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Growth of a high quality ZnO film on sapphire by atmospheric pressure halide vapor phase epitaxy using ZnO buffer layers

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Hexagonal ZnO films have been grown on a sapphire(0001) substrate by atmospheric pressure halide vapor phase epitaxy using ZnO buffer layers. The full width at half maximum of the X-ray (0002) diffraction peak for the ZnO films with the buffer layer was found to be smaller than that of the ZnO films without the buffer layer. Reflection high-energy electron diffraction measurements of the former revealed a diffraction pattern similar to that of a single crystal. The photoluminescence spectra showed a strong peak at 370 nm up to 180 K.

1 Introduction

ZnO is one of the most promising materials for light-emitting devices in blue, violet and ultraviolet regions because this material has a direct energy band gap of 3.37 eV.[1] For device fabrication, high-quality crystals with smooth specular surfaces are required, hence single crystals are usually grown on sapphire(0001) substrates.[2,3] However, epitaxial ZnO films of high quality with smooth surfaces which are free from cracks are not easy to grow because of the large lattice mismatch (*ca.* 13.4%) between ZnO and the substrate and the large difference in their thermal expansion coefficients. For this reason, a number of attempts have been made to grow high-quality single crystals. According to Amano *et al.*[4] and Nakamura,[5] the quality is improved greatly by prior deposition of a buffer layer on the substrate.

In a previous paper, we reported that hexagonal ZnO epitaxial layers can be successfully grown on a sapphire(0001) substrate by atmospheric pressure vapor phase epitaxy using a chloride source as the starting material.[6,7] We abbreviate this method to AP-HVPE hereafter. The obtained ZnO films showed a minimum full width at half maximum (FWHM) of the (0002) X-ray peak of 23.3 min and exhibited band edge emission at 370 nm. However, this FWHM is larger than that (3.6 min) of epitaxial ZnO deposited by MBE.[2] Therefore, further improvement (FWHM lower than 1.0 min) is required to obtain ZnO films by AP-HVPE which are suitable for practical application. In this paper we report the results of epitaxial growth of ZnO by AP-HVPE using a ZnO buffer layer on a sapphire(0001) substrate. The optical properties of such films are also reported.

2 Experimental

ZnO films were grown by AP-HVPE using $ZnCl_2$ and O_2 for starting materials, as described previously.[6] Growth of the hexagonal ZnO epitaxial layer was carried out in a horizontal quartz reactor at atmospheric pressure. Optical grade polished sapphire (10×10 mm) with (0001) orientation (*c*-face) was used as a substrate. The misorientation was within $\pm 0.5°$. The sapphire was degreased by successive cleaning in acetone and deionized water and chemically etched with a hot solution (160 °C) of H_3PO_4–H_2SO_4 (1 : 3) for 10 min before being dried in a stream of dry nitrogen. Afterwards, the sapphire substrates were placed on the susceptor in the reactor. High purity zinc chloride (99.999% $ZnCl_2$) and high purity oxygen gas (99.995% O_2) were used as the Zn and O sources, respectively. Thin films of ZnO were deposited onto the sapphire(0001) surface in the hot wall reactor by the reaction of $ZnCl_2$ with O_2 under atmospheric pressure. During the deposition, $ZnCl_2$ was evaporated from the source boat at a temperature of 480 °C, the vapour was then supplied to the growth zone. Purified N_2 was used as the carrier gas.

Fig. 1 shows a typical ZnO growth process using a ZnO buffer layer. It has two steps: the buffer layer of ZnO was deposited at 500 °C and then the epitaxial film was grown at 900 °C. After the first step, the buffer layer was annealed at

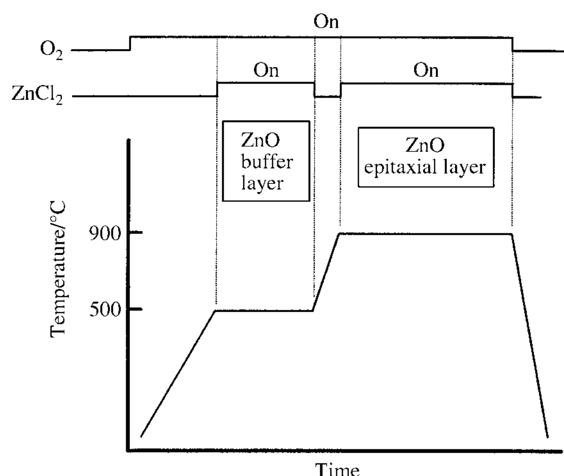

Fig. 1 Time chart of the AP-HVPE growth process using a ZnO buffer layer.

