

Rapid Growth of Thick ZnO Films with Room-Temperature Ultraviolet Emission by Means of Atmospheric Pressure Halide Vapor-Phase Epitaxy

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Materials classified as wide and direct band-gap semiconductors are of considerable interest for application to optical devices such as blue and ultraviolet (UV) light emitting diodes and laser diodes. One of the promising candidates for this purpose is ZnO with a direct band gap of 3.37 eV at room temperature, which has widely been used for transparent conductive films varistors, solar cell windows, and bulk acoustic waves devices.^{1–5} Key to the success of obtaining room-temperature emission lies in the techniques to prepare defect-free ZnO films with a variety of thicknesses ranging from a few hundred nanometers to a few hundred micrometers. This is because the oxygen and zinc vacancies, which show greenish yellow emission, are easily formed. Also, it is extremely difficult to grow “thick ZnO crystalline films (bulk)”. For this reason, a variety of techniques, such as laser molecular beam epitaxy (MBE), RF magnetron sputtering, and pulsed laser deposition, have been examined for the preparation of the ZnO films so far. Zu et al.⁶ and Chen et al.⁷ have observed an ultraviolet emission at room temperature from the ZnO thin films prepared under reduced pressure by laser MBE and plasma-enhanced MBE methods. On the basis of the growth rate reported, however, their deposition rate is too slow to prepare thick ZnO crystalline films (bulk). In a previous paper, we reported that the thin films of the hexagonal ZnO with room-temperature ultraviolet emission are grown epitaxially on a sapphire (0001) substrate by atmospheric pressure halide vapor-phase epitaxy (AP-HVPE)

using zinc chloride as a starting material.^{8–10} One would note that the AP-HVPE has a higher growth rate than those by other means. Therefore, this article focuses on the rapid growth of the thick ZnO films by the AP-HVPE using zinc iodide as a source.

Films of ZnO were grown by atmospheric pressure vapor-phase epitaxy (AP-VPE) using ZnI₂ and O₂ as starting materials. Purities of ZnI₂ and O₂ used were 99.999 and 99.995%, respectively. The setup used in the present study is illustrated in Figure 1. The growth of the ZnO epitaxial film was carried out in a vertical quartz reactor under atmospheric pressure. A polished optical-grade sapphire of 10 × 10 mm with the (0001) orientation (*c*-face) was used as a substrate, in which the misorientation was within ±0.5°. The substrate was degreased by successive cleaning in acetone and deionized water, followed by etching with a mixed solution of H₃PO₄–H₂SO₄ (1:3) at 433 K for 10 min before being dried in a stream of dry nitrogen. Afterward, the sapphire substrate was placed on a quartz susceptor in the reactor. ZnI₂ was transported to the reactor with N₂ as a carrier gas. Typical growth conditions are summarized in Table 1. As-deposited films were characterized by X-ray diffraction (XRD) analysis, XRD pole figure analysis, and atomic force microscopy (AFM). Photoluminescence (PL) spectra were measured by exciting the films with light of 325 nm using a He–Cd laser of 15 mW.

Table 1. Typical Growth Conditions

substrate	sapphire (0001)
ZnI ₂ source temperature	648 K
ZnI ₂ partial pressure	3.76 × 10 ¹ Pa
O ₂ partial pressure	2.03 × 10 ⁴ Pa
carrier gas	N ₂
total flow rate	2.0 × 10 ^{−4} m ³ s ^{−1}
growth temperature	1023 K

It was found that the growth for 60 min under the conditions given in Table 1 yields a film of about 100 μm, suggesting that the growth rate is 27.8 nm/s. Figure 2 shows a typical XRD profile of the as-grown films at 1023 K. A strong diffraction line appears at 34.47°, assigned to the (0002) diffraction of the ZnO with hexagonal structure. This implies that the ZnO films were grown epitaxially under atmospheric pressure using ZnI₂ as a source, analogous to those using ZnCl₂.^{8–10} The lattice constant was calculated to be *c* = 0.5215 nm utilizing the observed (0002) diffraction, which is slightly larger than a reported value of 0.520661 nm for the bulk ZnO crystal.¹¹ Also, a full-width at half-maximum (fwhm) value of the ZnO epitaxial layer of about 0.2° is 50% smaller than that of the films deposited by sputtering.¹² It should be noteworthy that the fwhm for the ZnI₂/O₂ system is comparable to that of the films deposited for the ZnCl₂/O₂

