Defect-related infrared photoluminescence in Ge\textsuperscript{i+}-implanted SiO\textsubscript{2} films

X. L. Wu\textsuperscript{a} and T. Gao
National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China

G. G. Siu
Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, Republic of China

S. Tong and X. M. Bao
National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China

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SiO\textsubscript{2} films with Ge\textsuperscript{i+} implantation at an energy of 60 keV and a dose of \(1 \times 10^{16} \text{ cm}^{-2}\), followed by annealing at different temperature, exhibit a broad infrared photoluminescence (PL) at room temperature under an excitation of the 514.5 nm line of Ar\textsuperscript{+} laser. With increasing the annealing temperature, the intensity of the infrared PL band decreases, its full width at half maximum increases, and its energy redshifts. Spectral analysis and some experimental results from Raman scattering, electron spin resonance, and infrared spectroscopy strongly suggest that the infrared PL is mainly related to interfacial oxygen-deficient-type defects between the oxide and Ge nanocrystals.

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Studies on the SiO\textsubscript{2} films embedded with Si nanocrystals have lasted for a long time, and red, green, and blue photoluminescence (PL) has been observed due to the quantum confinement effect (QCE) or some defect centers.\textsuperscript{1,2} Since bulk Ge has a large dielectric constant and small carrier masses compared to bulk Si, the QCE of Ge nanocrystals will be more pronounced than that of corresponding Si.\textsuperscript{3,4} Recently, Kanemitsu, Uto, and Masumoto\textsuperscript{5} fabricated a kind of Ge-embedded SiO\textsubscript{2} matrix by magnetic co-sputtering and observed a 550 nm PL band due to the QCE of Ge nanocrystals. Scheglov et al.\textsuperscript{6} and Min et al.\textsuperscript{7} reported a broad PL band peaked at 500–900 nm from Ge-implanted SiO\textsubscript{2} films and attributed the PL to the QCE of Ge nanocrystals and the radiative defect centers in the SiO\textsubscript{2} matrix, respectively. We recently reported a strong violet PL from Ge-implanted SiO\textsubscript{2} films.\textsuperscript{8} The PL band was assigned to the \(T_1\rightarrow S_0\) transition in the GeO. In this letter, we report a near infrared PL from the same material. Its origin is discussed.

A layer of SiO\textsubscript{2} film with a thickness of 360 nm was formed on p-type (100) oriented crystal Si by thermal oxidation. Ge ions were implanted into this SiO\textsubscript{2} layer with a dose of \(1 \times 10^{16} \text{ cm}^{-2}\) and at an energy of 60 keV. The implanted samples were annealed under various temperatures (\(T_a\)) in N\textsubscript{2} for 30 min. PL spectra were obtained on a 44 W monocular meter using an excitation of the 514.5 nm line of Ar\textsuperscript{+} laser. The electron spin resonance (ESR) signals were measured using a Bruker ER-200D X-band spectrometer, operating at a low microwave power of 6.4 mW to avoid saturation. Infrared absorption spectra were obtained under normal incidence using a Nicolet 170 SX Fourier-transform infrared (FTIR) spectrometer. The SiO\textsubscript{2} films on the reverse sides of the substrates were etched off in order to prevent infrared absorption by the nonimplanted films. All spectral measurements were run at room temperature.

Figure 1 shows the PL spectra of three typical samples annealed at 400, 600, and 1100 °C, measured at 77 K. The three spectra all exhibit a broad infrared PL band at \(800, 850, \text{ and } 900 \text{ nm}\), respectively. With increasing \(T_a\), the PL peak energy redshifts clearly, the PL intensity decreases, and the PL full width at half maximum (FWHM) increases. In the \(T_a = 1100 \text{ °C}\) sample, the PL intensity is almost 70% of that in the \(T_a = 400 \text{ °C}\) sample. Since no infrared emission was observed in both pure SiO\textsubscript{2} film and as-implanted SiO\textsubscript{2} film, we can infer that the PL is closely related to both Ge\textsuperscript{i+} implantation and subsequent annealing.

Previously, we have known that annealing leads to the absorption of the nonimplanted films. All spectral measurements were run at room temperature.

Figure 1. PL spectra of the samples with \(T_a = 400, 600, \text{ and } 1100 \text{ °C}\). An obvious redshift of the PL peak can be observed with increasing \(T_a\).

