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AP-HVPE growth of ZnO with room-temperature ultraviolet emission

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Thin films of ZnO were grown on a sapphire(0001) substrate by atmospheric pressure halide vapor phase epitaxy. A double-crystal X-ray diffraction study showed a minimum full width at half maximum of the hexagonal ZnO(0002) line after 1212 s for the film deposited at 1023 K. The room-temperature photoluminescence spectrum displays an ultraviolet emission at 381.0 nm due to the recombination of free excitons.

1 Introduction

It is known that some metal oxides have unique properties such as high temperature superconductivity[1] and colossal magnetoresistance.[2] Amongst the metal oxides, zinc oxide has a variety of interesting characteristics such as excellent piezoelectric properties, high transmittance and good thermal and chemical stability. As a result, ZnO films have been applied for surface acoustic wave devices, piezoelectric transducers, transparent conducting films and gas sensors.[3–6]

Recently, a new application has been proposed: epitaxial ZnO films, which show an emission in the blue–ultraviolet region, are one of the most promising compound semiconductors because they not only have a wide direct band gap of 3.37 eV, but also a high exciton binding energy of 60 meV at room temperature.[7,8] In particular, it is worth noting that the binding energy of such films is larger than their thermal energy at room temperature, so that the stabilized exicton would lead to room temperature laser emission.

It is not easy to prepare the defect-free ZnO films which are required for non-radiative relaxation and/or deep level-based emission in the visible range, which occurs at 450–570 nm.[9] Zu *et al.*[10] and Chen *et al.*[11] observed ultraviolet emission at room temperature from ZnO films grown by laser molecular beam epitaxy (MBE) and plasma-enhanced MBE, respectively. To date, there is no literature on the preparation under atmospheric pressure of ZnO films showing room temperature ultraviolet emission. In previous work, we examined the epitaxial growth of ZnO films on sapphire(0001) substrates formed by atmospheric pressure halide vapor phase epitaxy (AP-HVPE) using zinc chloride as the zinc source.[12–14] Such films showed a band edge emission at 370 nm up to 180 K, but nothing at temperatures above 180 K. A detailed analysis of their photoluminescence spectra suggested that there might be trace amounts of chloride ions trapped in the films. In this paper, therefore, we report the results of an investigation into the growth of ZnO thin films using zinc iodide, since the iodide ion is more easily reduced to iodine than is the chloride ion to chlorine.

2 Experimental

The zinc iodide and oxygen gas were of 99.999% and 99.995% purity, respectively. The set-up used for the AP-HVPE in this study is illustrated in Fig. 1, together with the temperature profile of a horizontal-type quartz tube reactor. The sapphire(0001) substrate (10 mm × 10 mm) was degreased by successive ultrasonic cleaning in acetone, methanol and deionized water, and then chemically etched in a mixed solution of $H_2SO_4 : H_3PO_4 = 3 : 1$ at 333 K for 600 s before being dried under a flow of dry nitrogen gas. Afterwards, the substrate was placed on a susceptor in the quartz tube reactor. ZnI_2 was evaporated and introduced into the reactor using purified N_2 as the carrier gas. ZnO films were deposited onto the sapphire substrate by the reaction of ZnI_2 and O_2 under atmospheric pressure. Typical growth conditions are summarized in Table 1.

The thickness of the ZnO films was estimated based on scanning electron micrographs recorded on a Shimadzu

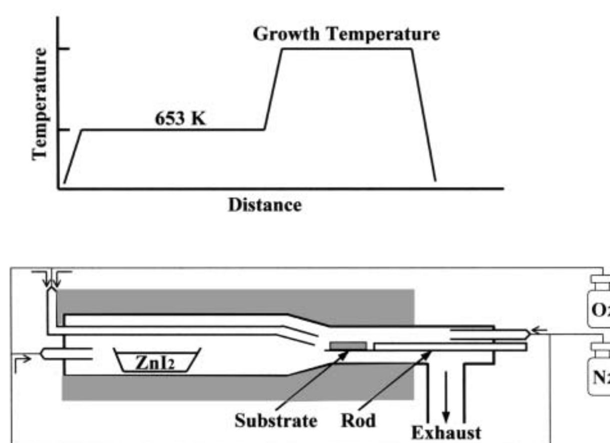

Fig. 1 Schematic diagram of the set-up used for the epitaxial growth of ZnO and the temperature profile of the furnace.

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Table 1 Typical growth conditions employed for the preparation of the ZnO films

Substrate	Sapphire(00001)
ZnI_2 source temperature	653 K
Partial pressure of ZnI_2	11.8 Pa
Partial pressure of O_2	3.04×10^4 Pa
Carrier gas	N_2
Total flow rate	1.0×10^{-5} m^3 s^{-1}
Growth temperature	773–1123 K

Superscan instrument. Crystallinity was evaluated both by double-crystal X-ray diffraction (DC-XRD) analysis and the reflection high-energy electron diffraction (RHEED) technique. XPS spectra were measured using a Shimadzu XRTOS-XSAM 800 X-ray photoelectron spectrometer. The electrical resistivity was determined by means of the four-probe technique using a Veeco Model FPP-100 instrument. Photoluminescence (PL) spectra were measured by excitation with light of wavelength 325 nm using an He–Cd laser with a power of 15 mW at temperatures ranging from 20 to 298 K. All the ZnO films examined in this study had a constant film thickness of 3 μm.

