



## Electroluminescence and photoluminescence of Ge + -implanted SiO 2 films thermally grown on crystalline silicon

Jia-Yu Zhang, Xing-Long Wu, and Xi-Mao Bao

Citation: Applied Physics Letters **71**, 2505 (1997); doi: 10.1063/1.120102 View online: http://dx.doi.org/10.1063/1.120102 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/71/17?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

High efficiency visible electroluminescence from silicon nanocrystals embedded in silicon nitride using a transparent doping layer Appl. Phys. Lett. **86**, 071909 (2005); 10.1063/1.1866638

Hot hole excitation of EuGa 2 S 4 electroluminescent thin films Appl. Phys. Lett. **85**, 923 (2004); 10.1063/1.1779337

Room-temperature visible electroluminescence of Al-doped silicon oxide films Appl. Phys. Lett. **78**, 4121 (2001); 10.1063/1.1382629

Red electroluminescence in Si + -implanted sol–gel-derived SiO 2 films Appl. Phys. Lett. **77**, 2952 (2000); 10.1063/1.1323551

Strong blue and violet photoluminescence and electroluminescence from germanium-implanted and siliconimplanted silicon-dioxide layers Appl. Phys. Lett. **71**, 2809 (1997); 10.1063/1.120143



## Electroluminescence and photoluminescence of Ge<sup>+</sup>-implanted SiO<sub>2</sub> films thermally grown on crystalline silicon

Jia-Yu Zhang,<sup>a)</sup> Xing-Long Wu, and Xi-Mao Bao

National Laboratory of Solid State Microstructure and Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China

(Received 4 February 1997; accepted for publication 2 September 1997)

Electroluminescent devices have been fabricated based on Ge<sup>+</sup>-implanted SiO<sub>2</sub> films thermally grown on crystalline silicon. Both room-temperature electroluminescence and photoluminescence spectra are found to have three luminescent bands peaked at 3.1, 2.1, and 1.6 eV. The electroluminescent devices have onsets for emission under forward bias of 5 V and under reverse bias of -13 V. Its emission is stable and reproducible. Spectral analyses suggest that the electroluminescent excitation of the 3.1 eV band may be related to the impact ionization by hot electrons, whereas that of the 2.1 and 1.6 eV bands to the radiative recombination of hole-electron pairs. © 1997 American Institute of Physics. [S0003-6951(97)03443-8]

Germanium-doped silica glasses have widely been investigated because they play an important role in optical fiber waveguides. Their photoluminescence (PL) has also been studied in order to explore the properties of the germanium oxygen deficiency center (GODC) in them.<sup>1</sup> Recently, much attention has been paid to Ge-nanocrystal-embedded silica glasses due to their excellent third-order nonlinear optical properties and the possibility for developing novel lightemitting devices.<sup>2,3</sup> Although porous Si is expected to be the most promising Si-based light-emitting material,<sup>4</sup> Genanocrystal-embedded silica glasses have their own advantage. Ge is much easier to change the electronic structure around the band gap than Si due to its larger exciton Bohr radius.<sup>2,3</sup> The nanocrystal/matrix interface is well passivated from the external ambient, and enables better control of nonradiative recombination processes.<sup>3,5</sup> So far, a series of techniques have been used to fabricate Ge nanocrystals embedded in SiO<sub>2</sub> matrices, including sol-gel,<sup>6</sup> cosputtering,<sup>2,7</sup> ultraviolet-assisted oxidation,<sup>8</sup> hyrothermal oxidation,<sup>9</sup> and ion implantation.<sup>5,10</sup> Especially, ion implantation is a favorable technique because it is compatible with convental silicon processing technology.<sup>5</sup>

To put the Ge-nanocrystal-embedded  $SiO_2$  materials into optoelectronic application, it is necessary to study their electroluminescent (EL) properties. Shchegiov *et al.*<sup>5</sup> have recently reported the visible broadband EL devices with Ge<sup>+</sup>-implanted Si/SiO<sub>2</sub>/Si structure, which have an onset for emission only under reverse bias.<sup>5</sup> In this letter, we report new EL devices with Ge<sup>+</sup>-implanted Au/SiO<sub>2</sub>/Si structure. The distinctive properties of the devices are that the EL devices have emission under both forward and reverse bias. Especially, a blue luminescent band peaked at 3.1 eV can be obtained from the devices.

