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Strong blue and violet photoluminescence and electroluminescence from germanium-implanted and silicon-implanted silicon-dioxide layers

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The photoluminescence (PL) and electroluminescence (EL) properties of Ge-implanted SiO_2 layers thermally grown on a Si substrate were investigated and compared to those of Si-implanted SiO_2 films. The PL spectra from Ge-implanted SiO_2 were recorded as a function of annealing temperature. It was found that the blue-violet PL from Ge-rich oxide layers reaches a maximum after annealing at 500 °C for 30 min, and is substantially more intense than the PL emission from Si-implanted oxides. The neutral oxygen vacancy is believed to be responsible for the observed luminescence. The EL spectrum from the Ge-implanted oxide after annealing at 1000 °C correlates very well with the PL one, and shows a linear dependence on the injected current. The EL emission was strong enough to be readily seen with the naked eye and the EL efficiency was assessed to be about 5×10^{-4}. © *1997 American Institute of Physics.* [S0003-6951(97)02745-9]

Because of its indirect band gap silicon is not suitable for fabricating light-emitting devices. The desire to adhere to the standard Si technology has motivated extensive research on the development of Si-related materials for optoelectronic applications. After the observation of efficient PL from porous silicon[1] much interest has been initially generated in this material. Many authors[2–5] have reported on EL in the red spectral region with wavelengths longer than 600 nm. However, the possible application for light-emitting devices in various chemical ambients or under thermal stress has focused the interest on alternative materials, which show better compatibility with current Si processing than porous silicon.

One promising approach of forming luminescent Si-based structures is the ion implantation of semiconductor species into thin SiO_2 films thermally grown on Si substrates, because of the robustness of the matrix and the very good control over the fabrication process. Furthermore, ion implantation is a dry process which, as distinct from the wet procedures utilized in the production of porous silicon, is fully compatible with microelectronic technology. Various studies have used the implantation of Si to obtain structures exhibiting PL in the red region.[6–9] Recently, results pertinent to blue PL from Si-implanted SiO_2 layers have been reported.[10–14] Bao *et al.*[15] have shown that violet PL can also be achieved from Ge-implanted SiO_2 layers, but no comparison between the Ge-induced PL intensity and that from Si-implanted SiO_2 has been attempted. To date, there have been only a few EL studies of Si-or Ge-implanted SiO_2 layers. Shcheglov *et al.*[16] have implanted Ge at very high doses into thermally grown SiO_2 and have recorded a broad EL spectrum peaking in the infrared region.

In the present study we demonstrate that the violet PL from Ge-implanted SiO_2 is much higher in intensity than the blue PL from Si-implanted SiO_2. Furthermore, we show that the Ge-rich structure exhibits strong EL with the same emission characteristics as the PL.

500-nm-thick SiO_2 films on (100) *n*-type Si substrates were grown in a wet ambient at 1000 °C. The SiO_2 films were implanted with Ge^+ ions at an energy of 350 keV to a dose of $3\times10^{16}\ cm^{-2}$ followed by a second Ge implant at 200 keV to a dose of $1.8\times10^{16}\ cm^{-2}$. As calculated by transport of ions in matter (TRIM), under these conditions a broad implant profile of an average density of excess Si or Ge atoms of about 3 at. % would be achieved over a depth region of 100–400 nm below the oxide surface. The substrate temperature during implantation was maintained between -120 and -150 °C by mounting the samples on a LN_2-cooled stage. For the sake of comparison, Si^+ ions were implanted at an energy of 200 keV followed by a second Si implant at 100 keV using the same doses and substrate temperatures as in the case of Ge. After implantation the structures prepared for PL measurements were furnace-annealed (FA) in the temperature range of 400–1200 °C for 30 min in a N_2 ambient. The SiO_2 films to be examined for EL were annealed at 1000 °C for 60 min in a N_2 ambient to recover the SiO_2 network using the same temperature as for the oxide growth. Metal–oxide–semiconductor (MOS) dot structures for EL studies were prepared using sputtered layers of indium tin oxide (ITO) and Al as front and rear side electrodes with a thickness of 300 nm, respectively. The oxide on the rear side of the wafer was removed before Al metallization. The transmission of ITO is higher than 80% in the wavelength region from 340 nm to 2 μm. The dot matrix with a dot diameter of 1 mm was made by photolithographic patterning. Finally, an annealing procedure of 400 °C for 30 min was performed to improve the ohmic behavior of the contacts. EL and PL measurements were performed at room

