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Cathodoluminescence of crystalline and amorphous SiO_2 and GeO_2

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Abstract

Cathodoluminescence (CL) and its temperature-dose behaviour are presented for different crystalline and amorphous modifications of SiO_2 and GeO_2 as well as for Ge-doped SiO_2 layers. The crystalline samples include four-fold coordinated Si and Ge in hexagonal quartz and quartz-like crystals, respectively, as well six-fold coordinated atoms in tetragonal rutile-like crystals. The detected luminescence bands, in general, are attributed to three optical active luminescence centres: the two-fold coordinated silicon (=Si:) and germanium (=Ge:) centre, respectively, the non-bridging oxygen hole centre (NBOHC) and the self trapped exciton (STE). The first ones, the oxygen deficient centres (ODC), are especially developed in both, in the tetragonal crystal rutile-like modifications as well as in glassy states. The huge violet luminescence in Ge-implanted SiO_2 -layers is attributed to the two-fold coordinated Ge in the silica matrix. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The electronic structure of solid materials in different structural modifications is still a problem of contemporary solid state physics. SiO_2 and GeO_2 can exist in quartz-like (hexagonal) crystalline structure or in rutile-like (tetragonal, perovskite-like) structure as well as in glassy amorphous states. SiO_2 and GeO_2 are promising in applications as optical materials, now widely used in optical fibers for telecommunications. Thin amorphous SiO_2 layers as gate or field oxides are

the basic dielectric or insulating material in microelectronics. Doped with Ge atoms these layers are favoured as electroluminescence devices in silicon technology, see e.g. [1], and fabrication of planar waveguides.

The peculiarities of Ge related properties can be studied, e.g., by comparison of Ge doped silicon dioxide with glassy and crystalline germanium dioxide.

In the present paper, microelectronic and electroluminescence SiO_2 -layers pure as well as doped with Ge, respectively, have been investigated by means of cathodoluminescence (CL) in dependence on the electron excitation dose and the temperature. For direct comparison similar measurements were carried out at SiO_2 and GeO_2 quartz and rutile-like crystals in order to correlate the luminescent centres and their precursors with

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defects in four-fold or six-fold coordinated crystal atoms, respectively.

2. Experimental

The CL measurements were performed in a digital scanning electron microscope via a parabolic mirror collector, a spectrograph and a CCD camera, Fig. 1. CL spectra ranging from 1.5 to 6.5 eV were accumulated in single shot mode within a short time of 1 s and with a spectral resolution of 4 nm. A cooling and heating temperature stage provides sample temperatures between 80 and 670 K. In general, the CL excitation was performed with electron energies of 5–30 keV and electron doses up to 0.2 As cm^{-2} . More details of the measurements are given in [2].

Samples under investigation were SiO_2 and GeO_2 , first in hexagonal and tetragonal crystalline states: quartz and rutile-like, then in amorphous state as silica and germanate glass, see Table 1. Furthermore, we have used amorphous, thermally grown SiO_2 layers, 500 nm thick and wet oxidized at 1000°C on $\langle 100 \rangle$ oriented Si substrate. The layers partially were doped by ion implantation with Ge^+ ions of an energy of 350 keV and with doses of $(0.5\text{--}5.0) \times 10^{16} \text{ ions cm}^{-2}$ leading to an atomic Ge fraction of about (0.4–4.0) at.% in the depth of the mean projected ion range of 250 nm. The post implantation annealing was done for 1 h at temperatures $T_A = 950^\circ\text{C}$, 1000°C and 1100°C in dry nitrogen.

Table 1

Samples of SiO_2 and GeO_2 modifications under investigation

crystalline		amorphous
SiO_2	quartz	silica glass
	stishovite (tetragonal)	
GeO_2	rutile-like (tetragonal)	layer $\text{SiO}_2 : \text{Ge}$
	quartz-like	
		germanate glass

The high purity silica samples of the type KS-4V were prepared by electrofusion of synthetic cristobalite, more detailed and described in [3].

