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Effects of Ion-Bombardment-Assist and High Temperature on Growth of Zinc Oxide Films by Microwave Excited High Density Plasma Enhanced MOCVD

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1. Introduction

Radical reaction based semiconductor manufacturing has been applied to silicon device processes using microwave excited high-density plasma with very low electron temperatures. The reactivity of the radical itself such as oxygen radicals and NH-radicals enables the formation of high quality films at low temperatures [1-2].

Zinc oxide (ZnO) is a wide-band-gap semiconductor with great potential for a variety of commercial applications in short-wavelength optoelectronic devices. It is an extensively studied transparent conductive film that is a valid alternative to indium tin oxide. High quality ZnO film formation is required, as some papers have recently reported [3-4]. Metal organic chemical vapor deposition (MOCVD) is a suitable technique for industrial mass production and is frequently employed for the growth of ZnO films [5-6].

We applied radical based semiconductor manufacturing to the ZnO growth; it showed that active species of plasma are effective for the formation of film [7]. In this paper, we demonstrate the advantageous effects of ion-bombardment-assist using RF bias and high temperatures on the growth of ZnO films by microwave excited high-density plasma enhanced MOCVD.

2. Experiments

Fig. 1 shows the schematic view of our developed experimental setup. The electron temperatures at the excitation region and the diffusion region are very low (~<2.0 eV), while the electron density at the excitation region is very high (>10^{12}cm-^{3}). RF power is applied to the RF electrode under the substrate to generate negative voltage self-bias in this microwave excited high-density plasma. The frequencies of RF power used in this study were 13.56MHz and 40.68MHz. Two types of stage, with different electrode areas, were used to change the RF power density. Fig. 2 shows the measured result of the substrate voltage as a function of the RF bias power and the schematic view of the two types of stage, type B having an area ratio 16 times that of type A. The self-bias voltage depends on RF frequency and stage type. In the case of 40.68MHz and type B stage, the self-bias voltage is low and ion-bombardment is soft compared with 13.56MHz. The effect on ZnO film growth of ion-bombardment at a stage temperature of 400 °C, and the effect of high temperature from 400 °C to 550 °C were evaluated. The ZnO films were fabricated by using Ar gas, O_2 gas and dimethylzinc (DMZ) as plasma excitation gas, oxygen radical precursor and Zn precursor, respectively. A-plane sapphire of 33mm in diameter was used for substrate. The pressure and the microwave input power were 2 Torr and 4.3 W/cm^2, respectively. The crystalline structures, morphology, impurity, electric properties, and thermal resistance of the films were investigated by X-Ray diffraction (XRD), a field emission scanning electron microscope (FE-SEM), secondary ion mass spectroscopy (SIMS), hall effect measurement at room temperature, and thermal desorption spectroscopy (TDS), respectively.

3. Results and discussions

Fig. 3 shows the SEM images of the film surface corresponding to the substrate voltage using ion-bombardment-assist. The positive ions such as Ar^+ and H^+ in the plasma are accelerated through the potential difference between the substrate voltage and the plasma potential, and impinge the film surface. When the substrate voltage is above –27V the surface morphology changes very little, but under –30V the grain growth is suppressed and the grain boundary becomes almost unnoticed on high impact. Fig. 4 shows the effect of ion-bombardment on crystallinity, mobility and carrier concentration. The frequency of RF is 40.68MHz and the stage type is B. As RF power is around 60W, the crystallinity, and the mobility are improved. It is considered that the grain boundaries were modified by a suitable bombardment. Fig. 5 shows the photo luminescence (PL) characteristic of the films shown in Fig. 4. The PL characteristic is dependent on RF bias power. At 45W and 60W it is improved by a suitable bombardment, but at 120W and 150W it is deteriorated by the irradiation-induced crystal defects. Fig. 6 shows SIMS profile of the films shown in Fig. 4. Both carbon and hydrogen concentrations are reduced at 60W. Fig. 7 shows the TDS of ZnO films. Similarly, at 60W the amount of desorbed gases from the film is low. It is considered that the adsorption of impurity in the grain boundaries is controlled by the bombardment. The desorption of O_2 from these films isn't detected. Fig. 8 shows the effects of high temperature growth on crystallinity, carrier and impurity concentration. At 550 °C the high quality film with an impurity level similar to ZnO-substrate can be obtained. It is considered essential that the migrations of precursors on the film surface are enhanced by the effect of thermal energy.