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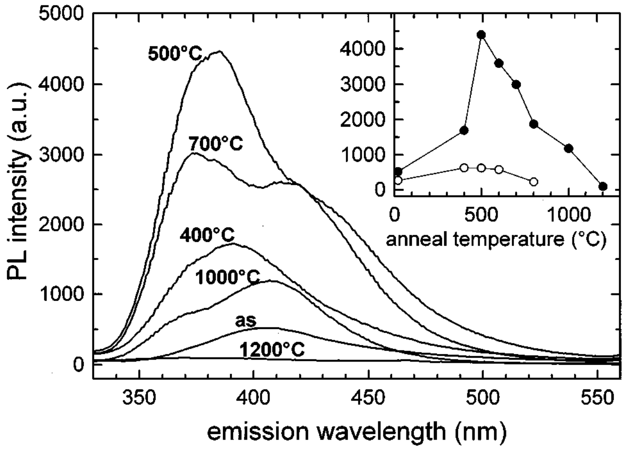

FIG. 1. The PL spectra from Ge-implanted SiO_2 films after implantation (as) and at different anneal temperatures under 240 nm excitation. The inset shows the PL intensity maximum from both Ge- (closed circles) and Si- (open circles) implanted SiO_2 films depending on anneal temperature.

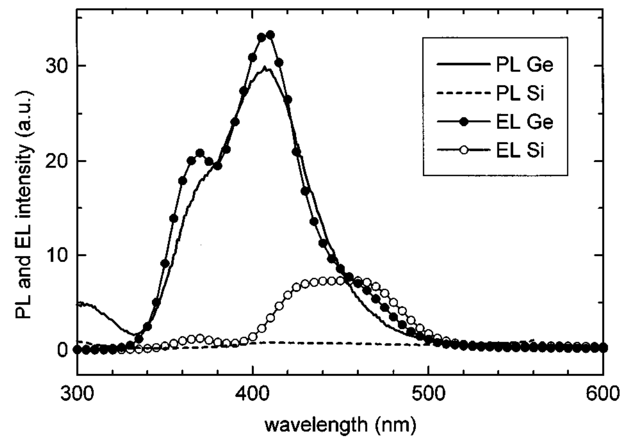

FIG. 2. The EL spectra from Ge- (closed circles) and Si- (open circles) implanted SiO_2 films in comparison to the PL spectra from Ge- (solid line) and Si- (dashed line) implanted oxide. All structures were furnace-annealed at 1000 °C for 30 min. The PL spectra for Ge- and Si-rich oxide were recorded under an excitation wavelength of 240 and 250 nm, respectively. The EL was stimulated using an injection current of about 100 nA by applying a voltage of 370 V (Si) and 380 V (Ge), respectively.

temperature in a Spex Fluoromax spectrometer with a R928 Hamamatsu photomultiplier.

Figure 1 shows PL spectra from Ge implanted SiO_2 films at different anneal temperatures under 240 nm excitation. The inset compares the PL intensity maximum from both Ge-(closed circles) and Si-(open circles) implanted SiO_2 films depending on anneal temperature. Maximum PL intensity is achieved for both Ge- and Si-implanted layers at 500 °C for 30 min, consistent with previous results.[14] At this anneal temperature the PL intensity for Ge exceeds that of Si by a factor of 7, thus becoming visible with the naked eye. The main emission from the Ge-implanted layers occurs between 350 and 450 nm, but the increase in the anneal temperature causes apparent changes in the shape of the violet PL spectra. This behavior differs distinctly from that of the Si-implanted oxide which always shows a single emission peak around 460 nm.[14] While the PL signal recorded from the as-implanted oxide exhibits a single broad peak of low intensity around 410 nm, after annealing at 500 °C a peak around 380 nm becomes dominant and a shoulder around 410 nm is also evident indicating the presence of a second peak. For $T > 600$ °C the bimodal behavior is retained, but the intensity ratio of these two peaks is seen to change in favor of the 410 nm peak, accompanied by a decrease in the overall intensity of the violet emission. At an anneal temperature of 800 °C the longer-wavelength peak now dominates in the PL signal and its maximum occurs at 407 nm.

Our previous investigations have shown that the PL from Si-implanted SiO_2 films is not simply caused by radiation damage, but is rather related to the nonstoichiometric composition of the silicon dioxide.[13] This was concluded from the very weak PL of the Ar-implanted oxide compared to the PL signal from Si-implanted SiO_2. Tohmon *et al.*[17] have interpreted the blue PL from Si-rich glasses in terms of oxygen-defect centers and suggested that the neutral oxygen vacancy is the main luminescent center. Recently, it has been shown that the neutral oxygen vacancy is also responsible for the blue PL in Si-implanted SiO_2.[11] This luminescing center is a product of Si–Si bond formation in the SiO_2 network and will be denoted hereafter as $\equiv$Si–Si$\equiv$ center.

