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Preparation of ZnO by a nearby vaporizing chemical vapor deposition method

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Abstract

ZnO films were prepared by a nearby vaporizing chemical vapor deposition (CVD) method using bis(2,4-pentanedionato)zinc as a source material. The deposition rate increased exponentially from 0.58 to 147 nm min^{-1} with increasing substrate temperature. The highest preferred orientation to c-axis was obtained under the conditions that the distance between substrate and source surface (D) was 5.0 mm and the substrate temperature (T_s) was 300 °C. When we used a sapphire (0001) substrate, an epitaxial ZnO film could be deposited on this condition.

Zinc oxide has been utilized widely in the field of scientific and technological applications. For example, highly oriented ZnO films are exploited as piezoelectric transducers in acoustic range, and as optical waveguides and laser oscillation devices in photonic range[1]. Although ZnO film is one of the important materials, there exist few chemical vapor deposition (CVD) sources. Although alkyl metal compounds such as dimethyl zinc (DMZ) and diethyl zinc (DEZ)[2-6] are only materials for conventional low temperature CVD processes, these compounds have dangerous property owing to their ignitability. Bis(2,4-pentanedionato)zinc was investigated previously by the present authors as a promising candidate for CVD source material without ignitability. However, a high substrate temperature of ca. 550°C is necessary for this compound to fabricate ZnO films of c-axis preferred orientation[7] by a conventional atmospheric CVD apparatus. The present report concerns the formation of ZnO films by a new modification of CVD method, in which vaporization of bis(2,4-pentanedionato)zinc takes place by radiant heat from the substrate without carrier gas. This deposition technique named "nearby vaporizing CVD" brings several advantages; low cost, energy saving, and easy control with few experimental parameters. Since no carrier gas is used, the present experimental set up is regarded as the simplest CVD apparatus in the world.

The schematic diagram of the apparatus of the nearby vaporizing CVD in atmospheric pressure are shown in figure 1, and Table I is a list of the preparation conditions. The substrate was heated by a hot Al suscepter with a resistance cartridge heater. The substrate temperature was sensed by a thermocouple inside the Al suscepter. A source material, bis(2,4-pentandionato)zinc [$Zn(C_5H_7O_2)_2$] was synthesized according to the literature[8]. To control the intensity of radiant heat from the nearby substrate, distance between the substrate and the surface of source material was adjusted by using a micrometer. The thickness and refractive index of the films deposited on Si(100) substrate were measured by an elipsometer (Mizojiri Optical DVA-36L) at 632.8 nm. The deposition rate was calculated for the film of ca. 50 nm in thickness. The surface morphology of the film was observed using a scanning electron microscope (SEM; JEOL-5310LVB) and an atomic force microscope (AFM; SII-SPI3700). The structure of the films was characterized by X-ray diffraction (XRD) and reflection high-energy electron diffraction (RHEED). Only for RHEED measurement, a sapphire substrate was employed.

Figure 2 shows the deposition rate and refractive index as a function of the substrate temperature (T_s) under the condition that the separation between substrate to the source material (D) was 5.0 mm. The deposition rate increases almost exponentially from 0.58 to 147 nm min^{-1} with the increase of the substrate temperature from 300 to 600°C. This observation that the deposition rate increases exponentially results from the fact that the vapor pressure of the source material increases exponentially with the temperature. The refractive index of the obtained ZnO films increased from about 1.38 to 1.95 as substrate temperature increased from 300 to 500°C, and decreased at 600°C. The first increase means the increase of the density of the films.

Figure 3 shows the X-ray diffraction patterns of ZnO films deposited at various substrate temperatures (T_s) ranging from 300 to 600°C. C-axis preferred orientation for ZnO films was obtained in the temperature range examined. For the deposition on fused quartz, the maximum preferred orientation was obtained at the substrate temperature of 300°C. This temperature is lower by 250°C than that obtained in the previous report[7] where the conventional CVD method was used. Since the present CVD apparatus needs no carrier gas, the process temperature for c-axis preferred orientation could be decreased.

Figure 4 shows the surface morphology of the films prepared at 300°, 400°, 500° , and 600°C. At the substrate temperature of 300°C, the films displayed hexagonal or triangle pole structure of about 2μm in diameter with many openings around the grains. This observation indicates the shortage of $Zn(C_5H_7O_2)_2$ vapor supplied at this substrate temperature. The surface roughness of the ZnO films decreased with the increase of the substrate temperature. This observation is explained by the increase of the nucleation density, which is caused by the increase of the vapor pressure of source material with radiant heat.

