Preparation and photoluminescence of undoped $ZnTiO_3$ thin films

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$ZnTiO_3$ thin films were prepared by radio frequency cosputtering of ZnO and TiO_2. It was found the as-prepared film is amorphous and the cubic phase $ZnTiO_3$ films form after annealing at temperature above 500 °C. The absorption spectra indicate that the optical band gap of the crystalline $ZnTiO_3$ film is about 3.70 eV. A strong photoluminescence band centered at 355 nm consisting of two emission peaks was observed in 800 °C annealed $ZnTiO_3$ thin film, and the peak positions of these two emission move to short wavelength with increasing annealing temperature. It was found the emission peak at ultraviolet zone is resulted from O^{2-} vacancy and that in the blue zone is attributed to Zn^{2+} vacancy. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3190820]

I. INTRODUCTION

TiO_2 and ZnO are both wideband semiconductors with excellent properties and extensive applications, and have attracted much interest on either single material[1–6] or $ZnO-TiO_2$ composites.[7–10] There are three compounds in $ZnO-TiO_2$ binary oxide system, i.e., Zn_2TiO_4, $ZnTiO_3$, and $Zn_2Ti_3O_8$,[11,12] and among them, $ZnTiO_3$ is a promising candidate as microwave dielectrics, gas sensor, white pigment and catalytic sorbents for desulfurization of hot coal.[13–22] $ZnTiO_3$ also has potential applications in nonlinear optics,[23] and as luminescent material.[24–26]

Many titanate-based perovskite-type oxides with $ATiO_3$ structure, such as $BaTiO_3$, $SrTiO_3$, and $MgTiO_3$, show the peculiar room temperature photoluminescence (PL) phenomenon related to certain defects in these compounds, such as oxygen vacancies.[27–30] On the other hand, as the component of $ZnTiO_3$, TiO_2 shows PL property in the visible or infrared light range due to the oxygen vacancy,[31] while ZnO exhibits a distinctive ultraviolet (UV) near-band-gap emission (3.3 eV) and a relatively broad visible (green) emission (2.3 eV), and the green emission was attributed to intrinsic defects such as oxygen vacancy (V_O), zinc vacancy (V_{Zn}), and interstitial zinc (Zn*i*).[32,33] There is no report on the PL of pure $ZnTiO_3$ in literatures, except the transitional metal ions doped $ZnTiO_3$.[24–26] $ZnTiO_3$ belongs to the limonite structure which is a derivative structure of corundum, Zn^{2+} and Ti^{4+} occupy 2/3 octahedral voids leaving the rest of the 1/3 octahedral void empty and the columbic repulsion between Zn^{2+} and Ti^{4+} ions causes each to move slightly toward the adjacent unoccupied octahedral site. The oxygen ions also shift slightly from idealized hexagonal closed-packed positions. In this paper, we report the preparation and PL property of pure phase $ZnTiO_3$ thin films.

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II. EXPERIMENTAL

$ZnTiO_3$ thin films were grown onto *n*-type (100) Si substrate by radio frequency magnetron cosputtering at room temperature. Pure TiO_2 (99.999%) ceramic target (60 mm in diameter) attached with several pieces of ZnO (99.999%) chip was used as the sputtering target. Pure argon (99.999%) with 16 (SCCM) (SCCM denotes standard cubic centimeters per minute at STP) flux controlled by mass flow controller was used as sputtering gas and the base pressure of the vacuum chamber is about 5×10^{-5} Pa. Sputtering was carried out at a pressure of 1.2 Pa with an input power of about 120 W. The distance between the target and substrate was kept at 50 mm.

Post annealing treatment was carried out at temperature from 200 to 900 °C for 2 h. The crystalline structures of the thin films were analyzed by grazing angle x-ray diffraction (XRD) measurements (Philips X'Pert Pro MPD, Cu $K\alpha$, 1.5406 Å). X-ray photoelectron spectroscopy (XPS) (VG ESCALAB U.K.) was applied to determine the chemical composition of the films. The surface morphology was observed by field-emission scanning electron microscopy (FESEM) (Sirion 200, resolution, 2.0 nm at 1 kV). Optical absorption spectra were obtained by a Carry 5E spectrometer in the wavelength range of 300–1200 nm. PL spectra were measured by Edinburgh Instruments FLS920 fluorescence spectrometer excited at variable wavelength using a 450 W Xenon lamp.

