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Violet photoluminescence from Ge^+-implanted Si-based nanoscale SiO_2 islands array

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Abstract

Ge ions were implanted into a SiO_2 nanoscale islands array at an energy of 200 keV with a dose of 1×10^{17} cm^{-2}. Violet photoluminescence (PL) bands peaked at 370, 396, and 415 nm from Ge^+ implanted SiO_2 nanoscale islands array were observed, and the violet PL spectra reached a maximum after annealing in N_2 ambient at 700°C. From photoluminescence excitation (PLE) spectra of samples we found an excitation band at around 270 nm besides a widely known excitation band at around 240 nm. We tentatively conclude that PLE band at around 270 nm and luminescence at 370 and 415 nm may be caused by Ge-associated neutral oxygen vacancy (denoted as ≡Ge–Si≡ and ≡Ge–Ge≡), while the 396 nm PL band arise from GeO color centers. © 2002 Elsevier Science B.V. All rights reserved.

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Silicon-based light emitting materials, which have been studied for a long time, are very important for full-color display, especially for the integrated optoelectronics [1]. Since the observation of efficient room-temperature photoluminescence (PL) in porous silicon [2], many new light emitting materials have been explored [3,4]. In application field, the blue–violet short wavelength emitting materials are especially required. The SiO_2/Si materials with nanocrystal embedded or impurities–defects radiative center is a kind of promising Si-based light emitting material.

The optical properties of Ge-doped silica have been investigated in the field of optical fibers for a long time [4,5]. Recently, Ge-doped SiO_2 films on Si substrate are intensively studied as a new kind of Si-based light emitting materials. Rebohle et al. [6] reported that Ge^+-implanted SiO_2 film can exhibit blue–violet luminescence. Bao et al. [7] also observed violet PL from Ge^+-implanted SiO_2 layers. Unfortunately, in both cases the distribution of light-emission bodies of Ge^+-implanted SiO_2 film is spatially disordered and thus their light emission should be a kind of microscale light source, not nanoscale one. Recently, many methods such as electron beam lithography [8] and ion beam lithography [9] have been employed to fabricate the distribution-ordered nanostructure of crystallites. These methods have many advantages, but they require huge and expensive fabrication systems. Instead of these methods, anodic alumina, as a natural lithography method, is a relatively simple and inexpensive

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technique for fabricating the ordered nanostructure by using its self-organization mechanism [10].

In this work, by using anodic alumina as a mask, we achieved a Si-based SiO_2 nanoscale islands array and further obtain a kind of Si-based nanoscale light source through Ge^+-implantation into the SiO_2 islands array. The presence of violet luminescence of this kind of Si-based nanoscale light source indicates its important applications in Si-based nano-optoelectronic integration.

A p-type, 0.5 Ω cm, ⟨100⟩-oriented silicon wafer was used as substrate. After cleaning and removing native oxidation layer, high-purity Al (99.99%) film with a thickness of 400 nm was deposited on the pre-treated Si wafer by electron-beam evaporation. The vacuum chamber was maintained under a pressure of 2.5×10^{-6} Pa. Accelerating voltage of electron beam is held essentially constant near 10 kV and electron gun current is 0.5 A. The deposited Al film is of good and clear surface and thus can directly be used to carry out anodization. Subsequently, the Al/Si film was anodized in 15 wt% dilute sulfuric acid electrolyte under a constant DC voltage of 20 V at 5°C. In the anodizing process, We can use the typical current density-etching time curve to control the formations of both anodic alumina mask and SiO_2 nanoscale islands array. Cross-sectional transmission electron microscope (TEM) observation (JEOL JEM-2000EX) was carried out on the anodic alumina mask, while planar scanning electron microscope (SEM) observation (JSM-6301F) was carried out on the SiO_2 nanoscale islands array. Subsequently, along the vertical channels of the anodic alumina mask, Ge ions were implanted into the SiO_2 nanoscale islands array at an energy of 200 keV and with a dose of 1×10^{17} cm^{-2}, and then the anodic alumina mask was removed by dipping treatment. Afterwards, the samples were annealed in N_2 ambient at 700, 800, and 1000°C for 30 min. The PL measurements were performed at room temperature by using a FluoroMax-2 photospectrometer.