4. Conclusions

The characteristics of ZnO film can be improved by moderate ion-bombardment and by raising the growth temperature to 550 °C in our plasma enhanced MOCVD. The ion-bombardment assist technique has possibilities to enhance the activation of dopant, and to reduce the process temperature. High temperature growth has the possibility to form single crystal film.

References

[1] T. Ohmi, et al., J. Phys. D: Appl. Phys., 39, R1, (2006).
[2] H. Tanaka, et al., Ext. Abst. of Int. Conf. on SSDM, (2003) p. 736.
[3] A. Tsukazaki, et al., Nat. Mater. Vol. 4, 42 (2005)
[4] Ozgur, et al., J. Appl. Phys. 98, 041301 (2005).
[5] B.P. Zhang, et al., J. Appl. Phys. A 78, 25 (2004).
[6] W.Z.Xu, et al., Appl. Phys. Lett. 88, 173506 (2006).
[7] H. Asahara, et al., Ext. Abst. of Int. Conf. on SSDM, (2007) p. 136.

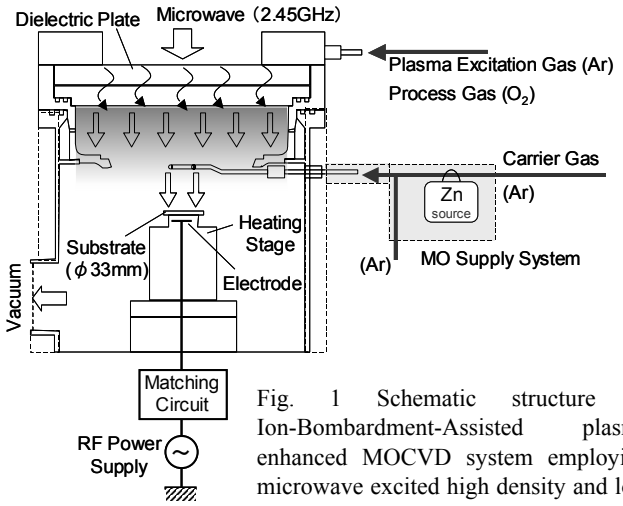


Fig. 1 Schematic structure of Ion-Bombardment-Assisted plasma enhanced MOCVD system employing microwave excited high density and low temperature plasma.

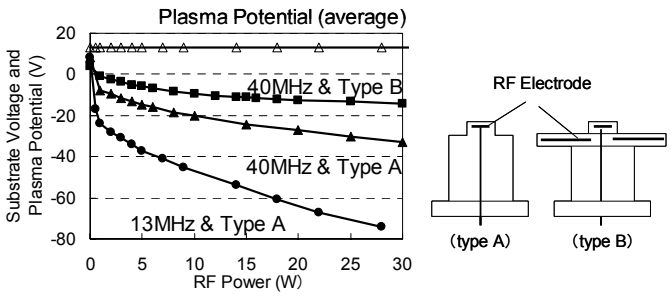


Fig. 2 Substrate voltage as a function of the RF bias power and the schematic view of the two types of stage, type B having an area ratio 16 times that of type A. The self-bias voltage depends on RF frequency and stage type. In the case of 40.68MHz and type B stage, the self-bias voltage is low.

V_{sub}=5V	-22V	-27V	-30V	-80V
RF = 0W	60W	150W	10W	28W
RF Frequency = 40.68MHz				13.56MHz
Stage type (B)			Stage type (A)	

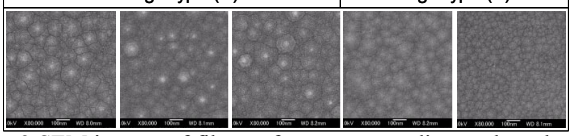


Fig. 3 SEM images of film surface corresponding to the substrate voltage using ion-bombardment-assist. When the substrate voltage is above –27V the surface morphology changes very little. Under –30V the grain growth is suppressed and the grain boundary becomes almost unnoticed.

