

Co-sputtered Aluminum Doped Zinc Oxide Thin Film as Transparent Anode for Organic Light-emitting Diodes

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ABSTRACT

Aluminum doped zinc oxide (AZO) is a promising transparent conducting oxide (TCO), which have the advantages of low material cost, low toxicity and chemical stability in reducing ambient over ITO. In this report, AZO was grown by sputtering Al target and ZnO target simultaneously, and the Al dopant concentration can be easily tuned by adjusting sputtering power set. The acquired lowest resistivity was $1.3 \times 10^{-3} \Omega \cdot \text{cm}$, with the Al concentration dopant as 4.8%. The transmittance of AZO is even better than commercial ITO glass. OLED devices based on TPD-Alq₃ were fabricated on AZO, and the device performance was competitive with that on commercial ITO. It was also proved that MTDATA matches better with AZO than CuPc, which served as hole injection layer.

Keywords: Aluminum doped zinc oxide, organic light-emitting diodes, co-sputtering

1. INTRODUCTION

Much research work has been done searching for other TCOs, the aim being to replace the ITO by cheap materials with less toxicity and higher transparency and conductivity. Aluminum doped zinc oxide (AZO) film, an n-type, highly degenerated, wide-gap semiconductor is expected to replace ITO films due to its high conductivity in the range of $10^{-3} \sim 10^{-4} \Omega \cdot \text{cm}$ and because it has a lower material cost than does indium [1]. They also have advantages in terms of their chemical stability in the reductive ambient containing H⁺ which is used for hydrogenated a-Si depositions [2].

Increasing research interest in AZO is not only because of its low resistivity, but also because of its optical characteristics. AZO thin film exhibits a sharp UV cut-off and a high refractive index in the IR range, and it is transparent in the visible range [3].

Many techniques such as reactive magnetron sputtering [4], pulsed laser deposition (PLD) [5], chemical vapor deposition (CVD) [6] and dip-coating technique [7], have been used for AZO deposition. Of these techniques, the magnetron sputtering is most often used due to its advantages of high growth rate and large area uniformity. It was reported that the Al dopant concentration plays an important role in the conductivity of AZO films, and most researchers agree that 2at% of Al in AZO ensures the highest conductivity [8]. But there are some variations for different deposition techniques. Kim and his coworkers reported that 0.8at% Al was the optimal concentration in

order to obtain the lowest resistivity in AZO samples grown using the PLD technique [9]. As for the target materials, usually the composite target sintered ceramic ZnO:Al₂O₃ (98:2) target is used for RF sputtering [10]. Alloy target containing 1.5wt% Al in Al-Zn is also used as the target material for AZO growth [4]. The reported resistivity of AZO varies greatly from $9.8 \times 10^{-2} \Omega \cdot \text{cm}$ to $1.5 \times 10^{-4} \Omega \cdot \text{cm}$, resulting from different deposition conditions [11-14]

In our research, a co-sputtering technique was used to deposit AZO from two separate targets, Al and ZnO. It was easy to tune the Al concentration by adjusting the sputtering power set.

2. EXPERIMENTAL DETAILS

Co-sputtering has the advantage of allowing an easy tuning and control of the percentage of Al in the AZO film. This is convenient when studying the effect of Al dopant within a large varying range.

High purity (99.99%) Aluminum and high purity ZnO (99.99%) served as the targets. The target dimension was two inches in diameter and 0.25 inch in thickness. The co-sputtering was carried out in the AJA International ATC 1200 sputtering system. The Al sputtering was carried out with DC power supply, and an RF power supply was used for the ZnO. The target-substrate distance was 20cm. The Al dopant concentration was tuned by adjusting the DC power set of the Al. It ranged from 20W to 60W, while the RF sputtering power for the ZnO was fixed at 200W.

The thickness of the film was measured with a Tensor P-10 surface profiler, and the sheet resistance measured with an automatic four point probe meter Model 280.

