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Photoluminescence study of ZnO films prepared by thermal oxidation of Zn metallic films in air

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Zinc oxide (ZnO) films were synthesized by thermal oxidation of metallic zinc films in air. The influence of annealing temperatures ranging from 320 to 1000 °C on the structural and optical properties of ZnO films is investigated systematically using x-ray diffraction and room temperature photoluminescence (PL). The films show a polycrystalline hexagonal wurtzite structure without preferred orientation. Room temperature PL spectra of the ZnO films display two emission bands, predominant excitonic ultraviolet (UV) emission and weak deep level visible emission. It is observed that the ZnO film annealed at 410 °C exhibits the strongest UV emission intensity and narrowest full width at half maximum (81 meV) among the temperature ranges studied. The excellent UV emission from the film annealed at 410 °C is attributed to the good crystalline quality of the ZnO film and the low rate of formation of intrinsic defects at such low temperature. The visible emission consists of two components in the green and yellow range, and they show different temperature dependent behavior from UV emission. Their possible origins are discussed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1577819]

I. INTRODUCTION

ZnO has a wide band gap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV.[1] The luminescent properties of ZnO have received considerable attention due to its potential application in ultraviolet light emitting devices and in flat panel displays as a low voltage phosphor.[2,3] The photoluminescence (PL) spectrum of ZnO is normally composed of two parts: excitonic near band edge emission with energy around the band gap of ZnO and defect related deep level emission in the visible range. The UV emission is due to excitonic related recombination.[4,5] The exact mechanism for deep level emission is still controversial; intrinsic defects such as oxygen vacancies, oxygen interstitial and zinc vacancies[6–8] and extrinsic impurities (Cu) (Refs. 9 and 10) are all considered as the origin. Optically pumped ultraviolet lasing has been demonstrated in random oriented and heteroepitaxial ZnO films.[2,11,12] Various techniques have been used to prepare ZnO films, such as pulsed laser deposition, chemical vapor deposition (CVD), molecular beam epitaxy (MBE), magnetron sputtering, and metalorganic chemical vapor deposition (MOCVD).[13–16] ZnO films can also be synthesized by oxidizing zinc-containing precursors; the sol–gel process is a typical method for this type of technique.[17,18] Recently, ZnS and metallic zinc have also been attempted as precursors for the synthesis of ZnO film by this method.[19–22] Preparation of ZnO film by oxidizing metallic zinc is an interesting method, because uniform large area zinc film can be deposited easily by many methods. ZnO films prepared by this method show excellent PL properties and room temperature lasing.[20] It is generally believed that the film quality improves with an increase of oxidation temperature, with the optimum annealing temperature for obtaining ZnO films with the best PL properties reported to be 1000 °C by Cho *et al.*[20] and 900 °C by Chen *et al.*[21] Such high temperature is not desirable for many processes and prevents wide application of this method. As of now, no detailed studies have been carried out on the PL properties of ZnO films prepared by annealing in oxygen ambient in the low temperature regime. The aim of the present work is to study the influence of the oxidation temperature on PL properties of ZnO films systematically, paying special attention to the low temperature range. Our experimental results reveal that, besides the high temperature regime, another optimum annealing temperature exists at a temperature as low as 410 °C.

II. EXPERIMENTS

Zinc films were deposited on silicon substrates at room temperature by the filtered cathodic vacuum arc (FCVA) technique which uses of an off-plane double bend filter. The apparatus used in this work is described elsewhere.[23] ZnO films can also be prepared by this technique.[23] Zinc ions are produced in a vacuum arc discharge between the cathode and the grounded anode. The cathode is a 60 mm diam 99.99% purity zinc target mounted on a water-cooled copper plate. A

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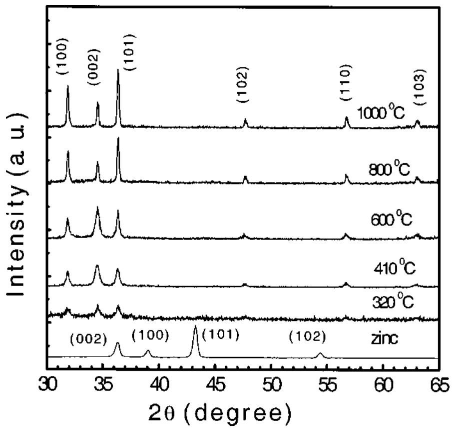