The morphology of a ZnO film obtained on sapphire(0001) at T_s = 300°C and D = 5.0 mm was continuous granular structure as observed in the AFM picture (fig. 5(a), 2.5 μm by 2.5 μm). The difference in specific thermal conductivity of the substrates may cause by the difference in the morphology from that deposited on Si(100) in figure 4(A). Figure 5(b) shows an RHEED pattern of this ZnO film. A distinct spotty pattern and very few arcs for polycrystalline layer are observed, indicating the formation of an epitaxial film on this condition.

ZnO films were prepared easily by newly developed nearby vaporizing CVD method under atmospheric pressure using bis(2,4-pentanedionate)zinc as a source material. The significant results of the present study are as follows:

The deposition rate increased exponentially from 0.58 to 147 nm min^{-1} with increasing substrate temperature. C-axis preferred orientation was obtained at the substrate temperature between 300 and 600°C. The maximum orientation was obtained under the conditions that the distance and substrate temperature are 5.0 mm and 300°C, respectively. By using a sapphire (0001) plate as a substrate, we could deposit an epitaxial film of ZnO.

References

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Table I. Preparation conditions

Source material:	Bis(2,4-pentanedionato)zinc [$Zn(C_5H_7O_2)_2$]
Substrate:	Si(100), fused quartz, and Sapphire(0001)
Dish of source material:	Ceramic, PTFE
Substrate temperature(T_s):	300−600℃
Distance between the substrate surface and the surface of the source material (D):	5.0 mm

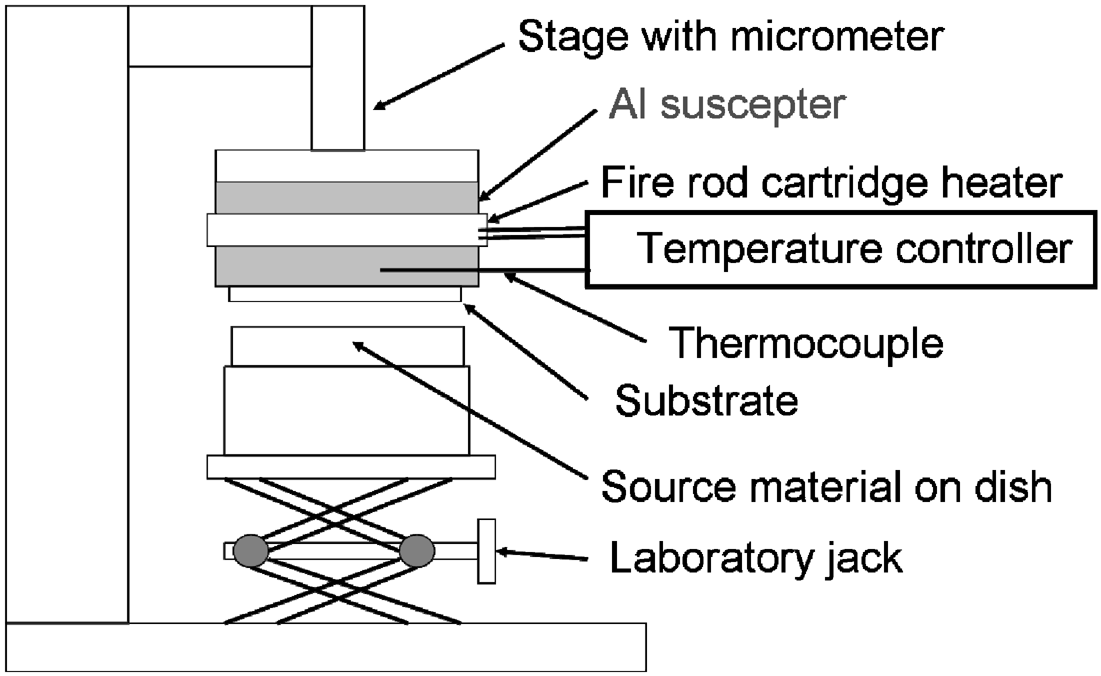


Figure 1. Schematic view of nearby vaporizing CVD apparatus.