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Table 1 Typical growth conditions

Substrate	Sapphire(0001)
$ZnCl_2$ partial pressure	1.3×10^{-3} atm
O_2 partial pressure	3.0×10^{-1} atm
$ZnCl_2$ source temperature	480 °C
Carrier gas	N_2
Total flow rate	600 cm^3 min^{-1}
Growth temperature of ZnO buffer layer	500 °C
Growth temperature of ZnO epitaxial layer	900 °C

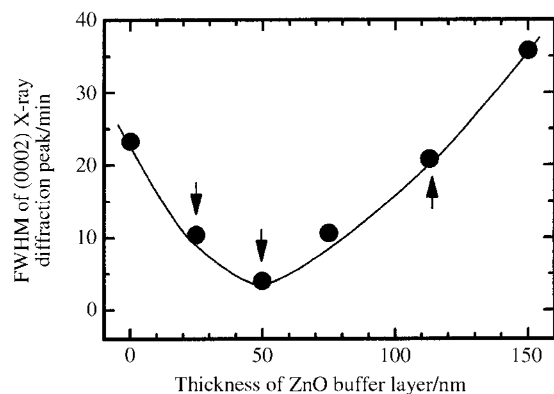


Fig. 2 The FWHM value of the (0002) X-ray diffraction peak of hexagonal ZnO as a function of the thickness of the ZnO buffer layer on sapphire(0001).

900 °C for 10 min under a flowing O_2 atmosphere. The buffer layer was found to be amorphous. For the second step, epitaxial ZnO layer growth was started by restoring the supply of both $ZnCl_2$ and O_2 to the reactor. Typical growth conditions are summarized in Table 1. In order to elucidate the effect of the ZnO buffer layer, the same experiments were also carried out without a buffer layer.

The crystallinity of the ZnO films was assessed by double crystal X-ray diffraction analysis and the reflection high-energy electron diffraction (RHEED) technique. The thickness and surface morphology of the films were evaluated by means of scanning electron microscopy (SEM) (Shimadzu superscan) and atomic force microscopy (AFM) (Shimadzu Co., SPM-9500), respectively. Photoluminescence (PL) measurements were carried out by exciting the samples with light of 325 nm provided by a He–Cd laser of 15 mW. All the measurements were performed using ZnO films of approximately 2.15 μm in thickness.

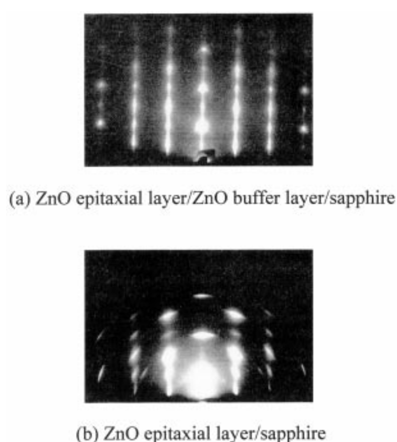
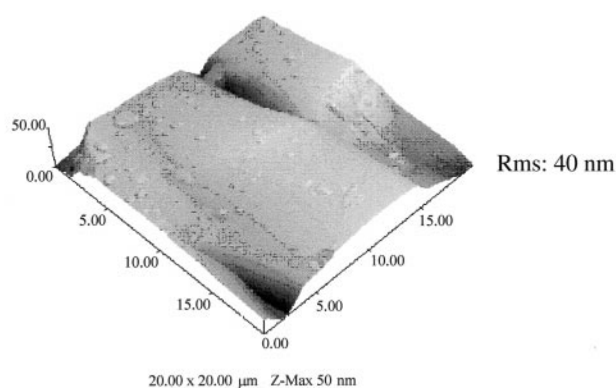
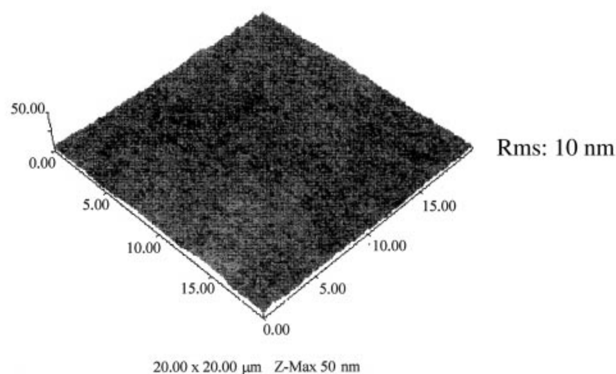


Fig. 3 RHEED patterns of ZnO epitaxial layers (a) with a ZnO buffer layer and (b) without a ZnO buffer layer.





