

PHOTOLUMINESCENCE FROM SiC NANOCRYSTALS EMBEDDED IN SiO₂

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Abstract. Silicon carbide nanocrystals embedded in a SiO₂ matrix on monocrystalline Si substrates were prepared by radio frequency (RF) co-sputtering with Si, C and SiO₂ targets, and subsequent high-temperature annealing. The structure of the films was determined by Fourier transform infrared spectroscopy. Photoluminescence (PL) from the composite films was studied as a function of annealing temperature. It was found that the PL spectra of the films are very sensitive to the annealing temperature. Blue band (490 nm) and green band (~546 nm) visible PL, originating from SiC nanoparticles and C nanoclusters, respectively, were observed at room temperature.

1. INTRODUCTION

Silicon-based light emitting materials have been of great interest since the discovery of strong visible light emitting at room temperature from porous silicon by Canham [1]. Besides porous silicon, many other materials, such as Si/SiO₂ superlattices [2], Si/Ge superlattices [3] and semiconductor nanoparticles Si, Ge or C embedded in amorphous SiO₂ films [4-6], etc, have also attracted much attention and been extensively studied. Visible PL has been observed from these systems, which opened up the possibility of the integration photonics with silicon-based microelectronics. The PL arising from most of these materials is located in the red or yellow-green spectral region [1-6]. The blue-violet PL from semiconductor nanoclusters embedded in a SiO₂ matrix has also been observed, which is presumably related to the oxygen-deficiency center [7-9]. However, the control of the formation of deficiencies is quite difficult and the stability of PL related deficiency is very low. So there is an urgent need to look for a novel types of blue-emitting, Si-base material.

Silicon carbide (SiC), a wide-gap semiconductor, has attracted much research interest due to its potential application in blue-green light-emitting diodes and UV photodetectors [10]. To improve the

light emitting efficiency, porous SiC similar to porous Si has been produced and from which intense visible PL has been observed at room temperature [11-13]. However, the low stability and reproducibility of porous SiC, greatly hindered its application in optoelectronic devices. Therefore, the synthesis of SiC nanocrystals embedded in SiO₂ films is of great significance in the development of optoelectronics [14-16]. The materials based on SiO₂ matrix are expected to offer some technological advantages, such as extremely high chemical and mechanical stability, and the compatibility in synthetic processes integrated with silicon planar technology. The existence of semiconductor nanocrystals could enhance the radiative recombination rates due to the quantum confinement effect of excitons in the nanoparticles.

In this paper, composite films were prepared by radio frequency (RF) co-sputtering with Si, C and SiO₂ targets and subsequent high-temperature annealing. The structure of the films was determined by Fourier transform infrared spectroscopy (FTIR). Blue PL, related to SiC nanocrystals, was observed at room temperature.

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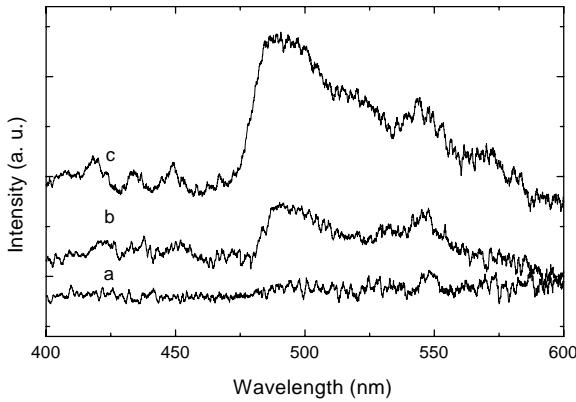


Fig. 1. Room temperature PL spectra for the annealed films, where curve a, b and c correspond to the films annealed at 800, 1000 and 1100 °C, respectively.

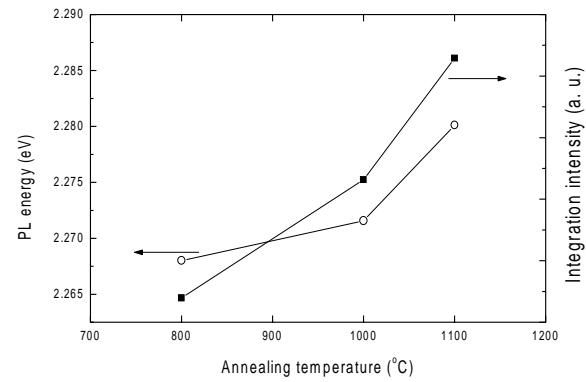


Fig. 2. The PL energy and integration intensity of the green band dependence on annealing temperature.