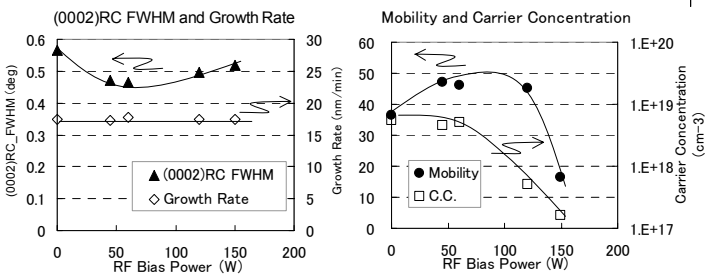


Fig. 4 Effects of ion-bombardment on crystallinity, mobility and carrier concentration. The frequency of RF is 40.68MHz and the stage type is B. As RF power is around 60W, the crystallinity, and the mobility are improved.

Fig. 5 PL characteristic of the films shown in Fig. 4. The PL characteristic is dependent on RF bias power.
At 45W and 60W it is improved by a suitable bombardment, but at 120W and 150W it is deteriorated by the irradiation-induced crystal defects.

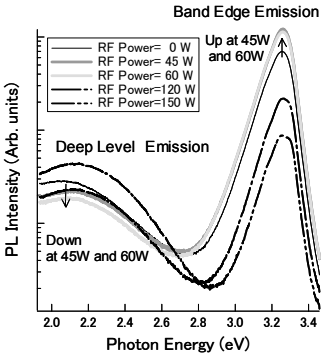
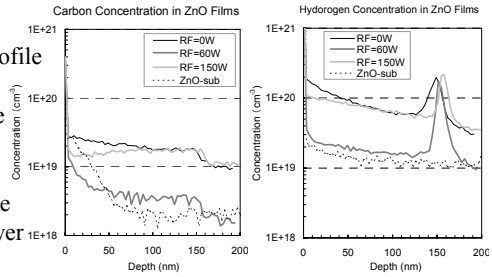


Fig. 6 SIMS profile of carbon and hydrogen in the films of Fig. 4.

The dependence on RF bias power appears.
Both carbon and hydrogen concentrations are reduced at 60W.



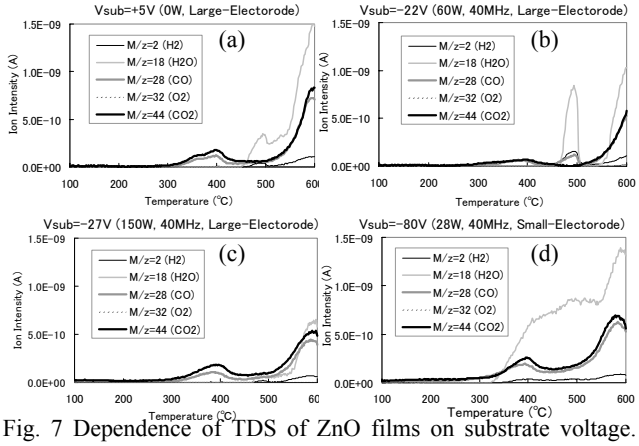


Fig. 7 Dependence of TDS of ZnO films on substrate voltage. (a) +5V (b) –22V (c) –27V (d) –80V The amount of desorbed gases from the film by moderate ion-bombardment-assist is low.

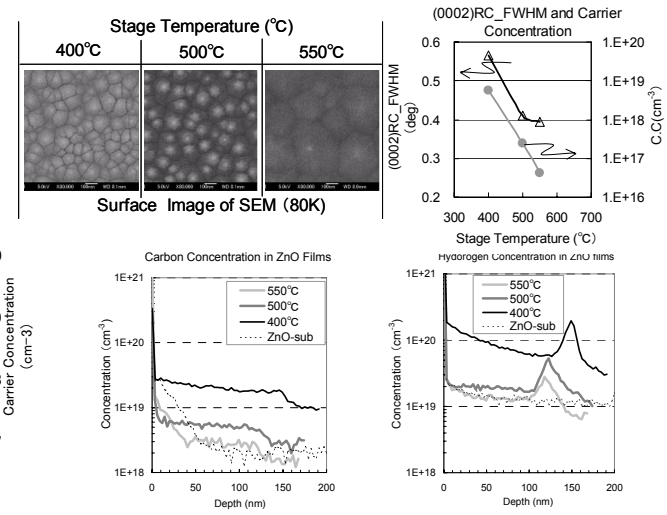


Fig. 8 Effects of high temperature growth on crystallinity, carrier and impurity concentration. At 550℃ the high quality film with an impurity level similar to ZnO-substrate can be obtained.