

Thermal decomposition and new luminescence bands in wet, dry, and additional oxygen implanted silica layers

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Abstract

Wet and dry silica oxide layers have been treated thermally up to $T_a = 1300$ °C and were investigated by cathodoluminescence (CL) spectroscopy. Whereas the dry oxides after high temperature treatment show an increase of the yellow–red spectra region, contrary, in wet oxides the UV–blue region is enhanced. Even a new strong band in the near-UV region (NV) at 330 nm (3.76 eV) is found for wet oxides at liquid nitrogen temperature (LNT), but much broader and with lower intensity for room temperature (RT) in a triple band structure UV: 290 nm, NV: 330 nm, and V: 400 nm. These violet bands should be associated with a thermally decomposed and rapidly cooled-down silica network in presence of OH groups or even dissociated oxygen. Additional oxygen implantation into dry silica with high doses up to 10^{17} ions/cm² and high thermal treatment $T > 1100$ °C leads as well to enhanced UV–NV–V luminescence emission bands supporting the fact that oxygen and structural decomposition play a decisive role in formation of near-UV luminescent defects in silica.

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1. Introduction

Silicon dioxide has revealed as an important material for microelectronics, optics, and even photonics. The performance of electronic and optical devices depends in a high degree on the presence of extrinsic as well as intrinsic defects in the atomic SiO₂ network.

Photoluminescence (PL), electron spin resonance (ESR), photoabsorption (PA), photoluminescence excitation spectroscopy (PLE) as well as cathodoluminescence (CL) are commonly used to study the structural and luminescent defects in silica materials [1]. A very special attention has

been paid to the PL and CL emission from the oxygen deficiency centers ODCs (like the oxygen vacancy) [2–4] and the non-bridging oxygen hole center (NBOHC) $\equiv\text{Si}-\text{O}^{\cdot}$ with an unpaired electron [5–9].

Two kinds of ODC species have been distinguished by their optical absorption and luminescence features; ODC(I): $\equiv\text{Si}-\text{Si}\equiv$ and ODC(II) which also has two proposed alternative models: the unrelaxed oxygen vacancy ($\equiv\text{Si}\cdots\text{Si}\equiv$) and the twofold co-ordinated silicon ($=\text{Si}:$) possessing a lone pair of non-bonding electrons [10,11]. A link between these ODC variants was put forward by the observation that under excitation of ODC(I), the UV emission band at 4.3 eV can be excited too which is attributed to ODC(II), this proposes the effectiveness of a conversion process between these two centers [12,13].

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According to the Skuja model of ODC(II) the twofold co-ordinated silicon =Si: possesses a fast singlet–singlet transition with the UV (4.3 eV) luminescence and the slow triplet–singlet transition of the blue B (2.7 eV) luminescence [12]. However, Meinhardi and Paleari [14] reported photoluminescence (PL) data on amorphous SiO₂ excited with synchrotron radiation, and their data indicate that the blue B band at 2.7 eV is independent of the UV band at 4.3 eV. These results are also reviewed by Leone et al. [15]. Morimoto et al. [16] have shown that the implantation of H⁺ ions reduces the magnitude of the B 2.7 eV blue emission whereas the UV emission is not affected. Even in a very recent work [17] X-ray excited luminescence (XRL) and successive thermally stimulated luminescence (TSL) show identical spectra but quite different in comparison to photoluminescence (PL) regarding the blue B (2.7 eV) and the UV (4.4 eV) luminescence bands. Moreover, the intensity of the blue emission B increases during electron beam irradiation whereas the UV emission remains nearly constant as we have observed in many CL dose experiments [18]. From this dose behavior the latter authors conclude that both centers of the blue and UV luminescence bands are not attributed to the same defect. The electron beam irradiation produces competitive reactions between luminescence center creation and destruction processes. During this competition reaction, the glassy network of SiO₂ changes also due to loss of oxygen [19] producing ODC's and even Si nanoclusters [20].