In the framework of our interpretation the PL may be explained as excitation from the singlet ground state, S_0, to the first excited singlet state, S_1, followed by intersystem crossing to the first excited triplet state, T_1, and a radiative deexcitation to the ground state. In the case of Ge-implanted SiO_2 films we believe that one or both Si atoms of the $\equiv$Si–Si$\equiv$ center are substituted by Ge atoms forming a $\equiv$Ge–Si$\equiv$ and $\equiv$Ge–Ge$\equiv$ center, respectively. The formation of two different defect centers can also explain the presence of two main subpeaks in the emission spectra of Ge-implanted material. As is known from the molecular spectroscopy,[18] substituting an atom of a given molecule with a heavier atom of isoelectronic configuration leads to an increase in the spin–orbit coupling. This in turn raises the probability of the triplet-to-singlet transition ($T_1 \rightarrow S_0$) and normally increases the transition energy as well. Therefore, assuming that the blue PL from a Si-rich oxide is due to a $T_1 \rightarrow S_0$ transition of the $\equiv$Si–Si$\equiv$ center, one would expect a blue shift of the peak position in the order $\equiv$Ge–Si$\equiv$ and $\equiv$Ge–Ge$\equiv$. The energy of the $S_0 \rightarrow S_1$ excitation band would not be influenced appreciably by the spin–orbit coupling and, in fact, we find only a small shift of the optimum excitation energy, namely from 250 nm (Si) to 240 nm (Ge).

Figure 2 shows the EL and PL spectra of Si- and Ge-implanted SiO_2 films. The EL was stimulated using an injection current of about 100 nA by applying a voltage of either 370 V (Si) or 380 V (Ge). The EL spectrum from the Ge-rich layers shows a double-peak structure with maxima at 366 and 407 nm, whereas the Si-implanted oxide exhibits a broader distribution between 420 and 470 nm. The EL intensity from the Ge-implanted SiO_2 films for the same current is by a factor of 5 larger than that in the case of Si-implanted structures, and for currents higher than 250 nA the EL emission becomes readily visible with the naked eye. It should be noted that the unimplanted SiO_2 films exhibit no EL.

The corresponding PL spectra from Ge- and Si-implanted layers shown in Fig. 2 were recorded using an excitation wavelength of 240 and 250 nm, respectively. For

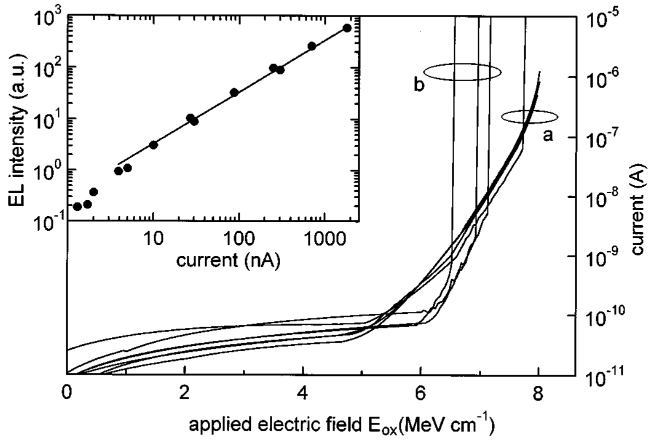

FIG. 3. The dependence of injection current on the applied electrical field E_{ox} for Ge-rich SiO_2 furnace-annealed at 1000 °C (a) and pure oxide (b). The inset shows the EL intensity for the Ge-implanted SiO_2 films as a function of current. The solid line represents a linear fit between 3.9 nA and 1.8 μA.

Ge-implanted layers a peak structure similar to that of EL is observed implying that both PL and EL of Ge-implanted SiO_2 films are caused by one and the same luminescing center. To verify this hypothesis, a basic peak fit analysis was carried out assuming that the peak structure can be described as a sum of Gaussian distributions on the energy scale. Both spectra can be fitted well by means of three subbands peaking at 3.39 eV (366 nm), 3.05 eV (407 nm), and 2.72 eV (455 nm). They differ slightly in two features: (i) the intensity ratio between the 3.39 and 3.05 eV peak is 1.66 for the EL spectrum, but 3.1 for PL spectra; (ii) all subpeaks in the EL spectra have the same full width at half-maximum (FWHM) of 0.3 eV, whereas in the PL spectra the FWHM of the 3.39 eV peak is broadened to 0.38 eV. On the basis of the preceding considerations we attribute the three subbands at 3.39, 3.05, and 2.72 eV to the ≡Ge–Ge≡, ≡Ge–Si≡, and ≡Si–Si≡ center, respectively. For the Si-implanted oxide layers annealed at 1000 °C only weak PL with a broad distribution between 400 and 500 nm was recorded.