All the samples underwent post-annealing in pure argon ambient and high vacuum (10^{-5} Torr) ambient. The temperature was set at 300°C, 400°C, 500°C and 600°C for the different samples. The effect of the post annealing on the AZO resistivity were studied.

With the AZO covered glass as starting the substrate and anode, OLED devices were fabricated and characterized. Commercial ITO served as the control sample. Different hole injection layers (HIL) were used in the device fabrication, the aim being to find a HIL that matches with AZO so as to acquire higher device efficiency.

3. RESULTS AND DISCUSSION

3.1. Resistivity of co-sputtered AZO films

When the DC power set for sputtering Al was varied from 20W to 60W, while kept the other parameters such as the

oxygen percentage in argon, the working pressure, the substrate temperature and deposition time unchanged. The deposition rate of Al varied with the power setting. The result was a variation of the Al concentration within the AZO film.

The Al concentration was detected using XPS technique which quantitatively gives the elements' percentage and binding energy. The relationship of the resistivity and the Al dopant concentration is similar as that shown in Figure 1. The resistivity shows a minimum when Al atomic concentration is 4.8%.

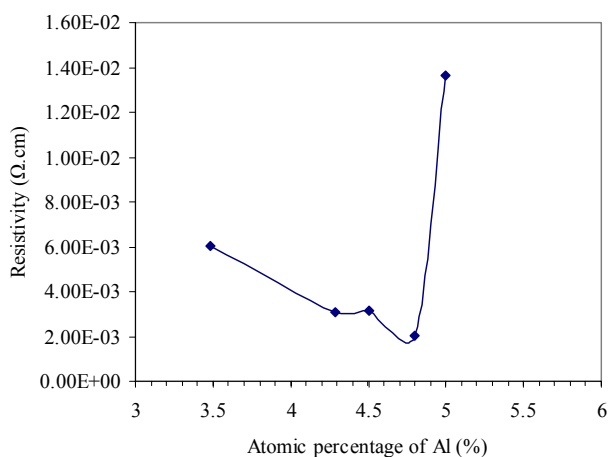


Figure 1 The effect of Al dopant on AZO resistivity, which is co-sputtered at 300°C

Post annealing is often used to activate the dopant so as to increase the conductivity of the samples [15]. All the annealing was done under a high vacuum, 2×10^{-5} Torr.

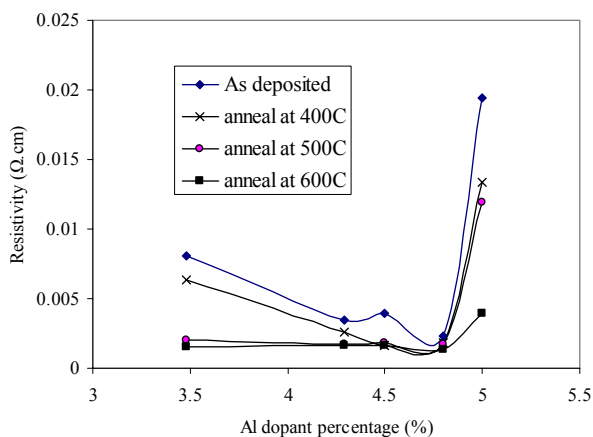


Figure 2. The annealing effect of different temperature on AZO samples

Figure 2 shows the annealing effect on AZO resistivity in comparison with the as-deposited sample, the annealing at 400°C for 30min does not improve the AZO conductivity much. When annealing under 400°C, the thermal energy provided to the doped atoms is not high enough for activation. When there is an increase in the annealing temperature to 500°C, the improvement in AZO conductivity is more significant. But, the conductivity with

a higher Al dopant is still very low; there is almost no change from that of the as-deposited samples. Further increasing the annealing temperature to 600°C greatly decreased the resistivity of the AZO samples with a higher 5% Al dopant concentration-from $1.9 \times 10^{-2} \Omega \cdot \text{cm}$ to $3.9 \times 10^{-3} \Omega \cdot \text{cm}$. The trend clearly proves that the activation of Al dopant contributes most to the conductivity with increasing annealing temperature. The lowest resistivity obtained is $1.3 \times 10^{-3} \Omega \cdot \text{cm}$. But, the annealing effect is not very significant on the AZO sample with an Al dopant as 4.8%, and even when the annealing temperature was high as 600°C.

