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Optical properties of $Si_{1-x}Ge_xO_2$ thin films prepared by radio frequency magnetron sputtering method

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$Si_{1-x}Ge_xO_2$ thin films were prepared by radio frequency (RF) magnetron sputtering and annealing treatment method. Ge/GeO_2 core-shell nanoparticals (NPs) embedded in SiO_2 matrix were identified by high resolution transmission electron microscope (HRTEM), with a size of ~4 nm in diameter. The affect of annealing temperature on the microstructural and photoluminescence (PL) properties of the thin films were investigated. Specimen exhibited red and near infrared light emission at room temperature. The position of 780 nm PL peak was independent with annealing temperature, which was ascribed to the electron transition in Ge-O related defects. As for ~900 nm light emission, quantum confinement effect was considered as a possible transition mechanism.

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Keywords: Photoluminescence, $Si_{1-x}Ge_xO_2$ thin films, Quantum confinement effect

1. Introduction

Group IV NPs embedded in a SiO_2 matrix have been studied extensively because of their potential for integrated optoelectronic device on silicon substrates [1]. In the past decades, in order to obtain room temperature Si-based light emission many methods have been developed such as ion implantion, chemical vapor deposition, cosputtering, and so on [2]. Among of those, it was a simple way to obtain luminescent Si NPs by thermal annealing of amorphous silicon suboxides (a-SiO_x). Since a-SiO_x was thermodynamically unstable, a decomposition reaction took place by annealing treatment and led to the formation of Si NPs/SiO_2 [3]. This process and the size of Si NPs were controlled by the excess Si atoms and annealing temperature (T_a). The light emission process has been discussed extensively and was attributed either to radiation recombination via quantum confined states, or to defect at anocrystalline/matrix interface or in the matrix itself [4]. The optical properties, for example, PL from of the isolated Ge NPs or Ge/GeO_x core-shell NPs embedded in SiO_2 matrix or have been reported earlier[5]. It is found that light emission is more prominent in the case of Ge/GeO_2 core-shell NPs. Wu et al. reported that Ge/GeO_2 core-shell structure embedded in SiO_2 matrix were prepared using the plused laser deposition method and the PL emission in UV region was obtained [6]. P. K. Giri et al. synthesized freestanding Ge/GeO_2 core-shell nanocrystals (NCs) with varying sizes and shell thicknesses were by a ball milling method, high-resolution transmission electron microscope images revealed the presence of strain in the Ge core and GeO_2 shell, which induced a strong phonon localization effect [7]. Yuan et al. reported Ge/GeO2 core/shell nanoparticles embedded in an Al2O3 dielectrics matrix. The phonon localization effect between the Ge core and GeO_2 shell, which leads to enhanced radiative recombination and thus it enhances the photoluminescence intensity [8].

In this paper, the $Si_{1-x}Ge_xO_2$ thin films were prepared by radio frequency (RF) magnetron sputtering method. The affect of T_a on the microstructural and PL properties of thin films were investigated.

2. Experimental

These thin films samples were fabricated by RF sputtering of Si and Ge composite target. A silicon wafer was used as substrate without heating. The chamber was evacuated with backing pump and turbo pump successively. After reached a pressure of 2×10^{-5} Pa in the sputtering chamber, Ar and O_2 gases were introduced into the chamber through two separate control valves. The working sputtering pressure was held constant at 5 Pa and the forward power was maintained at 150 W. After deposition, the $Si_{1-x}Ge_xO_2$ thin films were annealed at 700, 800, 900, 1000 °C in N_2 for 1 h (specimen were denoted by A1, A2, A3, A4). The gas flow rate is 300 sccm and the gas pressure is about 1.01×10^5 Pa with water sealed.

X-ray diffraction (XRD, X Pert PRO) measurements were carried out with a diffractometer (Cu Kα X-ray, λ=0.15406 nm). High resolution transmission electron microscope (HRTEM, JEM-2010) was used to determine the microstructure characterizations of NPs. The Raman spectra are acquired using a JY-T64000 spectrometer operating in backscattering geometry at an excitation wavelength of 325 nm. PL spectra were measured at room temperature using a He-Cd laser with a wavelength of 325 nm, equipped with a CCD detector.