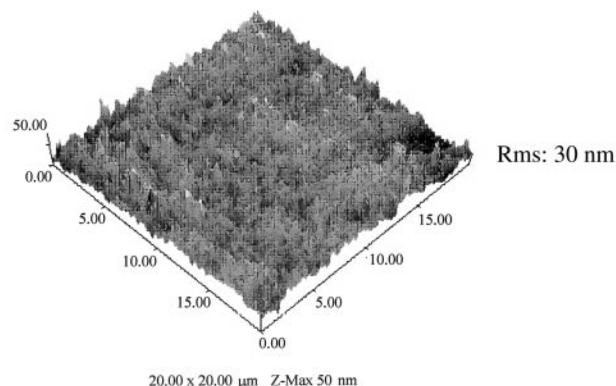


Fig. 4 AFM images of ZnO epitaxial layers. The thicknesses of the ZnO buffer layers are (a) 25, (b) 50 and (c) 100 nm.

3 Results and discussion

Fig. 2 shows the FWHM of the (0002) diffraction line for the obtained hexagonal ZnO films as a function of the thickness of the ZnO buffer layer on sapphire(0001). As is evident from Fig. 2, the FWHM decreases with the increasing thickness of the buffer layer up to 50 nm and then gradually increases. A minimum FWHM value of 4.3 min was obtained with a buffer layer thickness of approximately 50 nm. This value is comparable to that (3.6 min) of an epitaxial ZnO layer deposited by MBE,[8] implying that the optimum thickness for the buffer layer is around 50 nm.

A representative RHEED pattern for a ZnO film with a ZnO buffer layer thickness of 50 nm is shown in Fig. 3, together with that for a film without a buffer layer. It is immediately noticeable that the RHEED pattern of the ZnO film with the buffer layer shows streaks, indicating that the grown layer is of

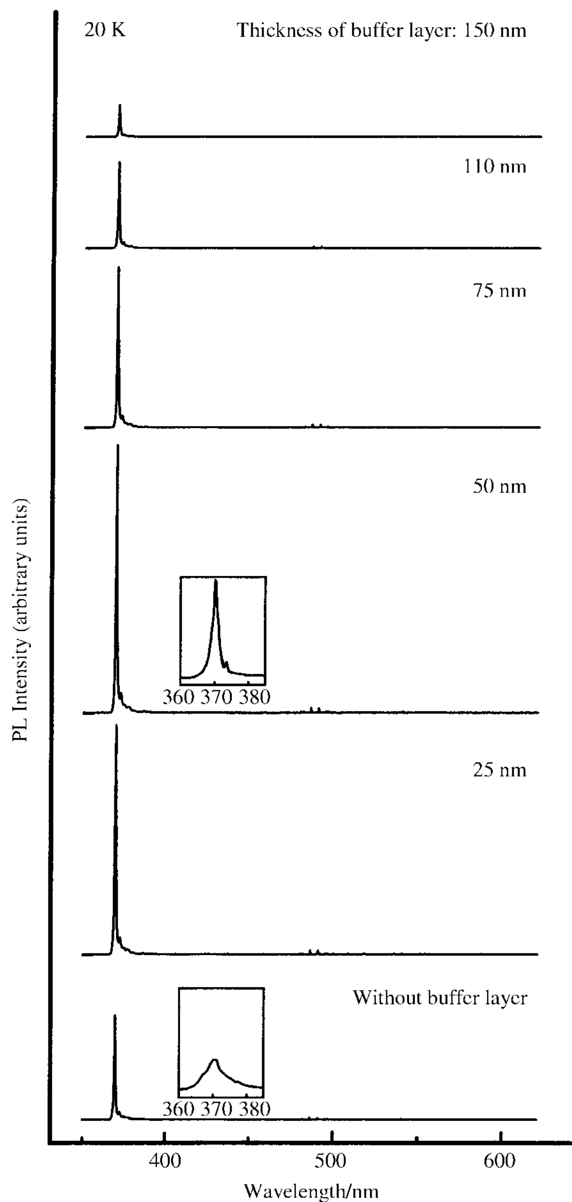


Fig. 5 Low temperature PL signals from hexagonal ZnO epitaxial layers on various thicknesses of ZnO buffer layer.

good crystallinity and some degree of roughness. On the other hand, the RHEED pattern of the ZnO film without a buffer layer shows rings, indicating that polycrystalline ZnO is formed. Therefore, the ZnO buffer layer is thought to be essential for growing a high quality ZnO epitaxial layer. Akasaki *et al.*[9] and Kuwano *et al.*[10] have pointed out that buffer layers play an important role in the relaxation of the lattice mismatch between the epitaxial layer and the substrate. Consequently, it is presumed that the high quality ZnO epitaxial layer obtained in this study is a result of the relaxation of the lattice mismatch by the ZnO buffer layer.

