phys. stat. sol. (a) **165**, 31 (1998)

Subject classification: 78.55.Hx; 78.60.Fi; S5.11; S10.1

Strong Blue and Violet Photo- and Electroluminescence from Ge- and Si-Implanted Silicon Dioxide

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(Received June 23, 1997)

The photoluminescence (PL) and electroluminescence (EL) properties of Ge-implanted SiO_2 films thermally-grown on a Si substrate have been investigated and compared to those of Si-implanted SiO_2 films. It is found that the blue-violet PL from both Si and Ge-rich layers reaches a maximum after annealing at 500 °C for 30 min. The PL and EL from Ge-implanted SiO_2 are distinctly higher than that from Si-implanted layers and well visible for the naked eye. The EL spectrum from the Ge-implanted oxide annealed at 1000 °C correlates very well with the PL one and shows a linear dependence on the injected current. The neutral oxygen vacancy is assumed to be responsible for the observed luminescence. In the case of Ge the microstructure after high temperature annealing is studied.

1. Introduction

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 [1 to 13], because of the robustness of the matrix and the very good control over the fabrication process. The ion implantation and annealing as dry techniques can be easier integrated in microelectronic processing lines than the wet procedures utilized for manufacturing porous silicon. Various studies used the implantation of Si to produce structures exhibiting PL in the red region [1 to 4]. Recently, results pertinent to blue PL from Si-implanted SiO_2 layers were reported [5 to 11]. Up to now there have been only few EL studies of Si- or Ge-implanted SiO_2 layers. Liao et al. [12] reported on red EL at 620 nm of Si-implanted SiO_2 films stimulated by a low electric field. Shcheglov et al. [13] implanted Ge at very high doses and obtained a broad EL spectrum with main emission in the near-infrared region. First promising results concerning blue-violet EL of Ge-implanted SiO_2 layers were reported in [10].

In the present study we demonstrate that the PL from Ge-implanted SiO_2 is distinctly higher than the PL from Si-implanted oxide. Furthermore, we show that the Ge-rich structure exhibits strong EL with the same emission characteristics like the PL. Additionally, the microstructure of Ge-implanted oxide after high temperature annealing was investigated.

2. Experimental

500 nm thick SiO_2 films on (100) n-type Si substrates were grown by wet oxidation at 1000 °C. The SiO_2 films were implanted with Ge^+ ions at an energy of 450 keV to a dose of 3×10^{16} cm^{-2}, followed by a second implantation of Ge^+ ions at 230 keV to a dose of 1.8×10^{16} cm^{-2}. As calculated by TRIM, under these conditions a broad implantation profile will be achieved within a depth region of 100 to 400 nm below the oxide surface. Single implantation of Ge at 350 keV to a dose of 5.0×10^{16} cm^{-2} was applied to investigate the Ge profile and microstructure in Ge-implanted SiO_2. For comparison, Si^+ ions were implanted at an energy of 200 keV, followed by a second implantation of Si^+ ions at 100 keV using the same doses and substrate temperatures as in the case of Ge. The substrate temperature during implantation was kept between −120 and −150 °C by mounting the samples on a LN_2-cooled stage. After implantation the structures prepared for PL measurements were furnace-annealed (FA) in the temperature range of 400 and 1200 °C for 30 min in an N_2 ambient. The SiO_2 films to be examined for EL were annealed at 1000 °C for 60 min in an N_2 ambient to recover the SiO_2 network using the same temperature as for the oxide growth. MOS dot structures for EL studies were prepared using sputtered layers of indium tin oxide and Al as front and rear side electrodes with a thickness each of 300 nm, respectively. EL and PL measurements were performed at room temperature in a Spex Fluoromax spectrometer with an R928 Hamamatsu photomultiplier. The EL was investigated using electron injection from the Si substrate into the oxide layer.

3. Results and Discussion

Previous investigations showed that the PL from Si-implanted SiO_2 films is not simply caused by radiation damage but is rather related to the non-stoichiometric composition of the silicon dioxide [8]. This was concluded from the weak PL of the Ar-implanted SiO_2 layers compared to the strong PL from Si- and Ge-implanted oxide.