III. RESULTS AND DISCUSSION

The sputtering rate of ZnO is higher than TiO_2, in order to obtain stoichiometric $ZnTiO_3$ thin film different area ratio of ZnO to TiO_2 in the cosputtering target was tried, and it was found that the $ZnTiO_3$ thin film with Zn/Ti atomic ratio of 1:1 can be achieved with the area ratio of ZnO to TiO_2 of about 1:26 in present sputtering conditions. XPS measurement confirmed that the as-deposited (Ti $2p$:1.000, Zn $2p_3$:1.016, and O $1s$:4.673) and the annealed (at tempera-

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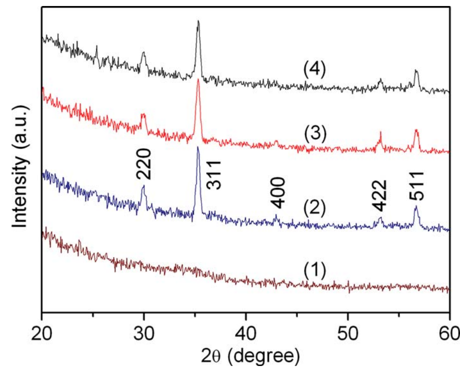

FIG. 1. (Color online) XRD patterns of $ZnTiO_3$ thin films annealed at (1) 400, (2) 500, (3) 800, and (4) 900 °C.

ture of 800 °C in air, Ti $2p$:1.000, Zn $2p_3$:0.976, and O $1s$:4.052) $ZnTiO_3$ thin films both have the atomic ratios of Zn to Ti of about 1:1.

Figure 1 shows the XRD patterns of $ZnTiO_3$ thin film annealed at different temperatures. The as-deposited thin film is in an amorphous state, and keeps in this state at the annealing temperature lower than 500 °C. At 500 °C the as-deposited thin film transforms to polycrystalline structure and the corresponding diffraction peaks at (220), (311), (400), (422), and (511) can be indexed to a cubic phase structure.[34] It was found at the annealing temperature from 500 to 900 °C, the films all have good cubic phase structures.

Figure 2 shows the absorption spectra of the $ZnTiO_3$ thin films in as-deposited state and annealed at 800 °C. One can see that the absorption edge of the crystalline thin film moves to longer wavelength as comparison with that of amorphous film. From the plot of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$, the inset in Fig. 2, one can get that the optical band gap of amorphous film is about 3.91 eV, and that of the cubic phase $ZnTiO_3$ film is about 3.70 eV, an obvious blueshift is observed. The best fitting of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ was obtained for crystalline films, indicating that the cubic phase $ZnTiO_3$ is an indirect band gap semiconductor, which is consistent with that reported in literatures.[7]

Figure 3 shows the PL spectra of the crystalline $ZnTiO_3$ thin films annealed at different temperatures excited at different wavelengths, in which a broad emission band in the

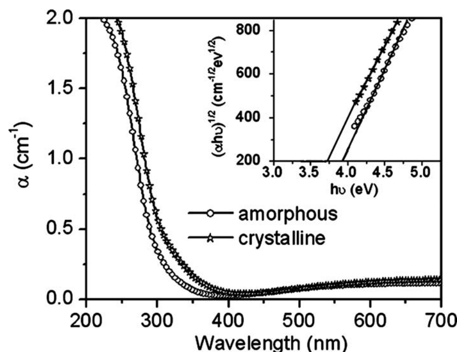

FIG. 2. Absorption spectra of amorphous $ZnO-TiO_2$ composite thin film and $ZnTiO_3$ thin film annealed at 800 °C. The inset is $(\alpha h\nu)^{1/2}$ vs $h\nu$ plot for α larger than 10^4 cm^{-1}.

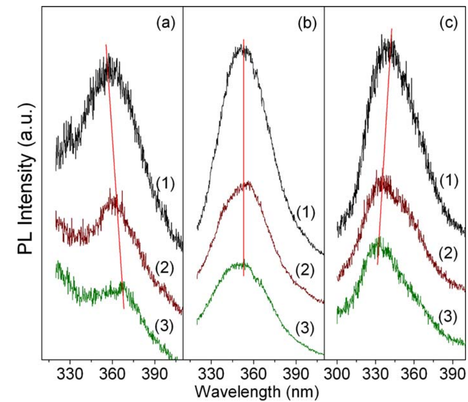

FIG. 3. (Color online) PL spectra of $ZnTiO_3$ thin films annealed at temperature of (a) 750, (b) 800, and (c) 850 °C in air excited at (1) 250, (2) 265, and (3) 280 nm.

