Origin of photoluminescence peaks in Ge–SiO₂ thin films

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Received 9 October 2001; revised 30 January 2002; accepted 30 January 2002

Abstract

Ge–SiO₂ thin films were prepared by the RF magnetron sputtering technique on p-Si substrates from a Ge–SiO₂ composite target. The as-deposited films were annealed in the temperature range of 300–1000 °C under nitrogen ambience. The structure of films was evaluated by X-ray diffraction, X-ray photoemission spectroscopy and Fourier transform infrared absorption spectroscopy. Results show that the content of Ge and its oxides in the films change with increasing annealing temperature (Tₐ); the photoluminescence (PL) characteristics are closely dependent on the contents of Ge and its oxides in SiO₂ matrix. The dependence observed strongly suggests that the PL peak at 394 nm is related to the existence of GeO and 580 nm to that of Ge nanocrystal (nc-Ge) in the films.

Keywords: Ge–SiO₂ thin films; Magnetron sputtering; Photoluminescence; Photoluminescence peak; Annealing temperature

1. Introduction

Silicon-based light emitting materials (mainly Si–SiO₂, Ge–SiO₂), are very important for full-color display, especially for the integrated optoelectronics technology. Recently, studies on optical properties of Ge–SiO₂ films and their photoluminescence (PL) mechanism have been reported [1,2]. It is not well understood about the sites of excitation and radiative recombination. An intensive debate about the origin of PL still exists [3]. It is elusive to understand the structure and optical properties of this kind of materials due to their complex amorphous structure; defects and interface chemical bonding states related to different preparation techniques. Nevertheless, it is of benefit to the further understanding of PL mechanism and investigating the relationship between the structure and PL peaks. In this paper, we report the effect of Tₐ on the structure and characteristics of PL from the sample films to clarify the relationship between them and to understand extensively the mechanism of luminescence from this kind of materials.

2. Experiment

The Ge–SiO₂ thin films were grown on (100) oriented p-type Si substrates with resistivity of 5–8 Ω cm using an RF magnetron sputtering technique, with a composite target of pure SiO₂ plate (50 mm in diameter) attached several Ge chips on the surface of it. Just before deposition, the Si substrates were dipped in 10% hydrofluoric acid to remove the surface native oxide, rinsed with a large amount of de-ionized water, dried in a flux of N₂, and immediately placed into the chamber. After vacuum pumping, the co-sputtering was performed with an Ar pressure of 2 Pa and RF power of 200 W at about 200 °C of substrate temperature in the chamber evacuated to 2 £ 10⁻⁴ Pa before argon gas in a flow of 40SCCM was introduced through a mass flow controller. The thickness of the films was about 300 nm. Post annealing was conducted under a flowing N₂ ambience in the temperature range of 300–1000 °C for 30 min. For comparison, SiO₂ films without Ge were also fabricated under the same conditions of deposition and post annealing.

X-ray diffraction (XRD) measurements were carried out with a Rigaku D/Max-3C diffractometer (Cu Ka X-ray, λ = 0.15406 nm). XPS spectra were measured with a PHI-550 photoelectric spectrometer after Ar⁺ sputtering of 5 min. IR absorption spectra were measured with a Nicolot AVATAR 360 Fourier transform IR system. PL spectra were measured by using 240 nm excitation light from a Xe lamp (Hitachi F-4010) and the monochromater with a resolution of 2 nm. All the measurements were conducted at room temperature.

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PII: S1468-6996(02)00024-4
3. Results

Fig. 1 shows the XRD patterns of films annealed at 500, 600, 800, and 1000 °C, respectively. When $T_a$ is higher than 600 °C, three obvious peaks of Ge(111), (220) and (311) appear, which indicates the formation of nc-Ge. With the increase of $T_a$, the XRD peaks become sharper and the full-width at half-maximum (FWHM) of each peak decreases. It means that the average size of nc-Ge increases. For the (111) peak, at $T_a$ of 600, 800, and 1000 °C, the FWHM is 2.2, 1.8, and 1.4°, respectively. The average size of nc-Ge evaluated according to Scherrer formula is about 3.9, 4.7, and 6.1 nm, respectively.

Fig. 2 shows the analytical results of XPS spectra of Ge3d electrons in samples annealed at different $T_a$. All the curves are unsymmetrical and the first three exhibit four obvious peaks located at about 28.6, 30.8, 31.6, and 32.5 eV which correspond to 3d electrons of Ge, GeO, Ge$_2$O$_3$, and GeO$_2$ [4], respectively. According to Gauss fitting, the proportion of each subband in total spectrum area represents the atomic ratio of its related content in total Ge-related components. For the sample annealed at 300 °C, the major content of the Ge related components is GeO$_2$, while the sample annealed at 1000 °C contains mainly elemental Ge accompanied with some content of GeO. The changes in the content of Ge oxides are due to the existence of silicon atoms, which come from the oxygen deficiency of silicon dioxides (SiO$_x$, $x < 2$) during sputtering the composite target of Ge–SiO$_2$, and the reaction between silicon and Ge oxides at elevated temperature [5].