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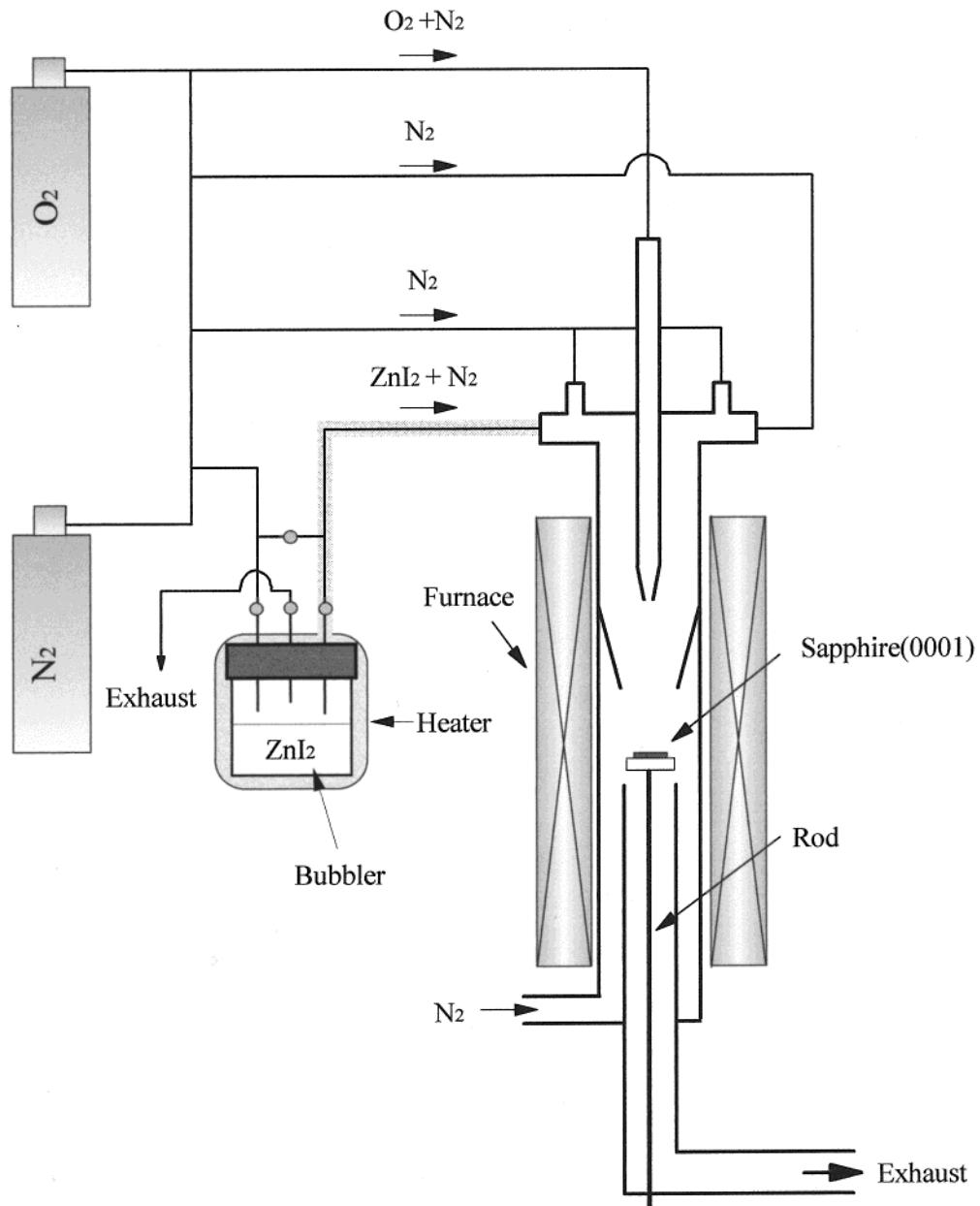


Figure 1. Schematic diagram of AP-HVPE.

