JOURNAL OF MATERIALS SCIENCE 17 (1982) 1364–1368

Correlation between film quality and photoluminescence in sputtered ZnO thin films

TADATSUGU MINAMI, HIDEHITO NANTO*, SHINZO TAKATA
Departments of Electrical Engineering and Electronics, Kanazawa Institute of Technology, Nonoichi-machi, P.O. Kanazawa-South, Ishikawa 921, Japan*

A red photoluminescence (PL) is observed in as-deposited ZnO thin films which are prepared by a conventional sputtering method. The PL intensity strongly depends on sputtering deposition conditions. In as-deposited and annealed films, it is found that there exists a correlation between the red PL intensity and the film quality. The origin of the red PL is attributed to the native defect induced during the sputtering deposition process. It is shown that the red PL measurement is effective as an evaluation method of the film quality.

1. Introduction

Sputtered ZnO thin film produced using the high rate depositing technique has been developed in recent years. This material shows promise for applications in acoustic, opto-electronic, display or sensor devices. There are few reports on photoluminescence (PL) in sputtered ZnO films, although the piezoelectrical and the electrical properties of this film have been extensively investigated for acoustic device application [1, 2]. In order to obtain optimum surface acoustic wave (SAW), optical wave-guide and luminescence properties, the sputtered film must simulate single-crystal properties. It is, therefore, important to evaluate the film quality based on the crystallographic properties such as orientation, crystallite size and grain size. The X-ray diffraction, reflection electron diffraction and scanning electron microscopy analyses have been conventionally used as a non-destructive evaluation method of the quality of sputtered films. In the present paper, we report the properties of the red PL which was observed in the as-deposited and the annealed ZnO films, and propose a simple evaluation method of the film quality using PL measurements.

2. Experimental procedure

Zinc oxide films were prepared using radio frequency (r.f.) diode sputtering under a d.c. magnetic field applied perpendicularly to a target, at a pressure of 3×10^{-2} Torr in a 20 vol % O_2/80 vol % Ar gas mixture. A sintered disc of ZnO (purity, 99.999 %) was used as the target. Sputtering deposition was carried out for 10 h at a deposition rate of about $0.1\,\mu\mathrm{m\,h}^{-1}$ on stainless steel, (1 1 1) silicon or $(1\bar{1}02)$ sapphire substrates in a temperature range from 120° C to 475° C. Sputtered films were evaluated using a conventional X-ray diffractometer with a copper target. The PL measurement was carried out by pulsed nitrogen laser (N_2-laser) or cw ultra-high pressure mercury lamp (Hg-lamp) excitations at room temperature (RT).

3. Results and discussions

Under N_2-laser or Hg-lamp excitations, the red PL ($\approx$ 650 nm) was observed in ZnO thin films which were deposited on silicon, sapphire and stainless steel substrates. Typical PL spectra in these sputtered ZnO films are shown in Fig. 1. Curves a, b and c show the spectrum of the film on stainless steel, sapphire and silicon substrates, respectively. The bumpy structures in the case of films on stainless steel and silicon substrates are thought to be due to interference effects. It was confirmed that there is no difference in the red

