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Annealing properties of ZnO films grown using diethyl zinc and tertiary butanol

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Abstract

ZnO films were grown by atmospheric metal–organic chemical vapour deposition and annealed at 900 °C in an oxygen environment. The annealing properties of the films have been characterized by means of x-ray diffraction, Raman scattering, Rutherford backscattering (RBS), elastic recoil detection analysis (ERDA) and photoluminescence spectra. The results indicate that high crystal quality ZnO film has been obtained after annealing. The full width at half-maximum of ω rocking curves is only 369 arcsec. The Raman spectra show a strong high frequency E_2 mode peak comparable to that for bulk ZnO. The intensity ratio of the $E_1(\text{LO})$ peak to E_2^{high} peak before annealing is 0.81 and after annealing 0.75. RBS and ERDA spectra indicate that a stoichiometric ZnO film is formed and the annealing only changes the H content in the ZnO film. After annealing all emission lines become sharper, as expected, which means a higher quality film has been obtained.

1. Introduction

ZnO is a direct, wide band gap semiconductor material with large exciton binding energy (about 60 meV). It has many interesting applications in optic–electronic devices, especially in the short wavelength region. In order to obtain high quality ZnO films, many growth techniques such as sputtering [1], pulsed laser deposition [2], MBE [3] and metal–organic chemical vapour deposition (MOCVD) [4] have been employed. The MOCVD method is an important way to grow optical material for optical–electric devices, so ZnO films grown by MOCVD attract the

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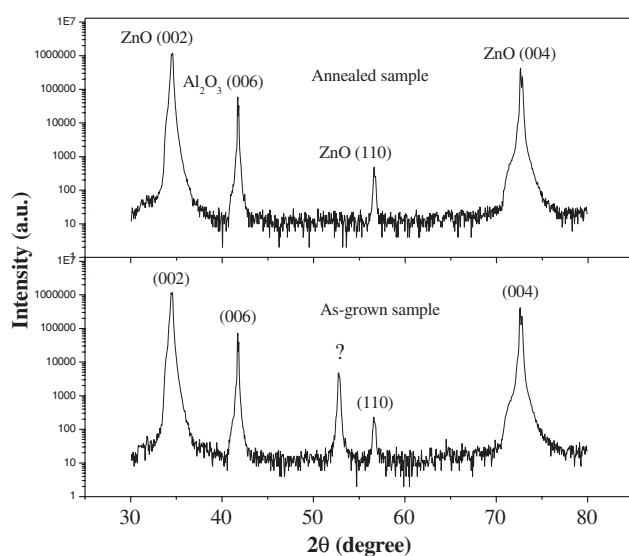


Figure 1. 2θ scanning spectra of the as-grown and annealed ZnO films.

most attention. Using tertiary butanol as precursor, ZnO films were grown by MOCVD and discussed in [5–7]. However, there is no report on the composition and annealing properties of ZnO film grown using tertiary butanol. In this paper, we report the influence of annealing on its composition and properties.

2. Experimental details

Epitaxial growth of ZnO is performed in a vertical, radio-frequency heated, water cooled quartz MOVCD reactor operated at atmospheric pressure. Diethyl zinc (DEZn) and the tertiary butanol are used as Zn and O precursors, respectively. The substrate material is *c*-plane sapphire and hydrogen is employed as the carrier gas. The film was grown under optimized conditions. After growth, the sample was divided into two pieces, and one was annealed at 900 °C in an oxygen environment for 0.5 h.

The crystal quality of the two samples was measured by means of high resolution x-ray diffraction (HRXRD). Raman scattering measurements were carried out at room temperature in backscattering geometry using an Ar⁺ ion laser (514.5 nm) as excitation. The composition of the samples was estimated from Rutherford backscattering (RBS) spectra obtained using ⁴He and H beams at 2 MeV. Elastic recoil detection analysis with a 2 MeV ⁴He beam was used to determine the H content. All the spectra from the samples were analysed in a consistent way with the code NDF [8]. Photoluminescence (PL) measurements at different temperatures were carried out with a He–Cd laser (325 nm) as excitation source, and a 325 nm band pass filter was used to attenuate lines other than the 325 nm laser line. The luminescence was dispersed by a Spex 1704 monochromator (1 m, 1200 mm⁻¹) and detected by a cooled Hamamatsu R928 photomultiplier.

