

# Enhanced green photoluminescence from ZnO films prepared by TFA-MOD method

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Received 4 February 2005; accepted 15 May 2005

Available online 6 June 2005

## Abstract

Preferentially (002) oriented ZnO films were prepared on Si (111) substrates at relatively low temperature by trifluoroacetate metalorganic deposition (TFA-MOD) method. The growth process, structure and photoluminescence properties were studied by thermogravimetric analysis, Fourier transform infrared absorption, X-ray diffraction, X-ray photoelectron spectra and photoluminescence. The green photoluminescence is enhanced remarkably and becomes visible by naked eyes with the formation of zinc silicate after 900 °C annealing. Furthermore, the oxygen partial pressure of annealing ambient also affects the green photoluminescence evidently. Our results support that oxygen antisite defect in ZnO is responsible for the green emission and a small amount of Zn<sub>2</sub>SiO<sub>4</sub> can enhance the green emission.

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PACS: 81.15-z; 78.55.Et

Keywords: Zinc oxide films; Trifluoroacetate metalorganic deposition; Luminescence; Defects

## 1. Introduction

Recently, ZnO has attracted great attentions due to its stimulated emission and optically pumped laser behavior [1–5]. Compared with other wide band gap materials, ZnO has a wide and direct band gap of 3.36 eV at room temperature and a higher exciton binding energy ~ 60 meV, which assures more efficient exciton emission at room temperature [6,7]. Generally, ZnO can emit three luminescence bands in the UV, green, and yellow spectral range [8]. The ~ 3.3 eV UV emission has been well understood to be due to the exciton recombination. Various mechanisms have been reported [9–12] for the emissions in the visible range. However, the exact mechanism is still in controversy.

It was reported that the emission properties of the ZnO films are dependent on the growth condition [13, 14]. Therefore, suitable methods to obtain ZnO films with prominent luminescence are of great benefit to current

research. Trifluoroacetate metalorganic deposition (TFA-MOD) method does not require any expensive vacuum apparatus during the whole process and is regarded as one of the most suitable candidates for fabricating oxide films [15]. In this letter, TFA-MOD method was used to prepare ZnO films on Si (111) for the first time. It was found that the green emission visible by naked eyes is strongly affected by the annealing temperature and ambient. The origins of the green and UV bands are discussed in the light of the experimental results.

## 2. Experiment

1.3 g zinc oxide powder (AR) and 3 ml trifluoroacetic acid (CP) were mixed in 8 ml methanol (AR) and reflux to form a homogeneous solution (pH 4). After aging for 24 h, the precursor solution was spin-coated on Si (111) substrates at 3000 rpm. The precursor films were calcined at 270 °C in moist oxygen to decompose Zn(CF<sub>3</sub>COO)<sub>2</sub> into ZnO. Annealing process was carried out at different conditions: 500 °C/O<sub>2</sub>, 750 °C/O<sub>2</sub>, 750 °C/air, 750 °C/Ar and 900 °C/O<sub>2</sub>.

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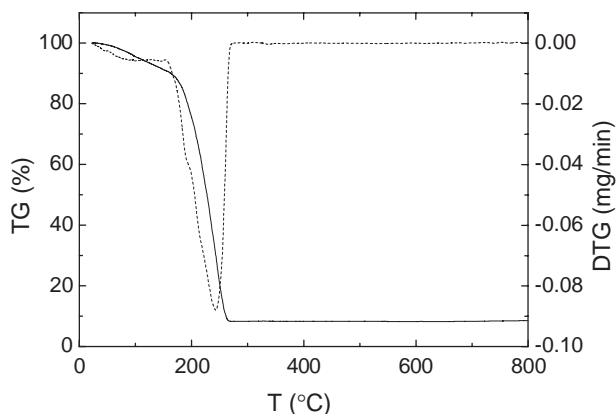
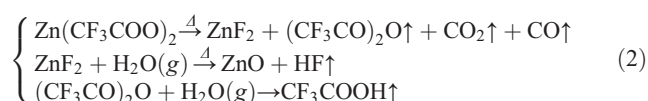


Fig. 1. TG–DTG curve of precursor gel.

Fourier transform infrared absorption (FTIR, MAGNA-750), X-ray diffraction (XRD, P/Max-RA, CuK $\alpha$ ) and X-ray photoelectron spectra (XPS, VG ESCALAB MK-II) were used to characterize the precursor gel and films. Thermogravimetric analysis (TG) measurement was carried out on Shimadzu TA-50 thermal analysis in oxygen. Photoluminescence (PL) spectra were acquired on a Hitachi 850 fluorescence spectrophotometer at RT excited with 210-nm light produced by a xenon lamp.