Fig. 1 shows the cross-sectional TEM image of the Si-based anodic alumina mask. It can be seen from this image that the parallel, straight, and uniform alumina nanochannels with a average diameter of about 14 nm have been fabricated on Si substrate. At the bottom of each channel, there always exists an island. These islands construct an island layer. Fourier transform infrared spectrum shows that this island layer mainly
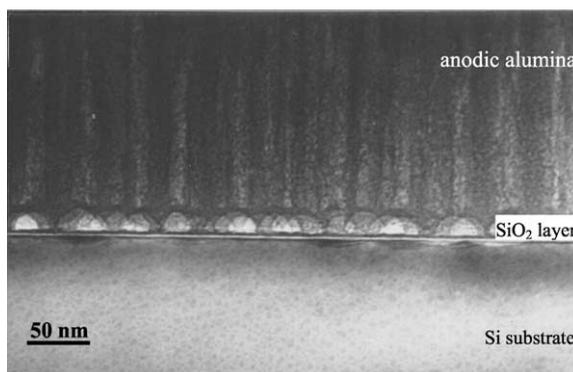
Fig. 1. Cross-sectional TEM image of the Si-based anodic porous alumina mask.

consists of SiO_2. Since the SiO_2 only exists at the bottom of each channel, we may obtain a SiO_2 island array by removing the anodic alumina membrane. Fig. 2 is the SEM photograph of surface of the SiO_2 nanoscale islands array. In the surface view, SiO_2 nanoscale islands can be observed over the entire measurable area. The island size is almost uniform and the interval of the islands is almost equal. Because of the expansion effect in process of the anodization of Si substrate, the average island diameter in the SiO_2 nanoscale islands array is about 25–35 nm, which is large than the nanochannel diameter of the Si-based anodic alumina mask. In addition, as the anodization time increases, the diameter and thickness of the SiO_2 nanoscale islands also increase.

Under 240 nm (5.16 eV) excitation, Ge^+-implanted SiO_2 nanoscale islands array emits obvious violet PL bands. Fig. 3 shows the PL spectra for the as-implanted sample and the sample annealed at different annealing temperature (T_{an}). The PL spectrum of as-implanted sample exhibits three luminescence bands peaked at 370, 396, and 415 nm. For the samples with different T_{an}, the positions of these PL peaks remain unchanged, but their intensities change with increasing T_{an}, reaching maximums in the sample with $T_{an} = 700$°C. In these samples with $T_{an} > 700$°C, the PL intensities dramatically decreases. This means that violet PL bands are related to some radiative defects formed by Ge implantation because implantation induced defects are annealed out by subsequent high temperature annealing. It can be seen from Fig. 3, the PL signal is weak and the PL signal-to-noise ratio is relatively low in comparison to the PL from Ge^+-
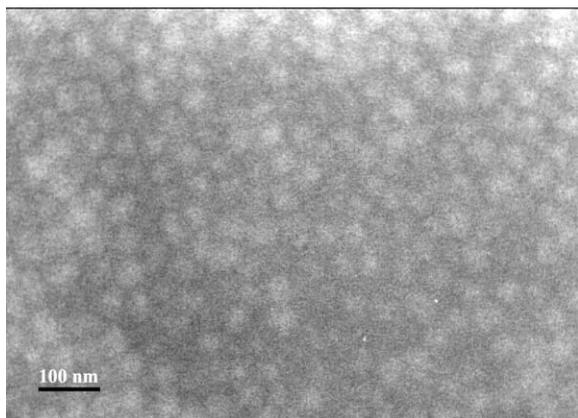
Fig. 2. SEM photograph of surface of the SiO_2 nanoscale islands array.
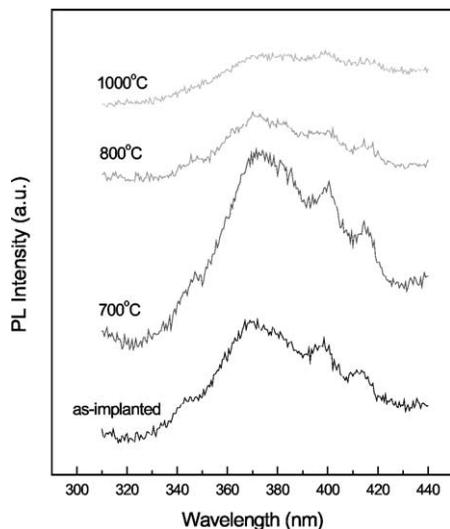
Fig. 3. PL spectra of as-implanted and the annealed SiO_2 nanoscale island array, taken under an excitation wavelength of the 240 nm.