The rare high temperature–pressure modification stishovite of SiO_2 in tetragonal, rutile-like structure has been selected from natural samples found in the famous US Arizona Crater.

Tetragonal GeO_2 crystals were grown from the melt of germanium dioxide powder by the ‘top-seed’ method [4]. The melt is cooled down a little bit below the fusion temperature of 1035°C , but kept above 1000°C . In such a way the transition of the hexagonal phase to the tetragonal one is achieved. The crystals were grown on a seed rod introduced to the liquid surface. The remaining fusion after cooling was in a glassy state. In this way also samples of glassy germanium oxide could be studied in comparison with crystalline modifications.

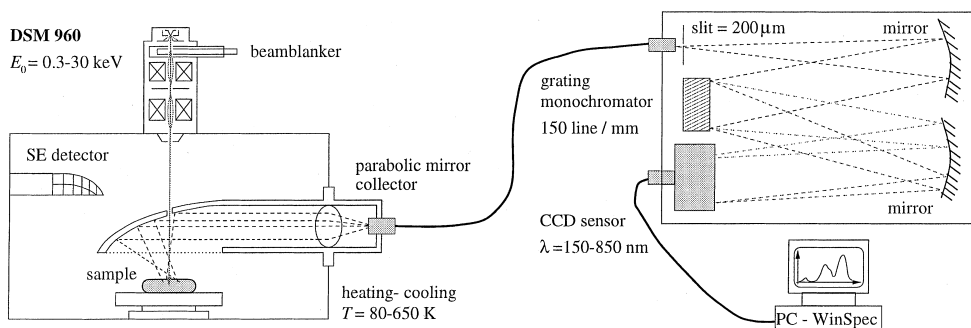


Fig. 1. CL spectrometer, installed in a digital scanning electron microscope.

3. Results

We find certain similarities in the spectra consisting in crystalline and amorphous SiO_2 with a red band (R) at 650 nm due to a band–band recombination centre, a blue (B) 460 nm triplet–singlet and an ultraviolet (UV) 290 nm singlet–singlet defect luminescence band. However, the latter one is not found in hexagonal quartz, but evidently in tetragonal stishovite. At low temperatures a green self trapped exciton (STE) peak appears at 560 nm, see Figs. 2 and 3. Moreover, at room temperatures, the CL spectrum of quartz is

completely different from that of silica. Only a broad red band is well developed, Fig. 2. The blue and the UV bands are partially undetectable. Even a long period of irradiation does not change this situation. Cooling down the crystal to 80 K leads to an appearance and strong increase of a broad structured band containing a dominating green maximum at 515 nm and the blue (B) band, both due to STE luminescence as already demonstrated in [5] as well as the common red (R) band. The green STE band is also found initially in the low temperatures CL spectra of thin film silica but it decays rapidly after the onset of the electron beam