### 3. Results

Fig. 1 shows the TG curves of precursor gel. The weight loss below 160 °C is ascribed to the evaporation of absorbed water. The main weight loss from 160 to 265 °C is due to the decomposition of Zn(CF<sub>3</sub>COO)<sub>2</sub>. We suggest two possible decomposition routes of Zn(CF<sub>3</sub>COO)<sub>2</sub>:



Regardless of which route is taken, the solid product is ZnO.

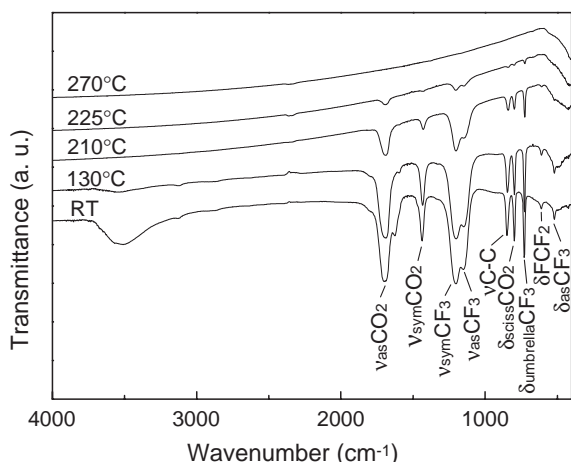


Fig. 2. FTIR spectra of precursor gel heated at different temperature.

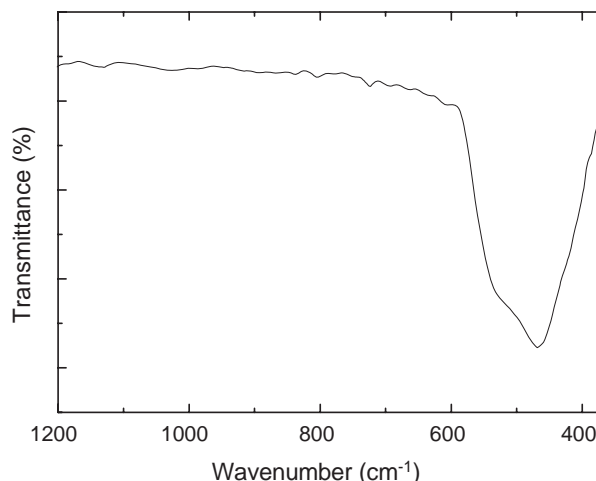


Fig. 3. FTIR spectrum of 500 °C heated gel.

The FTIR spectra of dried gel at different temperatures are shown in Fig. 2. The vibration peaks of CF<sub>3</sub>COO<sup>-</sup> agree well with that in literature [16]. Below 210 °C, the O–H vibration at ~3500 cm<sup>-1</sup> originated from absorbed water. It was also found that Zn(CF<sub>3</sub>COO)<sub>2</sub> decomposes into ZnO above 210 °C. The results of FTIR are consistent with that of TG.

Figs. 3 and 4(a) show the FTIR spectra and XRD pattern of 500 °C heated gel, respectively. The results indicate that pure wurtzite ZnO can be prepared by TFA-MOD method.

XRD pattern of TFA-MOD derived ZnO films after annealing at 500, 750 and 900 °C are shown in Fig. 4(b). The intensity of ZnO (002) peak increases with increasing annealing temperature. For the film annealed at 900 °C, there are some other peaks besides the ZnO diffraction peaks, denoted with solid triangles, indicating the formation of Zn<sub>2</sub>SiO<sub>4</sub>. Fig. 5(a) shows the PL spectra of the same series of ZnO films. One can see a strong peak at 520 nm

