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Raman scattering of ZnO films prepared by the laser molecular beam epitaxy

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A series of ZnO films have been prepared on Si (100) substrate at various oxygen pressures and at various substrate temperatures by using a laser molecular beam epitaxy system. Their structure was investigated by the Raman spectroscopy and X-ray diffraction. Raman spectra showed that only E_2 (low) and E_2 (high) modes were present in all ZnO films. The E_2 (low) mode peak changed from disperse to sharp at first and then became more dispersed as either the oxygen pressure or the substrate temperature increased. Its intensity reached a maximum either under the oxygen pressure of 1 Pa or at 773 K. The analyses showed that the sharper and stronger the E_2 (low) mode peak, the better the crystal quality, which was confirmed by the X-ray diffraction. Moreover, every E_2 (high) mode peak shifted to lower Raman frequencies compared with ZnO single crystal, implying that a tensile stress occurred in all films, which was also proved by the X-ray diffraction. All results indicated that Raman scattering is one of the most useful methods to investigate the structure of ZnO films. In addition, the intensity of Si Raman scattering was enhanced in our results, which might be due to surface-enhanced Raman spectroscopy.

Keywords: *Raman scattering; X-ray diffraction; ZnO films; laser molecular beam epitaxy*

1. Introduction

ZnO wjich has attracted much attention in recent years [1–4], is a versatile II–IV semiconductor material, with a variety of applications such as in ultraviolet (UV) emitters and detectors, surface acoustic wave (SAW) devices, gas sensors and transparent conducting electrodes. Many reports on ZnO films involved some techniques to study their structure, playing a key role in determining the properties of ZnO films. Raman scattering is considered to be a valuable technique for fast and nondestructive study of ZnO films. It can give information about the crystal structure at the scale of a few lattice constants. Any distortion of the lattice, excursion of the component, crystal defect and phase transformation can be shown in Raman bands. Therefore, the Ra-

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man spectroscopic technique is one of the most useful methods for gaining insight into the microscopic structural effects of ZnO materials. In this paper, we have used Raman scattering to investigate the effects of both oxygen pressure and substrate temperature on ZnO films.

2. Experimental

All ZnO films were prepared on single crystals Si (100) substrates by using a laser molecular beam epitaxy system. The laser source was a KrF excimer laser with the wavelength of 248 nm. The pulse of the laser was 5 Hz and the energy was 100 mJ per pulse. A ZnO ceramic target with the diameter of 40 mm and the purity of 99.99% was installed parallel to the substrate surface and the distance between the target and the substrate was about 5 cm. The base pressure was ca. 5×10^{-6} Pa. When in position, all KrF excimer laser pulses were focused by a lens and were directed onto a ZnO ceramic target. In order to improve the crystal quality of ZnO films and to compensate the oxygen atoms in ZnO films, the oxygen gas with a purity of 99.999% was put into a deposition chamber. Both the target and the substrate were rotated at 30 rev/min in order to make the ZnO films homogeneous. The deposition time was about 2 h for all samples. The microstructure of ZnO films was investigated using both a Raman spectrometer and an X-ray diffractometer (XRD) with Cu K_α radiation ($\lambda = 0.15406$ nm). The cross-section morphologies were characterized by scanning electronic microscopy (SEM). The thicknesses of ZnO layers could also be determined by observing the cross-section morphologies of ZnO layers. The results showed that all ZnO layers are ca. 800 nm.

3. Results and discussion

Figure 1 shows the Raman spectra of ZnO films prepared on Si substrate under various oxygen pressures. The substrate temperatures are all 773 K and all the results could be obtained by the subtraction of signals of the Si substrate from total signals. It can be seen that the E_2 modes corresponding to ZnO films are represented besides some Raman peaks corresponding to single crystal Si, and no other Raman peaks corresponding to ZnO were discovered. The E_2 modes include an E_2 (low) mode at about 99 cm^{-1} and an E_2 (high) mode at about 437 cm^{-1} [5]. It was clear from Fig. 1 that the ZnO film exhibited a dispersed E_2 (low) peak with low intensity at a low oxygen pressure of 10^{-5} Pa. As the oxygen pressure increased, the E_2 (low) peak first became sharp and then dispersed, reaching its sharpest profile at 1 Pa oxygen pressure. At the same time, the intensity of the E_2 (low) peak also reached a maximum. Meanwhile, it could be seen that the position of E_2 (high) peaks for all ZnO films shifted to a lower frequency compared with ZnO single crystal [5]. In addition, it should be noted that a very strong Raman signal of Si substrate was present even if the substrate signal was subtracted from the total signal. This might be attributed to the surface-enhanced Raman spectroscopy (SERS) [6] induced by the epitaxy layer ZnO films. Further comparative studies will be undertaken later.