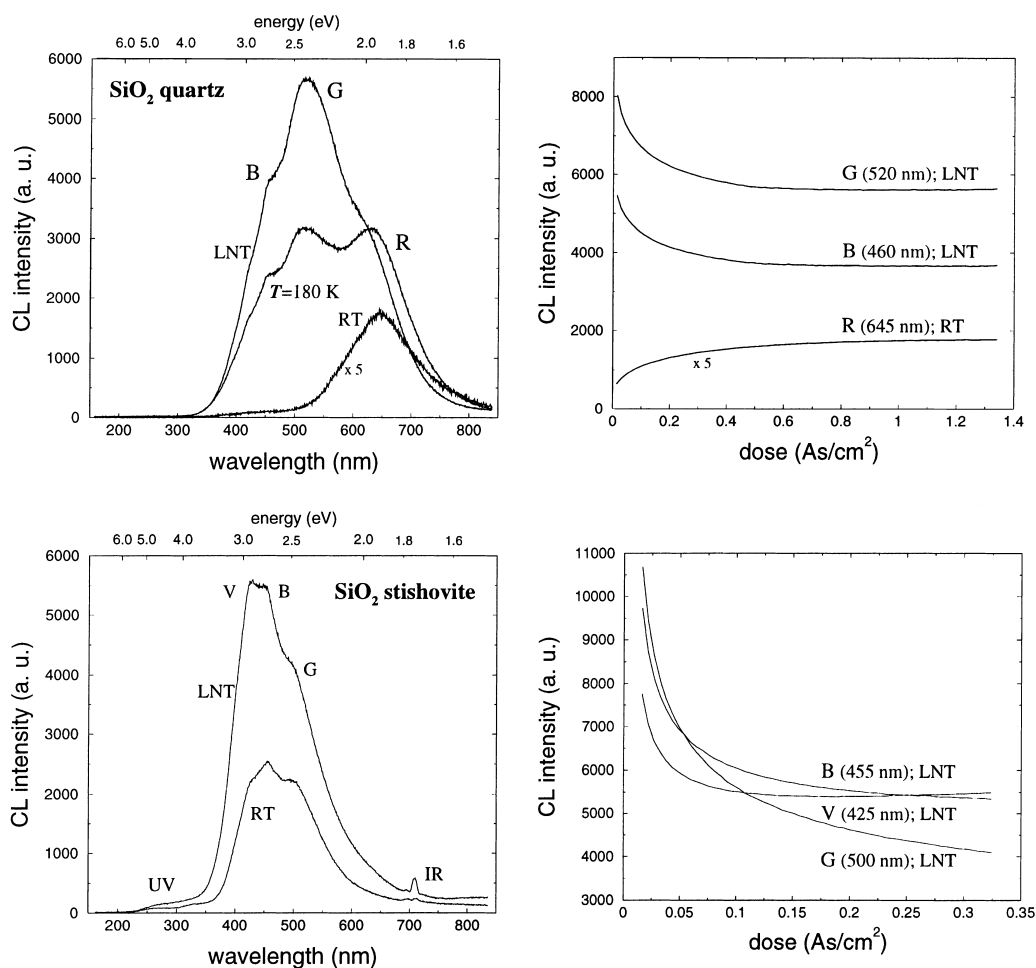


Fig. 2. CL spectra and selected bands dose behaviour of hexagonal SiO_2 quartz (above) and tetragonal rutile-like SiO_2 stishovite (below).