wavelength from 320 to 420 nm can be clearly seen. It is observed that the emission peak shifts to the shorter wavelength for the $ZnTiO_3$ film annealed at 750 °C with increasing excitation wavelength [Fig. 3(a)], while that shifts to longer wavelength for the film annealed at 850 °C [Fig. 3(c)], and no obvious shift for the film annealed at 800 °C [Fig. 3(b)]. This emission band is not a band to band transition because the peak position (at 353 nm, 3.5 eV for the film annealed at 800 °C excited at 250 nm) is smaller than the optical band gap of the crystalline $ZnTiO_3$ film (3.70 eV, 334 nm), the obvious shift of the emission band with excitation wavelength indicates that the emission might result from defects. Figure 4 shows the PL spectra of the $ZnTiO_3$ annealed at different temperatures excited at 250 nm, an obvious blueshift can be seen with increasing annealing temperature and the strongest emission is observed for the film annealed at 800 °C, which is considered the optimum annealing temperature is 800 °C for PL of pure phase $ZnTiO_3$ thin film.

Generally, in metal oxides the intrinsic defects such as oxygen vacancies and metal ion interstitials or vacancies often coexist. It is reported in $Ba_xSr_{1-x}TiO_3$ thin film two kinds of defect level exist due to the existence of oxygen vacancies and certain disorder structure, and the doped (or excited) electrons recombine with holes through the defect level.[27] In $ZnTiO_3$ thin film, there also exist intrinsic defects such as O^{2-} vacancy, Zn^{2+} interstitial and Zn^{2+} vacancy. To study the origin of the PL, the 800 °C annealed $ZnTiO_3$ thin film was

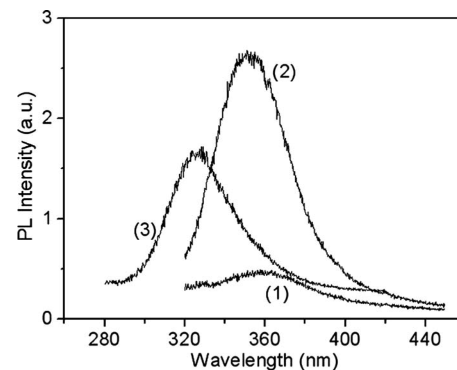

FIG. 4. PL spectra of $ZnTiO_3$ thin films annealed at temperature of (1) 750, (2) 800, and (3) 850 °C excited at 250 nm

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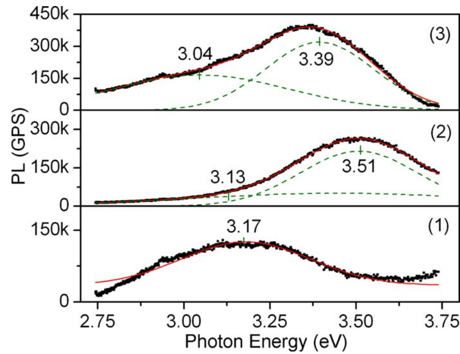

FIG. 5. (Color online) PL spectra of $ZnTiO_3$ thin films annealed at 800 °C in atmosphere of (1) H_2, (2) air, and (3) O_2 excited at 250 nm.

further heat treated in different atmospheres, which is regarded as an effective way to verify the existence of deficiency[35,36] and the PL spectra excited at 250 nm are shown in Fig. 5. The PL band consists of two PL peaks, one is very strong and situates at 3.51 eV and the other is very weak and situates at 3.13 eV (Gaussian fitting, see curve 2 in Fig. 5) when annealed in air. Moreover, the PL band only has one PL peaks centered at 3.17 eV and the other peak disappeared when annealed in O_2 (curve 1 in Fig. 5). When annealed in H_2, the PL band also consists of two PL peaks situated, respectively, at 3.04 and 3.39 eV, and both of the PL peaks move to lower energy (longer wavelength) and become stronger. The Gaussian fitting clearly indicates that the PL band annealed in air and H_2 atmosphere consists of two PL peaks, one is situated in the UV zone, and the other is in the blue region, while that annealed in O_2, there is only one weak PL band in blue region. This result shows the PL band is originated from two kinds of intrinsic defects.