0022–2461/82/051364–05$03.10/0

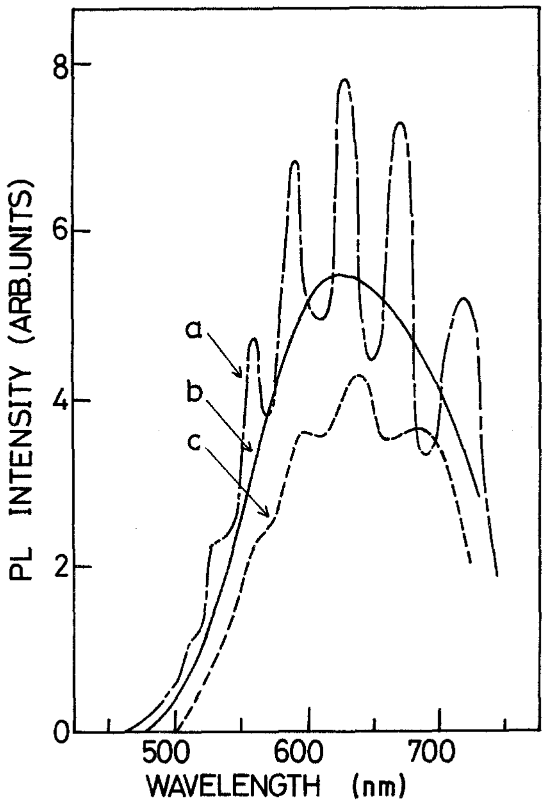

Figure 1 Typical PL spectra obtained from films on three different substrates. Curve a shows the spectrum of the film on stainless steel substrate. Curve b and c show those on sapphire and silicon substrates, respectively.

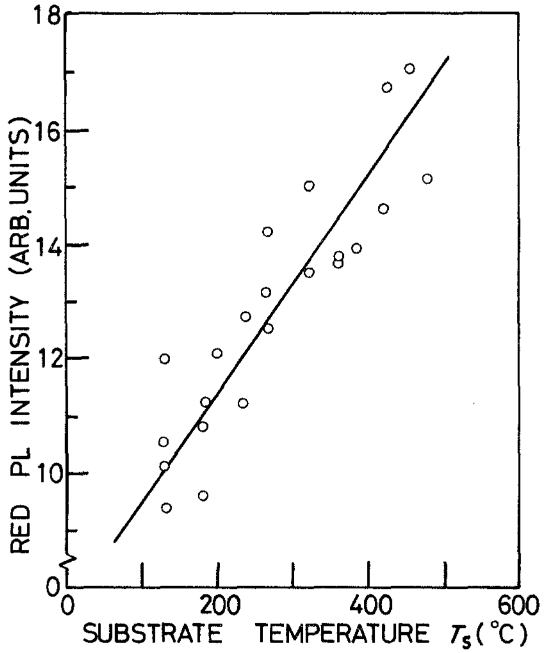

Figure 2 Total red PL intensity under N_2-laser excitation as a function of the substrate temperature.

PL spectral shape between N_2-laser and Hg-lamp excitations at RT. In as-deposited films, the red PL intensity strongly depended on the deposition conditions, particularly the substrate temperature. Films deposited on different substrates had different dependences of the red PL intensity on the substrate temperature. Here we are mainly concerned with the deposited films on silicon substrate because of the interesting structure for practical applications.

Fig. 2 shows the total red PL intensity for the as-deposited films on silicon substrate as a function of the substrate temperature. The total PL intensity was determined by integrating the corrected spectrum [3]. Figs 3 and 4 show the (0002) peak intensity and the half-width of X-ray diffraction as a function of the substrate temperature, respectively. The intensity of the (0 0 0 2) reflection is a direct indication of the volume of material oriented with (0 0 0 2) planes parallel to the substrate surface. In X-ray rocking curve tests, it was confirmed that the standard deviation of the rocking peak decreases with increasing substrate temperature, T_s, up to $T_s = 475°$ C. The standard deviation of the film which has the best (0 0 0 2) plane alignment was 0.53°. Peak broadening can be caused by a variety of factors such as crystallite size, non-uniform strain and stacking faults. The (0002) peak half-width depend only on crystallite size and non-uniform strain, although