The substrates used in this work were  $\langle 100 \rangle$  oriented *p*-type Si wafers with resistivity of 5  $\Omega$  cm. About 120-nm-thick SiO<sub>2</sub> films were grown on the wafers by thermal oxidation. Ge ions were implanted into the thermal SiO<sub>2</sub> films with a dose of  $1 \times 10^{16}$  cm<sup>-2</sup> and at an energy of 120 keV. During Ge<sup>+</sup> implantation, the substrates were kept at room

temperature. The Ge<sup>+</sup>-implanted films were subsequently annealed in N<sub>2</sub> ambient at 1100 °C for 30 min. To form a metal-insulator-semiconductor (MIS) structure, a 20-nmthick Au layer was deposited on the top of the Ge<sup>+</sup>-implanted SiO<sub>2</sub> films as a transparent electrode (the area of the Au electrode is  $\pi \times 1.5^2$  mm<sup>2</sup>). For comparison, MIS structures of SiO<sub>2</sub> films without Ge<sup>+</sup> implantation were also fabricated.

Rutherford backscattering spectra (RBS) were measured by using 2 MeV <sup>4</sup>He<sup>+</sup> beams at a scattering angle of 165°. The energy resolution was about 7 keV and the total dose of <sup>4</sup>He<sup>+</sup> was 3  $\mu$ C. Figure 1 shows the RBS spectra of the as-implanted film and the film annealed at 1100 °C. In the as-implanted SiO<sub>2</sub> films, Ge distribution is inhomogeneous. The maximal Ge density is at about 70 nm below the surface. The peak concentration of the Ge atoms is about 18 at. % at the projected range. Spectral analysis on RBS indicates that



FIG. 1. Rutherford backscattering spectra of the Ge<sup>+</sup>-implanted SiO<sub>2</sub> films. The two spectra correspond to the as-implanted film and the film annealed at 1100 °C.

<sup>&</sup>lt;sup>a)</sup>Electronic mail: jbchen@pine.njnu.edu.cn



FIG. 2. The current-voltage characteristics of a typical device. Curves a and b represent these under forward and reverse bias, respectively. It should be noted that the forward bias corresponds to a positive potential on p-type Si substrate.

the oxide film is a nonstoichiometry  $\text{SiO}_x$ , where  $1.8 \le x \le 1.9$ . In the annealed films, the diffusion of Ge atoms results in Ge accumulation at the oxide/Si interface, and the amount of Ge atoms is small in the layer below the surface due to out-diffusion. On the other hand, we know that this Ge<sup>+</sup>-implanted film is obviously a supersaturated solid solution containing a large amount of excess Ge.<sup>5</sup> Thus, if the film is annealed, Ge atoms will be precipitated to form Ge nanocrystals.<sup>3,7</sup> According to the RBS results, in the film annealed at 1100 °C, Ge nanocrystals are mainly distributed in the middle layer and the oxide/Si interface layer. Ge nanocrystals are lack in the layer below the surface.

EL devices were electrically characterized with a semiconductor parameter analyzer operating in current-voltage test mode. The current-voltage characteristic of a typical device is shown in Fig. 2, where curve a and b represent these under forward and reverse bias, respectively. The forward bias corresponds to a positive potential on *p*-type Si substrate. From Fig. 2, it can be seen that the rectifying behavior exists under forward bias, whereas a relatively broad breakdown feature occurs under reverse bias between -10 and -15 V. Under both forward and reverse bias, a relatively large series resistance can be observed. For MIS structures of SiO<sub>2</sub> films without Ge<sup>+</sup> implantation, no reverse bias breakdown phenomenon is observed and the current is very small within the voltage range for the parameter analyzer. These results above indicate that Ge nanocrystals in the SiO<sub>2</sub> films play an important role in charge motion of the EL device.

The EL can be observed with the naked eye in dark room under both forward and reverse bias. Under forward bias the EL is detected at voltage of 5 V, and under reserve bias the EL is obtained at voltage of -13 V. The obtained EL is stable and reproducible. The EL spectra are dependent upon the applied voltage, as shown in Fig. 3(a). Under forward bias, two luminescent bands peaked at 600 nm (2.1 eV) and 780 nm (1.6 eV) can be observed when the applied voltage is low, and the other luminescent band peaked at 400 nm (3.1 eV) appears when the applied voltage is above 12 V. Under reverse bias, there only exists the 400 nm luminescent band, and the 600 and 780 nm luminescent bands are almost



