Deposition of ZnO film by high power impulse magnetron sputtering (HiPIMS)

L. YANG, H. Zhang, Q. Chen and H. Zhang

Laboratory of Plasma Physics and Materials, Beijing Institute of Graphic Communication, Beijing, PR China

Abstract: ZnO films with c-axis preferential orientation were deposited by high power impulse magnetron sputtering (HiPIMS). The role of inductively coupled plasma (ICP) on the characters of ZnO films has been investigated by XRD, AFM and EDS. Only (002) peak was observed in the XRD patterns. Furthermore, Langmuir probe and optical emission spectrum (OES) was applied to diagnostics the sputtering process.

Keywords: Plasma diagnostics, HiPIMS, film, ZnO, Langmuir probe

1. Background

With the characterization of wide band gap of 3.37 eV and large exciting binding energy of 60 meV, ZnO has been regarded as one of the most promising candidates for the next generation of ultra-violet light-emitting diodes (LED) and laser diodes (LD) [1,2]. However, it is critical to prepare high crystal quality ZnO thin film for the foundation of investigating and applying. At present, reactive magnetron sputtering (MS) is one of important deposition techniques for oxide or nitride preparations. However, ZnO film deposited by MS usually had low crystalline quality and needed a high substrate temperature. In present work, we proposed inductively coupled plasma (ICP) assisted high power impulse magnetron sputtering (HiPIMS) to prepare high crystal quality ZnO film at room temperature. The ICP has been used in MS to increase the fraction of the ionized sputtered species for tuning the film properties. The role of ICP on ZnO film quality was explored in detail. Furthermore, Langmuir probe and optical emission spectrum (OES) were applied to diagnostics the sputtering process.

2. Experimental setup and methods

The deposition of ZnO thin film was carried out in an ICP assisted HiPIMS system. The ICP was equipped above the target, and the substrate was located right above the ICP coils. The Zn (99.9999 % in purity) target was employed as Zn source and the oxygen gas as O source. The diameter of the target was 95 mm. Before deposition, the glass substrates were cleaned in ultrasonic bath with de-ionized water, ethanol and acetone for 15 minutes respectively, and dried by nitrogen (99.99 % in purity) stream before mounted in the chamber. The base pressure of the chamber was < 2×10^{-3} Pa, and work pressure was 0.5 Pa. The distance between the target and substrate was approximately 15 cm. Before ZnO growth, the target was cleaned at 700 V, 400 Hz, 50 μs of pulse width and 1.3 Pa pressure for 10 min. When ZnO depositing, the mixture gas of argon and oxygen was introduced into the chamber through mass flow meter control (MFC) and kept the work pressure at 0.5 Pa. The power of ICP was set at 100 W. The OES were used to analyse the plasma feature with ICP. The frequency and pulse width of power supply were set at 200 Hz and 50 μs, respectively. The Langmuir single probe was used to determine the variation of plasma electron temperature and density with different voltages and air pressure. Probe diameter was 0.195 mm and was placed on the substrate surface.

3. Results and discussion

ZnO films could be easily deposited in HiPIMS system with or without ICP. Fig.1 shows the x-ray diffraction (XRD) patterns of the ZnO films. One can see that when ICP was 100 W, only one diffraction peak of ZnO was observed. It is preferential orientation crystal in wurtzite structure (36-1451) (002). When the film was deposited without ICP, there were three diffraction peaks corresponded to (100), (002), and (101) in the pattern, which indicated that it was a Polycrystalline ZnO. It means that the ZnO films with ICP possessed better crystal quality than ones without ICP. Due to the Zn and O atoms got extra power from ICP and these atoms could migrate more quickly among the substrate surface. Therefore, high quality crystal ZnO thin film could be deposited with the assistant of ICP.

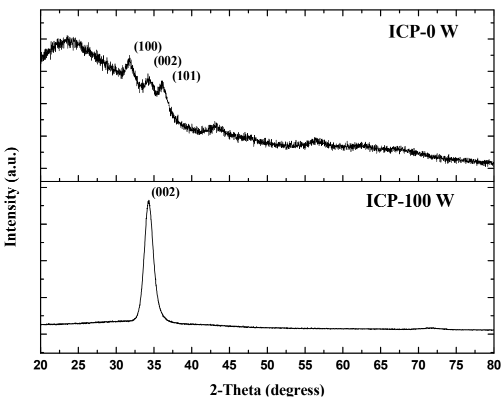

Fig.1. XRD of ZnO films deposited at 0 W and 100 W of ICP, respectively.

