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Growth and optical properties of Ge oxide thin film on silicon substrate by pulsed laser deposition

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Abstract

Germanium oxide thin films on silicon substrate were produced using pulsed laser deposition method under adjusted substrate temperature and oxygen pressure. There existed two PL bands observed in our samples, violet and blue bands. We attributed both of them to the neutral oxygen vacancy (NOV) but of different types: ≡Ge–Ge≡ and ≡Ge–Si≡, respectively. Fourier transform infrared spectra (FTIR) measurements in our samples not only proved the Ge–O–Si vibration but also assigned the peaks around 1000 cm^{-1} in Si–Ge oxide system qualitatively.

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Ge-doped SiO_2 films with efficient photoluminescence (PL) have been investigated for a long time because of their applications in Si-based optoelectronics [1,2]. In this system, there are two main possible mechanisms for its light emission: quantum confinement of Ge nanocrystals and defects in Ge oxide [1]. In spite of the numerous number of the reports about Ge-doped SiO_2 system [1–3], the origin remains as a controversial subject. Much attention was paid to the silicon oxide matrix and few works were related to pure Ge oxide and its optical property [3,4], which could be helpful to identify the PL mechanism.

Another interesting phenomenon in this system is its Fourier transform infrared spectra (FTIR) [2,3,5–9],

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because of the similarity of peak positions in Ge and Si. So they should be checked and identified with suitable experiments. Our results may give a clear assignment to different peaks.

In this Letter, we fabricated Ge oxide thin films on silicon substrate utilizing pulsed laser deposition (PLD) method at adjusted substrate temperature. There existed two PL bands observed in our samples, violet and blue bands. We attributed both of them to the neutral oxygen vacancies (NOVs) but of different types: $\equiv$Ge–Ge$\equiv$ and $\equiv$Ge–Si$\equiv$, respectively. FTIR measurements in our samples not only proved the Ge–O–Si vibration but also assigned the peaks close to 1000 cm^{-1} qualitatively.

Pulsed laser deposition (PLD) was performed by KrF excimer pulsed irradiation with a wavelength of 248 nm ($\tau = 20$ ns and $f = 5$ Hz) and a laser energy of 5.5 J/cm^2. Germanium single crystal was used as target for depositing Ge oxide films on (1 0 0)-oriented Si substrates. The deposition was run under an oxygen pressure of $\sim$ 6.5 Pa for 15 minutes. The substrate temperature was maintained on adjusted temperatures from room temperature to 400 °C during PLD. The thicknesses of the deposited films were about 100 nm. Finally, the films were cooled down to room temperature under the same oxygen environment. The as-deposited samples were annealed in N$_2$ (99.99%) environment from 600 °C to 1000 °C for 30 minutes. Because the growth temperature can reach 400 °C, the annealing at 400 °C was ignored. The PL properties of our samples were studied using an excitation wavelength of 325 nm at room temperatures. The films were primarily characterized by FTIR (Perkin–Elmer, FT-IR 1600) in a transmission mode. The X-ray photoelectron spectroscopy (XPS) measurement was conducted using a monochromatic Al K$_\alpha$ excitation line 1486.6 eV.

Fig. 1(a) shows the PL spectra of as-deposited sample deposited at 200 °C and the samples subsequently annealed at 600–1000 °C for 30 minutes. One can see that two peaks appear at $\sim$ 416 (violet) and $\sim$ 470 nm (blue) with little shift in different as-deposited or annealed samples. In previous results [3,4], a similar broad peak at $\sim$ 410 nm was observed in Ge oxide film, which was attributed to the NOV center of Ge oxide. So we may deduce that the violet band is related to NOV center because of their similarities which is confirmed by the PL behavior on annealing temperature. Its intensity reaches maximum after annealing at 600 °C and decreases with higher annealing temperature. This kind of annealing behavior is in good agreement with that of the NOV center [10,11].

