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Achieving high mobility ZnO:Al at very high growth rates by dc filtered cathodic arc deposition

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Abstract. Achieving a high growth rate is paramount for making large-area transparent conducting oxide coatings at a low cost. Unfortunately, the quality of thin films grown by most techniques degrades as the growth rate increases. Filtered dc cathodic arc is a lesser known technique which produces a stream of highly ionized plasma, in stark contrast to the neutral atoms produced by standard sputter sources. Ions bring a large amount of potential energy to the growing surface which is in the form of heat, not momentum. By minimizing the distance from cathode to substrate, the high ion flux gives a very high effective growth temperature near the film surface without causing damage from bombardment. The high surface temperature is a direct consequence of the high growth rate and allows for high quality crystal growth. Using this technique, 500-1300 nm thick and highly transparent ZnO:Al films were grown on glass at rates exceeding 250 nm/min while maintaining resistivity below $5 \times 10^{-4} \Omega\text{cm}$ with electron mobility as high as $60 \text{ cm}^2/\text{Vs}$.

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Currently, indium supply can meet the demand, even in the United States where no indium is mined and little is actually recycled. However, building energy efficiency must be improved world wide and smart, multi-functional windows requiring transparent conductive oxide (TCO) coatings will play an important role. About 10^8 m²/year of TCO coated glass is already required for the flat panel display and solar cell industry. Smart windows will require TCO coatings over areas of the same order of magnitude, and the photovoltaic market is also expected to grow. This will require a very substantial increase in the indium supply if indium tin oxide (ITO) and other In based materials remain the TCO of choice. Such an increase in the demand of ITO will have a profound impact on the indium price which is already subject to large swings. Furthermore, indium has very unique properties which make it useful for many other important applications which will inevitably suffer. For example, indium is used for coatings for aircraft parts, for cryogenic and vacuum applications, in optoelectronic devices for fiberoptic communications, etc.

Aluminum doped ZnO (AZO) is one of the leading candidates to replace ITO but several obstacles must first be overcome. Aside from AZO being less resilient to moisture and acids, the electrical properties of AZO deposited onto glass are not as good as ITO. Epitaxial AZO grown on sapphire by pulsed laser deposition (PLD)[1] has shown mobility as high as 70 cm²/Vs but mobility is 40-50 cm²/Vs when deposited on glass[2, 3]. The resistivity was a record low 0.8×10^{-4} Ωcm in the study by Agura et al.[2] but PLD has a very low growth rate and is not well suited for large area deposition.

Magnetron sputtering is the current standard for large area glass coating by physical vapor deposition. It can produce AZO/glass with resistivity as low as 5×10^{-4} Ωcm, but typically the mobility is limited to about 30-40 cm²/Vs.[4] This means a high carrier concentration is present, which limits transmission of the solar infrared that could be used to heat a building in cold climates or help power a solar cell. There is one publication where an exceptionally high mobility of 53 cm²/Vs was reported for as-deposited rf sputtered AZO which was 780-900 nm thick.[5] However, the growth rate was relatively slow at 15 nm/min. Reactive dc sputtered AZO has achieved a mobility of 46 cm²/Vs, but no information on the growth rate was reported.[6] Considering that the films were only 300-400 nm thick and that the rate wasn't even mentioned, it may be reasonable to assume that the growth rate was not considerably higher than that of rf sputtering.

There are a few reports of substantially higher growth rates, reaching 580 nm/min, for AZO grown by reactive magnetron sputtering but the mobility is limited to 20 cm²/Vs at best.[7] For AZO, ZnO, and many other crystalline materials, film quality judged by several metrics seems to be inversely proportional to the growth rate of the technique. Atomic layer deposition can produce high quality crystals (of a handful of materials) at very low rates, followed by MBE, and PLD. Then comes RF sputtering, then reactive sputtering, and then ultra high rate techniques like atmospheric plasma torches which are best suited for amorphous materials and thick porous films.