3.2. Transparency of co-sputtered AZO films

The acquired AZO samples are very good in regard to their optical transparency. The average transmittance in the visible ranges is more than 90%. This is even higher than that of commercial ITO. Figure 3 shows the transmittance of the AZO sample in comparison with that of commercial ITO.

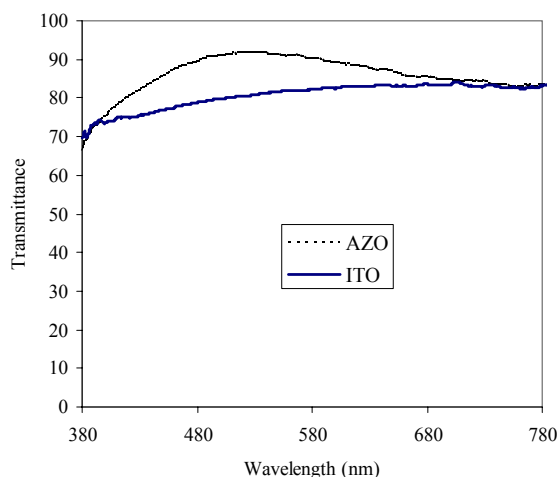


Figure 3. The transmittance of AZO sample in comparison with commercial ITO

3.3. Characterization of OLEDs fabricated on co-sputtered AZO films

Both the transparency and conductivity of the obtained AZO samples were suitable for OLED fabrication, but the work function of the AZO is 0.2~0.3 eV lower than the generally used ITO. This could have been a problem if the AZO was to serve as an anode for the OLED device. As our knowledge, only a few papers have been published which in relation to OLED performances with the AZO as anode [16], and the results were far from those of on ITO. In our work, OLED devices were also fabricated on AZO so as to make a comparison with commercial ITO. The focus is on determining the hole injection materials which matches AZO well, and exhibits higher efficiency. At the least, we sought AZO was competitive with commercial ITO.

The OLED devices were fabricated as usual, and their optimized configuration, based on experiment results [17], was 20nm, 40nm and 50nm for CuPc, TPD and Alq₃ respectively. With AZO as anode and CuPc as HIL, the device efficiencies are very low, which are 1.6cd/A and 0.2 lm/W. The current-voltage characterization is shown in Figure 4.

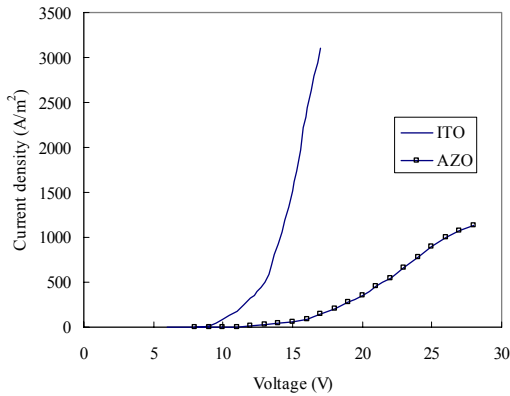


Figure 4. I-V characterization of OLED device with CuPc as HIL, fabricated on AZO and commercial ITO

As can be observed, the hole injection is the bottle neck for the device fabricated on AZO. Another hole injection layer, 4,4',4''-tris(N-3-methylphenyl-N phenyl-amino)-triphenylamine (MTDATA) was used for device fabrication. This hole injection material has been proved to greatly enhance the hole injection for OLED with ITO as the anode material [18,19].