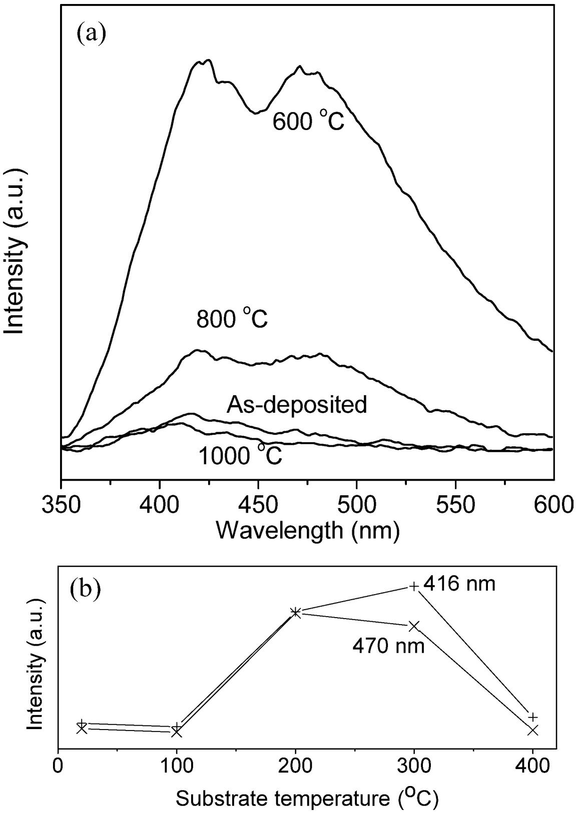

Fig. 1. (a) PL spectra of as-deposited sample deposited at 200 °C and the samples subsequently annealed at 600–1000 °C in N$_2$ for 30 minutes; (b) dependence of the PL (416 and 470 nm) maximal intensity on substrate temperature.

The violet band can be assigned to the NOV center of Ge oxide (O$\equiv$Ge–Ge$\equiv$O), while the blue band is a new peak in Ge oxide system. Fig. 1(b) is the dependence of the PL maximal intensity on substrate temperature (T_s). The maximal intensity means the strongest PL intensity selected from the as-deposited and annealed samples. One can see that both bands follow the same rule on the function of T_s. The intensity of the samples deposited at 200 °C or 300 °C and subsequently annealed is much stronger than the others, which implies that this temperature range is suitable to produce NOV center in our films. In order to reveal the PL mechanism of the blue band, FTIR and

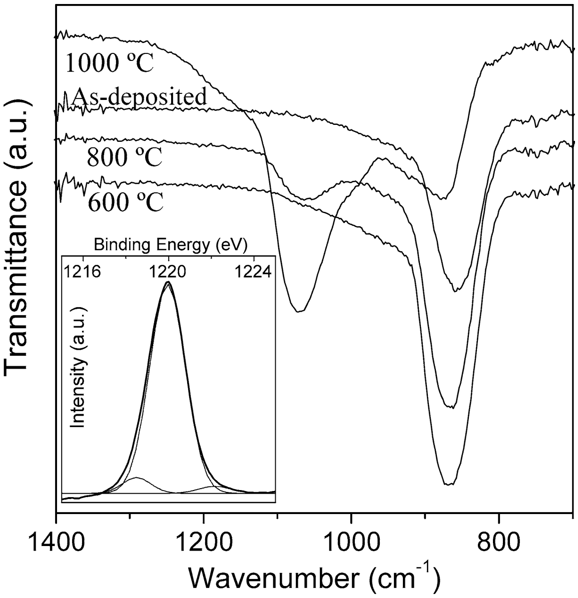

Fig. 2. FTIR spectra of Ge oxide film deposited at 200 °C and the samples subsequently annealed at 600–1000 °C in N_2 for 30 minutes; the inset shows the XPS results of Ge oxide film deposited at 200 °C and subsequently annealed at 800 °C in N_2 for 30 minutes.

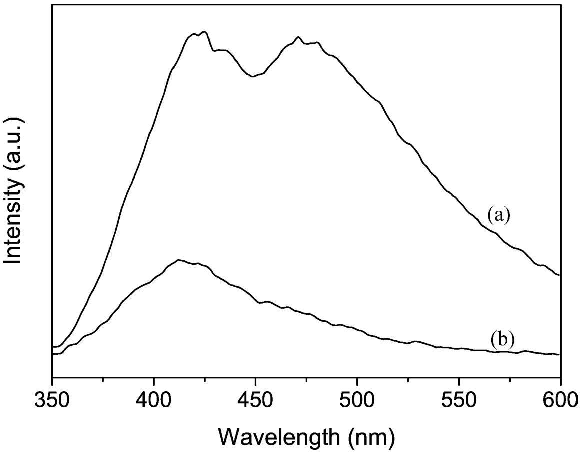

Fig. 3. PL spectra of Ge oxide film deposited (a) at 200 °C under oxygen pressure of ∼ 6.5 Pa and annealed at 600 °C, (b) at room temperature under oxygen pressure of ∼ 100 Pa and annealed at 800 °C. (Their intensities are strongest in their corresponding group samples.)

XPS measurements were conducted as shown in Fig. 2 and its inset with the sample deposited at 200 °C. Although Ge–O–Ge related vibration is observed and in agreement with the PL intensity of the violet band on annealing temperature, no further information can obtained. The XPS results change little with a series of samples. Three peaks decomposed by Gaussian fit are from the Ge oxide. There is no obvious change (see a typical spectrum in the inset of Fig. 2). The electron spin resonance (ESR) measurement only shows weak signals in our samples for thin film or no resonance.