To investigate whether the different luminescent centers are related to oxygen or to silicon, we have compared non-stoichiometric SiO₂ layers produced by direct ion implantation. Based on these findings we have proposed a model of defect creation by stressing the role of mobile oxygen in defect transformation [18]. Similar results were obtained after Si⁺ and O⁺ implantation by photoabsorption measurements [21]. In the present paper we want to investigate how strong thermal treatment with beginning dissociation of wet and dry silica acts to the luminescence behavior of those and what role plays additionally implanted oxygen.

2. Experimental

The CL spectra and related excitation dose measurements were performed in a digital scanning electron microscope via a parabolic mirror collector, a spectrograph and a CCD camera, see e.g. [18,20]. CL spectra ranging from 1.5 to 6.5 eV were accumulated in single shot mode within a time of 1 s and with a spectral resolution of 4 nm. A temperature controlled sample stage provides sample temperatures between 80 K (liquid nitrogen temperature, LNT) via room temperature (RT) up to 380 °C. In general, the CL excitation was performed with an electron energy of 10 keV and a beam current of $I_0 = 500$ nA. This beam is scanned over an area of (106×110) μm² providing a current density of $j_0 \approx 5$ mA/cm².

The samples under investigation were 'wet' and 'dry' oxidized SiO₂ layers on Si (111) substrate. The dry oxida-

tion has been performed at a temperature 1100 °C in O₂ ambient with a residual water content of ~4 ppm by weight. For wet oxidation the oxygen flow was passed through de-ionized water at 95 °C. The thicknesses of dry and wet oxide layers were 200 and 250 nm, respectively. The mass density of wet oxidized layers is $\rho = 2.18$ – 2.20 g/cm³, of dry oxidized ones $\rho = 2.25$ – 2.27 g/cm³. Both types of layers are of microelectronic quality prepared in the Research Center Rossendorf in Dresden. Further on, dry oxidized layers have been implanted additionally by oxygen ion O⁺ with doses $D = 1; 5; 10 \times 10^{16}$ ions/cm². This ion implantation technique is described more detailed in [18].

Afterwards, the samples have been thermally treated (in case of ion implantation one may say as well post-annealed) for 1 h in vacuum at temperatures $T_a = 700, 800, 900, 1000, 1100, 1200,$ and 1300 °C. After switching-off the heating the rapid cooling-down process to room temperature RT can be described by an exponential law $T(t) \sim (T_a - RT) \exp(-t/\tau) + RT$ with a mean chilling time of $\tau \sim 90$ s.

3. Results

The CL measurements of wet and dry as well as dry silica layers implanted additionally with oxygen ions are presented in Figs. 1–5.

3.1. Spectra of wet and dry oxides

The high thermal treatment of dry oxide layers at a temperature of $T_a = 1300$ °C in the present work in Fig. 1(top) shows the same effect of the enhanced red–yellow luminescence as described before in a previous work for SiO_x [20]. The yellow band Y is especially developed when measured at room temperature RT. However, here not SiO_x but dry full stoichiometric SiO₂ layers are investigated. Furthermore, we observe only slightly elevated UV and violet V regions. Looking to the wet oxide in Fig. 1(bottom) we see an increase of the yellow region too, but additionally a huge increase of the near ultra-violet (NV) region forming even a new NV band at 330 nm (3.76 eV) when measured at liquid nitrogen temperature LNT, Fig. 1(bottom, left). Moreover, at RT (right) we see a broad band extended from the UV region 250 nm up to the blue region 470 nm. Thereby it exhibits three subbands: the well-known UV band at 290 nm, the new near-UV (NV) band at 330 nm and a violet band at about 400 nm.

In Fig. 2 we see the different bands on their T_a dependences. In dry oxide the yellow–red bands are increasing for $T_a > 1100$ °C; in wet oxide contrary, the blue–UV bands are arising beyond 1100 °C. However, under electron beam irradiation of $j_0 = 5$ mA/cm² these new bands live only a short time $t < 100$ s as can be seen in Fig. 3. Afterwards the spectra resemble each other and possess almost the same common shape of silica CL spectra as to be seen in Fig. 4.

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