FIG. 1. XRD patterns of the as-grown zinc film and the ZnO films prepared at temperatures ranging from 320 to 1000 °C.

turbomolecular pump evacuates the chamber to a base pressure of 1×10^{-6} Torr before deposition. The film thickness was measured to be around 200 nm by a surface profiler. The zinc films were annealed in a thermal tube furnace in open air. The annealing temperature changes from 320 to 1000 °C. The films were transferred into the furnace when the temperature reached the set point. The annealing time was fixed to 1 h. After thermal oxidation, the sample was removed from the furnace and cooled quickly in air. The crystal structure of the films was characterized by x-ray diffraction (XRD) (Shimadzu-600), and the wavelength of the x-ray beam used was 0.154 nm. Surface morphologies were characterized by field emission scanning electron microscope (JEOL-6340F). PL spectra were acquired in the wavelength range of 350–850 nm at room temperature; the excitation light was the 325 nm line of a He–Cd laser.

III. RESULTS AND DISCUSSION

Figure 1 shows XRD spectra of the as-grown zinc film and the ZnO films prepared by oxidizing zinc films in air at temperatures of 320, 410, 600, 800, and 1000 °C, respectively. The as-grown zinc film is polycrystalline with a hexagonal close packed crystal structure, and no amorphous phase is detected. After oxidizing in air for 1 h, the diffraction patterns of zinc disappear, and the metallic zinc is completely transformed into ZnO. Six peaks appear at 2θ from 30° to 65° in the spectra of the ZnO films, and they correspond to the (100), (002), (101), (102), (110), and (103) directions of the hexagonal ZnO crystal structure. With an increase in oxidation temperature, the diffraction peaks become more intense and sharper, which suggests that the grain size becomes larger and the crystal quality has improved. The relative intensity of the (002) peak decreases with an increase of the annealing temperature. The average grain size in the films can be estimated by the Scherrer formula using the full width at half maximum (FWHM) value of the XRD diffraction peaks. The Scherrer formula[24] is

$$d=0.9\lambda/B\cos\theta, \qquad (1)$$

where d, λ, θ, and B are the mean grain size, the x-ray wavelength of 0.154 nm, Bragg diffraction angle, and the FWHM of the diffraction peak of the (101) direction at 43.2° for zinc film and (101) direction at 36.3° for ZnO films, respectively. Instrumental broadening was determined by measuring the line broadening of (111) oriented monocrystal silicon wafer, and its value is subtracted from the measured half width value. The mean grain size of the as-grown zinc film is estimated to be about 31 nm. The mean grain sizes are calculated to be about 21, 22, 26, 32, 40, 43, 49, 55, and 64 nm for the ZnO films prepared at temperatures of 320, 410, 500, 600, 700, 800, 900, and 1000 °C, respectively. The XRD peak can also be widened by internal stress and defects, so the mean grain size estimated by this method is normally smaller than the actual value, and this discrepancy can be seen in scanning electron microscopy (SEM) images.

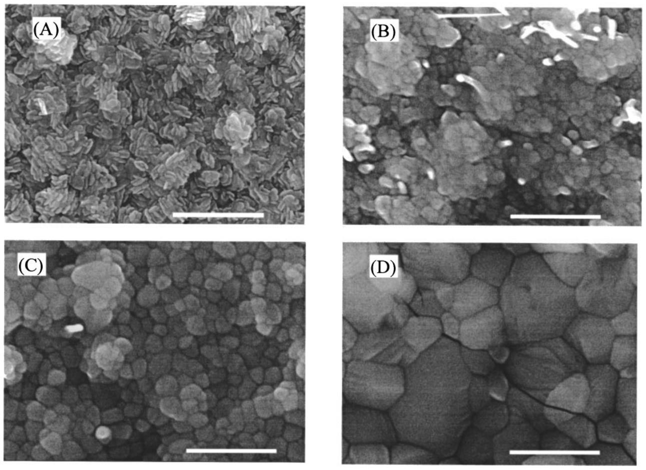

FIG. 2. SEM photographs showing the morphology of the (a) as-grown zinc film and zinc oxide films prepared at various temperatures: (b) 410, (c) 700 and (d) 1000 °C, respectively. The scale bars shown are 200 nm.