3. Results and discussion

For comparison, figures 1 and 2, respectively, show 2θ scanning and ω rocking curves of the as-grown and the annealed ZnO film. As seen from figure 1, all spectra show very strong (002), (004) plane of ZnO and (006) plane of sapphire diffraction peaks, which means that ZnO films were grown in (001) orientation on *c*-plane sapphire substrates. The experimental data indicate

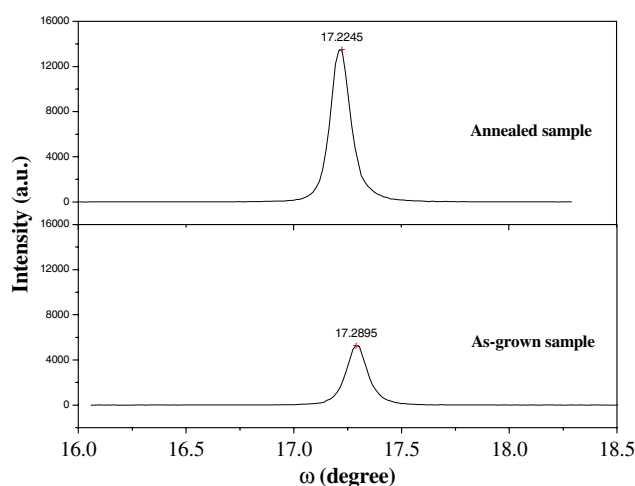


Figure 2. Rocking curves of the as-grown and annealed ZnO films.

that there is no obvious difference for (002) and (004) peaks of ZnO between before and after annealing. However, we can see that the intensity of the sapphire (006) peak decreases a little upon annealing. Besides these three peaks, two other weak peaks are observed, at 52.77° and 56.66° , respectively. The peak at 52.77° disappears upon annealing at 900°C in an oxygen environment; its origin is not clear. Perhaps it results from carbon or hydrogen contamination in the ZnO film. As for the second peak, it comes from ZnO(110) plane diffraction. The spectra show that the (110) peak becomes a little stronger upon annealing, which may be caused by the combination of ZnO columns and strain relaxation during annealing. Figure 2 indicates that the ZnO(002) peak becomes much stronger and sharper after annealing. Its intensity increases more than two times and the FWHM decreases from 403 to 369 arcsec. Furthermore, the peak position moves to about 17.22° , which is in good agreement with bulk ZnO, indicating that annealing relieved most of the strain in the film.

As is known, group theory predicts that the E_2^{low} , E_2^{high} , A_1 and E_1 phonon vibration modes in ZnO are Raman active. Furthermore, A_1 and E_1 modes are respectively divided into $A_1(\text{TO})$, $A_1(\text{LO})$ and $E_1(\text{TO})$, $E_1(\text{LO})$ due to the electric field associated with the longitudinal phonon [9]. The vibration modes in the ZnO film have been examined. Raman scattering spectra of the as-grown and the annealed film were recorded in the range from 70 to 700 cm^{-1} , and are shown in figure 3. In order to compare with bulk ZnO, we also show the Raman spectrum of ZnO substrate material supplied by EaglePitcher. As seen, the spectra of the films all show two typical E_2^{low} and E_2^{high} Raman peaks at about 98 and 438 cm^{-1} , respectively. Furthermore, these two peaks become stronger and sharper after annealing. However, in contrast to the bulk ZnO case, the spectra of the both samples show a very weak $E_1(\text{LO})$ peak at 581.9 cm^{-1} . Generally, this vibration mode is not allowed in the backscattering geometry (laser beam parallel to c -axis ZnO), so the presence of the weak $E_1(\text{LO})$ peak indicates that there are still some defects and a little disorientation in the films even if they have a high crystal quality. For comparison, the intensity ratio of the $E_1(\text{LO})$ peak to the E_2^{high} peak was calculated for the as-grown and annealed films. The corresponding ratio is 0.81 and 0.75, respectively. It is clear that the ratio decreases upon annealing, which means that the crystal quality has been improved by annealing. Furthermore, these conclusions are all in accordance with the sample XRD changes.

