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Characterization of Zinc Oxide Films Grown by a Newly Developed Plasma Enhanced MOCVD Employing Microwave Excited High Density Plasma

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1. Introduction

The radical reaction based semiconductor manufacturing has been developed using microwave excited high density plasma with very low electron temperatures where reactions are promoted by the reactivity of the radical itself such as oxygen radicals (O^*) for surface oxidation and NH-radicals (NH^*) for surface nitridation so that the process temperatures are lowered compared to those of current molecule reaction based semiconductor manufacturing, such as high quality silicon surface oxidation at around 400 °C and high quality silicon nitridation at around 600 °C [1]. It has been reported that high quality CVD-SiO_2 and CVD-Si_3N_4 film can be formed by this plasma equipment [2-3].

On the other hand, there has been a great deal of interest in zinc oxide (ZnO) materials lately. ZnO is an extensively studied transparent conductive film as a valid alternative to indium tin oxide for different applications, ranging from flat panel displays and solar cells to thin film transistors and optoelectronics, while ZnO has a direct wide band gap of 3.37 eV. Owing to the strong exciton binding energy of 60 meV, ZnO is recognized as a promising photonic material in the UV region. High quality ZnO film formation at low temperature is required for light emitting device and transparent conductive film, and some papers has been reported, recently [4-5].

In this paper, we demonstrate that the newly developed plasma enhanced metal-organic CVD (MOCVD) [1] applied a compound semiconductor such as ZnO firstly, and characteristics of ZnO films are very good, by optimization of equipment and process conditions. This method has possibilities to form very high quality ZnO film at low temperature.

2. Experiments

Low electron temperature and high-density plasma equipment was used for the plasma enhanced MOCVD (PE-MOCVD).

Fig. 1 shows the schematic view of the equipment. Microwave (2.45 GHz) is introduced into the chamber through the dielectric plate of quartz. As a result, high-density plasma is excited immediately below the dielectric plate. Plasma excitation gas (Ar) and process gas (O_2) are introduced into the plasma excitation region. The lower shower nozzle for the supply of material gases (Zn, Ga precursor) is set at the diffusion plasma region with low electron temperature. Fig. 2 shows electron temperature and electron density of this equipment measured by single probe method. The electron temperature at excitation region and diffusion region are very low (~<2.0 eV). Electron density at excitation region is very high (>10^{12}cm^{-3}). Material gases are carried from MO supply system. For accurate and stable supply of material gases, temperature, pressure and gas flow rate in the system are exactly controlled. Using the lower shower nozzle having many small gas injection holes, material gases are supplied toward the wafer. Since the plasma excitation region is limited to the space immediately below the dielectric plate, the CVD process region is completely separated from the plasma excitation region. Therefore, the equipment can control the decomposition of metal organic gases in a diffusion plasma region by control of an electron temperature and plasma density. The ZnO films were fabricated by using Ar gas as plasma excitation gas and O_2 gas and Zn precursor gas. Fig. 3 shows comparative table and vapor pressure curve of Zn precursor materials. MOPD, Diisopropylzinc (DIPZ) and Dimethylzinc (DMZ) were estimated. A-plane sapphire (a-sapphire) and corning glass were used for substrate. Ga doped ZnO transparent conductive films were fabricated by using Triethylgallium (TEG) as Ga precursor gas.

3. Results and discussions

Fig. 4 shows results of X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) of ZnO films on a-sapphire substrate using MOPD for Zn material. It turned out that Crystal structure of the film is wurtzite structure, and the film consists of Zinc and Oxygen. The composition of the film is similar to bulk ZnO grown by hydrothermal method.

Fig. 5 shows the FWHM of (0002) rocking curve as a function of process parameter. MOPD and glass were used as Zn source and substrate. The FWHM can be reduced as microwave power increases and oxygen gas flow rate increases. There is reducing trend of FWHM as wafer-stage temperature increases. At power is 1500W (4.3W/cm^2), there isn't so much difference between 400 °C and 300 °C. It is considered that radical reaction generated by the plasma contributes to crystal growth of film.

Fig. 6 shows SIMS profile of carbon content in the films. There are material dependency and process condition dependency. Film using DMZ contains the much carbon. The carbon content can be reduced as microwave power increases and oxygen gas flow rate increases. Carbon concentration is less than the detection limit of percent order in XPS.