Figure 2 shows typical SEM images of the as-grown zinc film and the zinc oxide films prepared at temperatures of 410, 700, and 1000 °C. The as-grown zinc film is rugged and is composed of particles of about 50 nm, and the surface of the particles display a small pallet structure of several tens of nanometers. The surface morphologies of the ZnO films change greatly with an increase in oxidation temperature. At oxidation temperature of 410 °C [Fig. 2(b)], the film consists of fine grains; these grains agglomerate together so grain boundaries cannot be distinguished clearly some rod-like structures also formed on the surface. For films oxidized at 700 °C [Fig. 2(c)], the grains can be distinguished clearly, and they are distributed in a narrow range of 45 nm, which is consistent with the XRD analysis. A significant change in surface morphology is observed in the film annealed at 1000 °C [Fig. 2(d)], well facet grains are observed; their size becomes larger, with a wide range of distribution from several tens to 200 nm. Such high temperature stimulates migration of grain boundaries, and causes the coalescence of small grains and the formation of large grains. As expected, the XRD analysis underestimates the mean grain size. Cracks are also observed in the film, and they probably originate from the different thermal expansion coefficients of the ZnO film and the substrate.

Figure 3 presents room temperature PL spectra of the

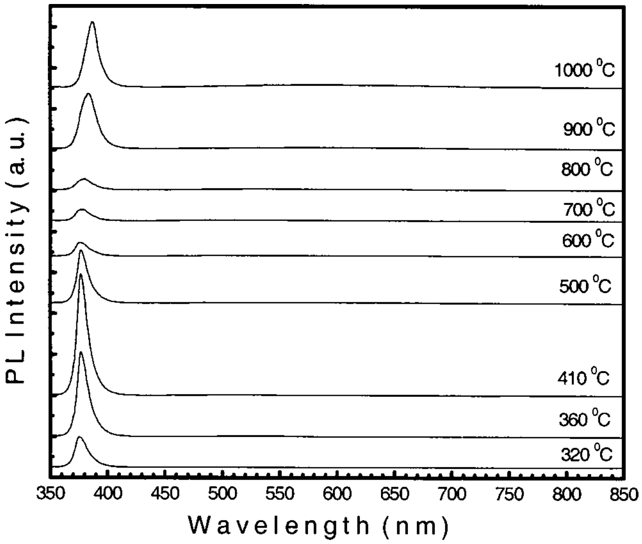

FIG. 3. Room temperature PL spectra of the ZnO films prepared at various temperatures.

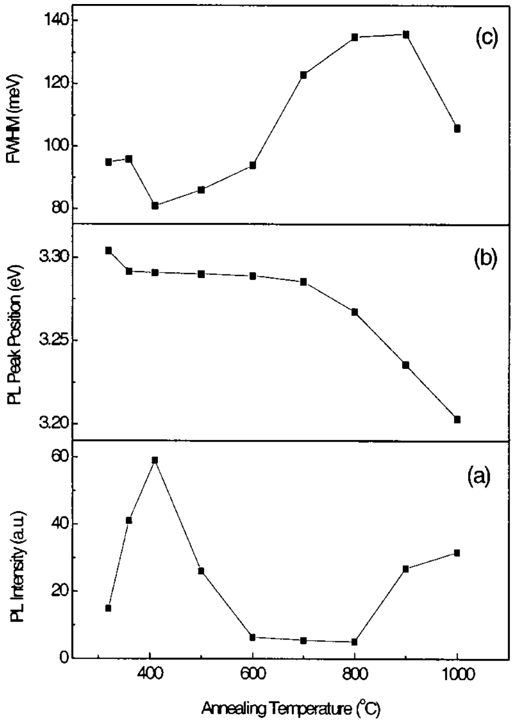

FIG. 4. (a) Variation of UV emission intensity with the annealing temperature. (b) Peak position vs annealing temperature. (c) FWHM variation with the annealing temperature.