Fig. 1 shows the PL spectra of Si-implanted SiO_2 layers depending on annealing temperature (T) under 250 nm excitation. The as-implanted oxide exhibits a blue peak at

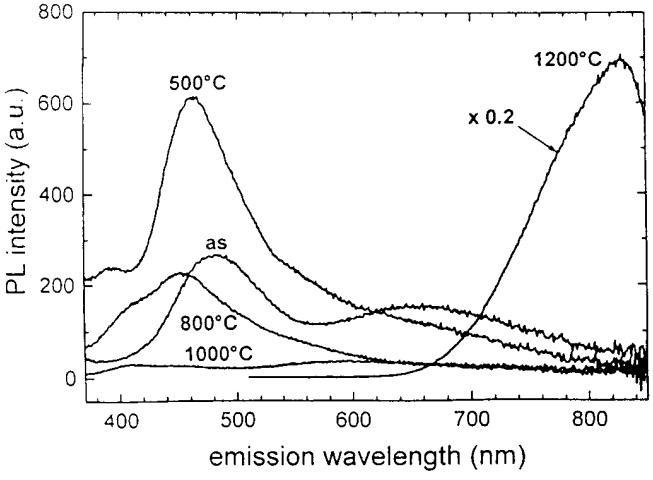

Fig. 1. PL spectra (in arb. units) of Si-implanted SiO_2 films at different annealing temperatures

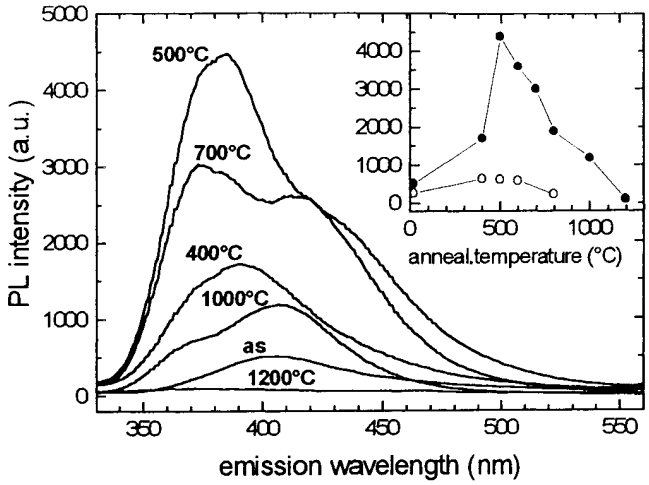

Fig. 2. PL spectra (in arb. units) of Ge-implanted SiO_2 films at different annealing temperatures. The inset compares the PL intensity maximum from both Ge- (closed circles) and Si- (open circles) implanted SiO_2 films depending on annealing temperature

480 nm and a broad red PL band around 660 nm. With increasing annealing temperature the intensity of the blue peak reaches a maximum at 500 °C, accompanied by a shift of its position to 460 nm, whereas the red PL is continuously quenched. For $T > 600$ °C the PL intensity decreases and is nearly diminished at 1000 °C. Finally, at 1200 °C an intense infrared peak appears at 830 nm.

Fig. 2 shows the PL spectra of Ge-implanted SiO_2 films at different annealing temperatures under 240 nm excitation. Similar to Si, the maximum PL intensity is achieved at 500 °C, but the spectral shape and annealing behaviour differ significantly from that of Si-implanted SiO_2 films. Firstly, no PL was detected in the red and infrared region for wavelengths shorter than 900 nm. Secondly, the main emission from the Ge-implanted layers occurs between 350 and 450 nm, but the increase in the annealing temperature causes apparent changes in the shape of the violet PL spectra. Contrary to the PL spectra of Si-implanted oxide, the spectra of Ge-implanted SiO_2 are characterized by the presence of at least two subpeaks whose relative intensities depend strongly on the annealing temperature. The inset of Fig. 2 compares the PL intensity maximum from both Ge- (closed circles) and Si- (open circles) implanted SiO_2 films depending on annealing temperature. Maximum PL intensity is achieved for both Ge- and Si-implanted layers at 500 °C for 30 min, where the PL intensity for Ge exceeds that of Si by a factor of 7.