3. Results and discussion

Fig. 1 shows the XRD pattern from the thin films annealed with different T_a. The broad weak peak around ~25° originates from the amorphous SiO_2. When T_a =800 °C, XRD diffraction pattern show intensive peaks at the positions of 26.1 ° and 27.6 °. They correspond to the characteristic peak of the GeO_2 (101) and Ge(111), meaning the formation of crystal structure of GeO_2 and Ge structure. With the increase of T_a, the intensity of characteristic peak from Ge(111) increases gradually, which indicates the enhancement in crystalline quality of Ge NPs.

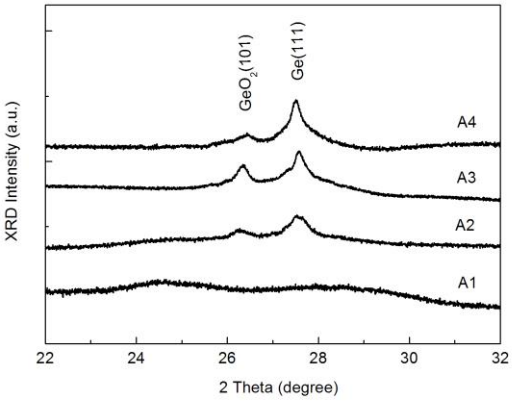

Fig. 1. XRD diffraction pattern of specimen A1, A2, A3 and A4.

The formation of NPs is also verified by the HRTEM observation. Fig. 2(a) presents the images of sample annealed at 900 °C (A3). Spherical NPs can be identified in the amorphous SiO_2 matrix. We estimate that the mean radius of NPs, which is about ~4 nm. The result is similar with the conclusion draw from the XRD diffraction pattern. According to HRTEM image, the lattice distances are 0.32 nm in core region and 0.34 nm in shell region, respectively. Which correspond to the lattice planes of Ge(111) and GeO_2 (101). Furthermore, the compositions of sample annealed at at 900 °C are detected by the EDS examination (as shown in Fig. 2(b)), O, Si and Ge peaks are visible in the EDS spectra for this sample. Ge oxide includes GeO, GeO_2, and Ge_2O_3, and which are easy to decompose during high temperature processing [9]. The following two reactions are easy to carry out: $GeO_x \rightarrow Ge + GeO_2$ and $GeO_2 + Si \rightarrow Ge + SiO_2$ during annealing process. From a thermodynamics point of view, Ge NPs is prone to dissolve in GeO_2 matrix rather than in SiO_2 matrix. Therefore, we thought the Ge/GeO_2 core-shell NPs were formed after annealing treatment.

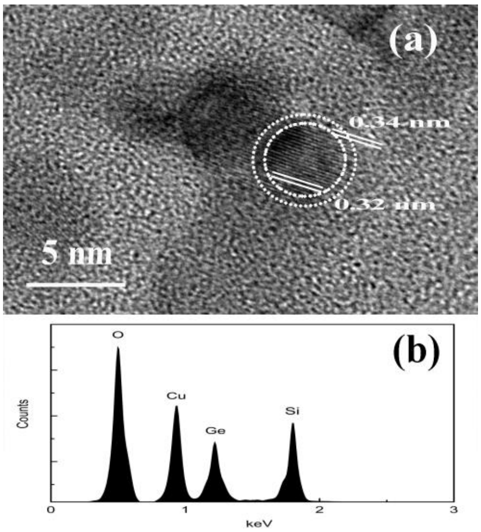

Fig. 2. HRTEM image of sample A3 (a) and the spectrum of EDS (b).

Fig. 3 shows Raman spectra of samples A1, A2, A3 and A4. Specimen exhibits three Raman peaks centered at 261, 298 and 440 cm^{-1}. The vibration peak at 298 cm^{-1} is attributed to the first-order transverse optical (TO) phonon mode of crystalline Ge [10]. The peaks centered at 261 and 440 cm^{-1} are the characteristic Raman active modes of crystalline GeO_2 [5]. From Fig. 3, the intensities ratio of 298 cm^{-1} to 440 cm^{-1} Raman peaks are enhanced with the increasing of T_a, which indicates the GeO_2 transferring to Ge gradually. As for 298 cm^{-1} Raman peak, its FWHM becomes acute with the increasing of T_a. The line width narrowing is caused by size distribution of Ge NCs and phonon confinement effect in the Ge NCs, which is known to be inversely proportional to the size of the NCs.

