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Work Function Engineering of Functionally Graded $ZnO+Ga_2O_3$ Thin Film for Solar Cell and Organic Light Emitting Diodes Applications

Yong-Taeg Oh, Won Song, Seok-Eui Choi, Bo-Ra Koo, and Dong-Chan Shin

***Abstract*—**$ZnO+Ga_2O_3$ functionally graded thin films (FGTFs) were examined for their potential use as Solar cell and organic light emitting diodes (OLEDs). FGTF transparent conducting oxides (TCO) were fabricated by combinatorial RF magnetron sputtering. The composition gradient was controlled up to 10% by changing the plasma power of the two sputter guns. A Ga_2O_3+ZnO graded region was placed on the top layer of ZnO. The FGTFs showed up to 80% transmittance. Their surface resistances were reduced to < 10% by increasing the Ga_2O_3: pure ZnO ratio in the TCO. The FGTFs' work functions could be controlled within a range of 0.18 eV. The controlled work function is a very promising technology because it reduces the contact resistance between the anode and Hall transport layers of OLED and solar cell devices**.**

***Keywords*—**Work Function, TCO, Functionally Graded Thin Films, Resistance, Transmittance.

I. INTRODUCTION

THE considerable research on ZnO thin films has sought their application as transparent electrodes and channel materials in OLEDs, LCDs, solar cell and transparent TFTs on account of their good crystallinity at low temperatures and low manufacturing cost [1-2]. However, their electrical properties can be changed considerably by altering the stoichiometric ratio of Zn and O in the thin film. Many researchers have added Al, Ga, In, B and P dopants to ZnO thin films in an attempt to overcome this disadvantage and enhance the charge transfer characteristics of the OLED devices [3-8]. Recently, Heo *et al.* added B and P ions to ZnO and AZO thin films [9-11]. They could control the work function and enhance the charge transfer characteristics between the transparent electrode and hole transfer layer of the OLED device but the added ions increased the thin film's resistance. In this study, transparent functionally graded thin films (FGTFs) with a composition gradient of Ga_2O_3 in ZnO was deposited using combinatorial RF magnetron sputtering to obtain a low resistance and controlled work function. The electrical and optical properties, work functions and structures were examined to the reveal potential applications of FGTFs in OLED devices.

II. EXPERIMENTAL CONDITIONS

ZnO (99.9 %) and Ga_2O_3 (99.99 %) were used as targets. Corning 1737 glass was used as the substrate and cleaned using acetone, ethanol and deionized (D.I) water before use. The FGTFs were deposited at room temperature under 0.14 Pa Ar gas. The substrate to target distance was 90 mm. The RF power to the ZnO target was maintained at 250 W while that of Ga_2O_3 were 100 W, 75 W and 50 W. Fig. 1 shows the combinatorial RF magnetron sputtering system. The thin films deposited on three positions are denoted as P1, P2 and P3. Pure ZnO thin films deposited at the three positions are denoted as Z1, Z2, Z3 and Z4 and FGTFs are denoted as F1, F2, F3 and F4.

Sheet resistances were measured using a four-point probe (CMT-SR 1000N, ChangMin Tech.). Resistivities, carrier concentrations and Hall mobilities were investigated using a Hall Effect measurement system (HL5500PC, Accent Opt. Tech.). The transparencies of the FGTFs were measured between 300 - 800 nm by UV-Vis-Nir spectroscopy (Hitach, U-1400). Their work functions were measured using a Kelvin probe system (KT6500, McAllister Technical Services).

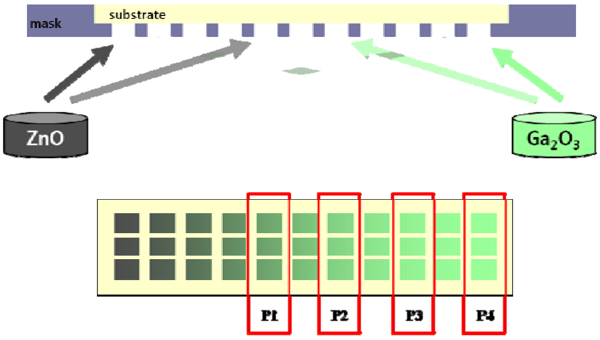

Fig. 1 A schematic diagram of combinatorial sputtering system

D. C. Shin is with the Department of Advanced Materials Engineering, Chosun University,375 Seosuk-dong, Dong-gu, Gwangju, 501-759, Korea (corresponding author to provide phone: +82-62-230-7191; fax: +82-62-236-3775; e-mail: dcshin@chosun.ac.kr).