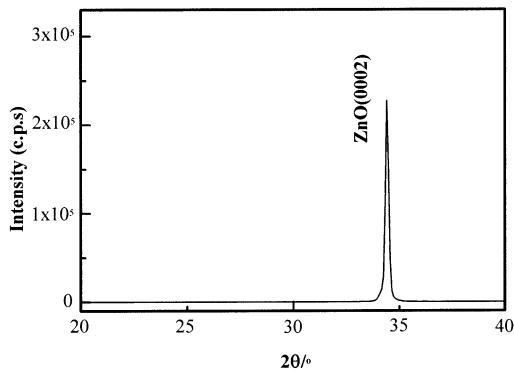


Figure 2. XRD pattern of the as-grown ZnO film deposited on a sapphire (0001) substrate.

system despite the fact that the former deposition rate is higher than the latter one.^{8,9} Therefore, it is deduced that the epitaxial ZnO films by AP-HVPE using ZnI₂ not only have a high growth rate but also are of high quality.

Further examination was carried out using XRD pole figure analysis to elucidate the in-plane alignment of the film. The hexagonal ZnO crystal with a *c*-axis orientation has 6-fold symmetry. Thus, six poles should appear in the pole figure if it has a homogeneous in-plane alignment. As presented in Figure 3, the observed six poles, separated by an angle of 60°, are evidence that the *c*-axis is perpendicular to the film. Also, it supports the homogeneous in-plane alignment of the epitaxially grown ZnO film.

The surface roughness of the ZnO film was evaluated by AFM microscopy. The mean square roughness (R_{ms}) evaluated for a $30 \times 30 \mu\text{m}^2$ of the ZnO film with a thickness of $100 \mu\text{m}$ was $<12.5 \text{ nm}$, suggesting that the surface is flat and smooth. Also, it is found that the surface morphology is smoother than that of ZnO films prepared on sapphire (0001) by CVD.¹³

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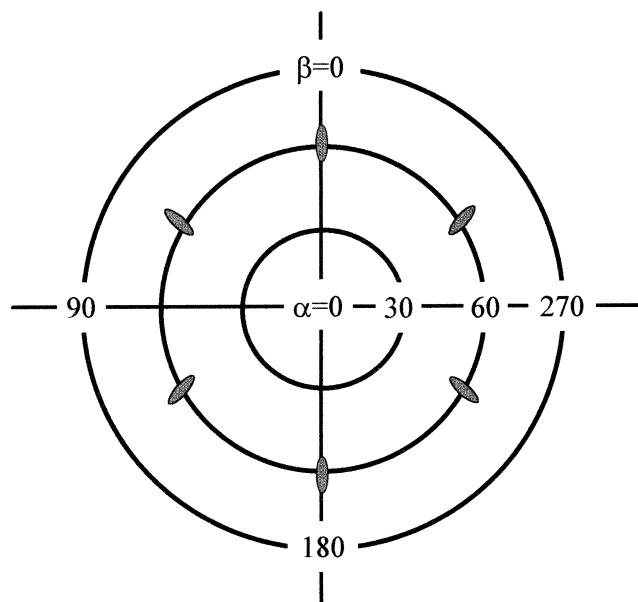


Figure 3. Pole figure of the as-grown ZnO film deposited on a sapphire (0001) substrate.

A room-temperature PL spectrum of the ZnO film is shown in Figure 4. It is worth noting that only an emission appearing at 381.0 nm is observed in the ultraviolet region. No emission was observed in the

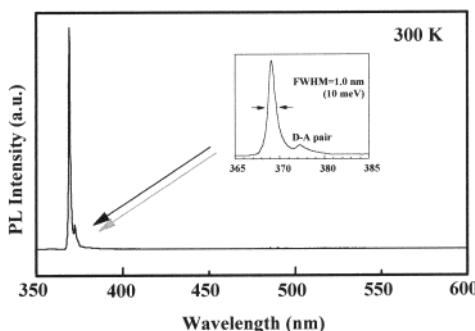


Figure 4. Room-temperature PL signal from a ZnO epitaxial layer.

visible region. The full-width at half-maximum value of the emission peak was ≈ 1.0 nm (10 meV). Taking into account the facts mentioned above, it is presumed that the epitaxial ZnO films grown are of excellent optical quality. Also, they have no deep-level impurities and/or lattice defect in them.

We have succeeded in the preparation of an epitaxially grown ZnO film with 100- μ m thickness. The films showed a room-temperature ultraviolet emission without any emission in the visible region. In conclusion, the AP-HVPE is an excellent method for preparing high-quality ZnO films with a rapid growth rate.

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