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Transitions of microstructure and photoluminescence properties of the Ge/ZnO multilayer films in certain annealing temperature region

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Abstract

The Ge/ZnO multilayer films have been prepared by rf magnetron sputtering. The effects of annealing on the microstructure and photoluminescence properties of the multilayers have been investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier-transform infrared (FTIR) spectrometry and photoluminescence (PL) spectrometry. The investigation of structural properties indicates that Zn_2GeO_4 has been formed with (2 2 0) texture and Zn deficiency from Ge/ZnO multilayer films in the process of annealing. However, lower Zn/Ge ratio can be improved by annealing. The annealed multilayers show three main emission bands at 532, 700, and 761 nm, which originate from the transition between oxygen vacancy (V_o^*) and Zn vacancies (V_{Zn}), the radiative recombination of quantum-confined excitons (QCE) in Ge nanocrystals, and the optical transition in the GeO color centers, respectively. Finally, the fabrication of thin film Zn_2GeO_4 from Ge/ZnO multilayer films by annealing at low temperature provides another approach to prepare the green-emitting oxide phosphor film:Zn_2GeO_4:Mn.

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Keywords: Ge/ZnO multilayers; Microstructure; Photoluminescence; Annealing

1. Introduction

As a wide band gap semiconductor, ZnO has been studied extensively for a long time due to its important application in optoelectronic devices such as UV light-emitting diodes and lasers, surface acoustic wave devices, and window material for display and solar cells [1–3]. ZnO generally emits a strong UV luminescence band around 370 nm ascribed to band edge emission [4] and several other visible bands in the blue, green and yellow wavelength resulting from defect emission [2,5]. However, the exact origin of the visible emission is still in controversy. Except for the most common UV band and the green band, other type of emission bands, such as yellow and red emitting, two essential types for white-light emission diodes, appear rarely for ZnO [6,7].

To satisfy the different requirements in devices, a number of approaches have been taken to modulate optical properties of ZnO. Recently, there are intensive studies on the subject by doping exotic dopants or depositing multilayer structures to realize above purpose, and now Er, Ce, Ga, Ge, Al, In, Na, Li, etc., as foreign materials have been investigated [6,8–10]. In contrast to other materials, group IV elements have an indirect band gap and energy difference between indirect gap and direct gap. In particular, Ge has a smaller energy difference ($\Delta E_g = 0.12$ eV) comparing with Si, which leads to tuning the electronic structure around band edge more easily [8]. On the other hand, ZnO ternary compounds formed with group IV, such as Zn_2SiO_4 and Zn_2GeO_4, have the potential applications as oxide phosphors in optoelectronics [11,12]. The violet and the blue light emissions from Ge-doped ZnO films have been reported previously [8,13,14]. But few attentions have embarked on other visible light emission band, and it is also necessary to clarify the development of the microstructure of this compound in the period of processing.

In this study, we report on the microstructure and the photoluminescence (PL) features of the Ge/ZnO multilayer films in annealing process in certain temperature region. The

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possible origins of the three PL emissions from the film along with their dependence on the annealing conditions have been studied. Finally, an important luminescence phosphor, Zn_2GeO_4 compound, has been synthesized successfully at low temperature from the Ge/ZnO multilayer films.

2. Experimental details

Ge/ZnO multilayer films were prepared on quartz substrates by sputtering a ZnO target (99.995%) at 100 W and a Ge target (99.999%) at 80 W alternately using rf magnetron sputtering system (JGP-500) at substrate temperature of 300 °C to form a four periodic multilayer structure. The distance between the target and the substrate is 8×10^{-2} m. Films were grown at working pressure of 1.0 Pa with O_2/Ar = 1 and pure Ar ambient for ZnO and Ge films, respectively. The thicknesses for each ZnO and Ge layer were 200 and 50 nm, respectively, and the total thickness of the structures was about 1 μm, which has been confirmed by spectroscopic ellipsometry (M-2000). After the deposition, the Ge/ZnO multilayers were annealed at N_2 ambient for 60 min at various annealing temperature (T_{an}) from 550 to 680 °C in a horizontal quartz furnace.

The structural properties were characterized using X-ray diffraction (XRD) with Bruker D8 X-ray diffractometer equipped with Cu Kα radiation (0.154 nm wavelength), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) and energy dispersive X-ray spectroscopy (EDX) equipped in a FEI Tecnai-20 TEM. Infrared absorption spectra were obtained ranging from 900 to 4000 cm^{-1} under ATR mode using a Nicolet Nexus 670 Fourier-transform infrared (FTIR) spectrometer at room temperature for investigating chemical bond signatures. Room temperature PL spectra were obtained with an Ar^+ laser excitation source (488 nm) and wavelength ranges from 500 to 900 nm by JY-HR800.