Figure 3 shows variation of the current with applied electrical field E_{ox} for Ge-rich SiO_2 (a) and pure oxide (b). The curve is divided into three different regions. For low E_{ox} a nearly constant displacement current below 100 pA is measured. For high E_{ox} the potential difference between the oxide surface and the Si substrate is so high that a considerable amount of electrons can cross the oxide layer via Fowler–Nordheim (FN) tunneling, and the current increases following an exponential law. Finally, E_{ox} is high enough to induce a breakdown of the oxide layer (marked with a vertical line). In comparison to the pure oxide the region of FN tunneling for the implanted oxide starts at a lower E_{ox}, the current increases with a slightly lower exponential constant and the breakdown voltage is higher. We assume that the luminescence centers will be excited by the impact of hot electrons. As can be seen from the inset to Fig. 3, the EL intensity shows a nearly linear dependence on the injection current. The EL spectra obtained at different injection currents are characterized by an identical spectral shape. The term ''EL efficiency'' is defined as the ratio of the light output power to the applied electric power, and the respective value obtained in our experiments is estimated to be about 5×10^{-4}.

In summary, we have demonstrated that Ge-implanted SiO_2 exhibits strong violet PL as well as intense EL, and that in both cases one and the same luminescence centers are excited. To the best of our knowledge, such a coincidence of PL and EL has been reported for the first time. The value of the PL efficiency has been estimated to be 5×10^{-4}. The PL and EL spectra consist of two main subpeaks which can be attributed to the presence of ≡Ge–Si≡ and ≡Ge–Ge≡ defect centers, respectively. The dependence of the EL on the injection current follows a linear relationship over a wide range of three orders of magnitudes, and can be explained by electron impact excitation of hot electrons injected from the Si substrate via FN tunneling. Both the PL and the EL from Ge-rich oxide layers are much higher in intensity than the respective emissions from Si-implanted oxides.

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[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
[2] A. Richter, P. Steiner, F. Kozlowski, and W. Lang, IEEE Electron Device Lett. **12**, 691 (1991).
[3] F. Kozlowski, M. Sauter, P. Steiner, A. Richter, H. Sandmaier, and W. Lang, Thin Solid Films **222**, 196 (1992).
[4] L. Tsybeskov, S. P. Duttagupta, K. D. Hirschman, and P. M. Fauchet, Appl. Phys. Lett. **68**, 2058 (1996).
[5] N. Lalic and J. Linnros, J. Appl. Phys. **80**, 5971 (1996).
[6] T. Shimizu-Iwayama, K. Fujita, S. Nakato, K. Saitoh, T. Fujita, and N. Itoh, J. Appl. Phys. **75**, 7779 (1994).
[7] H. A. Atwater, K. V. Sheglov, S. S. Wong, K. J. Vahala, R. C. Flagan, M. L. Brongersma, and A. Polman, Mater. Res. Soc. Symp. Proc. **321**, 363 (1994).
[8] T. Fischer, V. Petrova-Koch, K. Shcheglov, M. S. Brandt, and F. Koch, Thin Solid Films **276**, 100 (1996).
[9] G. A. Kachurin, I. E. Tyschenko, K. S. Zhuravlev, N. A. Pazdnikov, V. A. Volodin, A. K. Gutakovsky, A. F. Leier, W. Skorupa, and R. A. Yankov, Nucl. Instrum. Methods Phys. Res. B **122**, 571 (1997).
[10] P. Mutti, G. Ghislotti, S. Bertoni, L. Bonoldi, C. F. Cerofolini, L. Meda, E. Grilli, and M. Guzzi, Appl. Phys. Lett. **66**, 851 (1995).
[11] L. S. Liao, X. M. Bao, X. Q. Zheng, N. S. Li, and N. B. Min, Appl. Phys. Lett. **68**, 850 (1996).
[12] W. Skorupa, R. A. Yankov, I. E. Tyschenko, H. Fröb, T. Böhme, and K. Leo, Appl. Phys. Lett. **68**, 2410 (1996).
[13] W. Skorupa, R. A. Yankov, L. Rebohle, H. Fröb, T. Böhme, K. Leo, I. E. Tyschenko, and G. A. Kachurin, Nucl. Instrum. Methods Phys. Res. B **120**, 106 (1996).
[14] L. Rebohle, I. E. Tyschenko, H. Fröb, K. Leo, R. A. Yankov, J. von Borany, and W. Skorupa, Microelectron. Eng. **36**, 107 (1997).
[15] X. M. Bao, T. Gao, F. Yan, and S. Tong, Mater. Res. Soc. Symp. Proc. **438**, 477 (1997).
[16] K. V. Shcheglov, C. M. Yang, K. J. Vahala, and H. A. Atwater, Appl. Phys. Lett. **66**, 745 (1995).
[17] R. Thomon, Y. Shimogaichi, H. Mizuno, Y. Ohki, K. Nagasawa, and Y. Hama, Phys. Rev. Lett. **62**, 1388 (1989).
[18] S. P. McGlynn, T. Azumi, and M. Kinoshita, *Molecular Spectroscopy of the Triplet State* (Prentice-Hall, Englewood Cliffs, NJ, 1969).