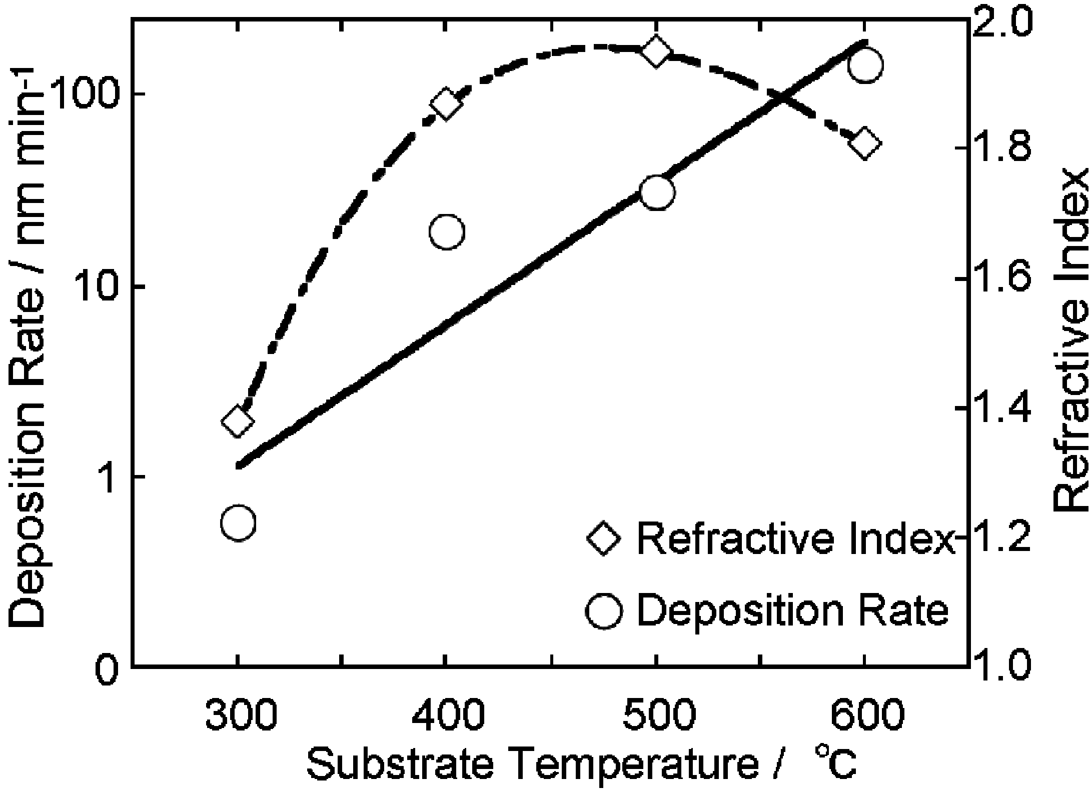


Figure 2. Dependence of substrate temperature on the deposition rate and refractive indices of ZnO films obtained on Si(100) at *D* = 5.0 mm.