ZnO films oxidized at different temperatures. The shapes of all the spectra, similar to those reported by others,[20,21] are dominated by strong near band edge UV emission and defect related deep level emission. The UV emission peak originates from free excitonic emission as shown by other researchers,[14] and it can be seen from Fig. 3 that the peak intensity and peak position of the UV emission vary with the annealing temperature. The film oxidized at 410 °C has the strongest PL intensity and the narrowest FWHM of the temperatures investigated. This does not agree with results of Cho *et al.*[20] and of Chen *et al.*,[21] in whose work the UV emission improved monotonically with an increase in annealing temperature from 320 to 1000 °C. The room temperature intensity ratios of UV emission to deep level emission are 13 and 200 for the samples annealed at 700 and 410 °C, respectively. This high intensity ratio manifests the low defect concentrations in the ZnO films obtained by this thermal oxidation method.

The intensity, position and FWHM of the UV emission peak are plotted as a function of the annealing temperature in Fig. 4. Figure 4(a) shows that the intensity of the UV emission increases with the annealing temperature first, and reaches a maximum at 410 °C; with a further increase of temperature, the intensity decreases quickly, and then increases again for annealing temperatures higher than 800 °C. The UV emission intensity of the film annealed at 410 °C is about two times that at 1000 °C. Figure 4(b) shows the peak position of the UV peak as a function of the annealing temperature. The UV peak shifts toward lower energies as the annealing temperature increases. The room temperature UV emission observed is attributed to free excitonic emission because of the high exciton binding energy of 60 meV, the reported typical peak position is at 3.26 eV.[14] From Fig. 4(b), we can see that the peak position redshifts monotonically from 3.30 to 3.20 eV with an increase of annealing temperature. XRD analysis shows the crystal size in the ZnO films increases from 21 to 64 nm with an increase of oxidation temperature from 320 to 1000 °C. According to quantum confinement theory, the energy band gap of a semiconductor depends on the crystal size; its value will increase with a decrease in crystal size. The analysis of Cho *et al.* gives band gap enhancement of 0.1 eV when the particle size decreases from 61 to 20 nm,[20] and this estimate is consistent with our results. The values of the FWHM of the UV peaks are in the range of 80–140 meV as shown in Fig. 4(c). It decreases to a minimum when the temperature reaches 410 °C, and then increases to a maximum value when the temperature is around 800–900 °C, and finally decreases again. The room temperature FWHMs are comparable with the values reported for bulk ZnO (115 meV),[25] heteroepitaxial ZnO film grown by MBE (117 meV),[14] and rf magnetron sputtered ZnO film (75 meV).[26] The small FWHM indicates that ZnO films, through thermal oxidization of zinc films in air, are of high crystal quality. The temperature dependent behavior of the FWHM indicated again that the film annealed at 410 °C has better crystal quality and is less defective than films prepared at other temperatures.

Figure 5 shows deep level emission spectra of ZnO films annealed at different temperatures. A broad visible emission band exists between 1.6 and 2.8 eV, with the shape of the band varying significantly as the annealing temperature increases. The small peak at ~1.68 eV is attributed to second-order diffraction of UV emission,[26] it appears only in the films with a strong UV emission peak and can barely be detected in the samples annealed at temperatures of 600–800 °C. The intensity of the broad PL band increases with an increase of the oxidation temperature; this temperature dependent relationship is different from that of the UV peak discussed above. The shape of the visible band indicates that

