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Characterizations of Tb:Zn_2SiO_4 films on silicon wafer prepared by sol-gel dip-coating and solid-phase reaction*

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Terbium-doped Zn_2SiO_4 films were successfully prepared on Si wafers by a simple sol-gel dip-coating and solid-phase reaction method of ZnO and SiO_2. X-ray diffraction (XRD) and UV–Vis absorption results revealed that films processed below 850°C were ZnO in wurzite structure, and films processed above 850°C were Zn_2SiO_4 in wellimite structure. Photoluminescence measurements of the Tb-doped Zn_2SiO_4 films showed two strong emission bands at 490 and 545nm. The photoluminescence lifetime was 4.6ms.

Keywords: zinc silicate, sol-gel, solid-phase reaction, photoluminescence
PACC: 7855, 7865, 7840

1. Introduction

Zn_2SiO_4 is a good luminescent host material.[1–11] By incorporating luminescence centres such as rare earth ions and transition metal ions, Zn_2SiO_4 films can emit blue, green and red lights.[12,13] Thin-film electro-luminescent devices made by ion-doped Zn_2SiO_4 were demonstrated by Refs.[14,15] In this paper, a simple sol-gel coating and high-temperature solid-phase reaction method is used to prepare terbium-doped Zn_2SiO_4 thin films on silicon wafers.

2. Experimental procedure

Tb-doped zinc silicate thin films were prepared by following steps. First, a sol-gel dipping and withdrawing process was used to coat the precursor films on silicon wafer, then the precursor films were pre-heated at 120°C for 30min, and finally, the films were heated at 750–950°C to form the zinc silicate by solid-phase reaction.

Zinc acetate was used as the source materials for zinc source, and terbium nitrate was used for terbium source. The solution was prepared as follows: 16.46g zinc acetate was dissolved in 100ml of 2-methoxyethanol; then 4ml of monoethanolamine ($NH_2CH_2CH_2OH$; Hea) was added; and after stirring for 1h at 60°C by a magnetic stirrer, terbium nitrate solution was added into the solution. Continuously stirring the solution for another 1h, a homogeneous and transparent solution was obtained. The final ratio of Tb:Zn_2SiO_4 was 3% in the solution.

Dip-coating was performed at a withdrawing speed of 1cm/min, which was precisely controlled by a pulse generator and step-motor. Two sets of samples were prepared by this method, one set on silicon wafer for x-ray diffraction (XRD) and photoluminescence (PL) measurements, and another set on quartz for UV-vis absorption measurement. The films were pretreated at 80°C and then processed between 750°C and 950°C in oxidizing atmosphere for 4h. The terbium-doped Zn_2SiO_4 films were analyzed using XRD (Rigaku Rotaflex D/max-rA, Cu$K\alpha$, 40kV, 100mA), PL spectrum (Hitachi-F4500 spectrophotometer at room temperature), and UV–Vis absorption (Lambda 20 spectrometer of Perkin Elmer).

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3. Results and discussion

3.1. XRD

Figure 1 shows the XRD patterns of the samples deposited on silicon wafers. It is found that when the annealing was carried out below 850°C, only diffraction peaks from ZnO were observed, indicating that the solid reaction between ZnO and SiO_2 did not take place at temperatures below 850°C. When the temperature rose above 850°, zinc silicate related diffraction peaks dominated the whole pattern, indicating that solid-phase reaction between ZnO and SiO_2 took place. The higher the temperature, the stronger and the narrower the diffraction peaks, which can be explained as a result of grain size increase. The results are similar to those reported in Ref.[13].