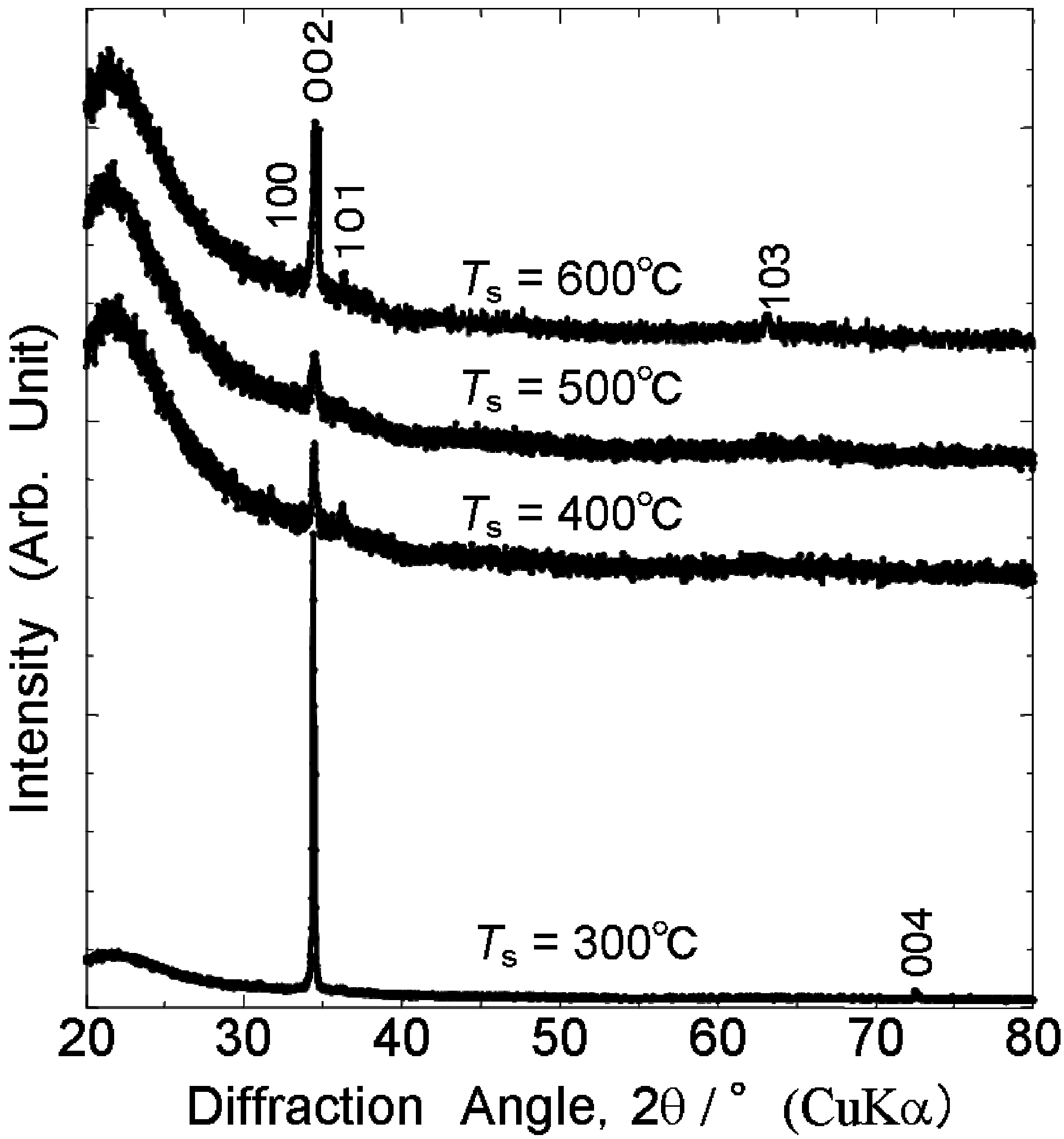


Figure 3. XRD patterns of ZnO films on a fused quartz obtained at various substrate temperatures.