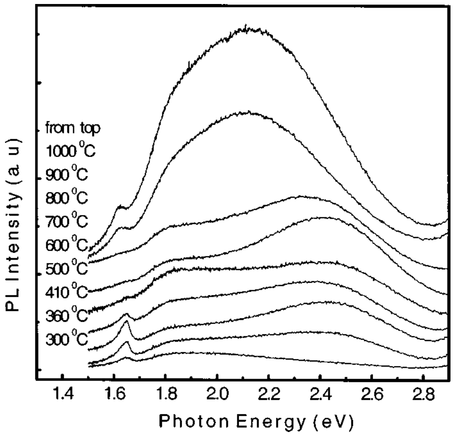

FIG. 5. Deep level PL spectra of the ZnO films at different temperatures.

it should consist of more than one emission peak. The broad band is fitted by Gaussian line distributions, and it can be fitted well by two peaks (excluding the harmonic peak of UV emission), located in the green and yellow energy range. Figure 6 shows the fitting results for the samples annealed at 410, 700, and 1000 °C. The position of the green peak depends strongly on the oxidation temperature, it redshifts with an increase of temperature: a shift of 0.3 eV is observed for the sample annealed at 1000 °C compared to the 410 °C annealed sample. On the contrary, the yellow peak (1.9 eV) displays weak temperature dependence. The intensity ratio of the green to yellow peak increases with the annealing temperature, especially at temperature higher than 900 °C. The origins of the defect related deep level PL band have been investigated for a long time, however, due to the complexity of the microstructure of ZnO, there is still no satisfactory consensus.[3,27–31] Extrinsic impurities such as Cu are considered as possible candidates for the green visible PL band.[9,10] Intrinsic defects, such as the oxygen vacancy and zinc vacancy, are also thought to be responsible for the green band.[28,30] For the oxygen vacancy especially, the work of Vanheusden *et al.*[3,6] has established a correlation between the green band and singly ionized oxygen vacancy. From our experiment, it can be seen that the concentration of the defect responsible for the green band increases with an increase of annealing temperature. If it is due to the extrinsic impurity, the intensity of the peak should mainly be determined by the impurity concentration, and it should not display such strong temperature dependence. The peak maximum of the green band generally decreases with an increase of annealing temperature, and it is located at 2.46 and 2.12 eV for samples annealed at 410 and 900 °C, respectively. This redshift can be partially explained by shrinkage of the energy band gap with an increase in particle size as suggested by van Dijken *et al.*[31] and by Wu *et al.*[32] However it should be noted that the shift of the green band with the annealing temperature is not as monotonical as it is in the UV peak. There are several anomalous temperature points, for example, for the samples annealed at 900 and 1000 °C, their UV peak positions are located at 3.24 and 3.20 eV, while their corresponding green bands are located at 2.12 and 2.15 eV, respectively. The yellow emission band has been observed in ZnO films by Studenikin *et al.*[17] at 640 nm (1.94 eV) and is attributed to oxygen interstitial.[17,32] The annealing temperature dependence behavior of the yellow band is different from that of the green band, since its peak position displays no systematic changes with the annealing temperature.

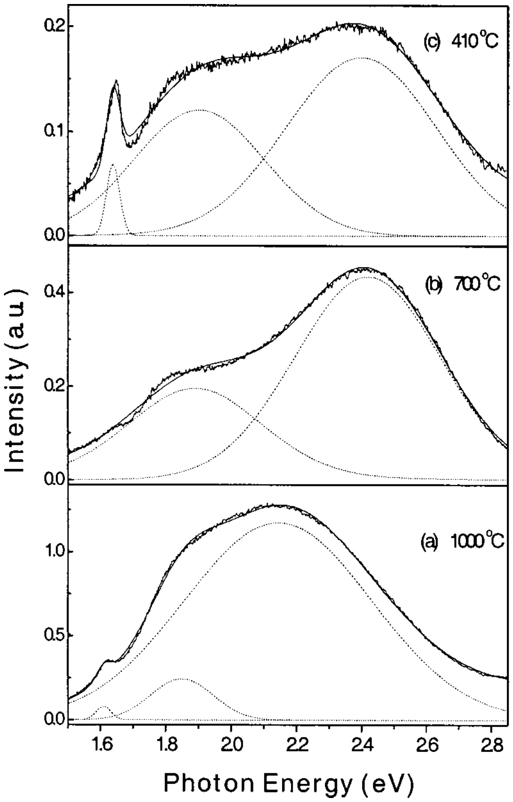

FIG. 6. Fitting results of three typical deep level PL spectra from ZnO films oxidized at different temperatures: (a) 1000, (b) 700, and (c) 410 °C.