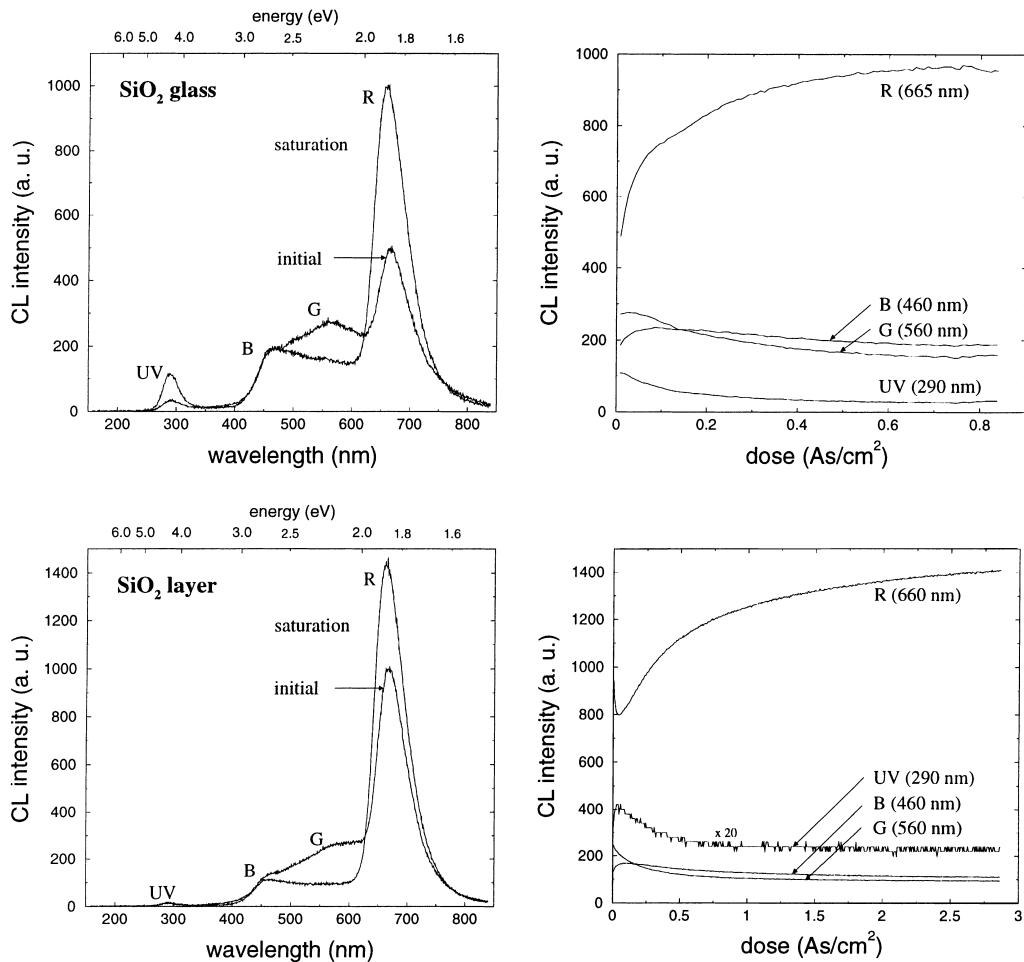


Fig. 3. CL spectra and selected bands dose behaviour of stoichiometric SiO_2 silica glass (above) and a 500 nm thin SiO_2 layer on Si (below) at LNT.

excitation [6]. In quartz even a long irradiation period at the low temperature of 80 K shows the green 515 nm STE band which only slightly decreases in intensity. Whereas a red band (R) appears in a position and with increasing dose behaviour analogous to that of silica glass, the UV band at 285 nm is not detectable in quartz, Fig. 2.

In the tetragonal stishovite we find a broad structured band where we may recognize three peaks at 420, 460, and 500 nm, see Fig. 2. These three peaks are also present in the hexagonal quartz spectra, however, a separate red peak (R) cannot be observed in stishovite. Instead of that we find a small and narrow near-infrared (IR)

band at about 710 nm. Furthermore, contrary to the quartz crystal, the ultraviolet band (UV) at 260 nm appears.

The samples, both crystals and glasses of GeO_2 possess green–yellow luminescence at about 550 nm, Fig. 4, and only in rutile-like GeO_2 a violet luminescence at 400 nm. The violet luminescence is the principal band under electron beam excitation. In [4] was found that the duration of the violet luminescence is in the order of ns whereas the decay kinetics of the green–yellow luminescence band at 550 nm are slightly non-exponential, but may be sufficiently well characterized by an exponential law. So at room temperature a mean decay