A frequently overlooked growth technique capable of high quality crystal formation is cathodic arc deposition. It is typically disregarded in major review papers on TCOs and has a low profile at most large conferences without a hard coating theme. Pulsed filtered cathodic arcs have produced AZO[8] with mobility above 40 cm²/Vs, but the growth rates are comparable to PLD. However, unlike PLD, cathodic arcs can be operated in a dc mode, giving much higher growth rates. AZO has been produced

by dc cathodic arc in the past,[9, 10, 11] but the quality was inferior to the films produced by reactive magnetron sputtering. This fact is likely why effort into dc arc growth of AZO and other TCOs seems to have diminished.

However, cathodic arc has the inherent advantage of producing a highly ionized plasma of cathode material. Energetic condensation from a plasma is known to give dense films due to both the kinetic and potential energy of the arriving ions.[12] Substrate biasing can control the kinetic energy of the arriving ions, but kinetic energy also brings momentum which can damage the growing surface. On the other hand, neutralization of the ion at the film surface releases the potential energy of the ion as heat, which can locally anneal and densify the films leading to better crystal quality. Thus, it is surprising that dc arc grown AZO did not previously outperform the sputtered-deposited films which condense from neutral atoms with very few ions in the arriving flux of particles.

As we will show, the limiting factor for previous work on dc arc grown AZO is the relatively large path the plasma followed from cathode to substrate. A long path is typically needed to make room for the magnetic plasma filter necessary to produce particulate-free coatings,[13] but it significantly reduces the ion flux. In this work, very high quality AZO with mobility as high as $60 \text{ cm}^2/\text{Vs}$ was produced at rates exceeding $250 \text{ nm}/\text{min}$ by minimizing the distance the plasma traveled. The high quality of these films compared to previous reports is attributed to the relatively high ion flux reaching the surface in the compact arrangement. The high flux locally raises the temperature *at the film surface* and allows for unusually high quality crystal growth at high rates.

Film deposition was done in a vacuum chamber which reaches a base pressure of 1×10^{-5} Torr when the substrate is at elevated temperatures. Oxygen gas was then fed in at a rate of 20-50 sccm with the total pressure in the range of 1-5 mTorr. Optimum oxygen pressure depends strongly on the arc current and these ranges were found to give the best balance for low resistivity and high visible transparency.

Readily available, very-low-cost Zn containing about 4 at % Al was used for the cathode (40 \$/kg). Arc currents typically used in this system are a relatively modest 25-70 A dc. The arc plasma was filtered using a helical quarter-torus open coil carrying 400 A dc and generating a magnetic field estimated to be 50 mT. Anode-filter separation as well as filter-substrate distance was minimized, with a 300 mm cathode-substrate separation.

Borosilicate microscope glass slides (25 mm x 75 mm, 1 mm thick) were used as substrates. They were cleaned with Liquinox, a widely used glass detergent containing ethylene diamine tetra acetate, designed to yield completely residue free surfaces. The samples were thoroughly rinsed with tap water and then the substrates were quickly dried using dry nitrogen, leaving a streak-free surface with no visible particulates or residues. Samples were pre-heated to an initial substrate temperature (T_s) of $425 \text{ }^\circ\text{C}$ at most, but excellent material could be deposited at $T_s = 200 \text{ }^\circ\text{C}$, and reasonably well performing material could be deposited on room temperature substrates. Before deposition the substrates were exposed to a 150 W oxygen plasma from a constricted plasma source[14] for 2 minutes, as a critical last step in the environmentally friendly cleaning procedure. Films were well adherent, even when grown up to several μm thick. Based on our personal experience in the lab growing more than 100 samples, this surprisingly simple cleaning procedure gave an initial glass surface equal to or better than those cleaned with solvents (ethanol and acetone) as judged by spurious residues on the surface. Growth time was usually 2 min and limited