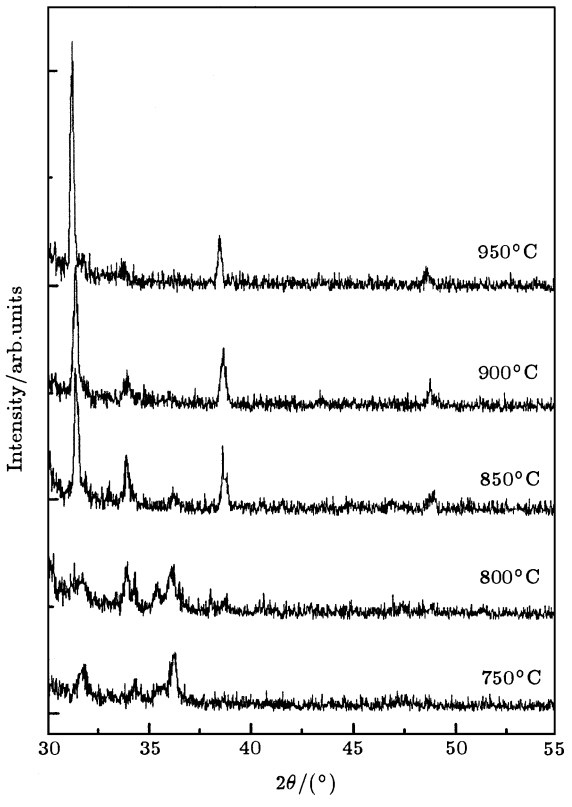


Fig.1. XRD patterns of Tb-doped films annealed at different temperatures.

3.2. UV–Vis absorption

Figure 2 shows two absorption spectra of the films prepared on the quartz glasses at 750°C and 950°C. For the film processed at 750°C, the absorption edge is at 385nm, a typical value for the bulk ZnO; while for the film processed at 950°C, the absorption edge is at 215nm (~5.7eV), which is the absorption edge of Zn_2SiO_4. The result is in agreement with the XRD results: i.e. at lower temperatures the precursor films transform to ZnO, while at higher temperatures, solid-phase reaction between ZnO and SiO_2 occurs and Zn_2SiO_4 is formed. The reaction formula is

$$ZnO + SiO_2 \xrightarrow{\Delta} Zn_2SiO_4.$$

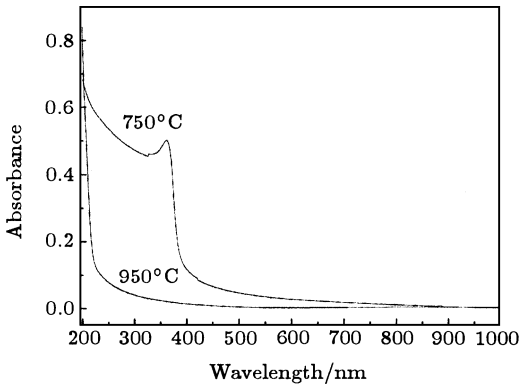


Fig.2. Typical UV–Vis absorption spectra of ZnO and Zn_2SiO_4 films.

3.3. Photoluminescence

The photoluminescence spectra for films annealed at different temperatures are shown in Fig.3. The excitation wavelength is fixed at 210nm. From the figure we can see that all the photoluminescence spectra of films have the same characteristic, i.e. there are mainly two emission bands, one at 545nm, and another at 490nm, which is similar to the results reported by Zhang *et al.*[13] It is clear that the higher the annealing temperature, the stronger the peaks intensity. As we knew from the results of XRD and UV–Vis absorption experiments, at temperatures below 850°C, the terbium-doped ZnO films were formed, while at temperatures above 850°C, the terbium-doped Zn_2SiO_4 films were formed. It is clear that the luminescence efficiency of terbium-doped Zn_2SiO_4 is much higher than that of terbium-doped ZnO. Another phenomenon is that the higher the annealing temperature, the stronger the emission bands, which can be explained by the crystalline quality improved as the temperature increases.