implanted SiO_2 film grown by thermally oxidation. In Ge^+-implanted SiO_2 nanoscale islands array, light-emission bodies only exist in individual nanoscale islands, while light-emission bodies of Ge^+-implanted SiO_2 film pervade the entire microscale film region. From the point of view of statistics, when equi-area samples are excited under the same excitation condition the luminescence intensities of the Ge^+-implanted SiO_2 nanoscale islands array are obviously lower than that of the Ge^+-implanted SiO_2 film. So the PL signal-to-noise ratio of the former is low. Since
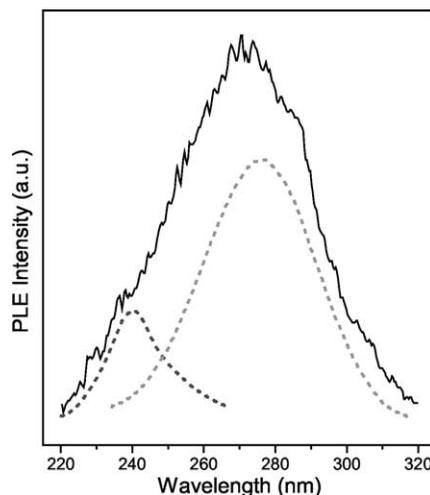
Fig. 4. PLE spectrum of the implantation sample annealed at $T_{an} = 700°C$, monitored at the emission wavelength of 396 nm.

no obvious PL was observed for the SiO_2 nanoscale islands array without Ge^+-implantation, we may infer that these PL bands originate from the SiO_2 nanoscale islands array with Ge^+-implantation.

Fig. 4 shows the PLE spectrum of the sample annealed at $T_{an} = 700°C$, which is monitored at the emission wavelength of 396 nm. The spectrum is obviously asymmetric. Through spectrum decomposition by using Gaussian functions, it is found that the PLE spectrum is composed of two bands located at about 240 nm (5.16 eV) and 275 nm (4.5 eV).

Many studies on germanium silicate glasses have confirmed that the well-known absorption band at 5 eV (the "B_2 band") is induced by oxygen-deficiency defect centers (GODC) [4,11]. Hosono et al. [11] have proposed that two types of defects contribute to the B_2 band: The neutral oxygen vacancy center (NOV) and GeO defects which introduce absorption bands at 5.06 and 5.16 eV (245 and 240 nm), respectively. Tohmon et al. [12] also reported the same results. The properties of the absorption band at around 240 nm (5.16 eV) were studied widely and the general conclusion has been that this absorption band is correlated with a singlet-to-singlet transition of GeO center [13–16]. The GeO center is a Ge atom in the Ge^{2+} valence state bonded only to two oxygen atoms instead of four as in the normal structure. On the other hand, it is well known that the 396 nm PL band from Ge-doped silica is mostly related to optical transition in the GeO

color center [17,18]. So in our case, we may draw a conclusion that the PLE band at around 240 nm arises from a singlet-to-singlet $(S_0 \rightarrow S_1)$ transition of GeO defects, which nonradiatively relaxes to a triplet state, then to ground singlet state $(T_1 \rightarrow S_0)$ and gives rise to the 396 nm PL.