According to OES results, Table 1 shows that the O and O/Zn were increased along with the oxygen flow rate, which meant more oxygen atom was generated at higher O_2 flow rate. The deterioration of crystal quality of ZnO at high oxygen flow rate might result from the formation of native defect, such as V_{Zn} and O_i, in O-rich condition [3] or the decreasing of mean energy of O atoms. When we increased the sputtering power by the voltage, varying from 900 to 1100 V, to increase the energy of O atom, the peak intensity was increasing and peak width at half height of (002) was narrower when voltage was over 900 V, as showed in the Table 2.

Table 1. The intensities of Zn, O, O/Zn and peak width at half height at different oxygen flows.

Peak width at half height	O_2 （sccm）	Zn (747.87 nm)	O (777.17 nm)	O/Zn
0.92	10	37.52	15.14	0.40
0.83	20	74.01	53.54	0.72
0.90	30	94.62	85.07	0.90
0.84	40	120.32	125.00	1.04

Experiment parameter：900 V，200 Hz，50 μs，Ar-80 sccm，0.5 Pa，ICP-100W

Table 2. The intensities of Zn, O, O/Zn and peak width at half height at different voltages.

Peak width at half height	Voltage （V）	Zn (747.87 nm)	O (777.17 nm)	O/Zn
0.90	900	115.77	110.33	0.95
0.74	1000	147.62	122.04	0.83
0.63	1100	119.39	94.52	0.79

Fig. 2 is the variation curve of electron temperature and density with applied voltage. It can be seen that the electron temperature and density increase with the applied voltages, the electron temperature of substrate surface is around 2 eV, and the electron density is 10^{16} m^{-3}. Here the electron temperature and electron density are relatively not very high, since the general high-power magnetron sputtering is in the 10^{18} m^{-3} order of magnitude. Fig. 3 shows variation curve of the electron temperature and electron density with air pressure. The electron temperature and density have a similar trend, with the increase of air pressure, the electron temperature and density rise first and then decrease, which is different from the results obtained by other researchers. Cloud A et al [4] demonstrated that the plasma electron density will increase and the plasma electron temperature decrease with the increase of air pressure.

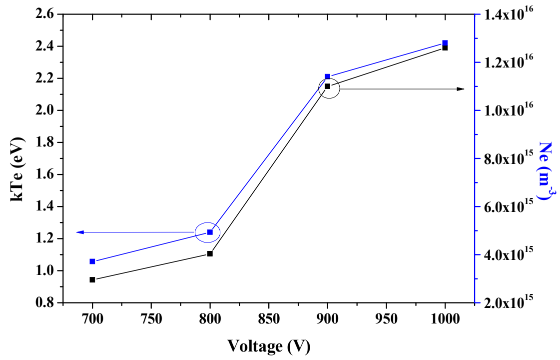

Fig. 2. Variations of electron temperature and electron density as function of voltage.

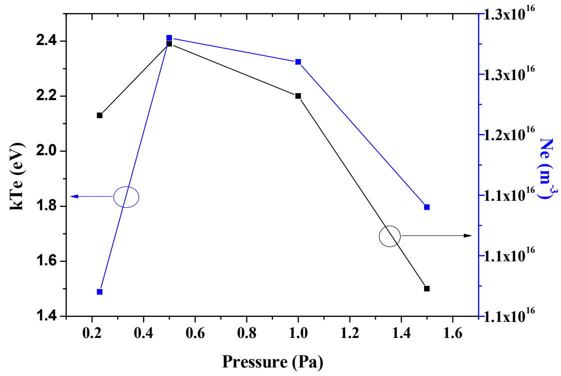

Fig. 3. Variations of electron temperature and electron density as function of gas pressure.

4. Conclusions

In summary, an inductively coupled plasma (ICP) assisted HiPIMS to deposit high quality crystal ZnO films. It was found that the crystal quality was greatly improved with ICP. We concluded that the ICP could improve the energy and number of oxygen atom, resulting in the better crystal quality. Furthermore, the sputtering process and plasma electron temperature and density were diagnosed by OES and Langmuir probe.

5. References

[1] Tang Z K, Wong G K L, Yu P, et al. Applied Physics Letters, **72**, 3270 (1998).

[2] Look D C. Materials Science and Engineering: B, **80**, 383-387 (2001).

[3] Chavillon B, Cario L, Renaud A, et al. Journal of the American Chemical Socie, **134**, 464-470 (2012).

[4] Cloud A, Jung S, Meng L. Journal of Vacuum Science & Technology A-Vacuum Surfaces And Films, **29**, 011024 (2011).