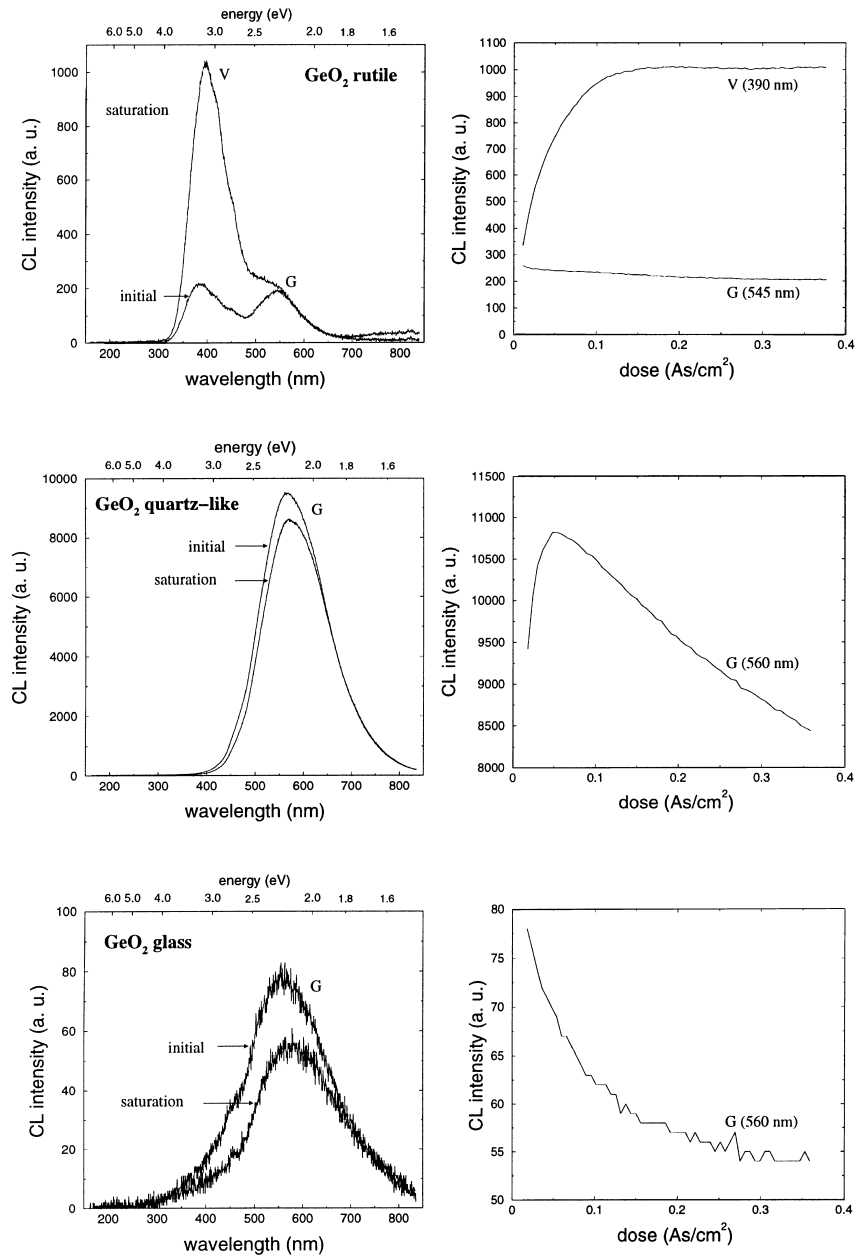


Fig. 4. CL spectra and selected bands dose behaviour of a tetragonal GeO₂ rutile-like crystal (above), a hexagonal GeO₂ quartz-like crystal (middle) and of a germanate glass (below), all at LNT.

time constant of about 130 μ s was found; for 80 K about 250 μ s. Thus the decay duration is decreasing with temperature. Together with the intensity–temperature dependence a thermal quenching processes should be assumed [4].

The spectra of Ge-doped amorphous SiO₂ layers are composed in a mixture, Figs. 5 and 6. Whereas the red luminescence (650 nm) from the SiO₂ matrix is conserved, the violet band at about 400 nm is overtaken from GeO₂ rutile indicating a

