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Preparation of ZnO Films by Low-pressure Organometallic Chemical Vapor Deposition

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Using zinc acetate as a precursor, ZnO films have been prepared on sapphire $(1\bar{1}02)$ substrates at pressures of 2.7×10^{-2} and 6.7×10^{-3} Pa. The deposition rate increased with substrate temperature. The crystal structure of ZnO film was dependent on the substrate temperature and H_2O partial pressure. In particular, oriented $(11\bar{2}0)$ ZnO films have been formed at 350 °C at 2.7×10^{-2} Pa.

In previous papers,[1)] we have pointed out that a strong electric field is necessary to suppress thermal reverse reactions for developing optical memories using photochromic oxide doped with transition metal ions. An electric field in the photochromic oxide can be provided not only by applying an external potential, but also by modified (or superlattice) doping. Such a modified (or superlattice) doping has been performed by molecular beam epitaxy (MBE).[2)] However, an apparatus for the MBE is very expensive, and in addition it is difficult to introduce many kinds of transition-metal ions into a host oxide. In recent years, a low-pressure organometallic chemical vapor deposition (LPOMCVD) was found to be a powerful technique for preparing devices with superlattice structures, as well as the MBE.[3,4)] Thus, we have attempted to prepare ZnO films as a host oxide for photochromic material by means of LPOMCVD using alkyl-zinc, zinc acetyl-acetonate, and zinc acetate dihydrate (ZnAc) as precursors of Zn source. From preliminary experiments, it was found that alkyl-zinc was very dangerous because of explosive reaction in air, and that no thermal decomposition of zinc acetyl-acetonate occurred at a fairly low temperature. Accordingly, we employed zinc acetate dihydrate as a precursor of Zn source. In this letter, we investigate the effects of both substrate temperature and H_2O partial pressure on the crystal structure of ZnO film.

A vaporizer for ZnAc powder was placed in a reaction chamber, while a vaporizer for H_2O was placed outside a reaction chamber. The reaction chamber was evacuated to 1.0×10^{-4} Pa using a diffusion pump, and then H_2O vapor was introduced into the reaction chamber up to 2.7×10^{-2} or 6.7×10^{-3} Pa; partial pressures of

Table 1. preparation conditions, film thickness, and deposition rate of ZnO films

Sample number	Pressure (Pa)	Sublimation rate (mg/h)	Substrate temperature (°C)	Deposition time (h)	Film thickness (Å)	Deposition rate (Å / h)
1	$2.7x10^{-2}$	3.0	250	4	1900	480
2	$2.7x10^{-2}$	3.0	300	4	2200	550
3	$2.7x10^{-2}$	3.0	350	4	3100	780
4	$5.7x10^{-3}$	1.5	250	4	1500	380
5	$5.7x10^{-3}$	1.5	300	4	2000	500
6	$5.7x10^{-3}$	1.5	350	4	2500	630

H_2O were $2.69x10^{-2}$ or $6.6x10^{-3}$ Pa, respectively. The sublimation rate of ZnAc was controlled by sublimation temperature which was varied from 100 to 180 °C. ZnO films were deposited on sapphire (1 $\bar{1}$02) substrates heated at 250, 300 and 350 °C. A ZnO film was placed in a X-ray diffraction (XRD) apparatus such that a maximum intensity of (11 $\bar{2}$0) reflection of ZnO was obtained (no reflections of a sapphire substrate were seen in XRD patterns because the (11 $\bar{2}$0) planes of ZnO inclined with respect to the (1 $\bar{1}$02) planes of sapphire). The thickness of ZnO film was measured by a surface roughness meter (Kosaka SE-30D). The absorption spectra of ZnO films were measured in the range of 200 to 1100 nm. In order to measure the sublimation rate of ZnAc, ZnAc powder of about 160 mg was packed into the vaporizer and then weight loss of ZnAc was measured at $2.7x10^{-2}$ Pa. In Fig. 1, weight of vaporized ZnAc is plotted as a function of time. The remarkable weight loss is observed up to 30 min at substrate temperatures of 130, 140, 150 and 160 °C. This is caused mainly by the loss of crystal water contained in ZnAc. As seen in Fig. 1, constant sublimation rate is obtained at time > 2 h. Accordingly, ZnO films were deposited after ZnAc was previously heated for 2 h. At pressure of $5.7x10^{-3}$ Pa, values of the sublimation rates are about one-half of those at $2.7x10^{-2}$ Pa (plots of vaporized weight vs. time are not shown here). Opaque films were frequently formed at sublimation rates higher than 4 mg/h, so that in this work the vaporizer temperature was kept constant at 150 °C (the sublimation rates were 3.0 mg/h at $2.7x10^{-2}$ Pa and 1.5 mg/h at $5.7x10^{-3}$ Pa, respectively). Preparation