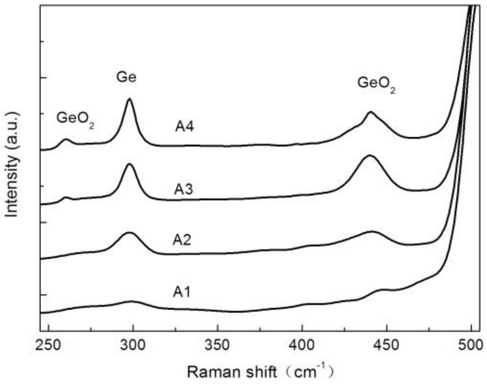

Fig. 3. Raman spectra of specimen A1, A2, A3 and A4.

The specimen exhibit two main PL peaks located at 780 nm and ~900 nm (as shown Fig. 4). The position of 780 nm PL peak is independent with T_a and its intensity reaches the maximum value when T_a =900 °C. However, the position of ~900 nm light emission is related with T_a and which red shifts from 887 nm to 921 nm. Commonly, the PL emission originated from the Ge NPs was scarcely reported. The reason was that there existed a mass of interface defects in Ge NPs/SiO_2 matrix. P_b center was thought to be one major defect, which could quench the PL emission from Ge NPs.

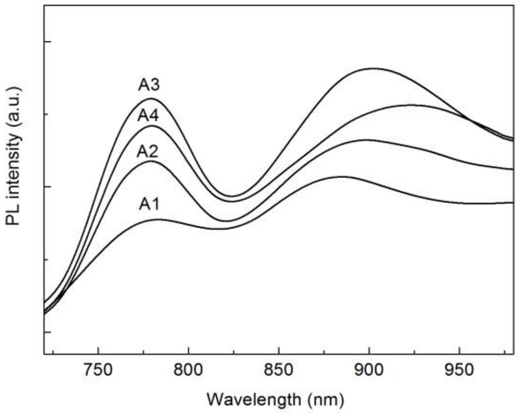

Fig. 4. PL spectra from specimen A1, A2, A3 and A4.

In this work, the thin films exhibited two PL peaks centered at 780 nm and ~900 nm. We assumed that the Ge/GeO_2 core-shell NPs be mainly composed of single crystal Ge. According to Brus's model [11], the energy gap of Ge NPs with a diameter of 4.4 nm was corresponding to the 900 nm light emission. The value was similar with the diameter obtained by HRTEM image. So the quantum confinement effect was considered as a possible mechanism for the 900 nm PL emission. Since thermal annealing treatment was benifical to the growth of Ge NPs, the PL emission peak red shifted from 887 nm to 921 nm.

From Fig. 4, the position of 780 nm PL peak is independent with T_a. This emission peak might originated from some kind of defect. Shen *et al.* have reported that the 780 nm PL was induced by the $T_\pi \rightarrow S_0$ transitions in Ge-O related defect [12]. The transitions in Ge-O defect were intra-transition which will not be affected by the environment, and were only related with the amount of defect. According to XPS results, the composition of GeO_x was easy to decompose during annealing treatment process [9]. The mount of Ge-O related defect was related with T_a, the intensity of 780 nm PL reach maximum value when T_a =900 °C also. Based on the discussion above, the 780 nm PL was ascribed to the transition of electron in Ge-O related defect.

4. Conclusions

In conclusion, $Si_{1-x}Ge_xO_2$ thin films were formed by RF magnetron sputtering and annealing treatment method. The affect of T_a on the microstructural and PL properties of thin films were investigated. Ge/GeO_2 core-shell NPs embedded in SiO_2 matrix were identified by HRTEM, with a size of ~4 nm in diameter. Specimen exhibit two strong PL peaks centered around 780 nm and 900 nm. The former was attributed to electron transitions in Ge-O related defect and the latter was ascribed to the quantum confinement effect.

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