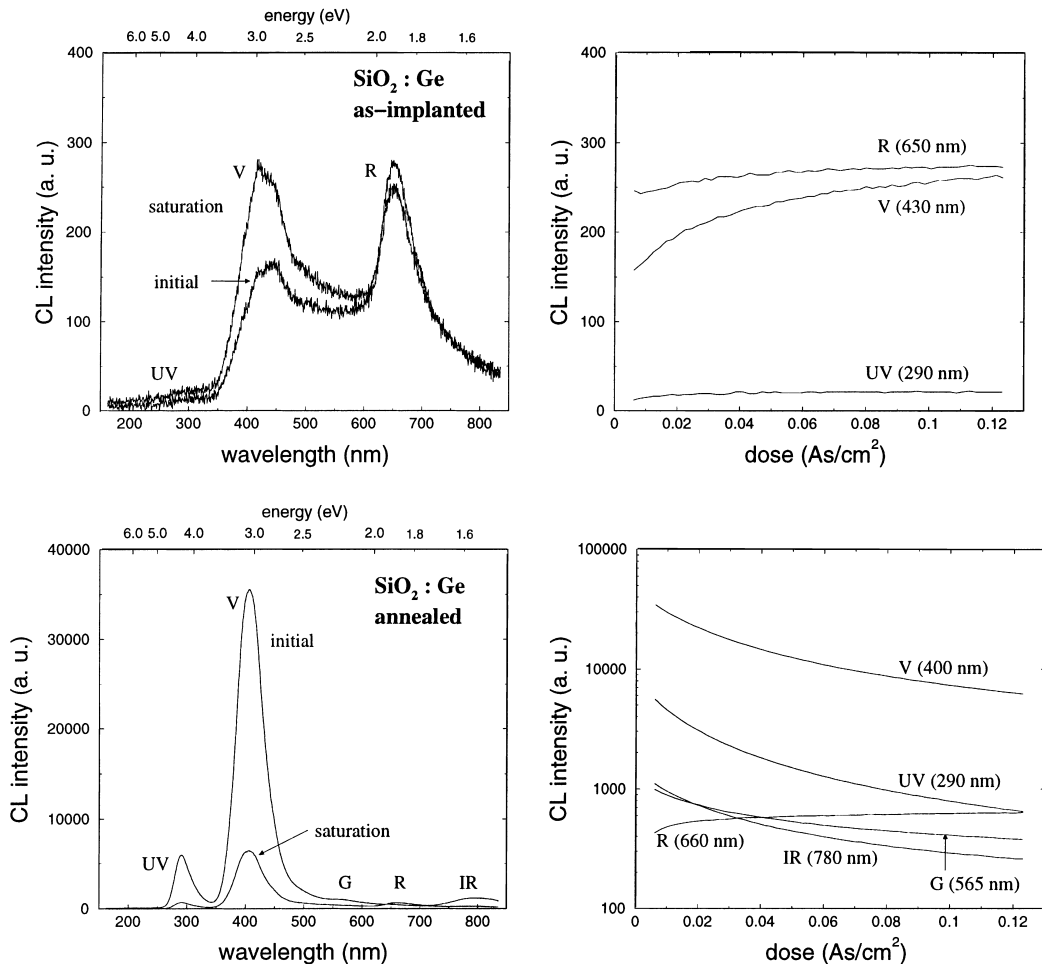


Fig. 5. CL spectra and selected bands dose behaviour of Ge^+ implanted SiO_2 layers on at LNT, implantation dose $5 \times 10^{16} \text{ cm}^{-2}$, as-implanted, not annealed (above) and thermally annealed at temperature $T_A = 1000^\circ\text{C}$ (below). The latter spectra show a huge violet emissivity.

strong defect luminescence at the Ge dopand centres.

After thermal annealing at temperatures $T_A = 950\text{--}1100^\circ\text{C}$ this violet band of the Ge doped silica is strongly increasing up to a factor of 200 and dominating the spectra, Figs. 5 and 7.

4. Discussion

According to the Skuja model [7], in SiO_2 and GeO_2 we assume the two-fold coordinated silicon =Si: and the two-fold coordinated germanium

=Ge:, respectively, as the triplet–singlet luminescence centres. One possible way of its generation is given by transformation from a simple oxygen vacancy due to electron beam induced bond cleavage and subsequent reordering [8]. This model of an oxygen vacancy does not contradict the Weeks model of interstitial oxygen [9,10], where the oxygen is replaced by ionizing radiation with energies greater than the band gap energy $E_g \approx 10 \text{ eV}$. However, the question remains whether the blue (B) and ultraviolet (UV) luminescence stems from Si or O-related centres. We should consider it in context with the Ge-doped SiO_2 -layers and Fig. 6. There we

