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An investigation on hysteresis process of ZnO film deposition and changes of surface morphology and wettability

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ABSTRACT

Plasma Optical Emission Spectroscopy was employed to investigate hysteresis process of reactive sputtering with high purity Zn target in the presence of Ar plus O_2 plasma. An optimal working point was obtained through analyzing hysteretic curve in order to deposit high quality ZnO film. Scanning Electron Microscope was used to characterize effects of various O_2 flow rate on surface crystal structure of samples. The SEM results indicate that the structure of ZnO film is strongly dependent on O_2 flow rate at constant pressure and power. Specially, At 1.6 sccm O_2 flow rate, the sample with best crystallite structure has been observed. Energy-dispersive X-ray Spectroscopy also demonstrates the relationship between the chemical compositions of ZnO films and O_2 flow rate. The film to 1.6 sccm O_2 shows the optimal atom ratio of Zn to O and the mass ratio of Zn to O. The water contact angle measurement also shows various O_2 flow rate strongly affects wettability.

1. Introduction

Recently, many groups are focusing on zinc oxide film due to its high exciting binding energy (60 meV), interesting piezoelectric and ferroelectric properties, high light transmission, and potential applications in UV emitters, detectors, surface acoustic wave (SAW), and even transparent electrodes [1–11]. A difficulty in deposition a high quality ZnO film by reactive magnetron sputtering is how to control nucleation and growth process [1,5–7]. Target poisoning and shift in deposition condition result in poor film quality, even operation failure. Despite extensive studies [1–11], a detailed understanding of hysteresis phenomenon in reactive sputtering for ZnO film interactions with crystal structure is only beginning to emerge. Especially, an optimal working point (operating condition) should be discerned prior to studying process control. We report here results of Zn (472 nm) spectrum based hysteresis curve measured by optical emission spectroscopy (OES) and the effect of O_2 flow rate on surface morphology, atom ratio and wettability of ZnO film. Un-doped ZnO samples deposited by DC reactive magnetron sputtering at various O_2 mass flow rate were characterized by SEM, EDS and water contact angle measurement. The data demonstrate a relationship between O_2 mass flow rate and ZnO film properties and an optimal working point has been observed.

2. Experiment

ZnO samples were deposited on glass substrates (10×10 mm^2) in a commercial DC magnetron sputtering system with Zn target (99.99%) at room temperature. The chamber was evacuated down to 6.7×10^{-4} Pa by a molecular pump backed with a rotary pump prior to introduction of Ar (99.999%) and O_2 (99.999%) controlled by MFC (SEVENSTAR, CHINA). The distance from target to substrate was kept at constant 60 mm. Hysteresis process was performed through target poisoning operation and the hysteresis curves were monitored by a Mini-Optical Fiber Spectrometer (EPP2000, 190–110 nm, resolution 0.1 nm, Stellarnet, USA). The surface morphology of samples was characterized by SEM (SSX-550, amplification factor 300000, accelerating voltage 30 kV, resolution 3.5 nm, Shimadzsu, Japan) with Energy Dispersive Spectrometer (EDS). Water contact angle measurement was carried out with a Contact Angle Meter SL200B instrument (resolution 0.01°, Solon Technol. Sci. Co., Ltd., USA).

3. Results and discussions

Plasma emission spectra [12,13] at 5 Pa pressure, and Ar (10 sccm)/O_2 (2 sccm) mixture are shown in Fig. 1. The observed relatively strong Zn lines include the atom Zn (472 nm, 481 nm, 636 nm), without desired Zn (468 nm, 333.5 nm) and Zn ion-related emissions due to different operating condition [12,13]. However, only these two Zn lines (472 nm, 481 nm) are enough to subsequent study of hysteresis curve owing to their relatively higher intensities (>150 arbitrary unit) [12–14]. Relatively more Ar lines (750.5 nm, 751.5 nm, 763 nm, et al.)

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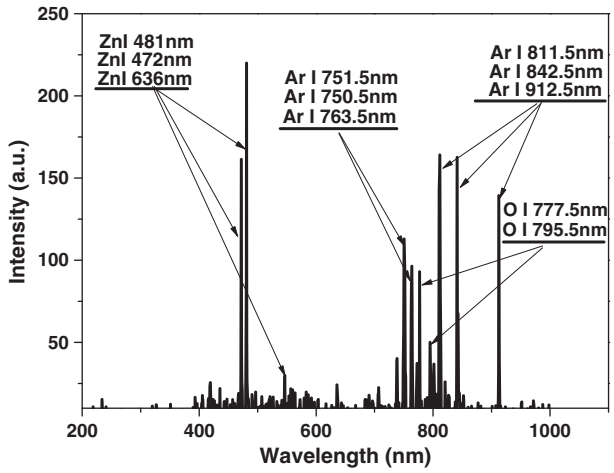

Fig. 1. Optical emission spectral of Ar (10 sccm)/O_2 (2 sccm) plasma with Zn target.