2. EXPERIMENTS

The semiconductor-doped glasses were prepared by the RF co-sputtering method, which is similar to the procedure for the preparation of Si or Ge nanocrystals embedded in SiO_2 [17]. Thin plates of pure carbon ($10 \times 1 \text{ mm}^3$) and Si wafer ($10 \times 10 \times 0.5 \text{ mm}^3$) were placed on a pure SiO_2 target (10 cm in diameter) mounted in a RF sputtering apparatus. To obtain the appropriate composition in the sample, the number of Si and C pieces can be adjusted. The ratio of the area of Si and C pieces used here was 1:3 and the area of the SiO_2 target was twice as large as the total area of Si and C targets. The carbon, silicon and SiO_2 targets were co-sputtered in Ar gas at 2 Pa by setting the RF power of 300 W. The substrates were (111) Si wafers and the temperature of the substrate was retained at 500 °C. After depositing a composite film with the thickness of 500 nm, a 100 nm Si cap was deposited. The as-deposited films were annealed between 800 °C and 1100 °C for 60 min in flowing N_2 atmosphere.

The PL experiments were performed at room temperature, exciting the sample with an ultraviolet He-Cd laser working at a wavelength of 325 nm. FTIR spectra were recorded with a Nicolet AVATAR 360 FT-IR system. The measurements were carried out at room temperature with resolution 4 cm^{-1} .

3. RESULTS AND DISCUSSION

Fig. 1 shows the PL spectra of the samples annealed at 800 °C, 1000 °C and 1100 °C. All PL spectra show a weak band around 546 nm (green band). After annealing at 1000 °C, a new PL band at 490 nm emerges (blue band), which was very strong and

wide. The blue band dominated the whole PL spectrum of the sample annealed at 1100 °C.

As shown in Fig. 2, when increasing the annealing temperature from 800 °C to 1100 °C, the green band shifted slightly to higher energy and its integration intensity increased. The visible luminescence from these semiconductor dopants embedded in the SiO_2 matrix probably originates from matrix defects and/or nanocrystals. If the PL originates from defect-related luminescence centers, the PL should not be shifted with the increasing annealing temperature. Our composite films presumably contained Si nanocrystals, C clusters and SiC nanoparticles. Various nanoparticles result in various PL bands, and we believe that the green band is assigned to C-rich clusters. The band blue shifted with the increase of annealing temperature, which directly disproves the notion that the green band PL comes from defects related to SiO_2 . A similar interpretation has already been proposed by Yu *et al.* [18], Hayashi *et al.* [6] and Gonzalez-Varona *et al.* [14] in their studies of carbon implanted thermal SiO_2 films, RF co-sputtering C-rich SiO_2 films and Si, C co-implanted SiO_2 films, respectively. According to the result of Barchava *et al.* [19], in the case of C-rich layers, a SIMS study has shown the progressive disappearance of the C content when annealing in a conventional furnace. C atoms can bind with either the O atoms present in the SiO_2 layer or even those coming from the atmosphere during annealing. The out-diffusion of C presumably originates from the formation of mobile CO and/or CO_2 molecules. Therefore, when increasing the annealing temperature, the size of C clusters may decrease, and thus according to the quantum confinement effect, the

blue shift dependence on increasing annealing temperature can be easily interpreted. This is similar to the blue shift PL related to C clusters in the reduction of C targets [6].

As seen from Fig. 1, the blue band cannot be observed for samples annealed at 800 °C, but abruptly appears after annealing at 1000 °C. The intensity also notably increased and no shift of the PL was observed with increasing annealing temperature. Given the stability of the blue-light emission with the annealing procedure at high temperature (1100 °C), an explanation of PL in terms of defects seems to be implausible. The PL arising from Si nanocrystals is generally located in the red and/or infrared spectral region (1.4-1.8 eV). Other groups have previously studied the PL originating from SiC related materials. The PL peaks from porous SiC reported by some researchers were located in a range of 2.4-2.7 eV [11-13]. Zhao *et al.* [15] and Gonzalez-Varona *et al.* [14] reported short-wavelength PL of 2.5 eV and 2.8 eV, respectively, from thermal SiO_2 films co-implanted with Si and C ions. The results of Liu *et al.* showed the intense blue-light emission (454 nm) from carbon-plasma-implanted porous silicon [20]. They attributed the blue PL band to SiC nanoparticles and/or SiC-related luminescence centers. Considering these previous studies, we tentatively assign the blue PL (490 nm, 2.54 eV) of our co-sputtering samples to the presence of SiC nanocrystals luminescence centers.