FIG. 3. (a) The electroluminescence (EL) spectra of the EL devices at voltage of -15, 8, and 15 V, respectively. (b) The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the Ge<sup>+</sup>-implanted SiO<sub>2</sub> film. The PL spectrum is under 248 nm excitation, and the PLE spectrum is monitored at the emission wavelength ( $\lambda_{em}$ ) of 400 nm. The vertical dashed line indicates the measuring limit by cutoff filters.

inhibited. For the MIS structure of SiO<sub>2</sub> films without Ge<sup>+</sup> implantation, a forward (or reverse) voltage is applied up to 20 V, but no EL can be detected. This indicates that the EL is connected with Ge<sup>+</sup> implantation. Figure 3(b) shows the PL and PL excitation (PLE) spectra of the Ge<sup>+</sup>-implanted SiO<sub>2</sub> films annealed at 1100 °C. The PL spectrum displays three luminescent bands peaked at 400, 600, and 780 nm under 248 nm excitation. [The vertical dashed line in Fig. 3(b) indicates the measuring limit by cutoff filters.] The PLE spectrum is monitored at the emission wavelength ( $\lambda_{em}$ ) of 400 nm, displaying a band peaked at 240 nm (5 eV). The PL, PLE, and EL spectra were measured at room temperature. From Fig. 3, it can be seen that the EL and PL spectra have same peak positions though their spectral shapes are different.

The origins of the three luminescent bands at 3.1, 2.1, and 1.6 eV are different. Ge<sup>+</sup> implantation and annealing induces not only Ge nanocrystals but also many defects in the oxide films.<sup>5,10-12</sup> Many studies on germanium silicate glasses have confirmed that the well-known absorption band at 5 eV is induced by GODC defects.<sup>1,13</sup> Some kinds of the GODC defects exhibit luminescent band at  $\sim 3 \text{ eV}$  under 5 eV excitation.<sup>13</sup> So we speculate that the 3.1 eV PL and 5 eV PLE bands come from the GODC defects in the SiO<sub>2</sub> film. On the other hand, it is well known that Ge nanocrystals in SiO<sub>2</sub> glassy matrices can show visible photoluminescence at room temperature.<sup>5-10</sup> In Fig. 3(a), since the 2.1 and 1.6 eV bands appear simultaneously under forward bias and are inhibited simultaneously under reverse bias, we speculate that both the 2.1 and 1.6 eV bands are related to Ge nanocrystals. The difference between them may come from different radiative relaxation procedures. The recombination of electronhole pairs in the Ge nanocrystals has several radiative relaxation procedures, emitting different luminescent bands.<sup>3,11,14</sup> The recombination may be within the Ge nanocrystals, or at the interface between the nanocrystals and the matrix, or at the defects of the SiO<sub>2</sub> matrix formed by implantation and annealing.<sup>3,11,14</sup> Further work is underway in order to understand the radiative relaxation procedures for the 2.1 and 1.6 eV bands.

Many causes can lead to the differences between the EL and PL spectra. An important cause is the difference in the mechanisms for the population of exciting states between electrical and optical pumping. Another important factor is that the photoluminescent and electroluminescent processes take place in different regions of the oxide films. In the photoluminescent process, the luminescence mainly comes from the pump absorption in the layer below the surface. The weak intensity of 2.1 and 1.6 bands in PL spectra is a result of the lack of Ge nanocrystals in the layer. In the electroluminescent process, the luminescence is controlled by both the carrier motion and the electric field distribution in the oxide film.