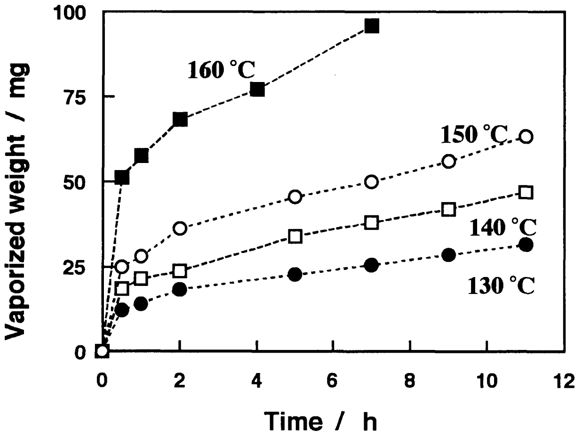

Fig. 1. Plots of weight of vaporized ZnAc vs. time at $2.7x10^{-2}$ Pa.

conditions, film thickness and deposition rate are listed in Table 1. Appreciable electric conductivity is observed for the ZnO films (3 and 6). As seen in Table 1, the deposition rate increases with substrate temperatures at either 2.7×10^{-2} or 5.7×10^{-3} Pa. The deposition rates for the ZnO films (4, 5 and 6) are slightly less than those for the ZnO films (1, 2 and 3), in spite of the remarkable difference in the H_2O partial pressure. This indicates that a reaction of $\mathrm{ZnAc} + H_2O \rightarrow \mathrm{ZnO} + 2\ CH_3COOH$ on a sapphire substrate is a rate-limiting process.

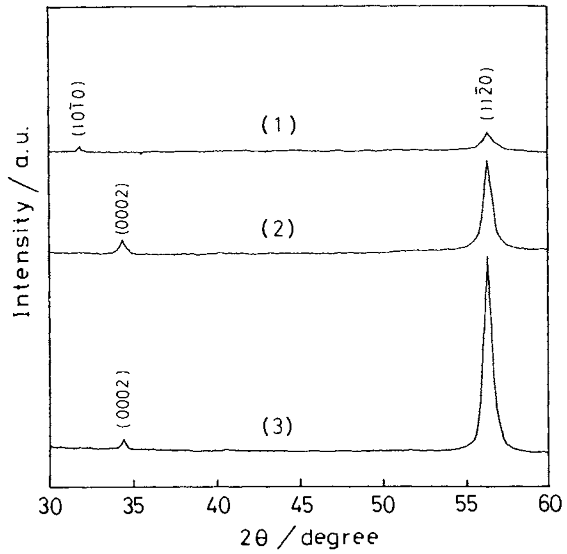

Fig. 2. XRD patterns of ZnO films (1, 2 and 3).

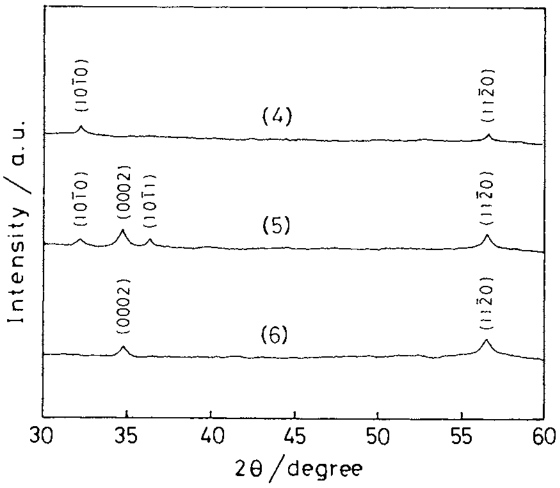

Fig. 3. XRD patterns of ZnO films (4, 5 and 6).