Thomon et al. [14] 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 was demonstrated that the neutral oxygen vacancy is also responsible for the blue PL in Si-implanted SiO_2 [6]. This luminescent center is a product of Si–Si bond formation in the silicon dioxide network and will be further described as $\equiv$Si–Si$\equiv$ center. In the case of Ge-implanted SiO_2 films we assume that one or both Si atoms are substituted by Ge atoms forming a $\equiv$Ge–Si$\equiv$ or $\equiv$Ge–Ge$\equiv$ center, respectively. The formation of two different defect centers may also explain the presence of two main subpeaks in the emission spectra of Ge-implanted material. Implanting Si or Ge may lead to the formation of paramagnetic E' centers which do not contribute to the observed PL. In the case of Si-implanted SiO_2 it has been reported [6], that the concen-

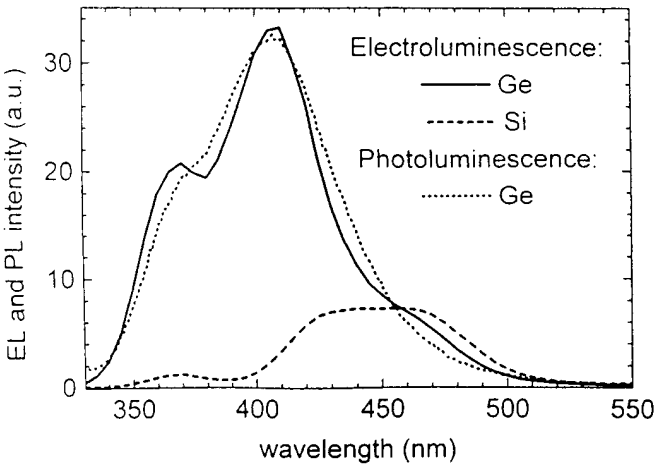

Fig. 3. EL spectra (in arb. units) of Ge-implanted (solid line) and Si-implanted (dashed line) SiO_2 films. For comparison, the PL spectrum of Ge-implanted SiO_2 layers (dotted line) is included

tration of these centers drops monotonically with increasing annealing temperature and vanishes completely at 600 °C. We suppose, that both E' and ≡Si–Si≡ centers are created during implantation, but that the E' centers will be transformed into ≡Si–Si≡ centers with increasing annealing temperature. At higher temperature the ≡Si–Si≡ centers also anneal out leading to the formation of larger agglomerates of excess Si. All these structural transformations result in the observed temperature dependence of the maximum PL intensity shown in the inset of Fig. 2.

For Ge, a similar scenario is assumed. Here, the implantation process generates E' centers and possibly Ge-related precursor defects, which will be transformed into ≡Ge–Si≡ or ≡Ge–Ge≡ centers. At higher temperatures these centers will be also annealed out forming larger Ge clusters or Ge nanocrystals. This is supported by the results of HRTEM investigations of Ge-implanted SiO_2 films annealed at 1000 °C. Here, a band of Ge clusters with a mean size of 5 to 6 nm is visible around the projected range of the implanted profile. The RBS measurements indicate the presence of two other Ge agglomeration of minor concentration at the Si/SiO_2 interface and around 50 nm below the oxide surface which are not observable by HRTEM.

Finally, the ability of the implanted oxide layers to exhibit EL was investigated. In Fig. 3 the EL spectra of Ge-implanted SiO_2 films at an injection current of about 100 nA are shown. The EL spectrum from the Ge-rich layer 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 film for the same current is up to 5 times larger than in the case of Si and well visible with the naked eye for currents higher than 250 nA. It should be noted that the unimplanted SiO_2 films exhibit no EL. The corresponding PL spectrum from the same Ge-implanted layer shown in Fig. 3 was recorded using an excitation wavelength of 240 nm. For Ge-implanted layers a peak structure similar to that of EL is observed. This indicates that both PL and EL of Ge-implanted SiO_2 films are caused by one and the same luminescence center. The EL was obtained for applied electrical fields higher than 6 MV cm^{-1} and shows a linear dependence on the injected current over three orders of magnitude. We assume that the luminescence centers will be excited by the impact of hot electrons crossing the oxide layer via Fowler-Nordheim tunneling.

4. Summary

We demonstrate that Ge-implanted SiO_2 exhibits strong violet PL as well as EL, and that in both cases one and the same luminescence center is excited. The PL and EL spectra consist of two main subpeaks which can be attributed to the presence of $\equiv$Ge–Si$\equiv$ and $\equiv$Ge–Ge$\equiv$ defect centers, respectively. The EL is directly correlated to the injection current over three orders of magnitude 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 distinctly higher than those from Si-implanted oxides.

Acknowledgements One of the authors (I.E.T.) would like to acknowledge the financial support of this research which has been provided by the Sächsische Staatsministerium für Wissenschaft und Kunst, Dresden. In addition, we thank R. A. Yankov and G. A. Kachurin for helpful discussion and critical remarks.

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