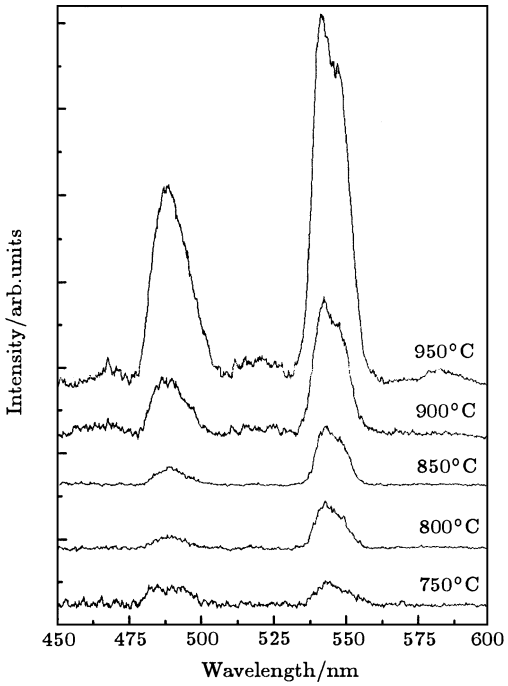


Fig.3. Photoluminescence spectra of Tb-doped films annealed at different temperatures.

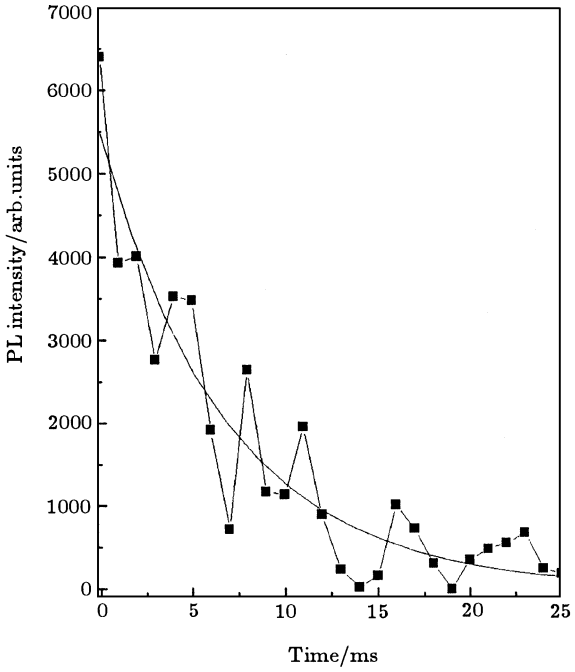


Fig.4. Decay kinetics of the green emission of terbium-doped film.

The emissions can be attributed to the $^5D_4 \rightarrow {}^7F_5$ transitions (545nm) and the $^5D_4 \rightarrow {}^7F_6$ transitions (490nm) of Tb^{3+} respectively.[13] The green emission ($^5D_4 - -{}^7F_5$) is stronger than the blue ($^5D_4 \rightarrow {}^7F_6$). This is obvious according to Judd–Ofelt theory,[16] because $(^7F_5 \| C^{(\lambda)} \| {}^5F_4)^2 > (^7F_6 \| C^{(\lambda)} \| {}^5F_4)^2$ for λ=2, 4, 6.[17]

The decay characteristic of the $^5D_4 - -{}^7F_5$ green emission at 545nm for the film processed at 950°C has also been studied, and the result is shown in Fig.4. The lifetime ($\tau_{1/e}$) calculated from the decay curve is 4.6ms.

In summary, the terbium-doped Zn_2SiO_4 thin films have been successfully fabricated on silicon wafers using a very simple method. The photoluminescence results showed that green emission ($^5D_4 - -{}^7F_5$) is dominant, and the lifetime of the blue emission is 4.6ms. Since silicate is a very stable and highly efficient luminescence material compared with other silicon-based photoluminescent materials, such as porous silicon and Si:H:O,[18,19] it is expected that transition and rare-earth metal ion-doped Zn_2SiO_4/Si have practical applications in silicon-based devices.

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