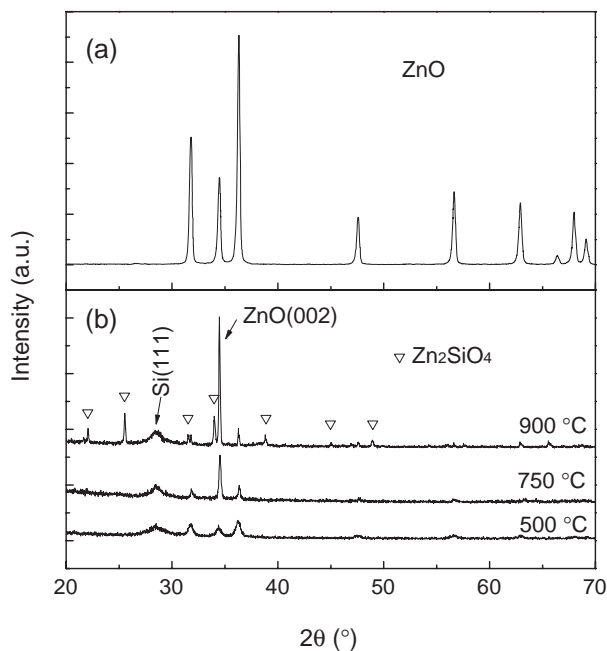


Fig. 4. XRD pattern of (a) 500 °C heated gel; (b) ZnO films heated at 500, 750 and 900 °C. The hollow triangles indicate the diffraction peaks of Zn<sub>2</sub>SiO<sub>4</sub>.

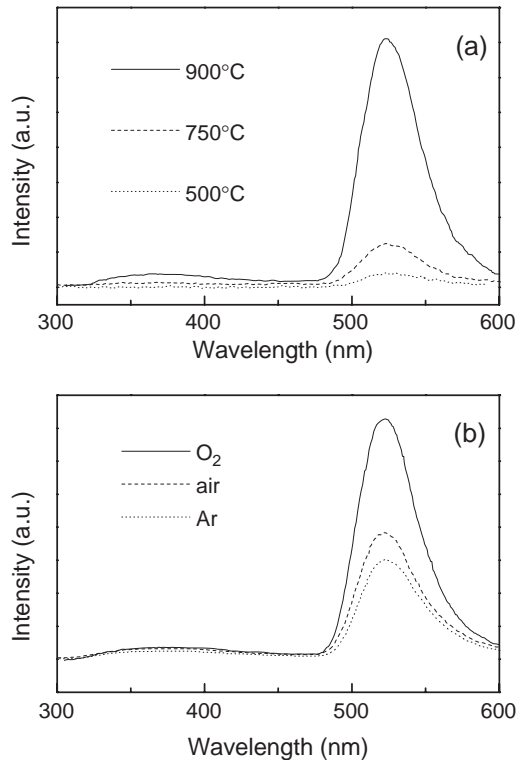


Fig. 5. PL spectra of ZnO films: (a) heated at 500, 750 and 900 °C; (b) annealed in Ar, air and O<sub>2</sub> at 750 °C.

(2.38 eV) accompanied with a weak UV band. The weak UV band is ascribed to the near band edge emission. The sharp peak of exciton recombination of ZnO (375 nm) is absent because our films contain a large number of defects which can quench the exciton emission. The green emission is enhanced remarkably with

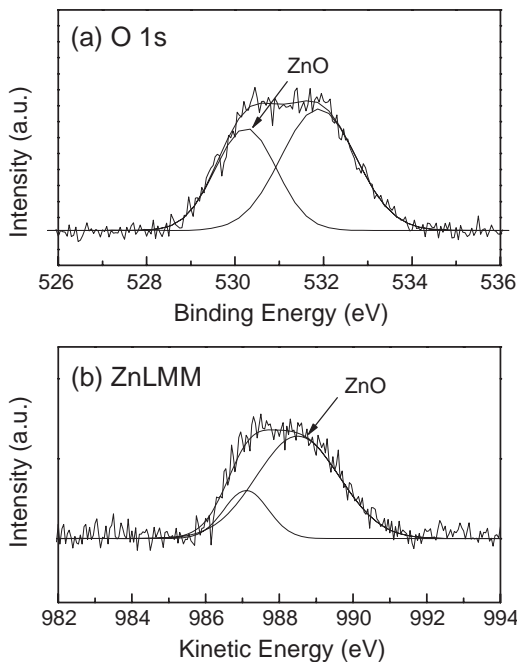


Fig. 6. XPS spectra of ZnO film after annealing at 900 °C in ambient oxygen: (a) O1s; (b) ZnLMM.

Table 1

XPS results of ZnO film after annealing at 900 °C in ambient oxygen				
Total O (at.%)	O in ZnO (at.%)	Total Zn (at.%)	Zn in ZnO (at.%)	O/Zn ratio in ZnO
60.0	24.1	28.3	22.7	1.06

increasing annealing temperature and becomes visible by naked eyes after annealed at 900 °C.