Because of the same rule of the two bands on T_s, we may consider the blue band is also due to the NOV center. In our film there exist three possible NOV centers: ≡Ge–Ge≡ (denoted as GG), ≡Si–Ge≡ (SG), and ≡Si–Si≡ (SS). In previous works [1,12], the band at ∼ 2.7 eV was generally assigned to ≡Si–Si≡ in Si or Ge-implanted SiO_2. However, we exclude this cause on account of the following explanation: When we increased the oxygen pressure (∼ 100 Pa), the intensity of blue peak is much weaker than that of violet one (Fig. 3), which means that the NOV center responsible for the blue band is tempered due to the abundance of oxygen. If the blue band is due to the SS NOV center, its intensity would increase for the relative thicker oxide layer for more oxygen (∼ 100 Pa). As far as we know, during our experiments the SS NOV can be produced by two processes—oxidation of Si during the growth of Ge oxide film or diffusion of O during post-annealing treatment. The latter can be ignored because of different PL behaviors with various samples after same treatments. Higher O_2 pressure supplied more oxygen during growth, which mean that more Si could be oxidized and trend to form SS NOV. But the intensity of blue band has no any obvious increase and decreases actually. So the SS NOV can also be ignored and the blue band is not cause by the SS NOV center.

So we attribute the blue band to SG NOV center, which is also confirmed by the Si–O–Ge vibration in FTIR. Fig. 4 shows the spectra of our samples after annealing at 1000 °C. There are five vibrational peaks (marked as 1: 1072 cm^{-1}, 2: 1039 cm^{-1}, 3: 987 cm^{-1}, 4: 910 cm^{-1}, and 5: 869 cm^{-1}) in our spectra. Peak 1 is due to the Si–O–Si stretching vibration of stoichiometric SiO_2. Peak 5 generally corresponds to Ge–O–Ge stretching vibration. The assignments about the above two peaks is authentic [2]. But, the peak around 1000 cm^{-1} is a little bit complicated [2,3,5–9]. In the study of plasma oxides of $Si_{1-x}Ge_x$ alloys, the peak at 1000 cm^{-1} was attributed to Si–O–Ge [5]. There existed a peak at 1020 cm^{-1} in the

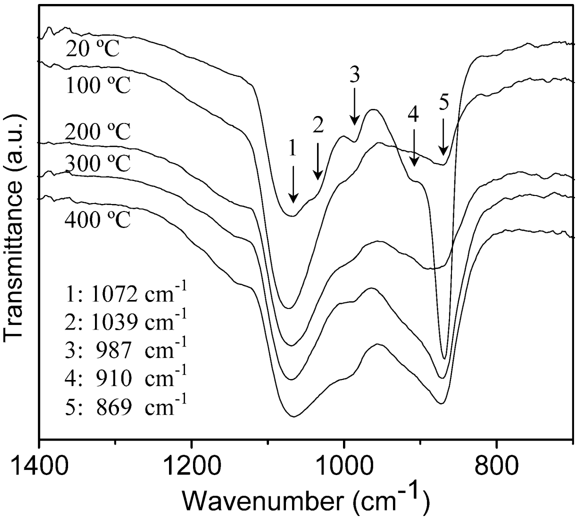

Fig. 4. FTIR spectra of Ge oxide film deposited at different substrate temperature [from room temperature (20 °C) to 400 °C] and subsequently annealed at 1000 °C in N_2 for 30 minutes.

spark-processed Ge, which was assigned to the Ge–O–Ge shoulder peak [6]. Another explanation about the 1020 cm^{-1} peak is related to non-stoichiometric SiO_y ($y < 2$) [3]. Based on the above explanations in their papers and our analysis, we assign peak 2, 3, and 4 to non-stoichiometric SiO_y or the shoulder peak of Si–O–Si, the vibration of Si–O–Ge, and the shoulder peak of Ge–O–Ge, respectively. As for the shift between the above works and our results, we may understand the difference from the ratio of Ge, Si and O [7]. So it should be careful to the FTIR assignment of Ge–Si oxide mixture. From the above analysis, the existence of Si–O–Ge vibration also confirms SG NOV center in our samples.

In summary, Ge oxide thin film on silicon substrate was produced using PLD method at different substrate temperature and under different oxygen pressure. There existed two PL bands observed in our samples, violet and blue bands. We attribute both of them to the neutral oxygen vacancy (NOV) of different types: ≡Ge–Ge≡ and ≡Ge–Si≡, respectively. FTIR measurements in our samples not only proved the Ge–O–Si vibration but also assigned the peaks around 1000 cm^{-1} in Si–Ge oxide system qualitatively.

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