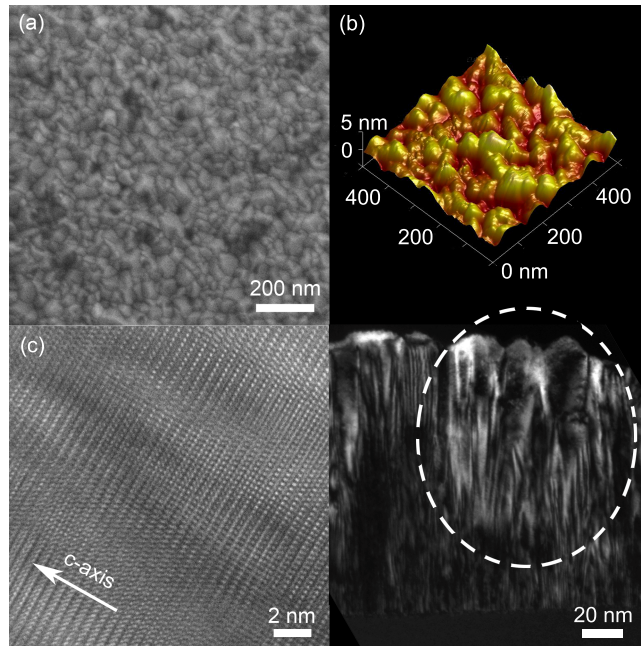


Figure 1. (a) SEM, (b) AFM, (c) cross sectional TEM, and (d) Dark field (002) TEM of AZO grown by dc arc. Images come from three different, typical samples with the TEM images taken on the same sample. A grain is circled in (d) with the dotted line.

to 5 min, sometimes by overheating of the substrate if the plasma flux was high.

AZO films grown by the compact dc filtered arc show a high degree of crystallinity and excellent crystallographic alignment of the grains, even for some samples deposited on room temperature substrates.[15] Al content in the films was measured to be 1.3 ± 0.3 at % using Rutherford backscattering spectroscopy. SEM, AFM, and cross sectional TEM images of samples grown at $T_S = 200$ °C are shown in Fig. 1. The (002) planes are very well aligned and the c -axis is normal to the substrate,[15] except for the first 80-100 nm which TEM shows as crystalline but with small grains and little overall alignment. SEM and AFM would suggest a very small lateral grain size, but the darkfield (002) TEM image shows the grains to be about 100 nm in diameter in the bulk of the film near the surface.

Optical transmission in the solar spectral range is high in these AZO samples, as shown by one of the better examples in Fig. 2. For 800-1500 nm photons, this AZO/glass stack shows at least 75% transmittance due to the low carrier concentration. A sheet resistance of 10.0 ± 0.3 Ω is possible for this 605 ± 15 nm thick sample (resistivity $\rho = 4.8 \times 10^{-4}$ Ωcm) due to the very high mobility of 50 ± 3 cm^2/Vs . Typical mobility for the samples produced in our system is 40-50 cm^2/Vs , with a 1300 nm film showing a record high 60 cm^2/Vs , the highest yet reported for as-deposited AZO thin films on glass substrates. For samples deposited at room temperature (RT), a mobility of 30 cm^2/Vs has been achieved which is much higher than typically reported for RT growth by sputtering[16] and PLD[17]. Properties of the more notable dc arc grown samples are summarized in Table 1.

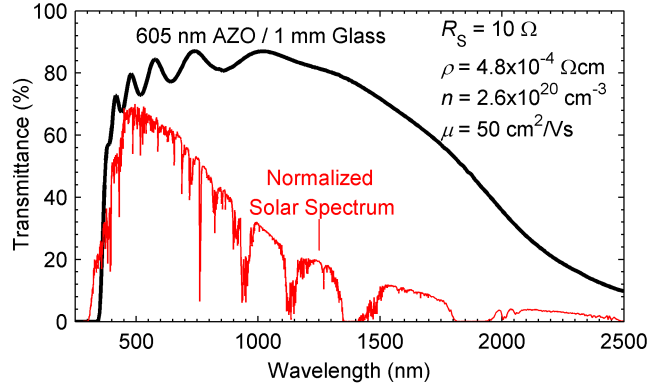


Figure 2. Transmittance of AZO/glass grown by the compact dc arc system (not corrected for the substrate). The AM1.5 solar spectrum is shown in relative units for comparison and the electrical properties of this film are in the upper-right corner.

Table 1. Properties of the more notable AZO samples produced by the compact dc cathodic arc system. T_{sol} is the transmittance over the entire AM1.5 spectrum shown in Fig. 2 through the AZO/glass stack. R_q is the surface roughness.