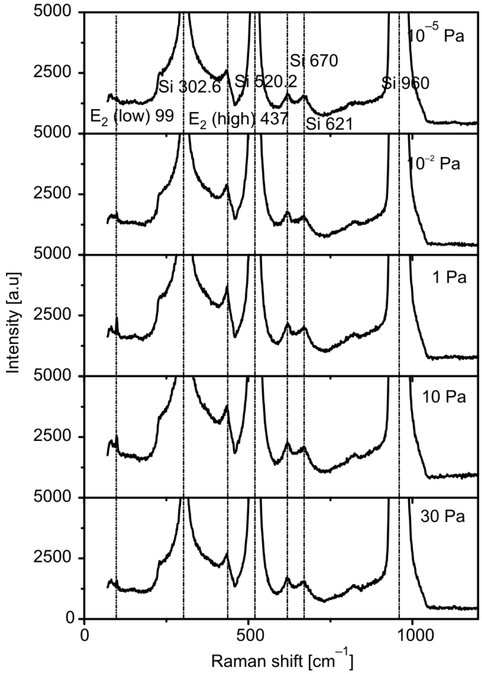

Fig. 1. Raman spectra of ZnO films prepared on Si substrate under various oxygen pressures. The substrate temperatures are all 773 K

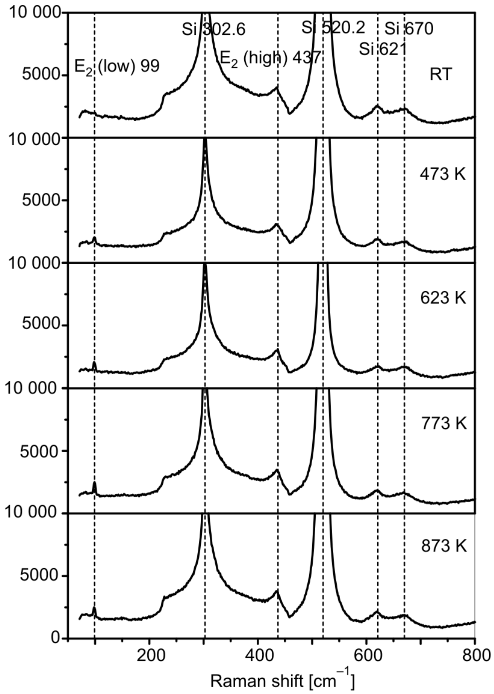

Fig. 2. Raman spectra of ZnO films prepared on Si substrate at various substrate temperatures. The oxygen pressures are all 1 Pa

Figure 2 shows the Raman spectra of ZnO films prepared on Si substrate at various substrate temperatures. The oxygen pressures were all 1 Pa and all the spectra were obtained by the subtraction of the Si substrate signal from the total signal. It can be seen that the results were similar to those in ZnO films prepared under various oxygen pressures. Besides some Raman peaks corresponding to single crystal Si, only E_2 modes corresponding to ZnO films were present in the spectra. At low substrate temperatures ZnO film exhibited a dispersed E_2 (low) peak with low intensity. As the substrate temperature increased, the profile of the E_2 (low) peak at first became sharp and then became dispersed, reaching its sharpest profile at 773 K. At the same time, the intensity of the E_2 (low) peak also reached a maximum. In addition, it can be seen from Fig. 2 that the position of each E_2 (high) peak also shifted to lower frequencies compared with ZnO single crystal [5].

