-5000. Surface morphology was studied with a Veeco MultiMode AFM in tapping mode and the structure was investigated with a Bruker x-ray diffractometer equipped with an area detector.

DISCUSSION

Pulsed cathodic arc has already proven to grow high quality AZO (3) but the growth rate is too slow to be industrially viable for large area window coatings. Running the arc with a continuous direct current (DC) substantially increases the growth rate. Film thickness for 2 minute growth is shown in Figure 1. However, this is known to affect the reproducibility of the growth rate since the cathode spot position fluctuates (8), altering the coupling of the plasma stream into the always-necessary magnetic plasma filter.

In this work, no clear correlation was observed between deposition rate and substrate temperature, oxygen plasma power, or any other growth parameter for that matter. A close look does show some evidence that the oxygen plasma increases the thickness, but with only 3 data points it is hard to remove outliers. Growth rate was between 100-400 nm/min, and also did not depend on the order in which the samples were grown (i.e. cathode erosion did not affect the growth rate in this experiment). Even on the low end, this rate is an order of magnitude higher than those typically achieved by reactive DC sputtering.

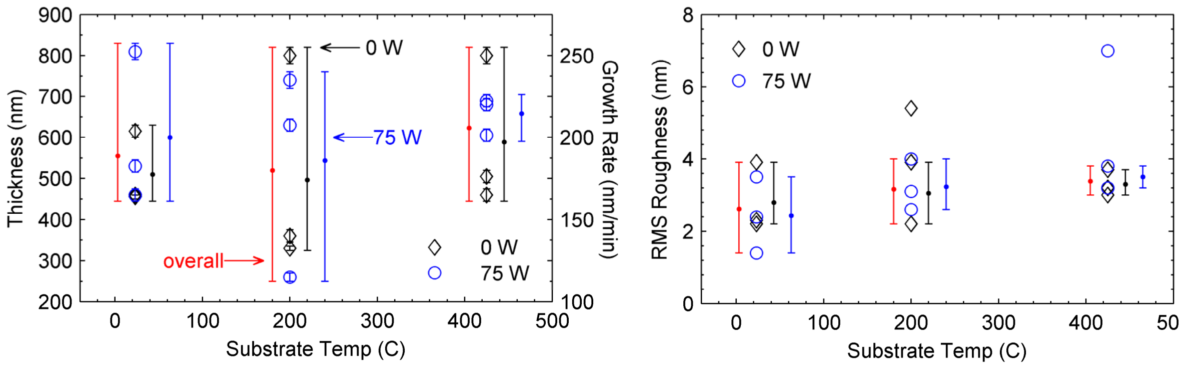

Figure 1 Thickness, growth rate, and RMS surface roughness of AZO films grown for 2 minutes with and without a 75 W oxygen plasma. Error bars on the data points show the measurement uncertainty. The error bars to the left show the overall error at each substrate temperature and the ones on the right show the spread for each oxygen plasma condition. Outlying data points are not included in the error bars to the sides of the data.

Surface roughness, measured with the AFM, was typically below 4 nm and all samples showed very similar morphology. No correlation between oxygen plasma power and surface roughness was observed. In this case, all 6 samples grown at a given temperature can be treated as equal and outliers can be identified. This is the case for the [425°C, 75 W] sample not included in the error bars. It was, however, observed that films could be made very smooth (less than 1 nm RMS) by reducing the arc current at the cost of the growth rate (to be published).

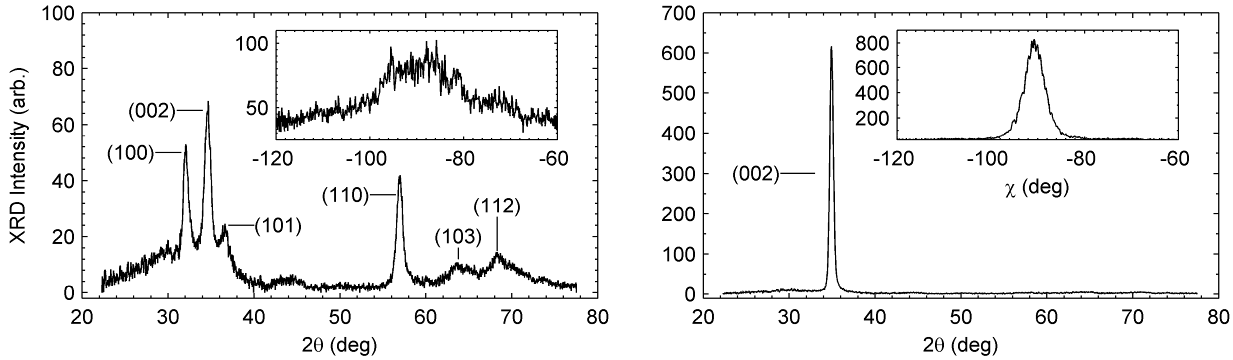

Figure 2 XRD spectrum of a poorly aligned sample grown at (left) room temperature and a well aligned sample grown at 425°C (right). Alignment did not strongly depend on substrate temperature but heating was beneficial to reproducibility. χ-scans are shown in the insets.