Fig. 7 shows scanning electron microscope (SEM) images before and after annealing treatment of ZnO films formed using DMZ and a-sapphire. By annealing treatment at 700 °C, crystalline and mobility are improved and grain boundary disappears.

Fig. 8 shows Ga content and electric property of Ga doped ZnO films on the sapphire and the glass. Ga content in GZO film, carrier concentration and Mobility of film can be controlled by quantity of TEG.

4. Conclusions

We showed the good characteristics of ZnO films grown by a newly developed plasma enhanced MOCVD employing microwave excited high density plasma.

By selection of material gasses, optimization of equipment and process conditions, this method can form high quality ZnO film because this method has possibilities to control dissociation of metal-organic materials. Using RLSA technology, substrate is possible to grow at very low temperature and for large display.

References

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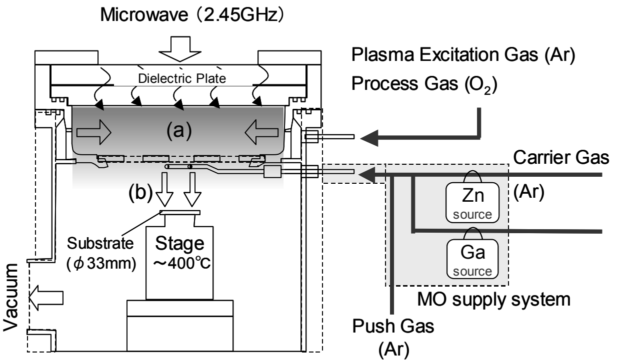
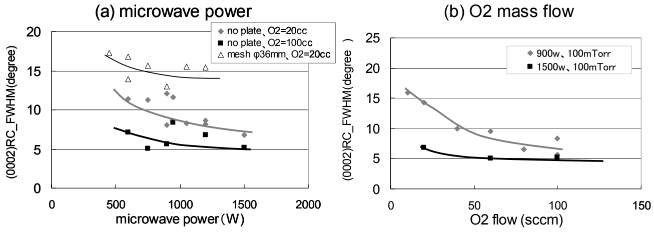


Fig. 1 Schematic structure of plasma enhanced MOCVD system employing microwave excited high density and low temperature plasma.



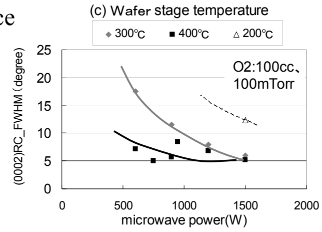


Fig. 5 Growth condition dependence of (0002)RC FWHM.
Zn source: MOPD, substrate: glass
(a) microwave power
: High power is better.
(b) Oxygen mass flow
: High O2 flow rate is better.
(c) wafer-stage temperature
: High temperature is better.

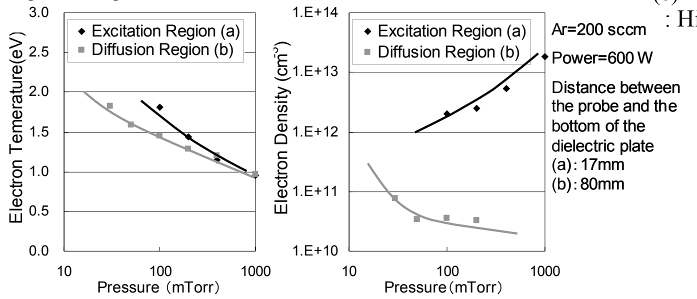


Fig. 2 Electron temperature and electron density as a function of the pressure. The electron temperature at excitation region and diffusion region are very low. Electron density is very high. (a) and (b) are the location shown in Fig.1.