In general, there are two kinds of electroluminescent mechanisms. One is impact ionization by hot carriers, and the other is the recombination of electron-hole pairs. To explore the electroluminescent mechanism, the carrier motion in the Ge-implanted SiO<sub>2</sub> films should be studied. Electron injection in SiO<sub>2</sub> film prevails over hole injection due to energy barrier height asymmetries of the contacting metal or the semiconductor with the oxide (the electron barriers are lower than the hole barriers).<sup>5,14–16</sup> The presence of Ge nanocrystals inside the SiO2 film allows direct carrier tunneling between nanocrystals.<sup>14–16</sup> In the moderate electric field range, the presence of Ge nanocrystals in the layer of the SiO<sub>2</sub> film at the Si/SiO<sub>2</sub> interface enhances carrier tunneling from the Si substrate into the SiO<sub>2</sub> film.<sup>14–16</sup> Therefore, we propose the motion of electrons and holes as follows: when the forward voltage is applied on the MIS structure, electrons are injected into the film from the Au/SiO2 interface. Meantime, hole tunneling from the Si substrate into the film is enhanced due to the presence of Ge nanocrystals in the layer at the Si/SiO<sub>2</sub> interface. The carriers then transport from nanocrystals to nanocrystals and recombine via different processes, emitting the 2.1 and 1.6 eV luminescent bands. The inhibition of these two bands under reserve bias is because Ge nanocrystals are lack in the layer at the Au/SiO<sub>2</sub> interface (the layer is near the positively biased electrode under reserve bias). On the other hand, when the EL device shows the 3.1 eV luminescent band, the average field strength in the film is about  $10^6$  V/cm. In fact, the electric field in some regions is above  $10^6$  V/cm, because the presence of nanocrystals in the SiO<sub>2</sub> film induces inhomogeneous distribution of the electric field.<sup>16</sup> Thus, we speculate that the mechanism for excitation of the GODC defect is related to impact ionization by hot electrons in the high field, similar to the electroluminescence in ZnS:Mn.<sup>5,14</sup>

In summary, Ge nanocrystal-based electroluminescent devices have been fabricated by using Ge<sup>+</sup> implantation and thermal annealing, a method compatible with a conventional silicon integrated circuit process. The PL and EL spectra display three luminescent bands peaked at 3.1, 2.1, and 1.6 eV. The 3.1 eV luminescent band is related to the GODC defect, and its electroluminescent excitation is related to the impact ionization by hot electrons. The 2.1 and 1.6 eV luminescent bands are related to Ge nanocrystals, their electroluminescent excitation is related to the hole-electron pairs.

This work was supported by the National Natural Science Foundation of China.

- <sup>1</sup>H. Hosono, Y. Abe, D. L. Kinser, R. A. Weeks, K. Muta, and H. Kawazoe, Phys. Rev. B **46**, 11 445 (1992).
- <sup>2</sup>Y. Maeda, N. Tsukamoto, Y. Yazawa, Y. Kanemitsu, and Y. Masumoto, Appl. Phys. Lett. **59**, 3168 (1991).
- <sup>3</sup>Y. Maeda, Phys. Rev. B **51**, 1658 (1995).
- <sup>4</sup>K. D. Hirschman, L. Tsybeskov, S. P. Duttagupta, and P. M. Fauchet, Nature (London) **384**, 338 (1996).
- <sup>5</sup>K. V. Shcheglov, C. M. Yang, K. J. Vahala, and H. A. Atwater, Appl. Phys. Lett. **66**, 745 (1995).
- <sup>6</sup>M. Nogami and Y. Abe, Appl. Phys. Lett. **65**, 2545 (1994).
- <sup>7</sup>M. Fujii, S. Hayashi, and K. Yamamoto, Jpn. J. Appl. Phys., Part 1 **30**, 687 (1991).
- <sup>8</sup>V. Cracium, C. B. Leborgne, E. J. Nicholls, and I. W. Boyd, Appl. Phys. Lett. **69**, 1506 (1996).
- <sup>9</sup>D. C. Paine, C. Caragianis, T. Y. Kim, Y. Shigesato, and T. Ishahara, Appl. Phys. Lett. **62**, 2842 (1993).
- <sup>10</sup> H. Hosono, N. Matsunami, A. Kudo, and T. Ohtsuka, Appl. Phys. Lett. 65, 1632 (1994).
- <sup>11</sup>G. Ghislotti, B. Nielsen, P. A. Kumar, K. G. Lynn, A. Gambhir, L. F. Di Mauro, and C. E. Bottani, J. Appl. Phys. **79**, 8660 (1996).
- <sup>12</sup>K. Kawamura, H. Hosono, and H. Kawazoe, J. Appl. Phys. 80, 1357 (1996).
- <sup>13</sup>V. B. Neustruev, J. Phys.: Condens. Matter 6, 6901 (1994).
- <sup>14</sup>D. J. DiMaria, J. R. Kirtley, E. J. Pakulis, D. W. Dong, T. S. Kuan, F. L. Pesavento, T. N. Theis, J. A. Cutro, and S. D. Brorson, J. Appl. Phys. 56, 401 (1984).
- <sup>15</sup>D. J. DiMaria and D. W. Dong, J. Appl. Phys. **51**, 2722 (1980).
- <sup>16</sup>D. J. DiMaria, E. Cartier, and D. A. Buchanan, J. Appl. Phys. 80, 304 (1996).