Figure 2 shows XRD patterns of the ZnO films (1, 2 and 3) prepared at 2.7×10^{-2} Pa. A distinct $(11\bar{2}0)$ reflection and a weak $(10\bar{1}0)$ reflection are seen in XRD pattern of the ZnO film (1). A weak (0002) reflection and a fairly strong $(11\bar{2}0)$ reflection are seen in XRD pattern of the ZnO film (2). In XRD pattern of the ZnO film (3), an intensity of (0002) reflection is slightly decreased whereas an enhanced intensity of $(11\bar{2}0)$ reflection is observed. From rocking curves for the $(11\bar{2}0)$ reflection of the ZnO film (3), it is found that the orientation of the $(11\bar{2}0)$ planes of ZnO can be approximated by the Gaussian distribution with the standard deviation of 1.5 degree, and that the $(11\bar{2}0)$ planes of ZnO incline by 2.2 degree with respect to the $(1\bar{1}02)$ planes of sapphire. The appearance of the weak (0002) reflection in XRD patterns of ZnO films (2 and 3) may be due to either the increase in a deposition rate or the generation of oxygen vacancies, because optimum O_2-partial pressure is required for the epitaxial growth of $(11\bar{2}0)$ ZnO film.[5] Figure 3 shows XRD patterns of the ZnO films (4, 5 and 6) prepared at 5.7×10^{-3} Pa. There exist weak $(10\bar{1}0)$ and $(11\bar{2}0)$ reflections in XRD pattern of the ZnO film (4). There are several reflections of $(10\bar{1}0)$, (0002) and $(10\bar{1}0)$ besides $(11\bar{2}0)$ reflection in the ZnO film (5). There are (0002) and $(11\bar{2}0)$ reflections in the ZnO film (6). A noticeable feature of XRD patterns in Fig. 3 is that the intensity of $(11\bar{2}0)$ reflections is significantly weaker than that of the ZnO films (1, 2 and 3). In particular, no epitaxial growth is found in the ZnO film (6) prepared at 350

°C. These results indicate that the pressure of 5.7×10^{-3} Pa is not a preferable condition for the epitaxial growth of ZnO film. The reason for the appearance of (0002) reflection in the ZnO film (6) is same as in the ZnO film (3). Irrespective of the H_2O partial pressure, $(10\bar{1}0)$ reflection is seen in the ZnO films (1 and 4). This is probably in connection with the thermal decomposition of ZnAc at a low substrate temperature because no $(10\bar{1}0)$ reflection is seen in XRD patterns of ZnO films prepared at 250 °C by sputtering technique.5)

The absorption spectra of the films are shown in Fig. 4. As seen in Fig. 4, values of the absorbance for the present ZnO films (1,3,4 and 6) are significantly large at wavelength less than 360 nm. The wavelength corresponding to the band gap energy of ZnO is 360 nm, so that strong absorption at wavelength less than 360 nm arises from the band-gap excitation. The formation of ZnO films is supported by these absorption spectra. No excitonic absorption is seen in the absorption spectra near 370 nm. The result can be explained by both the low degree of crystallization and the generation of oxygen vacancies acting as nonradiative recombination centers. No appreciable absorption is seen at wavelength longer than 400 nm for the ZnO films (1, 3, 4 and 6). This means that no formation of ZnO powders which may act as light-scattering centers occurred in the deposition processes.

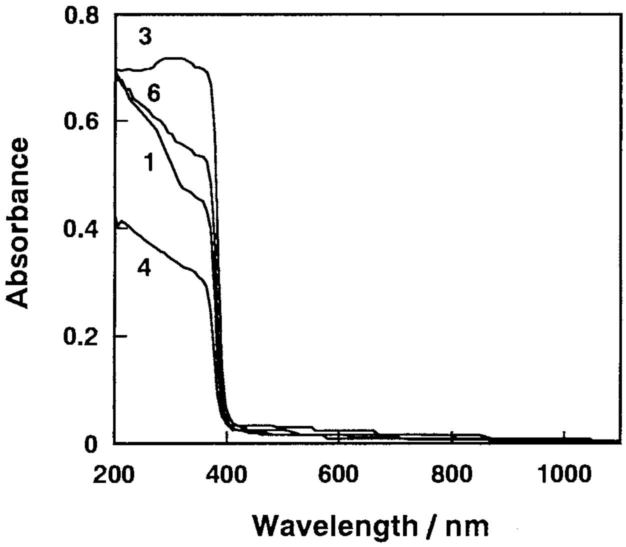

Fig. 4. Absorption spectra of ZnO films (1, 3, 4 and 6).

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