3 Results and discussion

XRD measurements confirm that the hexagonal ZnO films prepared by AP-HVPE using ZnI_2 are grown epitaxially on the sapphire(0001) substrate, similarly to those prepared using $ZnCl_2$ as the zinc source reported previously.[15] The XPS analysis suggests that the films contain C, N and I impurities at levels of less than 0.1 at%. This is consistent with the high resistivity of 2.5 kΩ m obtained for the films. Thus it is evident that the epitaxial ZnO films grown using ZnI_2 have less impurities and defects compared to those prepared from $ZnCl_2$.

Fig. 2 shows the dependence of the growth rate of the ZnO film on the growth temperature. It is noted that the growth rate increases monotonically from 0.06 to 0.83 nm s^{-1} with increasing temperature from 773 to 1123 K. In this temperature range, the activation energy for the epitaxial growth of the ZnO film is estimated to be 56.9 kJ mol^{-1} from the slope of the plot of growth rate against $1/T$ shown in Fig. 2. This implies that a surface reaction, such as adsorption of chemical species, is the rate-determining step for the epitaxial growth of the ZnO films.

Fig. 3 shows the variation of the full width at half maximum (FWHM) of the hexagonal Zn(0002) DC-XRD line as a function of the growth temperature. The FWHM decreases gradually to 1212 s as the growth temperature increases to 1023 K. A further increase in the growth temperature results in broadening of the FWHM, indicating that the best crystallinity is obtained at 1023 K.

Fig. 4 shows a representative RHEED pattern of the ZnO films grown at 1023 K in which the direction of the incident

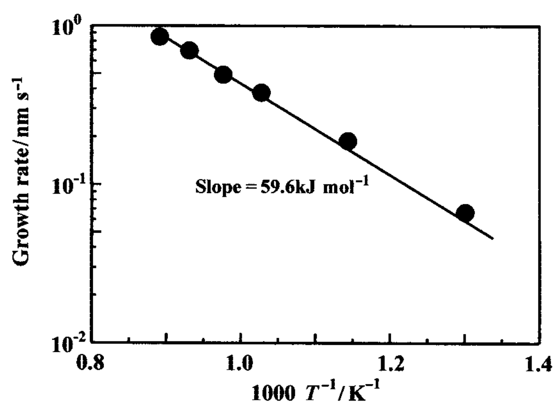

Fig. 2 Dependence of the growth rate of ZnO film on the growth temperature.

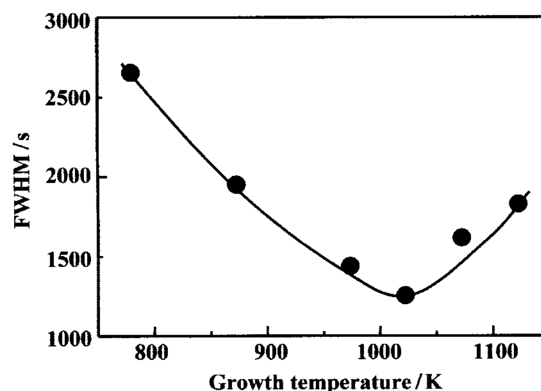

Fig. 3 Variation of the FWHM of the hexagonal ZnO DC-XRD diffraction line as a function of the growth temperature.

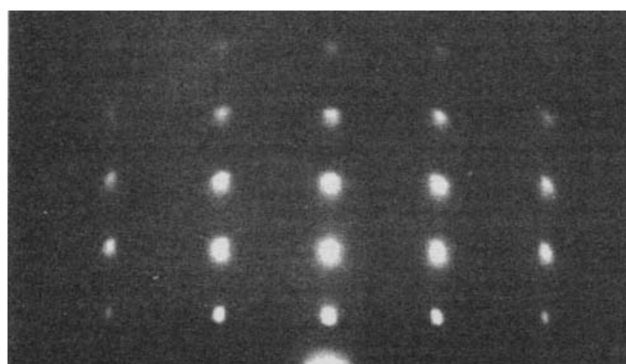

Fig. 4 The RHEED pattern of the ZnO film grown at 1023 K.