It is well known that ZnO with a hexagonal wurtzite structure belongs to the space group C_{6v}^4. The group theory predicts that optical phonons at the Γ point of the Brillouin zone belong to the following irreducible representation [7, 8]: $\Gamma = 1A_1 + 2B_1 + 1E_1 + 2E_2$. Both A_1 and E_1 modes are polar and split into transverse (TO) and longitudinal optical (LO) phonons with different frequencies, due to the macroscopic electric fields associated with the LO phonons. The two non-polar E_2 modes are Raman active only. The B_1 modes are infrared and Raman inactive (silent modes). As far as the phonon modes were concerned, different scattering geometry could generate different phonon modes in the Raman spectra. In this paper, the Raman spectra have been recorded with the scattering geometry in which incident and scattered polarizations are parallel. According to Raman selection rules [9], only the E_2 and A_1 (LO) mode can be observed in the above geometry. The reason why the A_1(LO) mode did not occur in our experiments might be due to the fact that the A_1(LO) mode was subsumed by the strong Si substrate mode [10].

Some researchers [11–13] reported that the E_2 (low) peak could determine the crystal quality of films, while the E_2 (high) peak had a close relationship with the intrinsic stress in ZnO films. If the E_2 (low) peak is sharpest and has the highest intensity, the sample has the best crystal quality. Moreover, if a tensile stress occurs in the films, the E_2 (high) peak can shift to lower frequencies compared with the bulk value of 437 cm^{-1}, while the E_2 (high) peak can shift to higher frequencies with respect to 437 cm^{-1} if there exists a compressive stress in the films. Therefore, according to the Raman results above, we can draw the conclusion that ZnO films prepared on Si substrate both under 1 Pa oxygen pressure and at 773 K have the best crystal quality, and all ZnO films exhibited tensile stress, which can also be confirmed by XRD results.

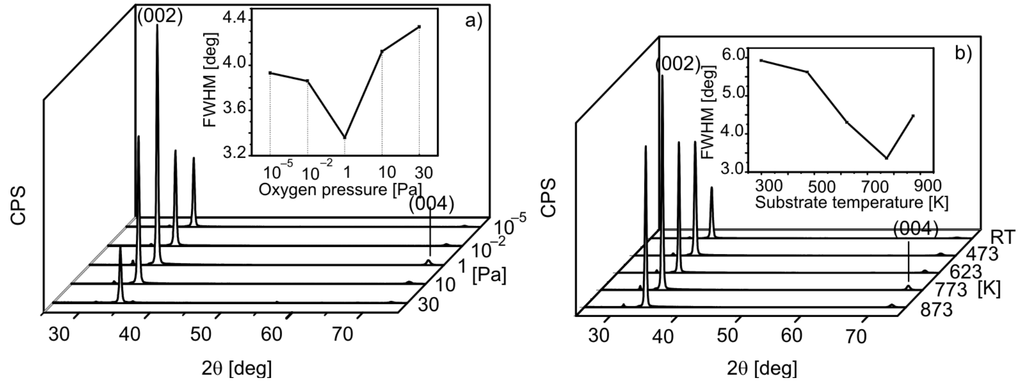

Fig. 3. XRD spectra of ZnO films prepared on Si substrate either at 773 K for various oxygen pressures (a) or under oxygen pressure of 1 Pa for various substrate temperatures (b). The inset shows the dependences of full widths at half maximum (FWHM) of the rocking curve of (002) diffraction peak on either the oxygen pressure (a) or the substrate temperature (b)

Figure 3 shows the XRD spectra of ZnO films prepared on Si substrate either at 773 K under various oxygen pressures or under 1 Pa oxygen pressure for various substrate temperatures. It can be seen that the ZnO films formed a wurtzite (*B*4) structure and there occurred a strong (002) diffraction peak at 2θ equal to ca. 34.5° for all ZnO films. A (004) diffraction peak also occurred for all ZnO films. However, its low intensity compared the intensity of the (002) peak implied that ZnO films have strong (002) texture and grew along the [002] orientation. This is confirmed by SEM observation (Fig. 4). Figure 4 shows the cross-section morphologies of ZnO films prepared both at 773 K and under oxygen pressure of 1 Pa. It was apparent that ZnO films with the thickness of ca. 800 nm formed columnar grains, indicating that ZnO films grew in columnar form. By comparison of the XRD spectra, one can draw the conclusion that ZnO films grew along the [002] orientation, which is perpendicular to the substrate surface.