X-ray diffraction (XRD) showed many of the samples to have a high degree of preferential (002) orientation perpendicular to the substrate, as shown in the spectra on the right hand side of Figure 2 with scans in the χ direction shown in the insets. The spectra indicate columnar grain growth perpendicular to the substrate and mainly proceeding along the (002) axis. The small full width at half maximum (FWHM) in the χ direction indicates very little tilting between grains in many of the samples. However, the intensity seems to show random variations similar to the growth rate; at most of the growth conditions one sample (or more) showed low intensity and significant reflections from several crystal planes. Even in these samples showing several planes, there was still some preferred (002) orientation as this peak does not dominate the spectrum of ZnO reference powder.

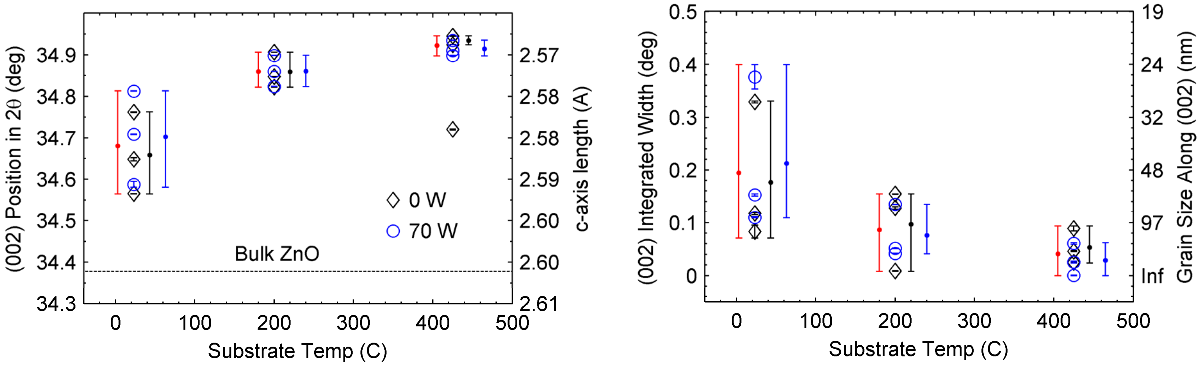

Figure 3 Peak parameters as found by a pseudo-Voigt decomposition. Integrated width (shown on right) has been corrected for instrumental broadening. About 50% of the samples had an average grain size along the (002) direction comparable to or larger than the film thickness.

Some correlation between the XRD spectra and substrate temperature can be seen in Figure 3 which shows the peak parameters as found by a pseudo-Voigt decomposition (WinPLOTR). As the substrate temperature was increased, the *c*-lattice parameter tended to decrease and, using the equation found in ref. (9) the stress in the films went from 0.5 to 3.3 GPa. This may be caused by differences in the thermal expansion coefficients between the AZO films and the glass substrate. A growth temperature is hard to define due to the substantial energy of the arriving ions and the film may have to cool from a few hundred degrees higher than the measured substrate temperature.

Integrated width of the (002) peak decreases with increasing substrate temperature, as shown in Figure 3b. Instrumental broadening was responsible for most of the peak width shown in Figure 2a and it was corrected for by analysis of a spectrum from a LaB_6 standard. Average grain size along the (002) direction is also shown in Figure 3, estimated by the Scherrer formula using a structure factor of 0.9 and the average (002) position of all the samples. About half of the samples show grain sizes which are comparable to (or even larger than) the film thickness. As such, many of the columnar grains extend all the way from the substrate interface to the film surface, especially when the substrates were heated. However, AFM and scanning electron microscope images show the average lateral grain size is much smaller (around 10-100 nm).

Electrical performance of the films was excellent, with sheet resistances as low as 6 Ω/□ and up to 60-70 Ω/□ in the least conductive samples grown at room temperature. Hall measurements show the carrier concentration to be in the $2\text{-}4 \times 10^{20}$ cm^{-3} range with no clear correlation to substrate temperature or oxygen plasma power. Resistivity is shown in Figure 4 and a clear decrease in resistivity and increase in mobility was observed with increasing substrate temperature. This is most likely due to the increased structural order of the films grown at higher temperatures. The best sample (425°C, 0 W, 505 ± 15 nm, 6.0 ± 0.3 Ω/□, 96% average visible transmittance) showed a mobility of 55 ± 3 cm^2/Vs, which is very competitive with the highest mobility samples reported in the literature.

Plotting the mobility against carrier concentration shows a fairly scattered plot with an upward trend. Such behavior is indicative of grain boundaries being the dominant scattering centers for free electrons. It is not surprising considering the small lateral grain size observed in both DC and pulsed arc deposited AZO (3) (4) (9). It must be noted that for thin films the electrical properties are known to depend on sample thickness but no correlation was observed in this sample set. As such, these films are all thick enough for the electrical (and structural) properties to have leveled off and thickness variations do not affect the trends shown in Figure 4.