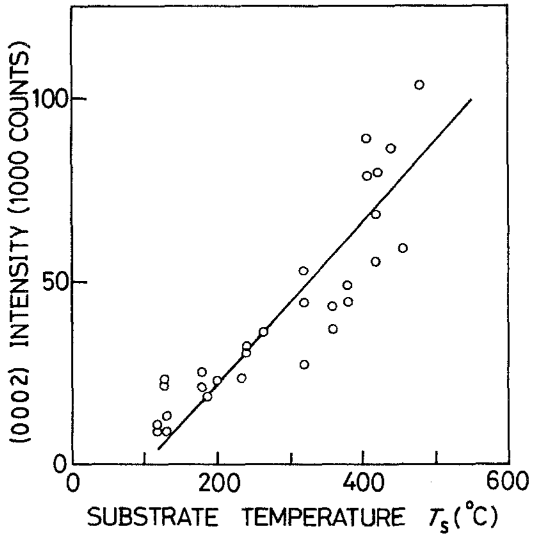

Figure 3 (0 0 0 2) X-ray diffraction peak intensity as a function of the substrate temperature.

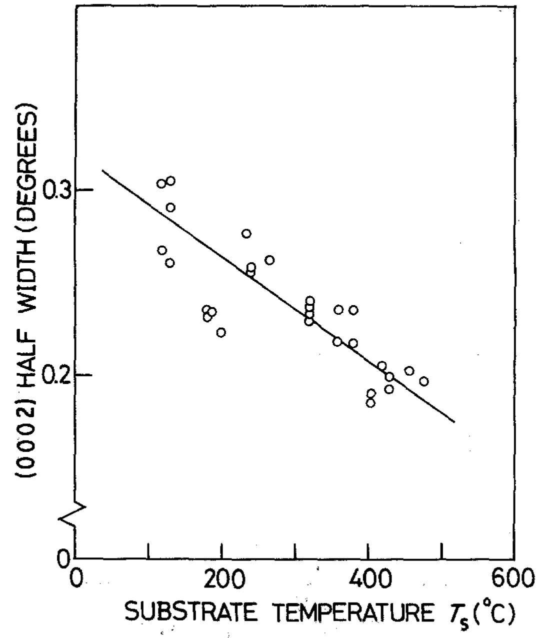

Figure 4 (0002) X-ray diffraction peak half-width as a function of the substrate temperature.

stacking faults may be present [4]. The large amount of the scatter of the data as shown in Figs 2, 3 and 4 can be ascribed to the non-reproducibility of plasma conditions and the spatial distribution of the temperature on the substrate surface. From Figs 2, 3 and 4, we see that there exists a correlation between the red PL intensity and the film quality in a substrate temperature range from 120 to 475° C. On the other hand, annealing at 400° C after deposition enhanced the red PL intensity regardless of the sputtered substrate temperature and annealed ambients (air, argon, hydrogen or vacuum). Also, annealing improved the film quality as evidenced by the increase in the intensity and the decrease in the half-width of the (0002) diffraction peak. The film thickness was not varied by annealing at 400° C. All of the films used in this work were deposited under identical sputtering conditions except for the substrate temperature. Data of film thickness measured by using a surface roughness detector were scattered in the range from 0.9 to 1.2 μm. This scattering may be ascribed to the non-reproducibility of plama conditions and the spatial distrubution of deposition rate on the substrate surface. We found that there is no correlation between the film thickness and the substrate temperature. If the film quality is affected by the thickness, the dependence of the film quality on the substrate temperature as shown in Figs 3 and 4 cannot be understood as the thickness effect. Within the limits of the results as described above, we can point out that a high film quality is associated with a stronger red PL intensity.

Fig. 5 shows the time-resolved red PL spectra and the dependence of the red PL spectrum on excitation intensity. From Fig. 5 we can see that the spectrum of the red PL is not shifted during decay and with excitation intensity. It was found that the stronger the PL is in intensity, the longer the PL takes to decay. The behaviour in annealing of the red PL and the above fact may suggest that a non-radiative process is dominant in this decay. The decay time was of the order of 0.1 to 2 μsec. Pierce and Hengehold [5] have reported that the cathodoluminescence of ZnO single crystals ion-implanted at 475° C exhibits