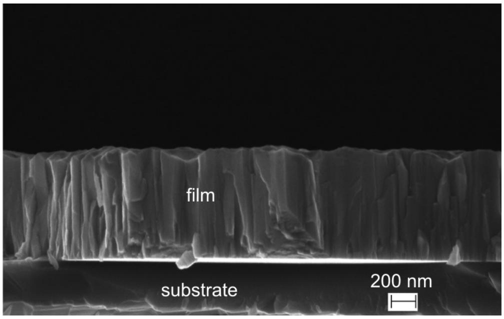

Fig. 4. The cross-section morphology of ZnO films prepared both at 773 K and at 1 Pa oxygen pressure

It is apparent from Fig. 3a that at a low oxygen pressure of 10^{-5} Pa, the intensity of the (002) diffraction peak was low. As the oxygen pressure increased, the intensity of the (002) diffraction peak increased and then decreased, reaching a maximum at the middle oxygen pressure of 1 Pa. In addition, at a low substrate temperature, the intensity of the (002) diffraction peak was also low. As the substrate temperature increased, the intensity of the (002) diffraction peak increased and then decreased, reaching a maximum at 773 K (Fig. 3b).

The intensity of a diffraction peak depends on both the crystal quality and the thickness of a film. Therefore it is insufficient to evaluate the crystal quality of ZnO films only from the intensity of the (002) diffraction peak. Another important factor is the full width at half maximum (FWHM) of the rocking curve of the (002) diffraction peak for ZnO films, through which we can easily determine the crystal quality of ZnO films prepared under various oxygen pressures. The smaller the FWHM, the better the crystal quality is. Accordingly, we measured the rocking curve of the (002) diffraction peak for ZnO films prepared under all conditions and showed the dependence of the FWHM values on either the oxygen pressure or the substrate temperature, as the insets in Fig. 3. It can be seen from the inset in Fig. 3a that as the oxygen pressure increased, the FWHM of the rocking curve of the (002) diffraction peak first decreased and then increased, reaching a minimum of about 3.36° at 1 Pa oxygen pressure, indicating that film had the best crystal quality. It can also be seen from Fig. 3b that as the substrate temperature increased, the FWHM of the rocking curve of the (002) diffraction peak first decreased and then increased, reaching a minimum of about 3.36° at 773 K, indicating that the film prepared at 773 K had the best crystal quality. All the above results showed that ZnO films prepared both at 1 Pa oxygen pressure and at 773 K have the best crystal quality, which is in good agreement with the Raman spectra and confirmed the accuracy of the Raman results.

For all ZnO films, the diffraction angle of all ZnO (002) diffraction peaks shifted to higher values compared with the standard XRD spectrum of ZnO powder ($2\theta = 34.43°$) [14], implying that the lattice constant c changed for all ZnO films. These changes were mainly caused by the intrinsic stress of ZnO films. For ZnO films with a wurtzite structure, the intrinsic stress could be obtained by the following formula [15]:

$$\sigma = \frac{2c_{13}^2 - c_{33}(c_{11} + c_{12})}{2c_{13}} \frac{c - c_0}{c_0} \tag{1}$$

where (i, j = 1, 2, 3) stands for the elastic constants in various orientations, c_0 is the lattice constant of ZnO films without defects and c is the lattice constant of ZnO film in our experiments, which can be computed by the following formulae:

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{d^2} + \frac{l^2}{c^2} \tag{2}$$

$$2d \sin\theta = \lambda \tag{3}$$

where $h = 0$, $k = 0$, $l = 0$ for the ZnO (002) diffraction peak, therefore, c is expressed as follows:

$$c = 2d_{002} = \frac{\lambda}{\sin\theta} \tag{4}$$

where d_{002} is the interplanar spacing of the ZnO (002) crystal plane. λ and θ are the X-ray wavelength and the Bragg diffraction angle, respectively.

Substituting the value of $c_{i,j}$ (i, j = 1, 2, 3) in Eq. (1) with c_{11} = 208.8 GPa, $c_{1,2}$ = 119.7 GPa, $c_{1,3}$ = 104.2 GPa, c_{33} = 213.8 GPa [16], we could obtain the residual stress σ [GPa] in ZnO film by the following formula:

$$\sigma = -233 \frac{c - c_0}{c_0} \tag{5}$$

Using the above formula, we calculated the intrinsic stress σ and the lattice constant c for various ZnO films, as shown in Fig. 5. Figure 5a showed the dependence of the intrinsic stress and the lattice constant on the oxygen pressure at 773 K and Fig. 5b the dependence of the intrinsic stress and the lattice constant on the substrate temperature under oxygen pressure of 1 Pa. The lattice constants of all ZnO films are smaller than that of bulk materials, thus resulting in tensile stresses in films, which was in good agreement with Raman data. These results confirmed that Raman scattering is a useful method for studying the structure of ZnO films. In addition, upon increasing the oxygen pressure, the stress first decreased and then increased, reaching a minimum at 1 Pa (Fig. 5a). As the substrate temperature increased, however, the stress increased monotonically (Fig. 5b).