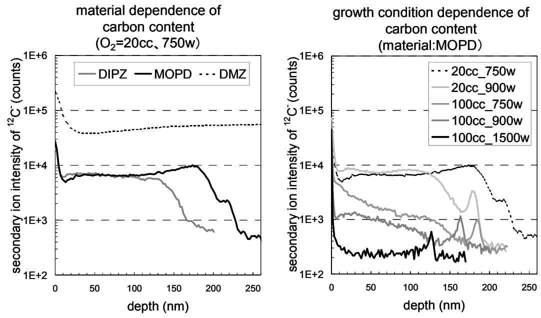


Fig. 6 Carbon content in ZnO film by SIMS. Film using DMZ contains the much carbon. The carbon content can be reduced as microwave power increases and oxygen gas flow rate increases. Carbon concentration is less than detection limit of %-order in XPS.

chemical notation	$Zn(MOPD)_2$	DIPZ	DMZ	DEZ
structure	$C_{18}H_{30}O_6Zn$	$(H_3C)_2HC-Zn-CH(CH_3)_2$	$H_3C-Zn-CH_3$	$H_3C-CH_2-Zn-H_2C-CH_3$
molecular weight	407.8	151.6	95.4	123.5
feature	No-pyrophoric	pyrophoric	pyrophoric	pyrophoric

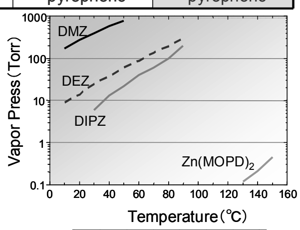


Fig. 3 Comparative table and vapor pressure curve of source materials for zinc. MOPD, DIPZ and DMZ have been estimated. we used TEG as Ga precursor gas.

anneal condition: argon atmosphere,60min

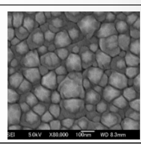
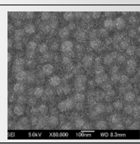
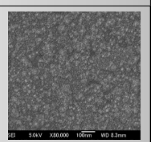
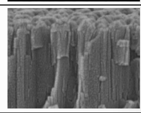
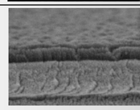
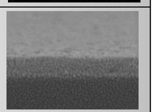
anneal temp	as Depo	600℃	700℃
Top view of SEM (×80k)			
Cross view of SEM (×80k)			
(002)RC_FWHM	0.36°	0.31°	0.35°
mobility	23 cm²/V･s		46 cm²/V･s

Fig. 7 SEM images of before and after annealing treatment of ZnO film formed using DMZ and a-sapphire. By 700 °C annealing treatment, mobility increased from 23 cm^2/Vs to 46 cm^2/Vs and grain boundary disappeared.

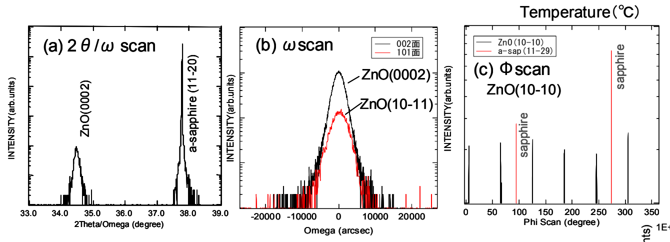
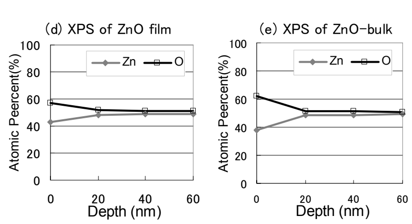


Fig. 4 Results of XRD and XPS of ZnO film using MOPD for Zn material on a-sapphire.



(a) (b) (c): The crystal ZnO film of wurtzite structure is grown.
(d) The film consists of Zinc and Oxygen.
(e) The composition at the surface of ZnO film are similar to bulk ZnO grown by hydrothermal method.

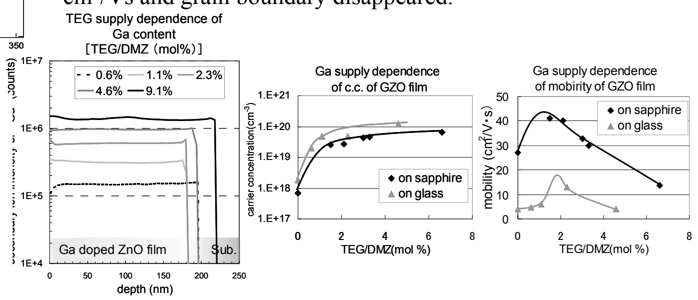


Fig. 8 Evaluation of Ga doped ZnO transparent conductive film on sapphire and glass. These are SIMS and Hall Effect measurement results. Regulating TEG supply quantity can control Ga content in GZO film, carrier concentration and Mobility of film.