W. Song was with the Department of Advanced Materials Engineering, Chosun University,375 Seosuk-dong, Dong-gu, Gwangju, 501-759, Korea (e-mail: gainax9999@naver.com).

S. E. Choi was with LED & OLED Research Center, Hanyoung Eng. Co. Ltd, Korea (e-mail: eui-op@nate.com).

B. R. Koo was with the Department of Advanced Materials Engineering, Chosun University,375 Seosuk-dong, Dong-gu, Gwangju, 501-759, Korea (e-mail: koobora88@gmail.net).

Y. T. Oh is with the Department of Advanced Materials Engineering, Chosun University,375 Seosuk-dong, Dong-gu, Gwangju, 501-759, Korea (e-mail: yto02@chosun.ac.kr).

III. RESULT AND DISCUSSION

Fig. 2 shows the electrical properties of the three specimens by Hall Effect measurements. In Fig. 2(a), Z1 and Z2 showed resistivities of 8.36×10^{-2} Ωcm and 3.34×10^{-2} Ωcm, respectively, whereas Z3 showed insulating characteristics. Among the FGTF TCO, F3 showed the lowest resistivity of 2.4×10^{-3} Ωcm.

Fig. 2(b) shows mobilities and carrier concentrations. All specimens showed only n-type characteristics. The Z1 specimen showed a higher mobility and low carrier concentration than Z2. This tendency is typical of intrinsic semiconductors. On the other hand, the mobilities of FGTFs increased gradually from F1 to F3. The carrier concentration also increased from 1.02×10^{19} cm^{-3} in F1 to 1.25×10^{20} cm^{-3} in F3. More interstitial Zn can be formed when Ga ions occupy Zn sites. The electrical properties of FGTFs are similar to those reported by S. B Zhang *et al.*[12], who suggested that Zn interstitials are the major carriers in ZnO. The higher mobility and carrier concentration of F3 resulted in the lowest resistivity.

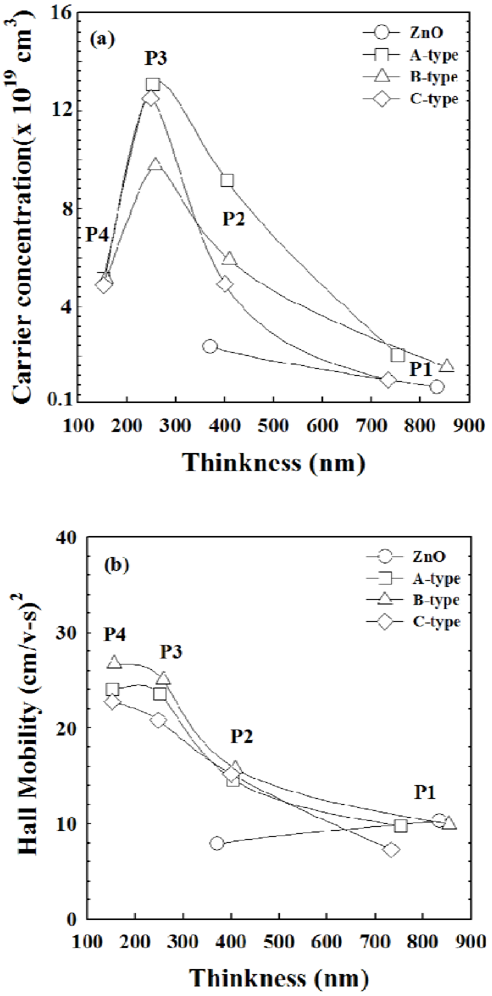

Fig. 2 Lattice parameter comparison between (111) plane of zinc blende structure of ZnS, (0001) plane of wurtzite structure of CdS, and (112) plane of chalcopyrite structure of CIGS

Fig. 3 shows the transmittances of pure ZnO and the FGTFs. All films showed > 80 % transmittance. Pure ZnO showed a blue shift from 2.4 eV for Z1 to 3.04 eV for Z3. The FGTFs of ZnO also showed a similar blue shift.

