ZnO:Cu Thin Films and p–n Homojunctions Grown by Electrochemical Deposition

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Abstract. ZnO doped with Cu thin films were deposited on indium tin oxide coated glass substrates by electrodeposition using an electrolyte consisting of Cu and Zn perchlorates dissolved in dimethylsulfoxide. The Cu/Zn ratio measured in the thin films is about twice the Cu/Zn ratio present in the starting electrolyte. Irrespective of the Cu content, all the ZnO:Cu films exhibit a hexagonal wurtzite structure typical of ZnO with a preferential orientation along (002) direction. The p-type behaviour of ZnO:Cu films is inferred from the change in the sign of the photocurrent observed for Cu concentrations greater than 2%. Furthermore, a p-n homojunction with a rectifying factor ~22 were prepared by electrodepositing of ZnO/ZnO:Cu layers.

Keywords: ZnO, p-type, electrodeposition.
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INTRODUCTION

Growth of p-type ZnO with low-resistivity has so far been found challenging and seen by some as controversial [1]. However, credible results of blue-green light emission have been reported with a p-ZnO/n-SiC device fabricated by molecular beam epitaxy where Cu has been the p-type dopant for ZnO [2]. A reliable low-cost fabrication of p-type ZnO will be a significant step in realizing the full potential of ZnO. Electrodeposition (ED) is low-cost process compared to conventional deposition techniques that can be used to deposit ZnO, as we have demonstrated recently with related materials [3, 4]. In the present work, p-type ZnO thin films were synthesized electrochemically by incorporating Cu in ZnO, and p-n homojunctions based on ZnO/ZnO:Cu were also fabricated by the same method.

EXPERIMENTAL DETAILS

ZnO:Cu thin films have been deposited on indium doped tin oxide (ITO) coated glass substrates by ED using an electrolyte consisting of Cu and Zn perchlorates dissolved in dimethyl sulfoxide (DMSO), where 0.1 M Potassium perchlorate [$KClO_4$] was used as a supporting electrolyte. The electrolyte solution was saturated with O_2 by bubbling molecular O_2 into the electrochemical cell. The [Cu]/[Zn] ratio of the starting solution was varied between 0 and 4% maintaining the sum of Cu and Zn cations at 25 mM. All chemicals were A.C.S. reagents, supplied by Sigma Aldrich and used without previous purification

RESULTS AND DISCUSSIONS

The composition of ZnO:Cu thin films was determined by Energy Dispersive Spectroscopy (EDS). The Cu/Zn ratio in the solid films was found to be twice that present in the starting electrolyte, which is related to the higher diffusion coefficient of Cu compared with Zn in DMSO.

Regardless of the different Cu content, ZnO:Cu films exhibit a hexagonal wurtzite structure typical of ZnO with a preferential orientation along (002) direction. However, a small shift was observed for the (002) peak position, which suggests the substitution of Cu in Zn sites. The wurtzite structure is maintained for samples deposited from electrolytes containing a Cu/Zn ratio below 4%. Higher Cu contents degrade the

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crystallinity of the films and the wurtzite structure is no longer observed.

Figure 1 shows the RT micro-Raman spectra of ZnO:Cu films, recorded on a Jobin-Yvon T64000 spectrometer in the frequency range of 200-800 cm^{-1}, using the 488 nm excitation line of an Ar+ laser and a backscattering geometry. The presence of the non-polar optical phonon (E2-high) mode at 437 cm^{-1} in the spectra confirms the ZnO structure with small crystallites. As can be seen, with doping, the E2 (high) mode widens and the A1(E1) mode increases in intensity and shifts towards lower wave numbers. Interestingly, we see the presence in all samples of the peak at 327 cm^{-1} , although well resolved for sample ZnO:Cu (1%) which is assigned to the second order Raman scattering arising from zone-boundary phonons E2(M) of ZnO. The normalized intensity ratio E2/A1 decreases strongly from approximately 0.2 (for ZnO, ZnO:Cu(1%) and ZnO:Cu(2%)) to 0.03 for ZnO:Cu (4%).

