Investigations on silver incorporated RF sputtered ZnO thin films

Melda Francis1,2, Anu Kuruvilla1,2, P Martin Francis3 and M Lakshmi2

1Department of Physics, Christ College, Irinjalakkuda, University of Calicut, Kerala, India.
2Department of Physics, Mercy College, Palakkad, University of Calicut, Kerala, India.
3Department of Chemistry, St. Thomas’ College, Thrissur, University of Calicut, Kerala, India.

Email: blooms88@gmail.com

Abstract: In this work, ZnO thin films were fabricated using RF Magnetron Sputtering technique on ITO substrates. The operating parameters time of deposition, Argon working pressure, distance between target and substrate, oxygen pressure, RF power etc. were optimized so as to get good quality ZnO thin films. The prepared films were characterised using various techniques like XPS, SEM, EDS etc. It was observed that the sheet resistance of the pristine ZnO film was around 200 MΩcm−1 even when coated on ITO substrates. For device level application the resistance of the film must be low. Therefore silver was incorporated by sputtering, and it served the purpose of reducing the sheet resistance of pristine ZnO film. The Ag incorporated films were also characterised by the above mentioned techniques. Detailed compositional analysis was done using depth profiling method of XPS. Resistance measurements were also done in these samples. The sheet resistance decreased (from ~ 200 MΩcm−1) to a range of about 500 Ωcm−1 by silver incorporation.

1. INTRODUCTION

ZnO is being widely investigated in recent years owing to its exciting properties and multifunctional behaviour. ZnO is a wide band gap semiconductor which generally shows n-type conductivity. Optical band gap of this material is around 3.37eV [1] at room temperature and it has high excitonic energy (60meV) [1] which makes it a promising candidate in opto-electronics devices. Other properties include piezoelectric nature [2], high carrier mobility, transparency in visible range, luminescence, high stability at room temperature etc. ZnO finds applications in the field of solar cells, transparent conducting oxides, rubber manufacturing, gas sensors, cosmetics, medicines etc. ZnO thin films can be synthesized in a variety of methods which include sputtering [3], spray pyrolysis [4], Chemical Bath Deposition [5], sol-gel method spin coating [6] etc. It is also reported that the optical and electrical properties are greatly enhanced by doping ZnO with suitable impurities like Ag, Al, Co, Mn etc. Semiconductor industry is making use of these advantages for meeting specific requirements like tuning the bandgap, improving electrical properties, etc.

In this work, ZnO thin films were prepared by RF magnetron sputtering technique. Good quality ZnO thin films with excellent chemical and thermal stability can be fabricated through sputtering. The films were transparent but the sheet resistance was very high in the range of ~200 MΩcm−1. This is not desirable for electronic applications. Therefore, a silver layer is incorporated on the substrate before the deposition of ZnO thin film and the stacked structure is annealed. This procedure considerably reduced the sheet resistance to about 500 Ω cm−1.
2. EXPERIMENTAL

The RF sputtering system used in this work was procured from Hind High Vacuum (Model BC-300) with a provision of Mass Flow Controller (MFC) for the controlled supply of gas. ZnO target with 99.999% purity was purchased from Kurt J Lesker, UK, and the substrate used was thoroughly cleaned ITO. The sample chamber was evacuated to about $6.6 \times 10^{-6}$ mbar base pressure before admitting the sputtering gas. Argon was chosen as the sputtering gas for initiating plasma. Oxygen gas was also supplied at 1 SCCM pressure through MFC in order to eliminate the possibility of oxygen deficiency during formation of thin film. Deposition parameters were optimized to get good ZnO thin films. Sputtering was carried out without substrate heating, at RF power of 80 W. The working pressure was maintained at $5.3 \times 10^{-3}$ mbar and the optimised time of sputtering was 15 minutes. Distance between substrate and the target was optimised at 7cms. The ZnO film obtained was transparent and it was annealed at $180^\circ$C for 1 hour.

In order to reduce the resistivity of the pristine ZnO samples, a very thin layer of silver was sputtered on the substrate prior to ZnO deposition. The thickness of the silver layer was very less so that transparency of the ZnO films was not affected significantly. Sputtering parameters for silver deposition were chosen as follows: Duration of sputtering - 2 minutes, RF power - 25 W, working pressure - $7 \times 10^{-3}$ mbar. Here oxygen supply was avoided and controlled Argon gas was supplied through MFC at a pressure of 20 SCCM. Other parameters were maintained similar to that of ZnO deposition. After the deposition of Ag and ZnO, the samples were annealed and characterised systematically.

3. RESULTS AND DISCUSSIONS

Pristine and silver incorporated ZnO films were characterised morphologically using SEM imaging, chemically using EDS and XPS analysis and electrically using LCZ meter.