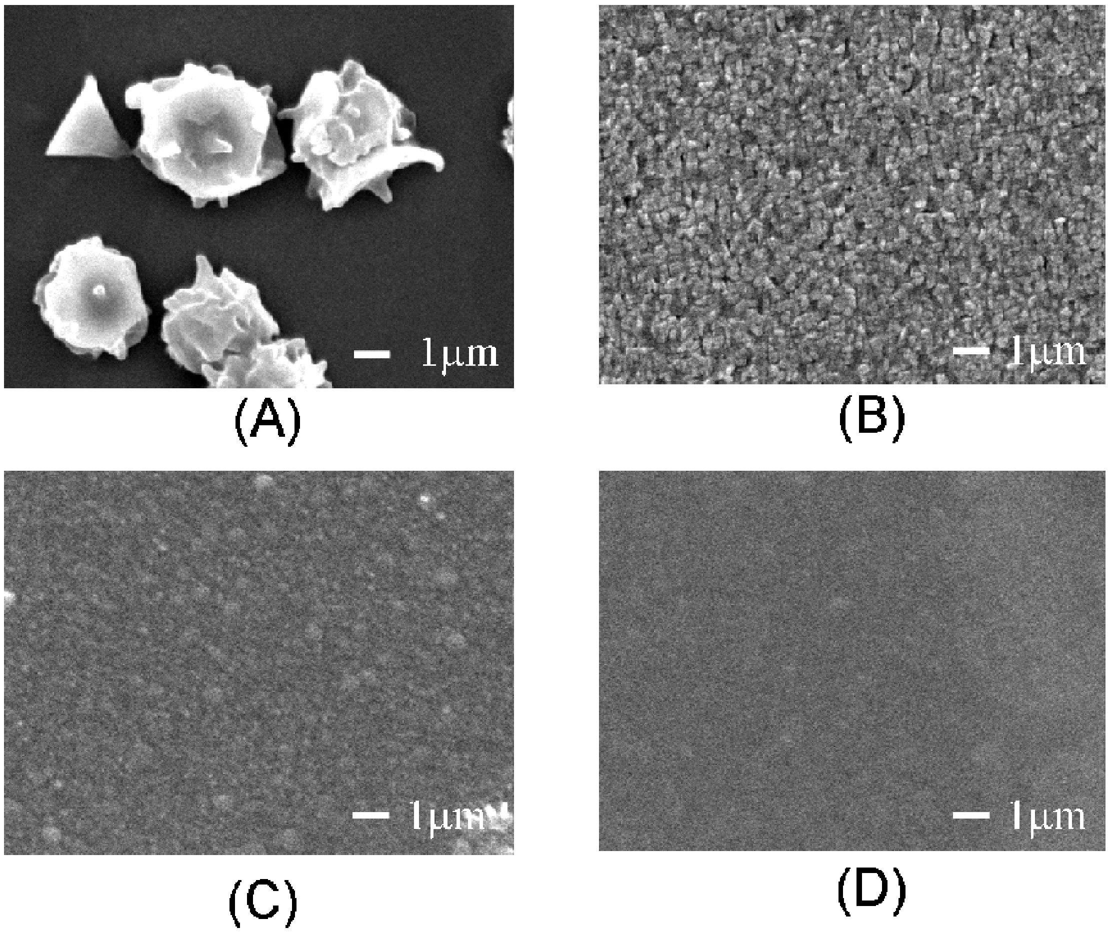
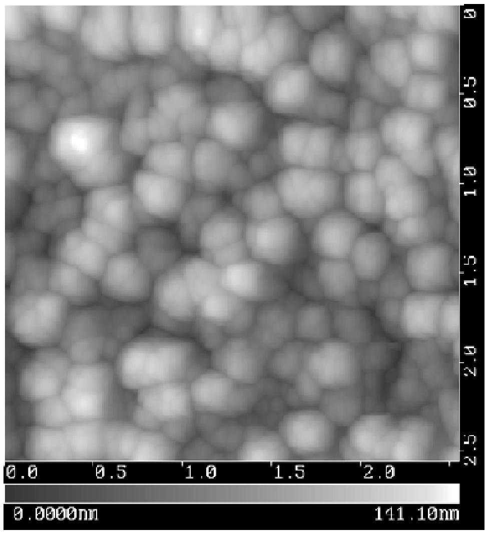
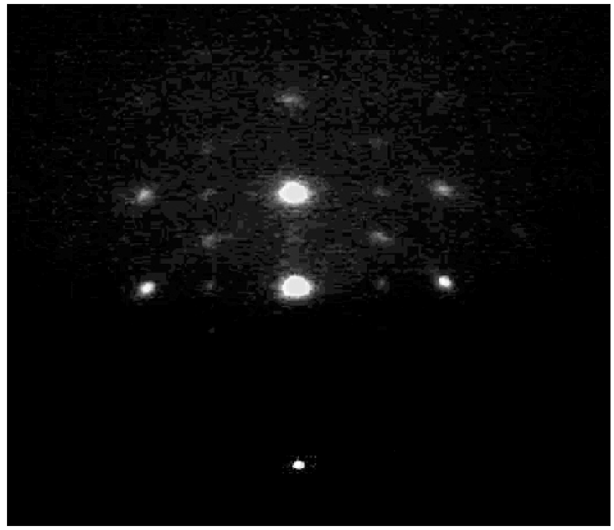


Figure 4. SEM photographs of ZnO films obtained on Si(100) substrate at (A) $T_s = 300$°C, (B) $T_s = 400$°C, (C) $T_s = 500$°C, and (D) $T_s = 600$°C under the conditions of $D = 5.0$ mm.



(a)



(b)

Figure 5. AFM image (a) and RHEED pattern (b) of ZnO film on sapphire(0001) substrate obtained at T_s = 300°C and D = 5.0 mm.