In the studies of optical absorption and luminescence properties of Ge-doped silica glass, much research has been done to the near 5 eV (the "B_2 band") absorption and excitation band. However, the 270 nm absorption and excitation band was hardly reported and investigated. In this Letter, we are interested in the occurrence of 275 nm excitation band shown in Fig. 4. This band was mentioned first in in [19] in 1982. Besides, an absorption band at 273 nm and two luminescence bands at 410 and 350 nm have been detected in Ge free N-doped silica glass [20]. As for the 275 nm excitation band shown in Fig. 4 and the 370 and 415 nm luminescence bands shown in Fig. 3, we deduce that these PLE and PL bands are closely related to the implantation-induced GeNOV centers. The neutral oxygen vacancy (NOV) is a result of Si–Si bond formation after removing one oxygen atom, which can be extended to Si–Ge and Ge–Ge bond formation in the case of Ge$^+$-implanted SiO$_2$. This results in three different type of oxygen vacancies, which are denoted as $\equiv$Si–Si$\equiv$, $\equiv$Ge–Si$\equiv$ and $\equiv$Ge–Ge$\equiv$ center, respectively. The 275 nm PLE band may be explained as singlet-to-singlet $(S_0 \rightarrow S_1)$ transition in the NOV centers, while the 370 and 415 nm PL bands may be attributed to triplet-to-singlet $(T_1 \rightarrow S_0)$ transition in the GeNOV centers. Since the SiO$_2$ becomes nonstoichiometric after Ge$^+$-implantation, the Si atom has a possibility for combining with other Si atom, which would form a Si–Si bond ($\equiv$Si–Si$\equiv$) in the SiO$_2$ islands. Further, we believe that one (or both) Si atom in the $\equiv$Si–Si$\equiv$ center might be substituted by Ge atom, which forms a $\equiv$Ge–Si$\equiv$ (or $\equiv$Ge–Ge$\equiv$) center. From the molecular spectroscopy [21], we may know that when Ge ions substitute Si ions in the $\equiv$Si–Si$\equiv$ center, the $T_1 \rightarrow S_0$ transition energy will increase and thus a blueshift of the PL peak from the ordered $\equiv$Ge–Si$\equiv$ or $\equiv$Ge–Ge$\equiv$ center can be expected compared with the 460 nm PL from the $\equiv$Si–Si$\equiv$ center. Therefore, we tentatively interpret the 370 and 415 nm PL bands as due to the $\equiv$Ge–Ge$\equiv$ and $\equiv$Ge–Si$\equiv$ defect center in the Ge$^+$-implanted SiO$_2$ islands.

When Ge ions are implanted into the SiO$_2$ islands, many Si–O bonds are destroyed and a great number of Ge, Si and O ions are produced. At low T_{an}, Ge–O (including GeO, Ge$_2$O$_3$, and GeO$_2$), Ge–Ge, Si–Si, and Ge–Si bonds can be formed. Therefore, the PL peaks related to these bonds can appear with large intensities. At higher T_{an}, these bonds will also be annealed out forming larger Ge clusters or Ge nanocrystals [22] and the Si oxide gradually becomes stoichiometric SiO$_2$. As a result, the observed PL band intensities decrease again.

In summary, we fabricated a Si-based SiO$_2$ nanoscale islands array, and then obtained a kind of Si-based nanoscale light source through Ge$^+$-implantation the SiO$_2$ nanoscale islands array. We found this kind of nanoscale light source array can exhibit violet luminescence. We tentatively conclude that the 275 nm PLE band and the 370 and 415 nm PL bands may be caused by Ge-associated neutral oxygen vacancy, while the 240 nm PLE band and the 400 nm PL band arise from GeO color centers.

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