3. Results and discussion

Fig. 1(a) shows the XRD patterns from the as-grown and annealed films. There is no new peak appearing when T_{an} is lower than 580 °C except for three peaks of ZnO (1 0 0), (0 0 2) and (0 0 4) located at $2\theta = 30.88°$, 34.21°, and 72.13°, respectively. At T_{an} = 580 °C, these three peaks shift toward larger angle apparently and their intensity has also enhanced slightly. This indicates that ZnO has a better crystallinity and some internal stress in the film has been released [8]. At the point, four other new peaks can be observed at $2\theta = 12.39°$, 24.97°, 27.28°, and 33.26°, which correspond to the diffraction peaks of Zn_2GeO_4 (1 1 0), Zn_2GeO_4 (2 2 0), Ge (1 1 1) and GeO, respectively. It is evident that the structural properties of the sample have changed. Amorphous Ge layer transform to polycrystalline while Ge and ZnO form a new compound of Zn_2GeO_4. With T_{an} increasing continually, the intensity of Zn_2GeO_4 (1 1 0), Zn_2GeO_4 (2 2 0) and GeO peaks and three ZnO peaks become much higher, whereas that of Ge (1 1 1) decreases linearly, which can be seen clearly in Fig. 1(b) and (c). After that, the intensity of ZnO peaks begins to decrease

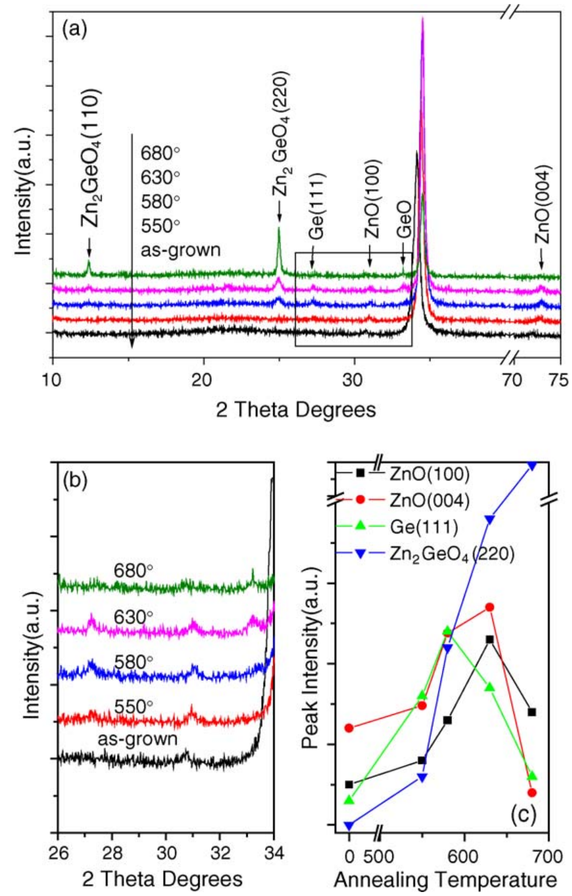

Fig. 1. The XRD patterns for the film in as-grown state and annealed at different temperatures (a); an enlarge image (b) of the square part in (a) shows the small peaks clearly; the dependence of XRD peak intensities on T_{an} (c).

gradually. At T_{an} = 680 °C, the Ge (1 1 1), ZnO (1 0 0) and (0 0 4) peaks almost disappear. The peak around 34° should be considered as a multiple peak of Zn_2GeO_4 (4 1 0) and ZnO (0 0 2) because we known that their positions are very close in XRD patterns and the intensity of this peak has a non-monotone change decreasing to a minimum value firstly when T_{an} increasing to 630 °C, and then it begins to increase quickly with T_{an} increasing to 680 °C. So, the facts shown in XRD measurements reveal that the change of structure for the prepared samples during annealing process. Thermal annealing cannot only fabricate Ge and GeO nanocrystals (7.2 and 5.8 nm, respectively) but also make another new compound, Zn_2GeO_4, from Ge/ZnO multilayer films in the end. In addition, the appearance of the peaks of Zn_2GeO_4 (1 1 0) and (2 2 0) implies the crystallization of Zn_2GeO_4 has the layered structure paralleling to the (1 1 0) facet.

The morphology and crystallinity properties of the Ge/ZnO multilayers annealed at T_{an} = 680 °C have been characterized by TEM, as shown in Fig. 2(a). The grain size is in between 4 and 10 nm obviously. The little white dots are rich in Ge while the large grey grains are rich in Zn and oxygen by the analysis of EDS. The small space between two different grains indicates that Zn_2GeO_4 would grow along certain crystallographic direction resulting in a column shape, which agrees well with