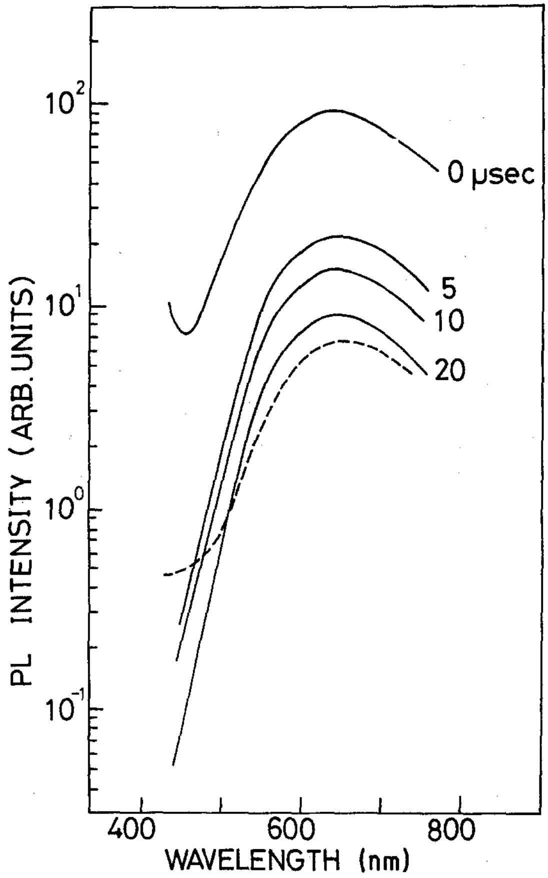

Figure 5 The time-resolved luminescence spectra under N_2-laser excitation (excitation power on the film surface $I_0 \approx 5$ MW cm^{-2}) at room temperature. The time delayed from the pulse excitation is shown in the figure. The dashed curve shows the PL spectrum of the same film at low excitation power ($I = 0.043 I_0$).

a peak near 650 nm. Since this red emission appears regardless of ion species implanted and is quenched by annealing at 900° C, they have concluded that the emission is attributed to damage defects. We found that the as-deposited films prepared by two different techniques such as magnetron sputtering (Zn target) [6] and chemical vapour deposition ($ZnCl_2$ source) [7] exhibit the red PL. The quality of these films was of the same order as one of the sputtered film in this work. The red PL of these films was dramatically quenched by annealing at above 900° C in air. The above facts imply that the radiative recombination centre responsible for the red emission is due to the formation of a native defect rather than arising from chemical impurity doping [8, 9]. We believe that the native defects such as interstitial zinc and/or oxygen vacancy are induced during the sputtering process [10, 11]. If there is a change of the amount of the radiative recombination centre with substrate temperature, its effect on the red PL is not important, because the transition mechanism is dominated by a non-radiative process rather than by a radiative one, as described above. On the other hand, many polycrystalline films, including ZnO, are known to contain a high concentration of non-radiative recombination centres which are caused by grain boundary and other defects. In order to decrease the amount of these defect centres responsible for the non-radiative process, the polycrystalline film must simulate the single-crystal properties. The quality of our films was improved with increasing the substrate temperature. The improvement of film qualities such as the crystallographic orienation and grain structure may be caused by annihilation of low-angle crystallite boundaries, stacking faults and other defects, with subsequent crystallite growth. The crystallite size can be estimated by the Scherer equation, based on the half-width and the peak-position of the X-ray profile. We found from the (0002) peak half-width in Fig. 3 that the crystallite size increases with substrate temperature and varies in a range from about 29 nm at T_s = 120° C to about 43 nm at T_s = 475° C. A grain, observed under a scanning electron microscope (SEM), is an aggregate of several crystallites which have grown to form a morphological unit which has distinct boundaries. We found that the grain size of our films, which were examined with a SEM, increases with substrate temperature and varies in a range from about 50 nm at T_s = 120° C to about 300 nm at T_s = 475° C. These results plotted as a function of the substrate temperature are shown in Fig. 6. Furthermore, the increases of the grain and the crystallite sizes by annealing at 400° C were also confirmed in the same manner as described above. As a consequence, the defect centres responsible for the non-radiative process are decreased as a result of improving the film quality. Therefore, we can conclude that the increase of the red PL intensity with increasing substrate temperature is attributed to the increase of grain and crystallite sizes.