Fig. 3 shows the Fourier transform infrared (FTIR) spectra. Each spectrum has three absorption bands around 460, 820, and 1090 cm$^{-1}$, which have been identified with rocking, bending and asymmetric stretching modes of Si–O–Si unit, respectively. For the as-deposited sample, there are other absorption bands around 580 and 870 cm$^{-1}$, which correspond to the bending and stretching modes of Ge–O–Ge unit [6,7], respectively. However, for the sample annealed at 1000 °C, these two bands disappear, which suggests that there are few of Ge oxides in the film and the majority of Ge exists in the form of nc-Ge.

From the results of XRD, XPS and FTIR spectra mentioned earlier, it is confirmed that Ge in the as-deposited film exists mainly in the form of Ge oxides, such as GeO, Ge$_2$O$_3$ and GeO$_2$. During annealing, because Si–O bond is stronger and more stable than Ge–O bond, the extra silicon atoms existing in the off-stoichiometric SiO$_x$ (x < 2) will react with the Ge oxides to produce Ge suboxides or elemental Ge. The relation of the contents of Ge oxides and elemental Ge to the $T_a$ are shown in Fig. 4. It can be seen clearly that the elemental Ge corresponding to the precipitation of nc-Ge in the film increases and the Ge oxides (GeO$_2$ and Ge$_2$O$_3$) decrease simultaneously. Since the increase of elemental Ge is related to a decrease of the Ge oxides, the relation mentioned earlier is reasonable. The relation of the content of GeO to $T_a$ is quite different to that of GeO$_2$ and Ge$_2$O$_3$ as indicated in Fig. 4 which may result from that GeO is also as one kind of the products of the reaction between elemental Si and GeO$_2$ (or Ge$_2$O$_3$), and...
GeO is more stable than GeO$_2$ and Ge$_2$O$_3$ at elevated temperature [4]. So the content of GeO increases in films annealed at the temperature of the beginning below 800 °C. But at $T_a$ above 800 °C, owing to the reaction between elemental Si and Ge oxides during the 30 min of annealing, GeO$_2$ and Ge$_2$O$_3$ are almost exhausted, and the reaction between the GeO and elemental Si may be more active, the content of GeO decreases dramatically.

The thermodynamical reactions produce a large amount of elemental Ge in the films during annealing at the elevated temperature, but according to the phase diagrams, a small amount of elemental Ge (less than 1 at.%) can dissolve in the SiO$_2$ matrices [8], so the increase of the elemental Ge results in phase separation, corresponding to precipitation of nc-Ge. $T_a$ is an important factor for controlling the particle size of nc-Ge. The average size of nc-Ge increases with $T_a$ from 300 to 1000 °C in our experiment.

Fig. 5 shows the PL spectra from the as-deposited film and the films annealed at different $T_a$. There are two main peaks which are centered at 394 and 580 nm in the spectra. All samples emit strong violet PL at 394 nm, and with the increase of the $T_a$, the intensity of the peak increases and reaches its maximum at $T_a$ about 800 °C, then decreases. The orange PL of 580 nm appears firstly at the sample annealed at 600 °C, henceforth its intensity keeps increasing with the increase of $T_a$ in our experiment range. The two peaks do not shift obviously with the annealing condition. For films without Ge, the violet and orange PL mentioned earlier were not observed.

4. Discussion

In general, PL consists of three processes, which are photo-excitation, energy transmission and radiative recombination of electron–hole pairs. For nc-Ge embedded SiO$_2$ films, the energy gap is much larger than that of bulk Ge due to the quantum confinement effect. There are two routes coexisting for the electron–hole pairs excited inside the nc-Ge to recombine and emit light. One is that they recombine just inside nc-Ge directly and emit light of corresponding wavelength. The other is that they transport out of the nc-Ge and then recombine to emit light via luminescence centers located at the interface with SiO$_2$ matrix or in the SiO$_2$ matrix. But the probability of the former is too low owing to the indirect energy gap of Ge to detect its light emission in the detectivity of our equipment. Most of electron–hole pairs move out of the nc-Ge and recombine via luminescence centers as mentioned in the latter route.

It must be noted from Figs. 4 and 5 that the content of GeO varies with the temperature in a similar manner to the PL peak intensity of 394 nm, and it is the same with the content of elemental Ge and the intensity of 580 nm. It indicates that the emission of peaks at 394 and 580 nm are related to the existences of GeO and Ge, respectively. In addition, for SiO$_2$ films without Ge, no obvious PL has been observed which indicates that SiO$_2$ matrix has nothing to do with the emission of these two bands in our experiment, and for as-deposited Ge–SiO$_2$ films there is no PL peak at 580 nm which indicates that the emission is related to the existence of nc-Ge. Based on our experimental results and the earlier analyses, it is reasonable to propose that the violet PL of 394 nm comes from the existence of GeO and the orange one of 580 nm from some luminescence center at the interface between the nc-Ge and SiO$_2$ matrix.

5. Conclusion

Ge–SiO$_2$ thin films were fabricated by the RF magnetron co-sputtering technique. The strong violet and orange PL from these films were observed. It is indicated that the violet PL of 394 nm comes from the existence of GeO and the orange one of 580 nm from some luminescence center at the interface between the nc-Ge and SiO$_2$ matrix.
Acknowledgments

One of the authors (C.N. Ye) thanks for the financial support by National Natural Science Foundation of China and partial support from the Ion Beam Laboratory of Shanghai Institute of Metallurgy, Academia Sinica.

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