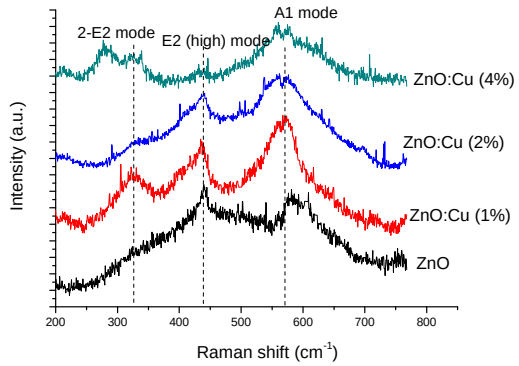

FIGURE 1. Micro-Raman spectra for ZnO:Cu electrodeposited films.

The conductivity type of ZnO:Cu films were evaluated using a photoelectrochemical (PEC) method. In particular, the sign of the photocurrent is the key parameter to determine the type of conductivity. The photocurrent of ZnO:Cu films registered in a three electrode configuration using KCl electrolyte confirms the films are n-type for a Cu/Zn ratio below 2% and p-type as this ratio surpasses 2%. The p-type character of ZnO:Cu was further assessed for Zn:Cu ratios 100:2 and higher. A p-n homojunction diode was fabricated by depositing a ZnO:Cu layer on top of an undoped ZnO layer. As the ZnO layer is intrinsically n-type, the rectifying behaviour of the diode further confirms the p-type doping. The I–V characteristics of such electrochemically prepared ZnO p-n diode is shown in Figure 2. In the forward bias, two distinct regions are observed. At low voltages, the current (I) is linear with the applied voltage (V) (ohmic behaviour) and at higher voltages $I \alpha V^2$, indicating the domination of space–charge limited current. This I–V characteristic follows the standard diode equation for forward bias below 0.35 V as given by, $I = I_o(\exp(qV/nkT)-1)$, where n is the ideality factor, q is the electronic charge, k is the Boltzmann constant and T is the temperature. Rectification factors for the best ITO/ZnO/ZnO:Cu/Au diode were 3 and 22 for ±1 and ±2 V, respectively.

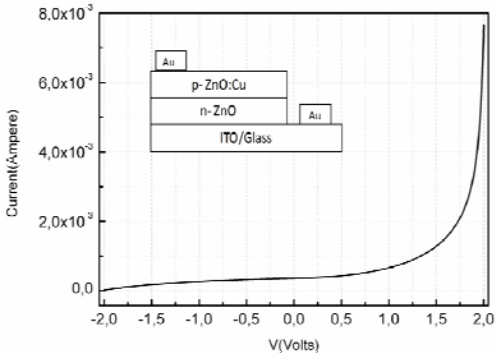

FIGURE 2. I-V curve of a ZnO/ZnO:Cu homojunction.

CONCLUSIONS

Cu-doped ZnO thin films were synthesized by an electrochemical approach. The Cu/Zn content in the films was found to be proportional to the Cu/Zn cation ratio in the starting electrolyte solution. A transition between n-type to p-type behaviour was observed in ZnO:Cu films as the Cu/Zn ratio surpasses 2%. The p-type character of the ZnO:Cu films allows the fabrication of p–n homojunctions by subsequent electrodeposition of two ZnO/ZnO:Cu layers.

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REFERENCES

1. M. D. McCluskey and S. J. Jokela, J. Appl. Phys. **106**, 071101 (1-13) (2009).
2. J. B. Kim, D. Byun, S. Y. Ie, D. H. Park, W. K. Choi, J-W. Choi and B. Angadi, Semicond. Sci. Technol. **23** 095004 (1-6) (2008).
3. M. Tortosa, M. Mollar, B. Marí, J. Crystal Growth **304**, 97-102 (2007).
4. M. Tortosa, M. Mollar, B. Marí, F. Lloret, J. Appl. Phys. **104**, 033910 (1-5) (2008).