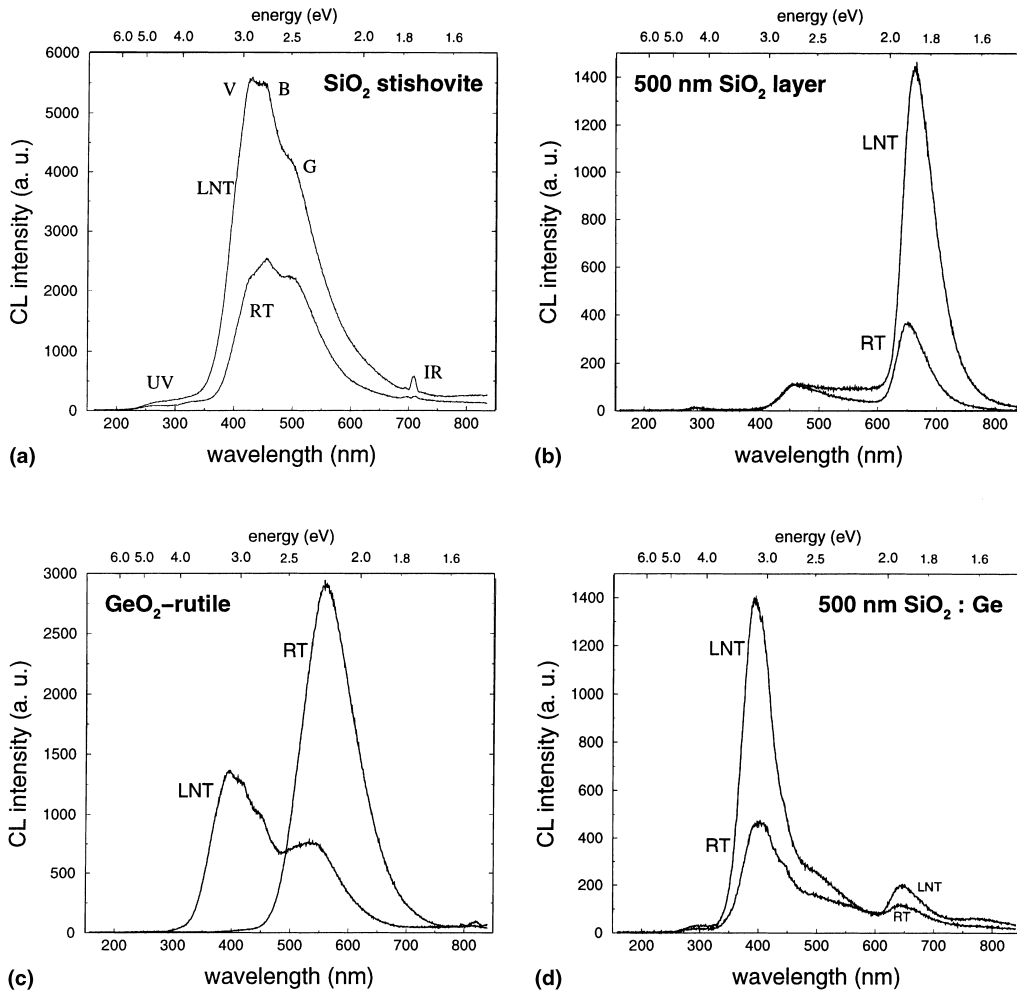


Fig. 6. Comparison of Si and Ge related CL spectra: (a) SiO₂ rutile-like crystal stishovite; (b) 500 nm SiO₂ layer on n-Si substrate; (c) GeO₂ rutile crystal; (d) 500 nm SiO₂ layer (sample b) but Ge-doped ($5 \times 10^{15} \text{ cm}^{-2}$); electron beam: $E_0 = 10 \text{ keV}$, $j_0 = 5 \times 10^{-3} \text{ A cm}^{-2}$, in deep saturation ($j_0 \times t_s \simeq 1 \text{ As cm}^{-2}$) at liquid nitrogen (LNT) and room (RT) temperature.

see that the main violet luminescence as well as the green–yellow luminescence, unambiguously, are related to the new species Ge and obviously not to interstitial oxygen in the host network of SiO₂. Moreover, in both crystalline phases of SiO₂ (Fig. 2) the short range dose behaviour of the blue (B) and the green (G) band shows a strong decay not supporting a creation of luminescence centres by electron impact displacement of regular oxygen atoms. Viceversa, the strong dose kinetics decay shows that the luminescence centres exist already in non-irradiated samples. This fact and the high CL yield may

demonstrate that these luminescence centres could be STE present in defect-less regions of quartz and stishovite. But here, still more investigation is expected in the next paper.