Fig. 4 shows AFM images of ZnO epitaxial layers of the thicknesses indicated by arrows in Fig. 2. As is shown in Fig. 4(b), a smooth surface with roughness of less than 10 nm was obtained with a ZnO buffer layer of 50 nm. The samples prepared with ZnO buffer layers of 25 nm and 110 nm in depth showed very rough surfaces. It is therefore evident that the surface morphology is significantly affected by the ZnO buffer layer.

Fig. 5 shows the PL spectra of the ZnO epitaxial layers at 20 K, for which the ZnO buffer layer was varied from 0 to 150 nm. It is worth noting that no emission peak is observed in

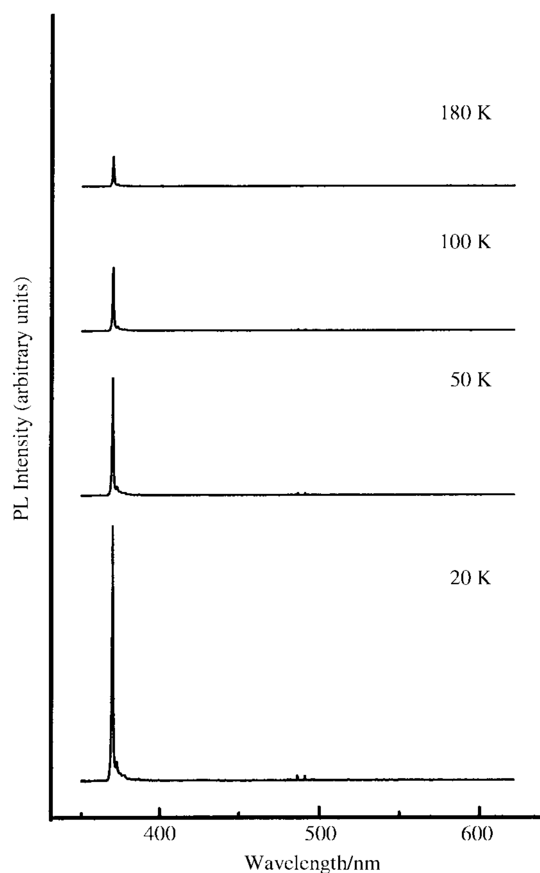


Fig. 6 PL signals at various measurement temperatures from epitaxial ZnO grown on a 50 nm ZnO buffer layer.

the visible region, suggesting that no deep-level impurities and/or lattice defects are formed in the films. This implies that the hexagonal ZnO epitaxial layers grown by AP-HVPE are of high optical quality. The strongest band edge emission was observed for the epitaxial ZnO grown on a ZnO buffer layer of 50 nm thickness. It was found that the intensity of emission is approximately 2.5 times stronger than that for the ZnO films without a buffer layer. The FWHM of the band edge emission showed a lowest value of 5 nm with a buffer layer thickness of 50 nm. This value is half that found for ZnO epitaxial films without buffer layers, but a little larger than for a ZnO epitaxial layer grown by MBE (0.56 nm).[2]

Fig. 6 shows the PL spectra of the epitaxial ZnO film with the buffer layer thickness of 50 nm in the temperature range of 20 to 180 K. An emission at 370 nm was observed up to 180 K in this study, while this band was only seen up to 80 K for the epitaxial layer without a ZnO buffer layer.[7] This confirms that the quality of the ZnO epitaxial layer is significantly improved by the prior deposition of a buffer layer. Consequently, it is found that the buffer layer is essential for growing a high-quality ZnO epitaxial layer. Bagnall *et al.*[2] and Zu *et al.*[3] have reported a strong sharp line at approximately 370 nm in the PL spectrum of a ZnO epitaxial layer at room temperature. Therefore, further investigation is in progress into the growth of ZnO films which display this room temperature emission.

4 Conclusions

The effect of a ZnO buffer layer on the epitaxial growth of ZnO by AP-HVPE has been investigated. X-ray diffraction, RHEED and AFM observations indicate that the optimum thickness of the ZnO buffer layer is 50 nm. The photoluminescence spectra exhibited a strong peak at 370.0 nm and the intensity of this emission for a ZnO epitaxial layer with a ZnO

buffer layer is approximately 2.5 times stronger than for a similar sample without a buffer layer. Furthermore, PL was observed up to 180 K for the ZnO epitaxial layer with a buffer of 50 nm. In conclusion, a hexagonal ZnO epitaxial layer of good quality is obtainable by prior deposition of a ZnO buffer layer. The key growth parameters are the deposition temperature and the annealing temperature of the ZnO buffer layer. In future research, we will concentrate on improving the crystallinity of the epitaxial layer by optimization of the buffer layer in order to grow the ZnO films which display room temperature PL emissions.

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