The device configuration was optimized based on MTDATA, TPD and Alq₃ was, aim to acquire the highest device efficiency. Figure 5 shows both the current efficiency and power efficiency of OLED device on AZO and ITO. The current efficiency was as high as 3.7cd/A. This was even higher than that of the control device on commercial ITO. The power efficiency was 1.2lm/W, almost the same as that of the control device. Both efficiencies prove that the AZO is a good anode material, which can be competitive with commercial ITO.

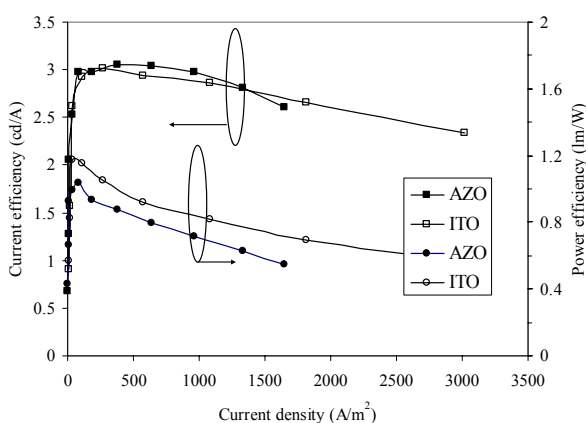


Figure 5. The efficiencies of OLED fabricated on AZO and ITO, in which MTDATA was used as HIL

With MTDATA as the hole injection layer, the device performance on AZO is greatly improved, and the efficiencies acquired is competitive with reported results of Alq₃ based OLED on ITO. This improvement of device performance should be attributed to the hole injection enhancement by MTDATA replacing CuPc, the I-V

characterization of OLED with MTDATA as HIL is shown in Figure 6.

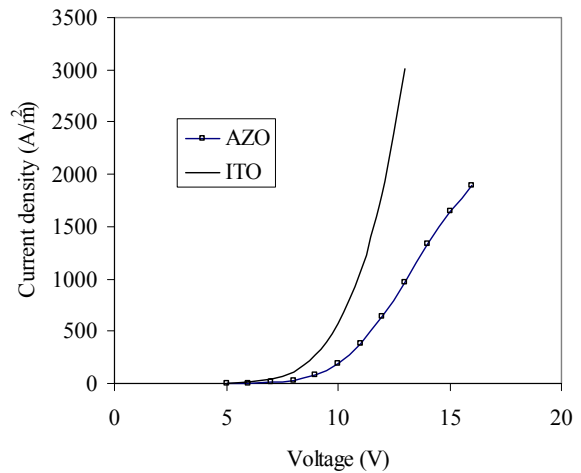


Figure 6. The I-V characterization of optimized OLED device with MTDATA as HIL

4. Conclusion

AZO thin films were successfully co-sputtered from two separate targets, Al and ZnO. The Al dopant concentration was adjusted by tuning the Al sputtering power set, and results show that the AZO resistivity is the lowest when the Al atomic concentration is 4.8%. AZO samples were grown both at room temperature and 300°C, and the transparency of the AZO thin film is better than that of commercial ITO.

Post annealing was done to reduce the AZO resistivity. For AZO samples grown at RM, post annealing at 500°C for 30min, significantly improved the conductivity. Results prove that the resistivity after annealing remained almost the same as the Al dopant concentration from 2.5% to 5%. For samples grown at 300°C, the annealing process ranging from 400°C to 600°C also reduced the AZO resistivity, but the results show that the AZO film with Al dopant concentration of 4.8% was still the lowest. The acquired lowest resistivity was $1.3 \times 10^{-3} \Omega \cdot \text{cm}$, with the Al concentration dopant of 4.8%.