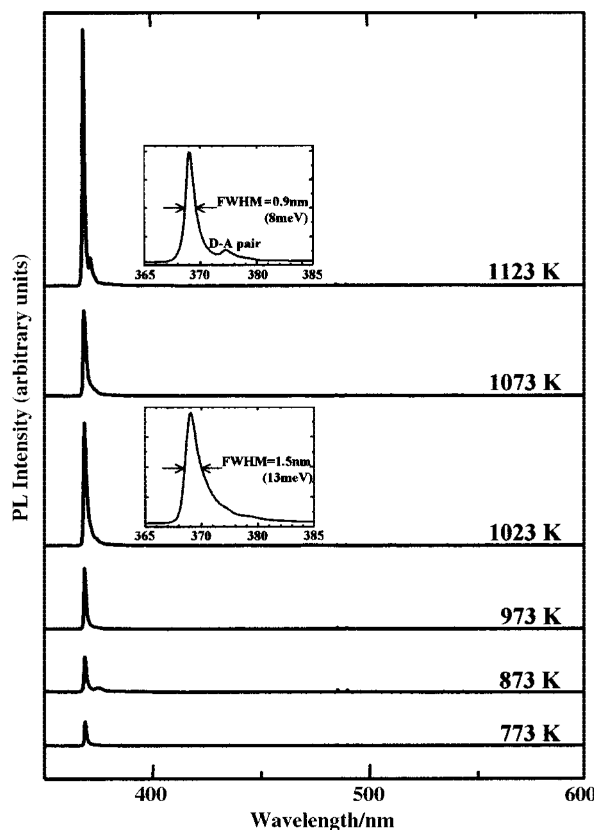

Fig. 5 Low temperature PL spectra of ZnO films deposited at various temperatures, recorded at 20 K.

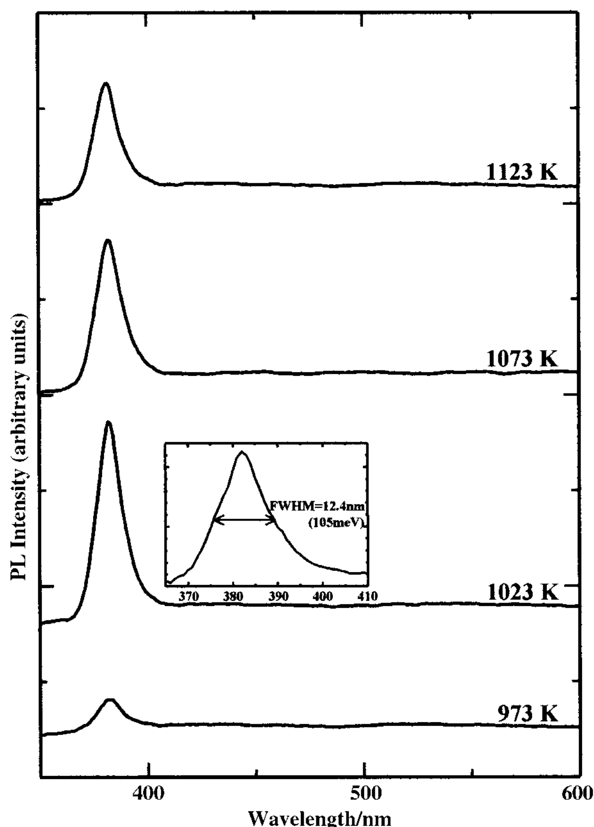

Fig. 6 Room temperature PL spectra of ZnO films deposited at various temperatures.

electron beam is parallel to [11$\bar{2}$0]ZnO. As can be seen from Fig. 4, the pattern consists of spots superimposed on sharp streak lines. This is typical of a RHEED pattern for ZnO films grown epitaxially.

Fig. 5 shows the low temperature PL spectra of ZnO films deposited at various temperatures, measured at 20 K. It is worth noting that no emission peak is observed in the visible region, implying that no deep levels due to impurities and/or lattice defects are formed in the ZnO films prepared by AP-HVPE.

The band edge emission that appears at 368.9 nm increases in intensity as the growth temperature is increased. The maximum PL intensity is observed at 1123 K, while the FWHM shows a minimum at 1073 K. In the enlarged PL spectrum, only a single strong emission at 368.9 nm due to bound excitons appears for the ZnO film prepared at 1023 K.[16] However, a weak emission at 372.1 nm associated with the recombination of the donor–acceptor pair is observed for the film prepared at 1123 K, although the edge emission at 368.9 nm is much sharper and stronger. The estimated FWHM of the band edge emission is 1.5 (13) and 0.9 nm (8 meV) at 1023 and 1123 K, respectively. Taking into account the data described above, it is presumed that impurities such as iodine are incorporated in the ZnO film at growth temperatures above 1023 K.

Fig. 6 shows the room temperature PL spectra of ZnO films deposited at various temperatures. An emission is observed at 381.0 nm, which is due to the recombination of free excitons.[16] From a comparison of their PL spectra, it is apparent that the ZnO film grown at 1023 K shows the strongest band edge emission of any film prepared in this study. It is important to note that this film has an FWHM value of 12.4 nm (105 meV) at room temperature, which is similar to that for the film grown by plasma-enhanced MBE (110 meV).[17]

4 Conclusions

We have succeeded in preparing epitaxially grown ZnO films that show an ultraviolet emission at 381.0 nm with an FWHM of 12.4 nm, due to the recombination of free excitons at room temperature. The AP-HVPE method using ZnI_2 is not only simple but also useful for the preparation of high quality ZnO films, despite the fact that it has a higher sample growth rate compared with other methods operated under reduced pressure.

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