PL emission efficiency is determined by the ratio of radiative and nonradiative transitions, and can be described by[28]

$$\eta = I_r / (I_r + I_{\mathrm{nr}}), \tag{2}$$

where η is the luminescence efficiency, and I_r and I_{nr} are radiative and nonradiative transition probabilities. In the case of ZnO, the nonradiative transition is induced by crystal imperfections, such as point defects, dislocations and grain boundaries. The radiative transition is composed of two parts as indicated above, near band edge excitonic related UV emission and deep level emission. Deep level emission is determined by the concentration of the corresponding defects. So there are two kinds of imperfections in ZnO, one induces nonradiative transition and the other induces deep level emission. To obtain ZnO with high UV emission efficiency, the two kinds of imperfections should be suppressed together. But for use as a green phosphor, the nonradiative defects should be suppressed while the concentration of the corresponding defects should be increased. It is generally agreed that the quality of ZnO films improves with an increase of annealing temperature.[20,21] However, the PL results shown here seem contradict to this conclusion, since ZnO films prepared at 410 °C possess better excitonic related UV emission than the films prepared at higher temperatures. This discrepancy can be understood by the fact that the key factors that influence XRD and PL spectra are different. In the case where the defect concentration in a material is not too high, XRD is mainly affected by the crystal size. For PL spectra, it is due to the small exciton Bohr radius of 1.8 nm; excitonic emissions are more sensitive to imperfections of the microstructure of a crystal. This discrepancy was also observed by Ryu *et al.*[33] on textured and epitaxial ZnO films. As shown in Fig. 4, the UV emission improves with an increase of temperature up to 410 °C, and then degrades quickly with a temperature increase to about 700 °C; finally it improves again with an increase of temperature to 1000 °C. A high annealing temperature (above 900 °C) facilitates the migration of grain boundaries and promotes the coalescence of small crystals, and thus favors a decrease of the concentration of nonradiative recombination centers. However, at the same time, high temperature increases the probability of the formation of radiative defects, which will compete with excitonic recombination and decrease UV emission efficiency. Why do the films annealed at around 410 °C have better crystal quality? This may originate from two factors, one is the low melting point of zinc (419 °C); below this temperature zinc stays in a solid state and can be oxidized at relative equilibrium conditions. When the temperature is higher than its melting point, oxidation is carried out at an unstable liquid state; more defects that are responsible for the nonradiative transition will be introduced into the films. This is why films annealed at around 700–800 °C show poorer UV PL emission: a large concentration of defects forms during the oxidation process, and this temperature range is not high enough to get rid of these defects. The second factor is the rate of formation point defects, which is responsible for radiative recombination, is low at low temperatures.

IV. CONCLUSION

ZnO films were prepared by annealing metallic zinc film in air at temperatures from 320 to 1000 °C. The dependence of the PL properties of these films on the temperature was investigated systematically. The films are polycrystalline without preferred orientation; the crystal size increases with an increase of oxidation temperature. The PL spectra are composed of a near band edge UV emission peak and a defect related deep level emission band, and the intensity of the deep level band is weak compared to UV emission for all films at room temperature. The deep level PL band can decompose into a green band and a yellow band. The intensity of the green band increases greatly at annealing temperature higher than 900 °C, which indicates that the defect center responsible for the green band in our samples is an intrinsic defect. The UV emission band shows anomalous annealing temperature dependent behavior; the optimum temperature range is around 410 °C. PL spectra of the films annealed at 410 °C display the strongest UV emission intensity and the narrowest FWHM among the annealing temperatures investigated, and these results are attributed to the low microdefect density in ZnO crystals formed at 410 °C.

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