With the co-sputtered AZO as the anode, OLED devices were fabricated. With CuPc as the HIL, the device performance was not competitive as that on ITO. With MTDATA as the HIL (replacing CuPc), the hole injection was significantly enhanced, and that proved that MTDATA is a better HIL matching with AZO anode. With an optimal device configuration, the OLED device based on MTDATA showed a similar or even higher efficiency, than that of the device on commercial ITO. The current efficiency was as high as 3.7cd/A. This was even higher than that of the control device on commercial ITO. The power efficiency was 1.2lm/W, almost the same as that of the control device.

In conclusion, the co-sputtered AZO shows very good optical transparency and conductivity. With co-sputtered AZO as the anode, the OLED device performance was also competitive with commercial ITO. The AZO is a very

promising anode material for OLED fabrication, with the advantages of low cost and low toxicity.

REFERENCES

1. J. M. Ting and B. S. Tsai, *Materials Chemistry and Physics*, 72 (2): 273-277 (2001).
2. F. J. Haug, Z. S. Geller, H. Zogg, A. N. Tiwari and C. Vignali, *Journal of Vacuum Science and Technology A-Vacuum Surface and Films*, 19 (1): 171-174 (2001).
3. J. M. Ting and B. S. Tsai, *Materials Chemistry and Physics*, 72 (2): 273-277 (2001).
4. M. Kon, P. K. Song, Y. Shigesato, P. Frach, A. Mizukami and K. Suzuki, *Jpn. J. Appl. Phys.*, Vol. 41, 814-819 (2002).
5. A. V. Singh and R. M. Mehra, N. Buthrath, A. Wakahara and A. Yoshida, *J. Appl. Phys.*, 90(11), 5661-5665 (2001).
6. J. Hu and R. G. Gordon, *J. Appl. Phys.*, 71, 880-884 (1992).
7. Radhouane Bel Hadj Tahar, Noureddine Bel Hadj Tahar, *J. Appl. Phys.*, Vol. 92, 4498-4501 (2002).
8. H. L. Hartnagel, A. L. Dawar, A. K. Jain, C. Jangadish, *Semiconducting Transparent Thin films*, IOP, (1995)
9. H. Kim, A. Piqué, J. S. Horwitz, H. Murata, Z. H. Kafafi, C. M. Gilmore and D. B. Chrisey, *Thin Solid Films*, 377-378, 798-802 (2000).
10. E. Fortunato, P. Nunes, A. Marques, D. Costa, H. Águas, I. Ferreira, M. E. V. Costa, M. H. Godinho, P. L. Almeida, J. P. Borges and R. Martins, *Surface and Coatings Technology*, 151-152, 247-251 (2002).
11. S. H. Jeong, J. W. Lee, S. B. Lee, J. H. Boo JH, *Thin Solid Films*, 435 (1-2): 78-82 (2003).
12. R. J. Hong, X. Jiang, B. Szyszka, V. Sittinger, A. Pflug, *Applied Physics Surface Science*, 207 (1-4): 341-350 (2003).
13. H. Kim, J. S. Horwitz, S. B. Qadri, D. B. Chrisey, *Thin Solid Films*, 420: 107-111 (2002).
14. G. J. Fang, D. J. Li, B. L. Yao *Vacuum*, 68 (4): 363-372 (2002).
15. G. J. Fang, D. J. Li and B. L. Yao, *Physica Status Solidi A-Applied Research*, 193 (1): 139-152 (2002).
16. J. Zhao, S. Xie, S. Han, Z. Yang, L. Ye, and T. Yang, 'Organic light-emitting diodes with AZO film as electrodes', *Synthetic Metals*, 114, 251-254 (2000).
17. C. F. Qiu, H. Y. Chen, M. Wong, H. S. Kwok, *IEEE Trans. Elec. Device*, 48 (9), 2131-2137 (2001).
18. L. S. Hung and C. H. Chen, *Material Science and Engineering R*, 39, 143-222 (2002).
19. N. von Malm, R. Schmechel and H. von Seggern, *Synthetic Metals*, 126(1), 87-95 (2002).