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Short Communication

Analysis of the properties of germanium/zinc silicate film growth through a simple thermal evaporation technique for hydrogen gas sensing and deep UV photodetector application

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ABSTRACT

Germanium/zinc silicate (Ge/Zn_2SiO_4) thin films were produced in a high-temperature horizontal tube furnace. Structural and optical properties of thin films were investigated by scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray diffraction. Room temperature Raman spectra were also obtained. Nickel (Ni) metal–semiconductor–metal (MSM) contacts were deposited on the Ge/Zn_2SiO_4 thin film by evaporating Ni using an appropriate MSM mask. Corresponding current–voltage characteristics of the Schottky diodes were recorded before and after (2%) hydrogen (H_2) gas exposure with different flow rates. The respectable response and sensitivity of the MSM to H_2 gas heighten the potential interest in future gas sensor devices. The strong photoelectric properties of the MSM in the deep ultraviolet demonstrate that the film contributes to photosensitivity. Therefore, Ge/Zn_2SiO_4 films are potential photodetectors in short wavelength applications.

1. Introduction

Zinc oxide (ZnO), a semiconductor material with a wide-band gap of 3.37 eV and a large excitation binding energy of 60 eV at room temperature, has attracted increasing attention because of its numerous prospective applications in many fields. To satisfy the different requirements in optoelectronic devices, ZnO films with various dopants such as erbium and gallium were studied [1,2]. Modified ZnO thin films doped with other materials have been attempted by many researchers. They can be used as gas sensors [3,4], photocatalysts [5], solar cells [6], light-emitting materials [7,8], and field-effect transistors [9].

Another possible material for doping with ZnO is germanium (Ge). Yu et al. [10] prepared a ZnO:Ge compound through the solid state reaction method and investigated its optical properties. Zheng et al. [11] deposited Ge/ZnO multilayer films by radio-frequency magnetron sputtering and fabricated a zinc germinate (Zn_2GeO_4) thin film from Ge/ZnO multilayer films through annealing. Pan et al. [12] grew Ge-catalyzed ZnO nanowires and found that Ge is a promising catalyst for growing high-quality oxide nanowires. We previously reported the structural, optical, and electrical properties of ZnO/Zn_2GeO_4 porous-like thin films and wires and demonstrated that the doping material is a potential photodetector in dual-ultraviolet (UV) wavelength applications [13]. Another promising compound with doped ZnO and Ge is the Ge/Zinc silicate (Zn_2SiO_4) mixture. Zn_2SiO_4 has a wide band gap of 5.5 eV and is a promising multifunctional material. Zn_2SiO_4-based nanostructures

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have been widely studied because of their great potential applications and importance in the study of size and dimensionality-dependent chemical and physical properties [14,15]. However, Ge/Zn_2SiO_4 compound applications such as hydrogen (H_2) gas sensors and photodetectors are not yet been explored and reported.

Thermal evaporation is a particularly interesting and simple way of producing Ge/Zn_2SiO_4 thin films. Thermal evaporation is a low-cost technique that only requires powders as source materials and not hazardous materials and gases. In this work, we characterized and studied the properties of a Ge/Zn_2SiO_4 thin film grown on an *n*-type silicon (Si) substrate using a horizontal tube furnace. An MSM photodiode with nickel (Ni) Schottky contacts was deposited using vacuum thermal evaporation to examine the H_2 gas sensing and photodetector properties of Ge/Zn_2SiO_4 thin films. Ge/Zn_2SiO_4 can be possibly integrated into future H_2 gas sensing and deep UV photodetector devices.

2. Experimental method

The Ge/Zn_2SiO_4 thin films were synthesized using a simple thermal evaporation method [13]. A mixture of Ge and ZnO (ratio 1:1) was used as source material and evaporated at 1145 °C for two and a half hours. The synthesized products were characterized using an X-ray diffractometer (XRD; PANalytical X'Pert PRO) and a scanning electron microscope (SEM, model JEOL JSM-6460LV with energy dispersive X-ray spectroscopy [EDX]). Room-temperature Raman spectrum was obtained with a Raman spectrometer (Horiba Jobin Yvon HR800), with Ar^+ as the excitation source, operating at a wavelength of 514.55 nm. The structure of the metal–semiconductor–metal (MSM) photodiode consists of two interdigitated Schottky contacts (electrode) with Ni Schottky contacts deposited using vacuum thermal evaporation [13]. The fabricated MSM structure was characterized using current–voltage (*I*–*V*) measurements. The experiments were conducted using a gas-sensing chamber. Five different flow rates of 2% H_2 in N_2 gas were used in the experiments starting from 30 sccm to 150 sccm. The test fixture was placed into the chamber with wires connected from the probes to the Keithley model 2400 to measure the *I*–*V* characteristics of the sample. The spectral responses of the MSM Ge/Zn_2SiO_4 were measured at different biasing voltages. A mercury light monochromator system was used to provide the light source from 220 nm to 300 nm.

