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Controlling preferred orientation of ZnO thin films by atomic layer deposition

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Wurtzite structured wide band gap ZnO thin films have been investigated extensively because of their interesting electrical, optical and piezoelectric properties. They have played an important role in various applications such as transparent conducting electrodes of solar cells and displays [1], surface acoustic wave devices [2], varistors [3], and sensors [4].

In growing ZnO thin films, it is of primary importance to control the preferred orientation for each application. ZnO having the (002) orientation normal to the substrate is especially important for piezoelectric applications whereas the one with (100) orientation is of benefit to transparent conductive oxide (TCO) applications due to the relatively larger grain size as compared to the films with the (002) orientation. There have been lots of reports on the fabrication method of ZnO films including sputtering, pulsed laser deposition (PLD), e-beam evaporation, sol-gel method, chemical vapor deposition (CVD), and atomic layer deposition (ALD) [5]. Among these technologies, ALD performed only by a surface reaction between precursors has been recognized as a unique fabrication technology by which high quality films with low structural imperfection can be obtained.

The ZnO films with (002) orientation have been usually observed for the films grown by various fabrication methods because the c-plane perpendicular to a substrate is the most densely packed and thermodynamically favorable plane in the wurtzite structure. In the ALD method using diethylzinc (DEZ) and water, however, it has been considered that the (100) orientation is favored at low deposition temperature [6]. The (002) preferred orientation of ZnO film by ALD can be obtained at a substrate temperature higher than 400 °C. Kaiya *et al.* recently reported ALD growth of ZnO film, with an intense diffraction peak assigned to the (002) reflection, by using $ZnCl_2$ and O_2 as precursor for Zn and O respectively at substrate temperatures higher than 450 °C [7]. Chaisitsak *et al.* reported that the orientation of ZnO film grown by ALD is strongly dependent on the DEZ flow rate at a substrate temperature of 165 °C [8]. On considering that ALD is rather insensitive to the precursor flux, that result was quite interesting. Although the effect of the substrate temperature on the crystalline growth direction of ALD grown ZnO films has been reported, detailed studies on the other process factors determining growth direction of the films are lacking. In this experiment, we have investigated the effects of oxygen precursor on the ZnO film growth by the ALD method.

The growth of ZnO films was carried out in a prototype F-450 (Microchemistry, Ltd.), i.e., a traveling wave type hot wall reactor for substrate as large as $12'' \times 16''$. With all other conditions fixed, the pulsing times were 1.65 s for the reactants and 4.4 s for the N_2 purge. The ZnO films were deposited by 3000 cycles at a substrate temperature of 180 °C on 200 nm thick Al_2O_3 coated Si wafer. The Al_2O_3 layer was deposited using trimethylaluminum (TMA) and water as precursors for Al and O, respectively. We carried out two different processes (designated as A and B) to deposit ZnO films. The sequence of one deposition cycle for process A consisted of four pulses; DEZ, N_2, water and N_2 (Film A). The process B included the following 5 steps; DEZ, N_2, O_2, water and N_2 (Film B). Crystallographic orientation of the ZnO films was determined by an X-ray diffractometer (XRD) with Cu K_α radiation and morphologies of the surfaces of the films were observed using a scanning electron microscope (SEM). The thickness of films was measured by the stylus method using an Alphastep 200.

Addition of an oxygen pulse between the DEZ/N_2 and water sequence during growth dramatically changed the preferred orientation and surface features of the ZnO films. The growth rate for the process A was 2.06 Å/cycle similar to the reported value[6] whereas a growth rate of 1.38 Å/cycle was obtained from the process B. The difference in growth rate came from the different film growth modes. In the process A, ZnO film with wedge-like shaped crystallites is obtained as shown in Fig. 1. On the other hand, the process B resulted in a ZnO film consisting of fine columnar crystallites. Fig. 2 shows XRD patterns of highly a-axis oriented Film A with a strong peak at $2\theta = 31.78°$ corresponding to the ZnO (100) plane and a highly c-axis oriented Film B with a peak at $2\theta = 34.4°$ indicating (002) orientation. The profound differences in crystallographical and

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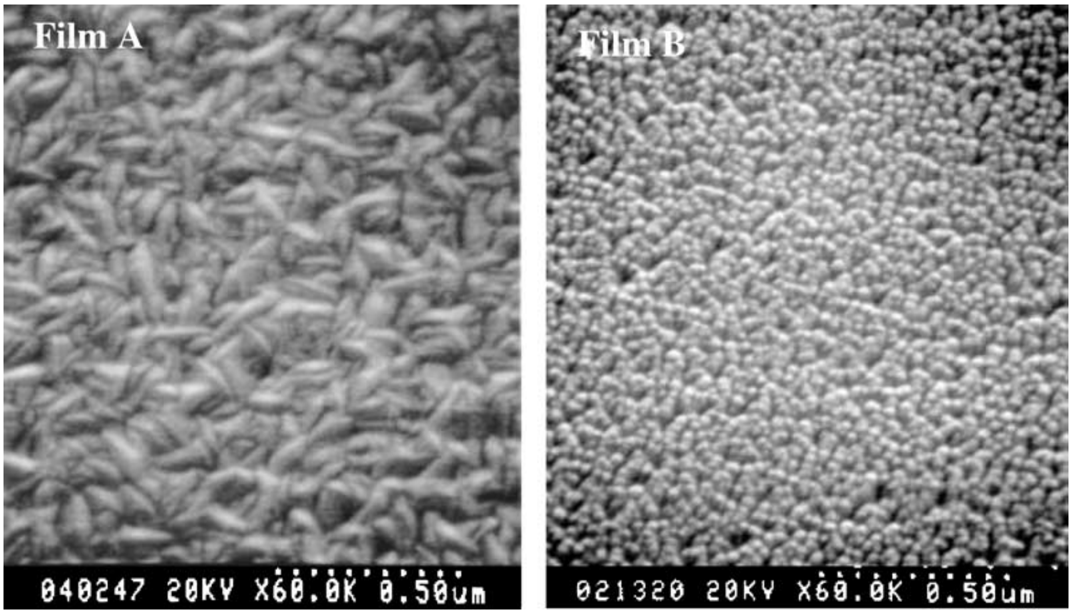