The RBS and ERDA spectra collected from the as-grown sample are shown in figure 4. The ^4He RBS spectrum is very sensitive to the actual surface of the sample, but does not probe

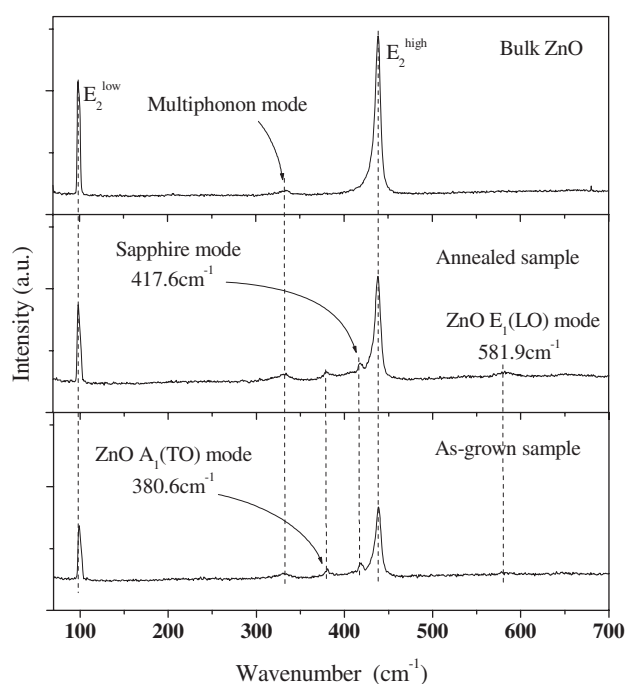


Figure 3. Raman backscattering spectra of the as-grown and annealed ZnO films and EaglePitcher bulk ZnO.

the entire film. In contrast, with the H beam we can determine the film thickness and also the O content with high sensitivity. Finally, the ERDA technique is only sensitive to the H content of the samples. The analysis shows that stoichiometric ZnO is formed, around $4 \mu\text{m}$ thick, using the ZnO bulk density of 5.675 g cm^{-3} , as shown in figure 5. The surface of the film is contaminated with light elements, mostly H, and possibly Al. A very small amount of C is also found at the surface. On annealing, the depth profile of the sample remains almost unchanged. The only difference is that the H content of the film near the surface is decreased by almost a factor of two. This supports the idea that the changes on annealing are connected not with a changing composition, but with an improvement in the crystalline structure of the ZnO.

PL spectra of the as-grown and the annealed film were recorded in the range from 3.1 to 3.4 eV under different temperatures. As shown in figure 6 the 7 K PL spectra of the as-grown and annealed films are very similar to ones observed for bulk samples using similar excitation conditions [10–12]. Despite the fact that the emission lines are slightly shifted to lower energies the general shape of the steady state PL spectra is coincident with the observed optically active centres in ZnO substrates. In the as-grown sample the low temperature emission is dominated by a broad D^0X line near 3.36 eV with a full width at half-maximum (FWHM) of 9 meV, followed by its two-electron satellites (TES) and LO phonon replicas. On the low energy side of these lines the 3.22 eV donor–acceptor pair (DAP) recombination assisted by LO phonon replicas is clearly resolved.

Annealing the sample promotes the observation of narrower emission lines as indicated in figure 6(b). Emission lines that were previously overlapped in the as-grown sample can now be clearly distinguished due to the increase of the film quality as also pointed out from the XRD measurements. With increasing temperature the 3.22 eV DAP recombination quenches for the temperatures above 40 K as observed from bulk samples [10–12], and a higher energy transition that is likely to be due to a second DAP as identified in bulk samples [12] is observed. Furthermore, the increase in temperature promotes simultaneously a decrease of the emission