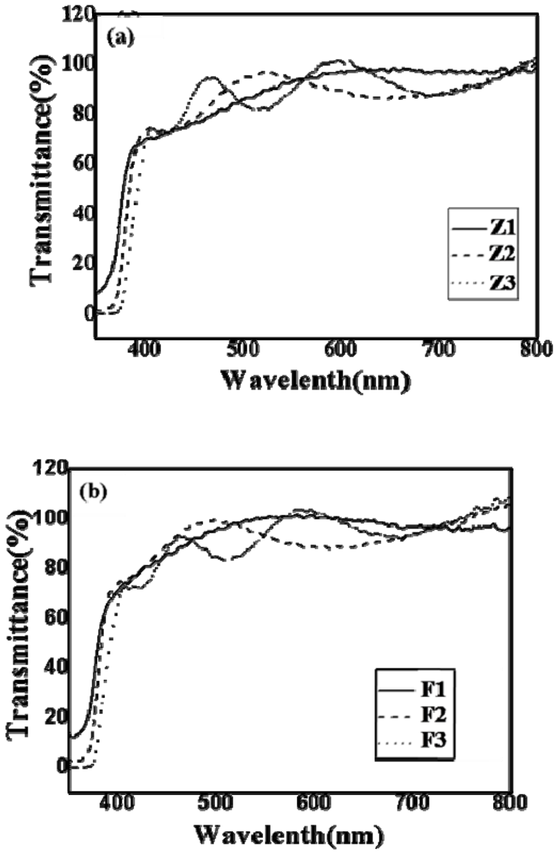

Fig. 3 Transmittances of (a) pure ZnO and (b) FGTF TCO deposited by combinatorial RF magnetron sputtering

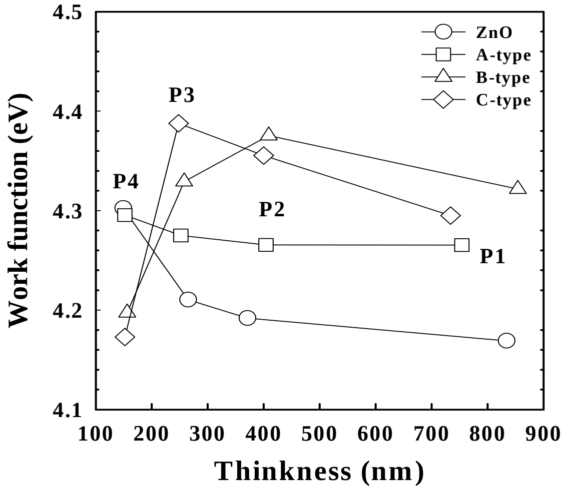

Fig. 4 Work function variation of pure and FGTF ZnO. Work function was evaluated by Kelvin probe

Fig. 4 shows the work functions of pure ZnO and the FGTFs measured by a Kelvin probe. All the FGTFs showed higher work functions than pure the ZnO. Among these, F3 had a work function of 4.39 eV, which is 0.18 eV higher than that of Z3. The increased work functions of the FGTFs can be explained by their lower Fermi levels. ZnO is an n-type semiconductor [9-11,13-14] When it is doped with Ga ions, the number of n-type defects will increase, as shown in Fig. 3. The donor defects of ZnO are oxygen vacancies and Zn interstitials. Ga doping can increase the number of Zn interstitials and decrease the number of oxygen vacancies. It can also lower the Fermi level because the Zn interstitials are deep level defects compared with the oxygen vacancies [10,13-14].

IV. SUMMARY

Ga ion graded FGTFs were fabricated by combinatorial RF magnetron sputtering to optimize their electrical and optical properties and work functions when compared with ZnO bare TCO to enhance their applicability in OLED devices. When the ZnO target to substrate distance was increased, the percentage of amorphous phase decreased and the crystallinity improved. The resistivity of F3 was lowest at 2.4×10^{-3} Ωcm. Its work function was 0.18 eV higher than that of pure ZnO. These FGTFs might be promising candidates for TCOs in OLED devices due to their low resistivities, high transmittances and higher work functions.

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