3. Results and discussion

The morphology and crystal structure of the grown Ge/Zn_2SiO_4 thin film on the Si substrate are shown in Fig. 1. The SEM image in Fig. 1(a) reveals that the film consists of stringy-shaped Ge/Zn_2SiO_4 structures covering the substrate. Further verification of the elemental distributions shows that the film consists of Ge, Zn, O, and Si on the Si surface (inset of Fig. 1a). The enlarged SEM image (inset) clearly shows that the Ge form tips located at the end of the stringy-shaped Zn_2SiO_4. The XRD pattern (Fig. 1(b)) shows

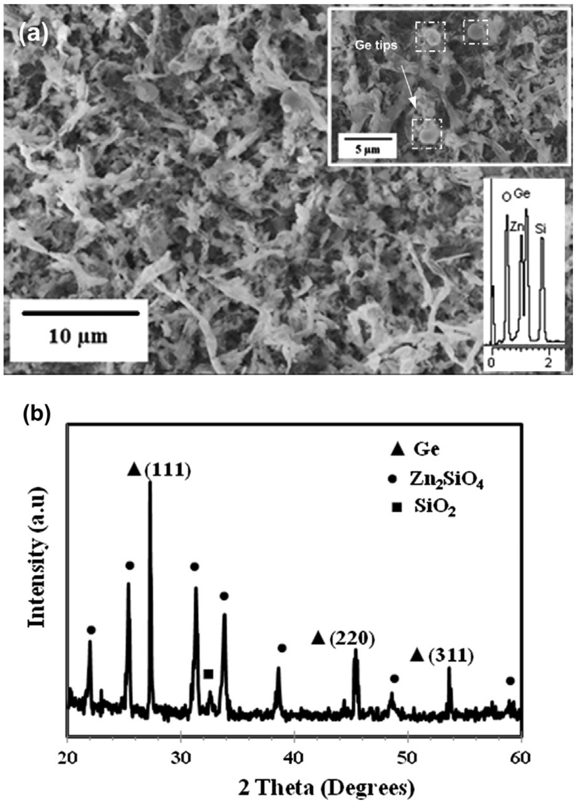

Fig. 1. (a) SEM images of the Ge/Zn_2SiO_4 thin film surface morphology, with EDX analysis and higher magnification image inset. (b) XRD results show crystalline structures in the grown product.

that the dominant peak of the thin film can be clearly indexed into a cubic Ge crystal structure (Joint Committee on Powder Diffraction Standards [JCPDS]: PDF file no. 03-065-0333). The Zn_2SiO_4 corresponded to the rhombohedral crystal structure (JCPDS: PDF file no. 01-070-1235), which was also detected in the structure. The crystallite size for Ge and Zn_2SiO_4 measured by Debye–Scherrer [16] is approximately 27 nm and 41 nm, respectively. Impurities such as SiO_2 were also detected in our sample from the Si substrate.

The room-temperature Raman spectrum of the Ge/Zn_2SiO_4 thin film is shown in Fig. 2. The 520 cm^{-1} peak is attributed to the optical phonon mode of the Si substrate [17], and the 298 cm^{-1} peak corresponds to the Ge optical phonons related to Ge–Ge bonds [18]. The peak at 400 cm^{-1} is related to the intermixing at the Ge/Si interface. These peaks correspond to the scattering of the optic phonons involving Si–Ge stretching motions [19]. However two new distinct peaks appear at 812 cm^{-1} and 863 cm^{-1}, respectively, which are not reported in the literature for the ZnO and Ge band. The inclusion of the spectrum from pure Zn_2GeO_4 (inset of Fig. 2) suggests that the appearance of the two peaks is attributed to the presence of the Zn_2SiO_4 compound. Therefore, further study is necessary to confirm this result. The broad Raman peak at the range of 950–1000 cm^{-1} is related to the SiO_2 from the Si substrate.

To examine the potential applications of the Ge/Zn_2SiO_4 thin film, Ni Schottky contacts were deposited through