Further XRD analysis of the $ZnTiO_3$ thin films annealed at 800 °C in different atmospheres, as shown in Fig. 6, indicates that for the films annealed in air and oxygen no obvious changes were observed except the relative intensity of the diffraction, while that annealed in H_2, there is only one diffraction peak corresponding to (511) plane of cubic phase $ZnTiO_3$ and the other two relative strong diffraction peaks situated at 25.3° and 48.0° and three relative weak diffraction peaks indicated by the arrows corresponding to anatase TiO_2.[37] This result indicates that phase separation of the

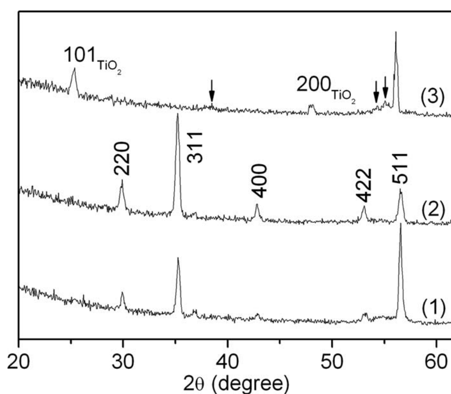

FIG. 6. XRD patterns of $ZnTiO_3$ thin films annealed at 800 °C in atmosphere of (1) air, (2) O_2, and (3) H_2.

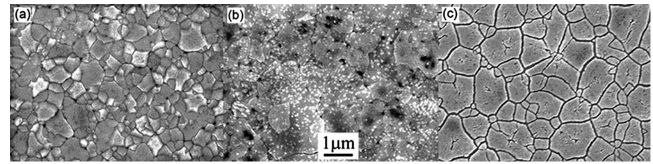

FIG. 7. FESEM images of $ZnTiO_3$ thin films annealed at 800 °C in atmosphere of (a) air, (b) H_2, and (c) O_2.

$ZnTiO_3$ phase occurs when annealed in H_2, in which the Zn^{2+} ions are partly reduced and separated out, leading to the formation of TiO_2 phase. The corresponding FESEM observations, as shown in Figs. 7(a) and 7(b), demonstrate that there are many cavities and bright particles in the film annealed in H_2 compared with that in air, the cavities are due to the evaporation of Zn, and the white particles are TiO_2 as proved by energy dispersive x-ray spectrometry (EDX) and XRD analysis. The grain size in the $ZnTiO_3$ film increases obviously when annealed in O_2 atmosphere, as shown in Fig. 7(c), leaving many gaps between grain boundaries due to the abnormal grain growth.

Above results indicate that the structure of $ZnTiO_3$ film changes with annealing atmosphere, which results in the variation of the concentration of intrinsic defects and leads to the changes of the relative intensity of the two emissions shown in Fig. 5. The emission peak in the UV zone quenches in O_2 and becomes stronger in H_2, so it is reasonable to ascribe this peak to O^{2-} vacancy in the $ZnTiO_3$ film. The reason lies in that the concentration of O^{2-} vacancy will increase when annealed in H_2 and decrease substantially in O_2, as reported in literature.[33] As for the weaker emission peak in the blue zone, the most possible origin is due to Zn^{2+} vacancy, because the $ZnTiO_3$ film was thermal heat treated at a high temperature of 800 °C, Zn^{2+} ions are easily reduced, and result in the formation of Zn^{2+} vacancies, which was confirmed by the XRD and FESEM analysis of the film annealed in H_2, in which the content of Zn obviously decreased after annealing. The shift of the two emissions to longer wavelength for the $ZnTiO_3$ film annealed in H_2 might result from the reduced defect levels due to the formation of TiO_2 phase in $ZnTiO_3$ film.

IV. CONCLUSION

Pure phase $ZnTiO_3$ thin films were prepared by cosputtering $ZnO-TiO_2$ composite films and post annealing treatment. The as-prepared film is an amorphous, and the cubic phase $ZnTiO_3$ films form after annealing at temperature higher than 500 °C. A strong PL band centered at 355 nm consisting of two emission peaks was observed in 800 °C annealed $ZnTiO_3$ thin film, and the peak positions of these two emission move to short wavelength with increasing annealing temperature. It was found the emission peak at UV zone is resulted from O^{2-} vacancy and that in the blue zone is attributed to Zn^{2+} vacancy. The PL of undoped $ZnTiO_3$ thin film was clearly observed and has been systematically studied, which provides more comprehensive knowledge of $ZnTiO_3$ material either in fundamental study or for potential applications in optics.

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