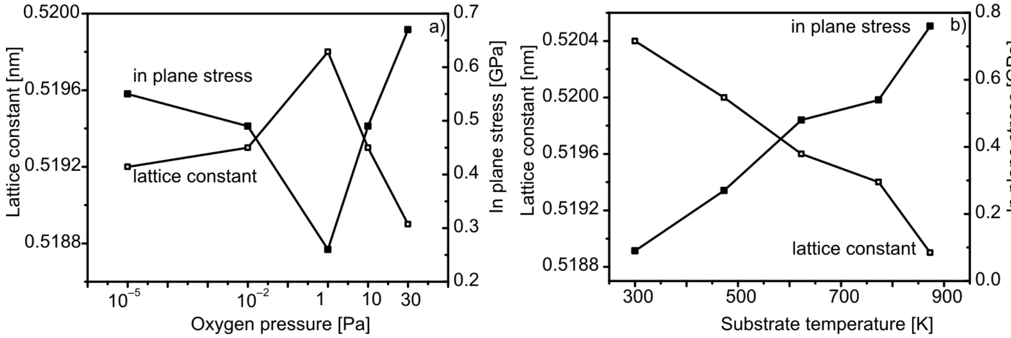

Fig. 5. Dependences of the lattice constant and the intrinsic stress on the oxygen pressure at 773 K (a), on the substrate temperature at 1 Pa oxygen pressure (b)

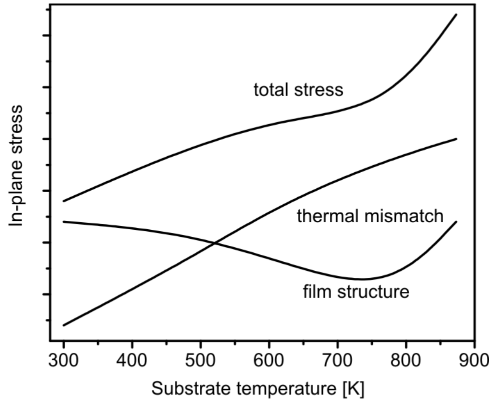

Fig. 6. Schematic illustration of the changes of stresses with the substrate temperature

In the ZnO film with the wurtzite structure, an intrinsic film stress in the direction perpendicular to the surface originated from a *C*-axis strain [17, 18]. Basically, this stress included an intrinsic stress originating from thermal mismatch between films and substrates and another intrinsic stress originating from the film structure. For ZnO films prepared with various oxygen pressures at 773 K, the intrinsic stress originating from thermal mismatch between films and substrates should be equal, while the intrinsic stress originating from the film structure changed non-monotonically with the film structure and should reach a minimum for films with the best crystal quality, thus resulting in the non-monotonic dependence of the stress on the oxygen pressure. For ZnO films prepared with various substrate temperatures under oxygen pressure of 1 Pa, two kinds of stresses changed with the substrate temperature. The intrinsic stress originating from thermal mismatch between films and substrates should increase monotonically as the substrate temperature increases, while another intrinsic stress originating from the film structure should change non-monotonically with the substrate temperature and should reach a minimum for film with the best crystal quality. Therefore, the sum of the two kinds of stresses might give rise to the monotonic change of the stress with the substrate temperature (Fig. 6).

4. Conclusions

The structure and intrinsic stress of ZnO films have been investigated by using a Raman spectrometer and the X-ray diffraction. The results showed that only the E_2 mode occurred in ZnO films prepared either at 773 K for various oxygen pressures or at 1 Pa oxygen pressure for various substrate temperatures. The analyses showed that the sharper and the stronger the E_2 (low) mode peak, the better the crystal quality, and the E_2 (high) mode peak in all films shifted to lower frequencies compared with ZnO single crystal, implying that a tensile stress occurred in all films. These results confirmed by X-ray diffraction indicated that Raman scattering is one of the most useful methods to investigate the structure of ZnO films. The changes in intrinsic stress were also analyzed in detail.

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