Sample	d (nm)	R_q (nm)	T_{sol} (%)	R_s (Ω)	ρ ($10^{-4}\Omega\text{cm}$)	n (10^{20}cm^{-3})	μ (cm^2/Vs)
Highest μ	1290	6.9	75	3.3	3.9	2.7	60
Lowest ρ	505	3.7	77	6.8	3.0	3.8	55
Smoothest	34	0.15	92	397	18.4	1.7	21
$d < 100$ nm	95	0.32	88	61	6.0	2.8	38
$T_s = 23$ °C	310	1.9	78	52	15.0	0.1	30

The optical and electrical performance of the films shown in Table 1 is noticeably superior to previous reports on dc cathodic arc grown AZO.[9, 18, 10, 11] It is very unlikely that the groups who published the reports simply missed the optimized process window. Since we used similar deposition conditions, there must therefore be an important difference in the geometry of the cathodic arc arrangement we used compared to other groups.

Film growth rate (G) is sensitive to the geometry of any physical vapor deposition system. For deposition of ZnO using a quarter-torus filter, growth rate is known to linearly increase with increasing arc current[19] (I_{arc}) and linearly decrease with increasing oxygen partial pressure[20] (P_{O_2}). For dc arcs, the growth rate is relatively independent of the substrate temperature (T_s) up to 425 °C.[15, 21] As such, one can approximate the effects of geometry on the ion flux reaching the target and the resulting growth rate by multiplying the current-normalized growth rate (G_C) by P_{O_2} .

As shown in Table 2, our G_C and $G_C \times P_{\text{O}_2}$ values are significantly higher than the others, proving that the much larger ion flux reaching the substrate (and higher G_C) is due to the geometry of our system. Published schematic drawings,[21, 22, 20] and pictures[23] suggest most other groups have a longer path from cathode to substrate due to the large filters (by an estimated factor of around 2). However, any extra distance the plasma must travel through the O_2 gas reduces its particle and energy

Table 2. Comparison of dc filtered (quarter-torus) cathodic arc growth rates of ZnO & AZO. ZnO reports are shown above the line, AZO below. I_{arc} is the arc current (A), P_{O_2} is the oxygen pressure (mTorr), G is the film growth rate (nm/min), and G_C is the current-normalized growth rate (nm/Amin).

Report	I_{arc}	P_{O_2}	G	G_C	$G_C \times P_{O_2}$
Xu[21]	70	1	20	0.3	0.3
Wang[22]	60	0.1	110	1.83	0.2
	60	1	30	0.5	0.5
David[19]	100	3	127	1.27	3.8
	300	3	650	2.2	6.5
Zhitomirsky[11]	200	5	130	0.65	3.3
This work	30	5	100 ^a	3.3	17
	70	5	300 ^a	4.3	21

^a Average of many samples

flux density by scattering and reduction of the mean ion charge state. Thus, a much greater percentage of the available energy of the cathodic arc plasma is utilized for film growth in the compact arrangement.

The large amount of available energy from the compact arc is critical for obtaining high mobility AZO. Atomic scale heating of the film surface leads to a *growth* temperature which can be higher than the *substrate* temperature.[12] During deposition, the heat from the growing surface can warm the substrate by up to 200 °C, but most of the energy is dissipated on ps time and nm length scales.[24] Therefore, in order to effectively heat the film surface, the ion flux must be high enough to ensure the individual thermal spikes from each ion are close in space and time.

In this compact arrangement the *growth* temperature may even exceed the melting point of the substrate without causing damage. AZO has a much higher melting point than glass, and the high *growth* temperatures reached by the compact arc promote the formation of high quality crystalline films with large grains. Such a situation cannot be attained by conventional substrate heating. This perhaps greatest advantage of cathodic arc deposition is substantially diminished as the plasma path length increases. Simply increasing the bias voltage on the substrate will lead to film damage and poor electrical performance due to the high kinetic energy of the arriving ions.

In summary, AZO thin films with mobilities in the 40-60 cm²/Vs range were deposited on glass substrates at rates exceeding 250 nm/min using a compact dc cathodic arc arrangement. The short plasma path was the key to maximizing the kinetic and potential energy flux of the condensing plasma, allowing significant transient heating of the growing film surface without overly heating the substrate. The low sheet resistance, high VIS-NIR transparency, and high growth rate of AZO grown by a compact cathodic arc arrangement could prove very competitive with commercially available TCOs used for large area applications.

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