3.1 SEM Analysis

Morphology of the prepared samples were analysed with SEM (JEOL Model JSM - 6390LV Scanning Electron Microscope). The micrographs of ZnO films and Ag incorporated ZnO films are given in figure 1(a) and 1(b) respectively. SEM images showed that pristine ZnO has granular nature, while silver doped samples were uniform, continuous and dense. The average grain size of ZnO film was around 200 nm.

![Figure 1. SEM Images of the samples (a) ZO and (b) AZO films.](image-url)
3.2 EDS Analysis
EDS analysis was carried out along with SEM analysis for better understanding of the chemical composition of prepared samples. The EDS spectra of ZnO and Ag doped ZnO samples are given in figure 2 (a) and 2 (b) respectively. It is found that the ratio of concentration of Zn to O is approximately 1:1 which confirms that the stoichiometry of the prepared ZnO sample. In the Ag doped ZnO sample, a small reduction of oxygen concentration was observed which may be attributed to the presence of Ag which was deposited in the absence of oxygen. The Ag signal is absent in the spectrum of the ZnO sample as expected. The EDS spectrum of Ag doped ZnO shows only a small peak of Ag which confirms that it is present only in doping level.

![EDS spectra of the samples (a) ZO and (b) AZO films.](image)

3.3 XPS Analysis
The XPS spectra of the films were recorded using Thermo Scientific K-Alpha X- Ray Photoelectron Spectrometer. The depth profile of ZnO and Ag doped ZnO films are given in figure 3. The figures 3(a), 3(b) and 3(c) shows the Zn 2p, O 1s and Ag 3d scans of ZnO films while figures 3(d), 3(e) and 3(f) shows Zn 2p, O1s and Ag 3d scans of Ag doped ZnO films. Layer-wise details are investigated by re-plotting specific etch cycles such as surface layer, 1st etch cycle, 5th etch cycle and 10th etch cycle wherever necessary. In the depth-wise scan, oxygen 1s scan of both ZnO and Ag doped ZnO films was almost similar. There is no Ag 3d signal in ZnO film as silver was absent. Layer-wise re-plotting is done only for Zn 2p scan of ZnO (figure 4a), Zn 2p scan of silver doped ZnO (figure 4b) and Ag 3d scan of Ag doped ZnO (figure 4c).
Figure 3. XPS depth profiles of sample ZnO and Ag doped ZnO films. (a) Zn 2p scan (b) O 1s scan (c) Ag 3d scan respectively of ZnO film. (d) Zn 2p scan (e) O 1s scan (f) Ag 3d scan respectively of Ag doped ZnO film.

Depth profiling was done to get detailed knowledge of layer wise composition of the prepared samples. Adventitious carbon binding energy correction was given for all peaks at 284.6 eV. The detailed XPS analysis of the ZnO and Ag doped ZnO films are discussed separately in the following subsections.

3.3.1 XPS Analysis of ZnO films

In this film, Zn 2p peaks has significant split in spin orbit components and the corresponding binding energies of $2p_{3/2}$ and $2p_{1/2}$ are observed at 1044.2 eV and 1021.1 eV respectively in figure (3a) [7,8,11]. It is observed that intensity of the peaks decrease as we proceed with etch cycles, which in turn means that the thickness of the ZnO film is less compared to the Ag doped ZnO film. In the O 1s depth profile, given in figure (3b), two binding energy peaks were observed at 531.5 eV 529.9 eV for the surface layer [7,9,12]. The first one is not prominent and it is attributed the binding energy of adsorbed atmospheric oxygen while the second one is more intense and it corresponds to the binding energy of Zn-O bond. From Ag 3d depth profile shown in figure 3c, it is clear that Ag is totally absent in the ZnO film.
3.3.2 XPS Analysis of Ag doped ZnO films

The Zn 2p depth profile of Ag doped ZnO film is shown in figure 3d. The binding energy peaks of Zn - O bond is observed at 1044.6 eV and 1021.6 eV corresponding to 2p\(_{1/2}\) and 2p\(_{3/2}\) respectively. Oxygen 1s peak of atmospheric oxygen is observed at 531.3 eV and that corresponding to Zn-O bond at 530.3 eV (figure 3e). Ag 3d peaks also showed well defined splitting to 3d\(_{3/2}\) and 3d\(_{5/2}\) at binding energies 373.6 eV and 367.6 eV respectively [7, 10, 13]. Presence of Ag is found to decrease considerably towards the last etch cycles which indicates the diffusion of Ag to the ZnO surface layers.