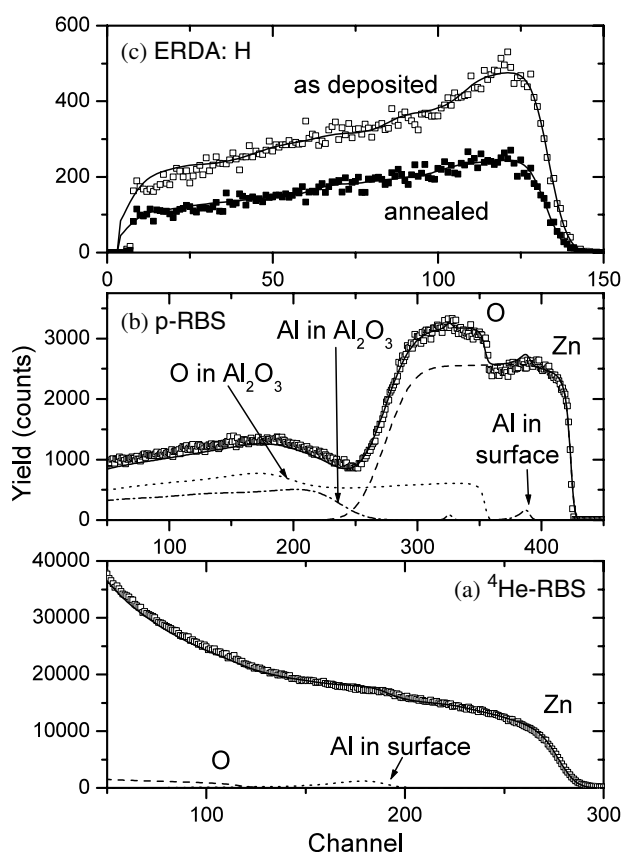


Figure 4. RBS spectra with (a) a ^4He beam and (b) a H beam, and (c) elastic recoil detection analysis (ERDA) spectra, for the as-grown sample. The ERDA spectrum for the annealed sample shows a decrease in H content.

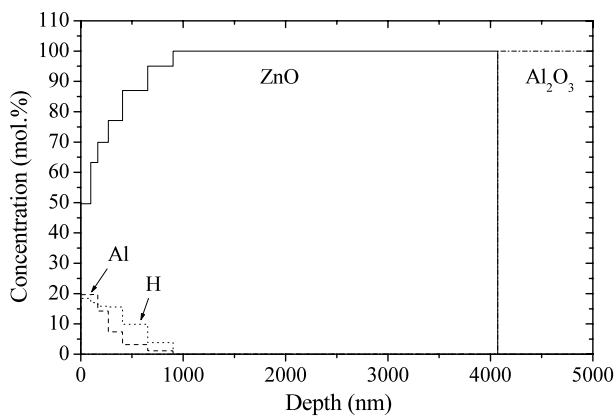


Figure 5. Compositional–depth profiles of the as-grown sample, as determined with RBS and ERDA. The annealed sample is very similar, showing only a decreased H content.

intensities and the overlap of the emitting centres. Also the shrinkage of the band gap is clearly observed at higher temperatures.

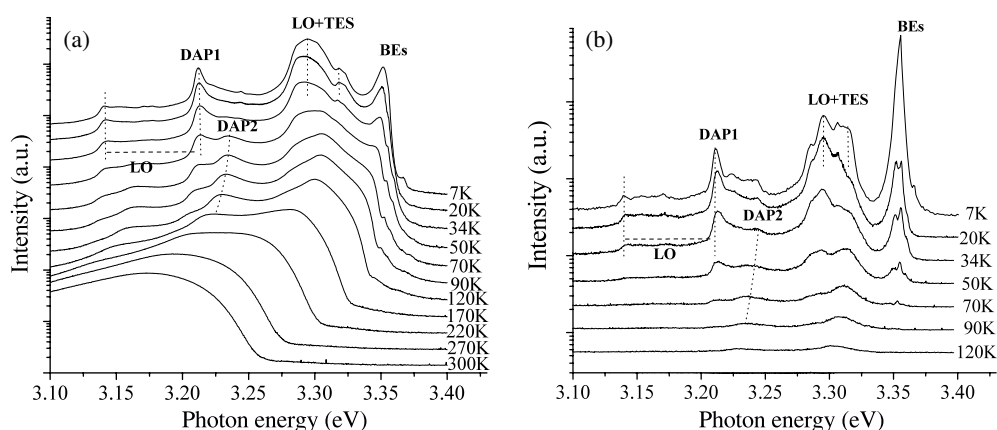


Figure 6. PL of ZnO films at different measuring temperatures. (a) PL of the as-grown film, (b) PL of the annealed film.

4. Conclusion

High quality ZnO films have been grown by the MOCVD method using DEZn and tertiary butanol as precursors. Furthermore, the annealing properties of ZnO films were studied in detail. RBS and ERDA spectra indicate that stoichiometric ZnO films were obtained and annealing only decreases the H content in the film. Also the crystal and optical quality have been improved by annealing. The FWHM of the rocking curves decreases to 369 arcsec upon annealing.

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