have been discerned here indicating that target sputtering can be maintained stably. The vital O_2 lines O (777.5 nm, 795.5 nm) [12,13] have also been detected in spite of relatively weak in intensities. These O_2 line finding also indicates that reactive O particles have presented in plasma predicting that ZnO-like component will be ascertained on samples after subsequent film deposition [13]. The OES spectra evolution apparently impacting on features of ZnO films upon exposure to such plasma [1,12,13] has also been investigated by this work in detail. The Zn lines evolutions as functions of discharge power, pressure and O_2 mass flow rate and changes in target voltage are shown in Fig. 2, respectively. For Zn (472 nm,481 nm), the changes in intensity are linearly dependent on target power (30–140 W) (Fig. 2(a)) showing that more Zn particles have been sputtered upon increasing target power.100 W power was determined finally according to both requiring high deposition rate and system safety [12]. Additionally, the data reported here demonstrate that the change in pressure can also affect emission of Zn (472 nm) for various Ar flow rate (2–20 sccm) as shown in Fig. 2 (b). And the data in Fig. 2(b) further indicates that a peak with a maximum at about 5 Pa apparently presents in curves and the curve for 10 sccm Ar flow exhibits highest intensity. So these OES data predicts a highest sputtering yield in the operating condition of around 5 Pa, 10 sccm Ar flow rate, and 100 W power. However, high deposition rate does not mean high quality ZnO film and so detailed experiments on Zn spectral evolution were performed to discover optimal working parameters. At 5 Pa pressure, 10 sccm Ar flow rate and 100 W power, the effect changes in O_2 flow rate (0–3.5 sccm) on Zn (472 nm) is shown in Fig. 2(c). The plot indicates that the Zn (472 nm) initially decreases (square in Fig. 2(c)) upon gradually increasing O_2 (0–3.5 sccm) and then subsequently increases (circle in Fig. 2(c), 3.5–0 sccm). The two curves can be partitioned into three regions named after metallic, transition and compound sputtering region, respectively [5–11]. The metallic sputtering region in which the Zn (472 nm) intensity slightly reduces linearly down to about 580 arbitrary unit upon O_2 firstly increasing from 0 to around1.4 sccm indicates high sputtering yield and plenty of Zn particles in plasma due to

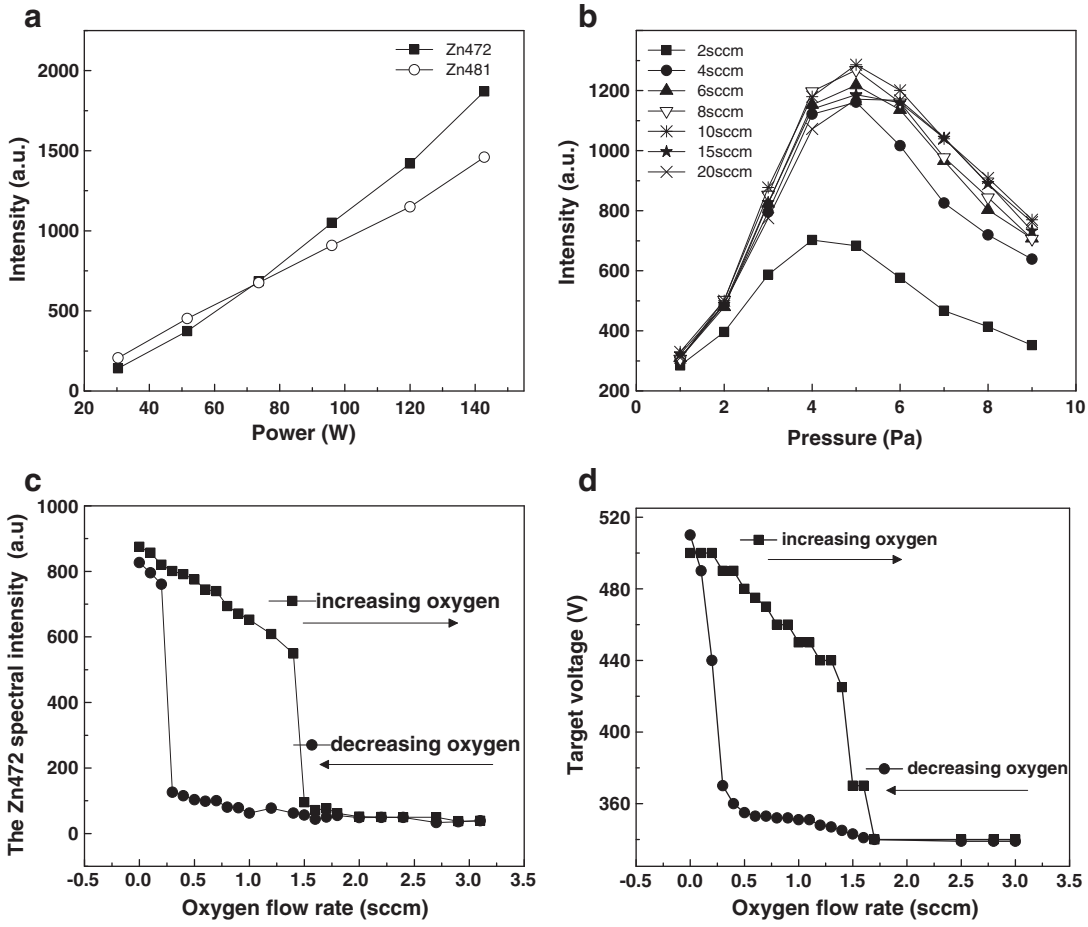

Fig. 2. Evolutions of Zn Spectral intensity and target voltage.