Figure 1 SEM photographs of ZnO Film A deposited by pulse sequence: DEZ/N_2/H_2O/N_2 and Film B deposited by the pulse sequence: DEZ/N_2/O_2/H_2O/N_2.

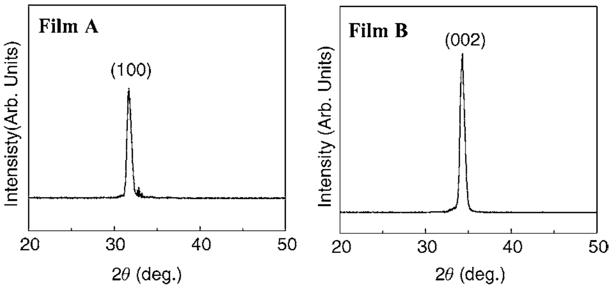

Figure 2 XRD patterns of ZnO Film A deposited by pulse sequence: DEZ/N_2/H_2O/N_2 and Film B deposited by the pulse sequence: DEZ/N_2/O_2/H_2O/N_2.

microstructural properties significantly influenced the electrical properties. The films composed of fine columnar crystallites had higher resistivity of 14.7 $\Omega \cdot$cm than the films with wedge-like shaped crystallites, 0.53 $\Omega \cdot$cm.

To investigate the effect of oxygen gas on the film growth, we carried out ZnO deposition by using DEZ and O_2 as a precursor for Zn and O respectively. No film was formed at a temperature of 180 °C and growth rates of 0.1 and 0.36 Å/cycle were obtained at 230 and 280 °C, respectively with an (002) orientation. These results imply that the oxygen source of ZnO Film B grown by process B comes not directly from the oxygen but from the water. ZnO film grown at a substrate temperature of 180 °C by the following 5 steps (process C); DEZ, N_2, water, O_2 and N_2, showed different surface features (Film C). Fig. 3 shows the XRD patterns and SEM image of the Film C. The film exhibits a peak at $2\theta = 31.8^\circ$ with similar intensity and a peak at $2\theta = 34.5^\circ$ with increased intensity compared to those of Film A. Although the microstructure of Film C seems to be a little different from that of Film A, XRD patterns are very similar to those of Film A. This indicates that oxygen gas plays some role before water

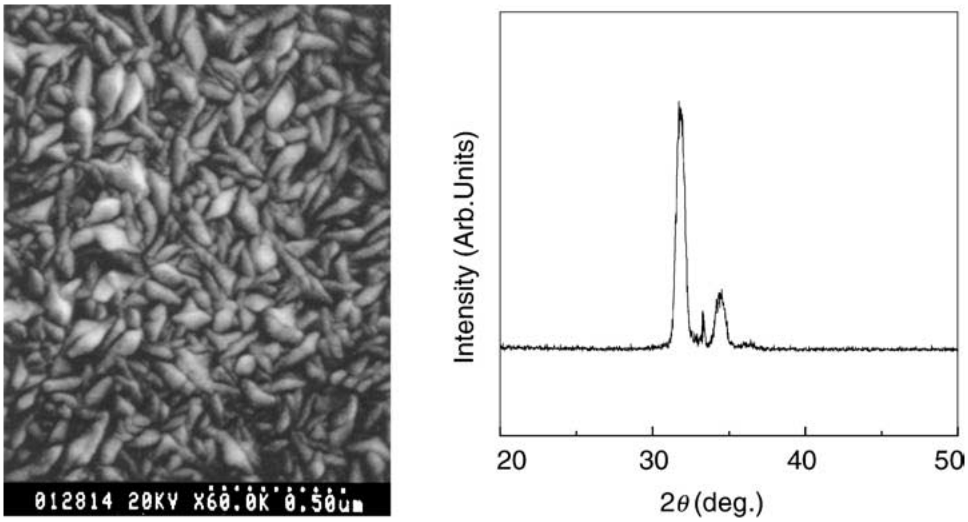

Figure 3 XRD patterns and SEM photograph of ZnO film deposited by pulse sequence: DEZ/N_2/H_2O/O_2/N_2.

reacts with surface-adsorbed O-Zn(CH_2CH_3), known as the reaction cite for the ZnO film growth. Further studies are under investigation to understand the effect of oxygen on the growth of ZnO film using DEZ and water.

In summary, we have shown that oxygen gas strongly influences the growth mode of ZnO film in the ALD method. The preferred orientation of the ZnO films can be controlled by the oxygen precursor. By pulsing oxygen gas before water source pulsing, a highly *c*-axis oriented ZnO film with granular crystallites and high resistivity was obtained with a growth rate of 1.38 Å/cycle.

Acknowledgment

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