![Figure 4](image_url)

**Figure 4.** Detailed cycles wise analysis of certain etch cycles of depth profiles (a) Zn 2p scan of ZnO film (b) Zn 2p scan of Ag doped ZnO film and (c) Ag 3d scan of Ag doped ZnO film.
3.4 Resistance Measurements
The sheet resistance of the ZnO and Ag doped ZnO samples was measured using HIOKI LCZ meter. The sheet resistance of the ZnO sample was around 200 MΩcm$^{-1}$. For thin film applications, especially for electronic and semiconductor applications, it is desirable to have very low sheet resistance. By introducing doping through very thin layer of sputtered silver, the sheet resistance reduced drastically to about 500 Ωcm$^{-1}$ without much loss in transparency of the film. Effect on sheet resistance with variation in duration of sputtering of silver is tabulated in Table 1. The same variation is graphically plotted in figure 5.

| Thin Film       | Doping time (minutes) | Measured sheet resistance (ohms per square cm) |
|-----------------|-----------------------|-----------------------------------------------|
| ZnO only        | -                     | ~200 M                                        |
| ZnO + Ag        | 1                     | 749.00                                        |
| ZnO + Ag        | 2                     | 638.94                                        |
| ZnO + Ag        | 3                     | 579.33                                        |

Table 1: Measured sheet resistances of ZnO and Ag doped ZnO films for various duration of silver deposition

![Figure 5. Variation of sheet resistance with various deposition times for silver sputtering.](image)

3.5 Optical Studies
Transmittance spectra were recorded using Intek UV- Vis spectrophotometer. Tauc plot was drawn plotting $h\nu$ along x axis and $(\alpha h\nu)^{2}$ along y axis from which band gap of the sample was obtained directly from the x intercept. Transmittance spectra and tauc plot (inset) of ZnO and Ag doped ZnO samples are given in figure (6a) and (6b) respectively. From the figures it is observed that there is no considerable decrease in the transparency of the sample on Ag doping. The band gap has slightly decreased from 3.21 eV to 3.17 eV and it can be attributed to the presence of impurity Ag level in the band structure.
Figure 6. Transmittance spectra and tauc plot (inset) of samples. (a) ZnO and (b) Ag doped ZnO

4. CONCLUSIONS

ZnO and Ag incorporated ZnO thin films were deposited using RF magnetron sputtering technique on ITO substrates. The chemical composition was studied using EDS and XPS analysis. The EDS analysis confirmed that the ratio of atomic concentration of Zn and O is 1:1. XPS depth profile was recorded for both the samples. Detailed investigation on chemical composition was carried out by re-plotting the etch cycle separately. The XPS analysis highlights the uniform presence of Zn, O and Ag and absence of any significant impurities. The sheet resistance was measured for ZnO and Ag incorporated ZnO with different duration of Ag sputtering. It was observed that the resistance reduced from 200 $\Omega \cdot cm$ to 500 $\Omega \cdot cm$ on incorporation of silver.

ACKNOWLEDGEMENTS

The authors acknowledge DST - FIST for providing financial support for procuring RF Sputtering System. The authors are thankful to Dr. Sadasivan Shaji and Dr. Bindu.K, Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León, Mexico for helping with X-ray Photoelectron Spectroscopy analysis. The services rendered by STIC, CUSAT, Cochin for the analytical facilities of SEM and EDS are also acknowledged.

REFERENCES

[1] D. EzgFr, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dog`an, V. Avrutin, S.-J. Cho and H. Morko A 2005, J. Appl. Phys., 98, 041 301.
[2] David A. Scrymgeour and Julia W. P. Hsu 2008, Nano Lett., 8, 8.
[3] Wei Gao and Zhengwei Li 2004, Ceramics International, 30, 7, 1155-1159.
[4] SA Studenikin, N Golego and M Cocivera 1998, Journal of Applied physics, 84, 2287.
[5] P. B. Taunk, D. P. Bisen, R.K.Tamrakar, Nootan Rathor 2015, Karbala International Journal of Modern Science, 1, 159-165.
[6] Nilam B Patil, Amol R.Nimbalkar and Maruti G.Patil 2018, Materials Science and Engineering B, 227, 53-60.
[7] John F. Moulder, William F. Stickle, Peter E.`Sobol, Kennethlf D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corporation, 1999
[8] https://xpssimplified.com/elements/zinc.php
[9] https://xpssimplified.com/elements/oxygen.php
[10] https://xpssimplified.com/elements/silver.php
[11] https://srdata.nist.gov/xps/EngElmSrchQuery.aspx?ETYPE=PE&CSOpt=Retri_ex_dat&Elm=Zn
[12] https://srdata.nist.gov/xps/EngElmSrchQuery.aspx?ETYPE=PE&CSOpt=Retri_ex_dat&Elm=O
[13] https://srdata.nist.gov/xps/EngElmSrchQuery.aspx?ETYPE=PE&CSOpt=Retri_ex_dat&Elm=Ag