Fig. 5(b) shows PL spectra of ZnO films after annealing in different ambient at 750 °C for 2 h. The green emission is enhanced evidently with increasing oxygen partial pressure.

Fig. 6 shows the XPS spectra of film sample after annealing at 900 °C in ambient oxygen. The O 1s spectrum can be fitted with two Gaussian peaks centered at ~530.2 and ~531.9 eV. The former is attributed to ZnO while the ~531.9 eV peak should be due to Zn<sub>2</sub>SiO<sub>4</sub> and surface contamination [17]. The Zn LMM spectrum is resolved as sums of two components which can be identified as Zn<sub>2</sub>SiO<sub>4</sub> and ZnO at ~987.1 and ~988.5 eV kinetic energies, respectively [17]. The O/Zn ratio in ZnO component can be calculated to be 1.06 from the areas of the fitting peaks. The results are shown in Table 1.

#### 4. Discussion

The 520 nm green emission was generally assigned to intrinsic defects of ZnO such as V<sub>O</sub>, Zn<sub>i</sub>, V<sub>Zn</sub> and O<sub>Zn</sub> [9–12]. According to our experiments (see Fig. 5(b)), the green luminescence center can not be O-deficient defects such as V<sub>O</sub> and Zn<sub>i</sub>. Xu et al. [18] calculated the energy level of several intrinsic defects in ZnO using full-potential linear muffin-tin orbital (FP-LMTO) method. The energy interval from the bottom of the conduction band to the V<sub>Zn</sub> level (3.07 eV) is much larger than that of the green emission, which indicates that O<sub>Zn</sub> also cannot be the green luminescence center. The energy interval from the bottom of the conduction band to the O<sub>Zn</sub> level (2.37 eV) is consistent with observed green emission energy. Lee et al. [19] pointed out that the formation energy of O<sub>Zn</sub> is very low under O-rich condition. In our experiments, the green emission is enhanced with increasing oxygen partial pressure. The XPS results (shown in Table 1) also prove that the films are O-rich. Accordingly, we suggest that the green emission in our ZnO films originates mainly from O<sub>Zn</sub> defect, in agreement with Ref. [11].

It is reported that hydrogen can passivate the defects in ZnO [20]. As shown in Fig. 2, 3, no hydrogen-related vibration was found at higher temperature. Therefore, we suggest that the effect of hydrogen passivation can be ignored in our samples.

Above 800 °C, Si can diffuse from substrate and react with O<sub>2</sub> and ZnO [21,22]. The reaction equation is probably as follows:



Pure Zn<sub>2</sub>SiO<sub>4</sub> does not show any PL emission [23]. But with formation of Zn<sub>2</sub>SiO<sub>4</sub>, green emission is enhanced evi-

dently. We suggest that the effect of  $\text{Zn}_2\text{SiO}_4$  on the enhancement of green emission probably consists of two aspects. First,  $\text{Zn}_2\text{SiO}_4$  grains are dispersed in ZnO films, leading to the increase of the interface and surface areas of ZnO. It was noted that the green luminescence center is generally near the surface [24,25]. Second, the formation of  $\text{Zn}_2\text{SiO}_4$  accelerates the outdiffusion of Zn from ZnO, resulting in more  $V_{\text{Zn}}$  which can easily transfer into  $\text{O}_{\text{Zn}}$  in O-rich condition. As a result, a small amount of  $\text{Zn}_2\text{SiO}_4$  can enhance the green emission.

## 5. Conclusion

In summary, ZnO films with preferred (002) orientation were prepared on Si (111) substrates by TFA-MOD method. The samples consisted of ZnO and  $\text{Zn}_2\text{SiO}_4$  after annealing at 900 °C and exhibited strong green photoluminescence visible by naked eyes. We suggested that the green emission center is oxygen antisite defect  $\text{O}_{\text{Zn}}$ . Effect of  $\text{Zn}_2\text{SiO}_4$  on the enhancement of green emission probably consists of two aspects: (1) increasing the interface and surface of ZnO; (2) accelerating the outdiffusion of Zn from ZnO to facilitate the formation of  $\text{O}_{\text{Zn}}$ .

## Acknowledgements

We are thankful to Dr. Haiping He, Jifeng Qu and Zhe Qu for the fruitful discussions. This project was supported by the National Natural Science Foundation of China under Grant no. 50372063.

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