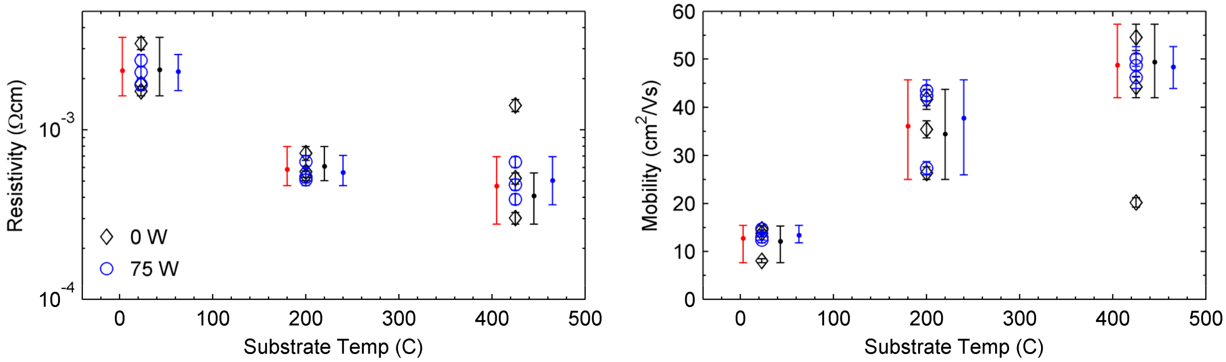

Figure 4 Resistivity and mobility measured by the Hall technique in the Van-der-Pauw geometry. One outlying sample with respect to electrical properties can be identified in the group of samples grown at 425°C.

Most of the samples were very clear to the eye and the average visible transmission of the film alone is shown in Figure 5a. Several of the samples had transparency over 90%, including the one showing the best electrical properties. Absolute reflectivity over the visible spectrum for all samples was between 10 and 20 %. Reflectivity did not correlate with substrate temperature or oxygen plasma power and the differences in the transmission were mainly due to absorption in some of the lower quality films. A commonly used empirical figure of merit for transparent conductors which accounts for both the optical and electrical properties of the films is shown in Figure 5a. Films grown at elevated substrate temperatures show high merit and good potential for applications where very thin films are not needed.

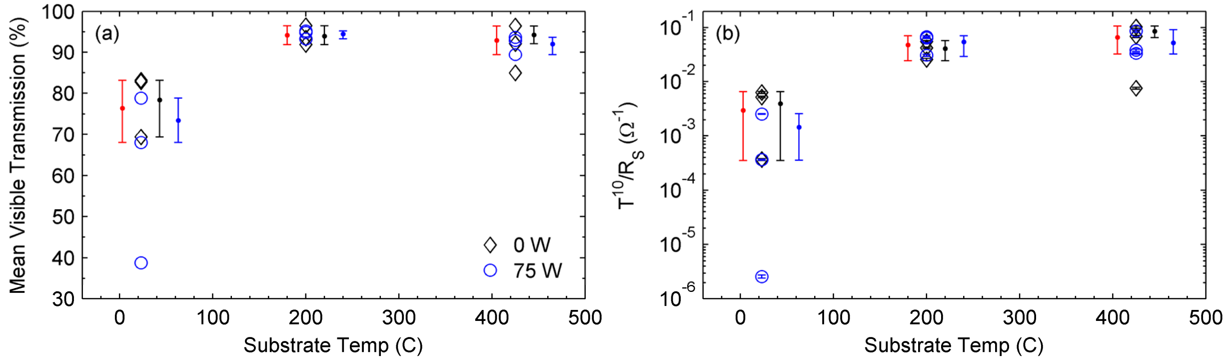

Figure 5: (a) Mean visible transmission measured from 400 to 750 nm after removing the contribution from the substrate. (b) Empirical transparent conductor figure of merit calculated from the mean visible transmittance and the sheet resistance.

CONCLUSIONS

Very high quality AZO can be produced at high rates by DC cathodic arc deposition. However, the variability in growth rate and structural properties will need to be reduced before yields will be high enough for window-scale production. Such variability also poses a problem for an accurate understanding of the effect of any of the growth parameters. Statistical studies involving large sample sets help to significantly improve the overall error bars and basic understanding of the film growth process. Such repeated measurements will be beneficial for growth of any material by any process.

Despite this variability, high quality AZO thin films with repeatable optical and electrical properties were produced. The best sample showed properties comparable to optimized PLD grown material at growth rates two orders of magnitude higher (425°C, 0 W, 2 minute growth, 505 ± 15 nm, 6.0 ± 0.3 Ω/□, 55±3 cm^2/Vs, and T=96%). Many other samples had similar characteristics, with substrate heating generally improving the quality. A low power (75W) oxygen plasma does not seem to affect the film growth but does allow for an inexpensive and environmentally friendly way to clean large area substrates.

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