\textsuperscript{a}Author to whom correspondence should be addressed; electronic mail: hksxlwu@netra.nju.edu.cn
formation of Ge nanocrystals. Raman results indicated that the sizes of Ge nano-crystals increase with \( Ta \), having a mean value of \( 3.6 \) (400 °C), \( 5.3 \) (600 °C), \( 5.7 \) (800 °C), and \( 6.4 \) nm (1100 °C).\(^ {9,10} \) This result, together with the PL red-shift with increasing \( Ta \), seems to imply that the infrared PL may arise from the QCE of Ge nanocrystals in the matrix. Further, Takagahara and Tapada\(^ {11} \) have also proposed a model about the quantum confinement effect on excitons in Ge and Si quantum dots. According to this model, the band gaps of Ge nanocrystals with sizes of \( 3.6, 5.3, \) and \( 6.4 \) nm are \( 2.1, 1.5, \) and \( 1.4 \) eV, respectively, basically consistent with our experimental results. However, such a key question for the PL origin should carefully be addressed. First, we should note that the obtained Raman spectra are noisy\(^ 9 \) and therefore an accurate peak fitting is rather difficult. Also, many assumptions in Raman calculations make the theoretical Raman profile and the resulting size qualitative. Therefore, the calculated mean crystallite sizes have some errors. Second, Takagahara’s calculation is based on uniform crystallite size and therefore the obtained emission energy will not necessarily be the same as that with the size distribution. In fact, the measured PL spectra are broader than the calculated ones. Also, the observed rate of increase in emission energy as a function of size is much less pronounced than what the theory predicts for zero-phonon transition. Third, the Bohr model,\(^ {12} \) which has widely been exploited to predict the PL peak energy, can predict the band gaps of Ge nanocrystals with mean sizes of \( 3.6, 5.3, \) and \( 6.4 \) nm to be \( 4.9, 2.7, \) and \( 2.0 \) eV, respectively, quite different from our experimental values of \( 1.55, 1.46, \) and \( 1.38 \) eV. In addition, Figs. 2(a) and 2(b) show the PL spectra of the sample with \( Ta=600 \) °C, measured at 300 and 77 K, respectively. The PL peak at \( \sim 600 \) nm in Fig. 2(a) has been described in our previous work.\(^ {13} \) For the infrared PL peak, although an apparent blue-shift of \( 0.07 \) eV from 300 to 77 K can be observed and explained in analogy to bulk Ge,\(^ {14} \) an increase in FWHM by more than a factor of 2 at 77 K cannot be elucidated simply on the basis of bulk material. The two peaks should have a different origin. These arguments above indicate that the infrared PL has an origin other than the quantum confinement on Ge nanocrystals. Three typical ESR spectra from the samples with different \( Ta \) are shown in Fig. 3. The as- implanted sample was found to involve a strong resonance line with a Lande \( g \) value of 2.000. Its spin density decreases with increasing \( Ta \) and almost disappears in the samples with \( Ta \) above 400 °C. The resonance line may be assigned to the \( E' \) defect center with a Si dangling bond.\(^ 1 \) The \( E' \) center is a nonradiative recombination center. Its decrease follows an increase of the infrared PL intensity, implying that some kind of diamagnetically radiative center defect produced by annealing is responsible for the infrared PL. Here we should point out that the disappearance of paramagnetic ESR signal in the sample with \( Ta > 300 \) °C does not imply that SiO\(_2\) has completely returned to its undamaged state, because partial damaged structures may have diamagnetic property, which cannot be detected in ESR experiments.

To identify structural damage to the SiO\(_2\) network caused by ion implantation and annealing, FTIR spectra were measured to determine the defect characteristics connected with the observed PL. Figures 4(a)–4(c) show three typical FTIR transmission spectra. In the stoichiometric SiO\(_2\) film, three vibrational bands exist at 470, 820, and 1086 cm\(^ {-1} \) (TO\(_ 3\) mode, corresponding to rocking, bending, and asymmetric stretching vibrations of Si–O–Si bond, respectively).\(^ {15} \) In the as-implanted film, two new bands appear at 580 and 870 cm\(^ {-1} \), corresponding to the bending and stretching vi-
be affected slightly by the oxygen shell bonded to the Ge atom, so its PL feature slightly depends on the fragment bonded to it. For the GeNOV defect, the PL bands arise from the transitions between the localized states resulting from the bonding and antibonding combination of \( sp \) orbits of the two Ge atoms, therefore the PL energies are strongly affected by the Ge–Ge distance. Our experimental results indicate that the observed PL-related defects should be connected with the GeNOV and TCGe. Annealing leads to the relaxation of Ge–Ge bond and then increases the Ge–Ge distance, which will cause a significant shift of the PL energy. Since the TCGe is bonded to the SiO\(_2\) network, structural changes in the network will lead to a change of bonding arrangement at the Ge\(^{2+}\) site. The broadening of the observed PL band is an indication of a statistical distribution of different bonding arrangements at each Ge\(^{2+}\) site.

In conclusion, for the SiO\(_2\) films with Ge\(^+\) implantation and followed by annealing, a near infrared PL can be observed. The PL obviously displays a redshift from 800 to 900 nm with increasing \( Ta \) from 400 to 1100 °C. Spectral analysis and some experimental results strongly suggest that the obtained infrared PL is closely related to the interfacial GeNOV and TCGe defects.

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