To identify the PL origin, we investigated the change of the microstructure of the samples annealed at different temperatures by FTIR measurements. Fig. 3 (a)-(c) show the corresponding results from the samples annealed at 800 °C, 1000 °C and 1100 °C, respectively. All these FTIR spectra clearly exhibit four vibrational bands at 460, 730, 820 and 1090 cm^{-1} . The 450 and 1090 cm^{-1} bands belong to Si-O-Si rocking and stretching vibrations of SiO_2 [21] and their intensities increase with the annealing temperature. The 730 and 820 cm^{-1} bands are related to amorphous SiC and crystalline SiC [22]. The intensity of SiC increases with the annealing temperature. This clearly indicates that the formation of SiC precipitates in our high-temperature annealed sample. The peak shift relative to the SiC phonon mode (wavenumber 794 cm^{-1}) was attributed to the size effects of SiC precipitates [22]. Because of the small size of the precipitates within the high dielectric constant SiO_2 matrix, interface absorption modes become significant and shift the mean band to higher frequencies (820 cm^{-1}). Furthermore, other factors such as strain, Si and/or C atoms on the surface of

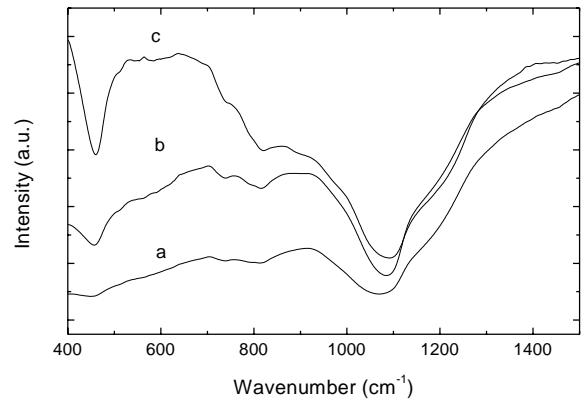


Fig. 3. FTIR spectra for films annealed at (a) 800, (b) 1000 and (c) 1100 °C .

the precipitates binding to O atoms, and disorder in the precipitates, may also affect this shift.

However, in C-contained SiO_2 composite films, the formation of Si-C bonds is difficult due to two factors. One is the ability of the carbon to interact with oxygen and then to out-diffuse as CO and/or CO_2 [19], and the other is that the Si-O bond is much stronger than that of Si-C bond [15]. The formation of SiC in our samples results from the following reasons. First, the out-diffusion of C atoms is restrained by Si atoms in the Si cap. As discussed above, we observed a decrease in size of C clusters originating from the out diffusion of C which we deduced from the slight blue shift of the green PL band. Second, excess C atoms are present in the deposited film. According to the various sputtering yields and different target areas, the ratio of C to Si atoms should be greater than 1.0 in the deposited film. It has been reported that nonuniformity of C throughout a SiO_2 matrix results in the formation of SiC [15]. In our experiments, the excessive C atoms are favourable for the formation of C clusters. The existence of C clusters and the nonuniformity of C would play an important role in the formation of SiC precipitates.

As seen from Fig. 3, the intensity of SiC absorption relative to that of the SiO_2 after annealing at 1100 °C is about twice as much as that after annealing at 800 °C, corresponding to the aggregation of SiC nanocrystals from the amorphous SiC phase and/or SiC precipitates.

Therefore, the blue PL band may originate from SiC nanocrystals embedded in the SiO_2 matrix. However, complexes containing Si, C and O such as binding between silicon carbide and oxygen, which

presumably contribute to the blue PL, may also exist at the interface between SiO_2 and SiC nanocrystals. Further research about the mechanism of PL and the formation of SiC nanocrystals are in progress.

4. CONCLUSIONS

Blue PL has been observed at room temperature from composite films prepared by RF co-sputtering Si, C and SiO_2 targets and subsequent high-temperature annealing. FTIR measurements confirmed the formation of SiC nanocrystals embedded in a SiO_2 matrix. We propose that the blue PL originates from SiC nanocrystals luminescence centers.

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