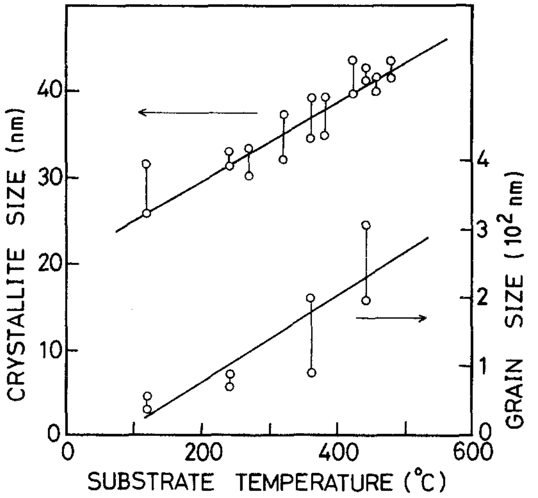

Figure 6 Grain size as determined by scanning electron microscope and crystallite size as estimated by the Scherer equation as a function of the substrate temperature.

4. Conclusions

We found that the red PL is observed in as-deposited and annealed films of sputtered ZnO and is attributed to the native defect induced during the sputtering deposition process. Since the film quality is improved by increasing the substrate temperature, the increase of the red PL intensity could be interpreted by the decrease of non-radiative recombination centres. In order to obtain optimum SAW, optical wave-guide and luminescence properties, the sputtered film must simulate single-crystal properties. On the practical applications for such devices, the measurement of the red PL is effective as an evaluation method of the quality of the sputtered ZnO film. This method is especially good because two-dimensional evaluation of the film quality is possible by a non-destructive manner, because it is easy to focus the exciting beam onto the film surface.

Acknowledgements

The authors would like to thank Professor Dr. H. Nagami for fruitful discussion on X-ray analysis, Mr Z. Yajima for his contribution to observation by SEM and Mr K. Shintani for his assistance in the film thickness measurement. They are indebted to Professor Dr N. Takeuchi of Kanazawa University for valuable discussion on X-ray rocking analysis and to Dr T. Hara of Kanazawa University for helpful suggestions on the magnetron sputtering apparatus.

References

1. F. S. HICKERNELL, Proceedings of the 1980 Ultrasonic Symposium, Boston, November 1980 (Institute of Electronic and Electrical Engineers, New York, 1980) p. 785.
2. N. CHUBACHI, Proc. IEEE **64** (1976) 772.
3. H. NANTO, T. MINAMI and S. TAKATA, *Phys. Stat. Sol (a)* **65** (1981) K131.
4. R. J. LAD, P. D. FUNKENBUSCH and C. R. AITA, *J. Vac. Sci. Technol.* 17 (1980) 808.
5. B. T. PIERCE and R. L. HENGEHOLD, *J. Appl. Phys.* **47** (1976) 644.
6. T. HATA, E. NODA, O. MORIMOTO and T. HADA, *Appl. Phys. Lett.* **37** (1980) 633.
7. T. TAKAHASHI, A. EBINA and A. KAMIYAMA, *Japan. J. Appl. Phys.* 5 (1966) 560.
8. O. F. SCHIRMER and D. ZWINGLE, *Solid State Commun.* 8 (1970) 1559.
9. D. ZWINGLE and F. GÄRTNER, *ibid.* **14** (1974) 45.
10. J. SCHOENES, K. KANAZAWA and E. KAY, *J. Appl. Phys.* **48** (1977) 2537.
11. J. O. BARNES, D. J. LEARY and A. G. JORDAN, *J. Electrochem. Soc.* **127** (1980) 1636.

Received 7 September
and accepted 5 October 1981