On the other hand, as well established, the red band (R) in different SiO₂ modifications is attributed to the non-bridging oxygen hole centre (NBOHC).

According to the blue luminescence in SiO₂ we should be authorized to ascribe the analogous nature of the green–yellow luminescence in hexa- and tetragonal GeO₂ crystals. The long duration

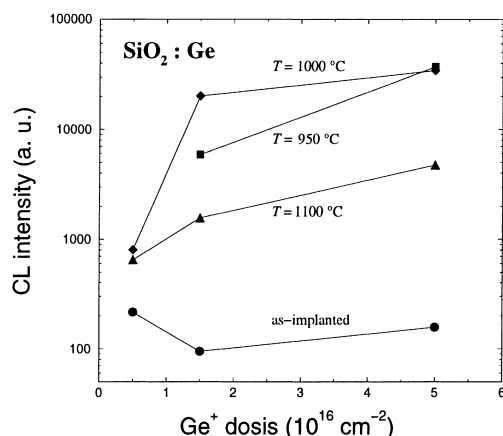


Fig. 7. Initial CL intensity of the violet 400 nm band of the Ge doped SiO₂ layer on Si at LNT in dependence on the Ge⁺ implantation dose and the annealing process over 1 h at different annealing temperatures T_A as parameter.

of the green–yellow luminescence ($\tau \approx 200 \mu\text{s}$) can be attributed to a triplet–singlet transition and the fast violet luminescence (ns) should be related to the singlet–singlet transition, both of the same luminescence centre. However, the relation between these two bands is not constant. The violet band is relatively small developed in X-ray excited luminescence but it becomes dominant in CL. The different behaviour of the triplet–singlet band and the singlet–singlet band under different excitation was also observed in the case of oxygen deficient centres (ODC) in pure germanium dioxide glasses [7]. It has been explained by complicated interactions with the surroundings of the centre in excited states and that these interactions are different for triplet and singlet excited states. Now we may use the same explanation for the centres in our GeO₂ samples studied here.

The nature of both the bands in tetragonal germanium dioxide crystals possessing slow (about 200 μs) and fast (ns) kinetics is ascribed to triplet and singlet transitions in ODC, here interpreted as the two-fold coordinated germanium centre = Ge:. Under nitrogen laser excitation only the green–yellow triplet–singlet transition is excited with a slow decay of luminescence.

So, we did not see any other luminescence band of tetragonal GeO₂, i.e., in the background of luminescence induced by oxygen deficiency. We

cannot support or refuse the existence of the STE, also in the case of tetragonal germanium dioxide crystals, although the STE luminescence of quartz-like germanium dioxide is situated in the same spectra range [11]. Therefore, the ODC may be produced only in tetragonal crystals with six-fold coordinated germanium and not in hexagonal ones with four-fold coordinated Ge atoms. Then the oxygen deficient centre in pure germanium dioxide may exist in parts of glassy structure more resembling six-fold coordinated germanium in a short range order. The same description can be given for SiO₂ with the two-fold-coordinated silicon centre = Si:, obviously, only present in tetragonal stishovite and evidenced by the appearance of the UV peak at 260 nm due to the singlet–singlet transition in this centre.

Once transformed the luminescence centres in the undoped SiO₂ samples are relatively stable. At room temperature there is no measurable change in CL intensity after an irradiation break of several hours. Even a post-annealing in vacuum at 600 K for about 1 h does not change the CL intensity. On the contrary to the undoped samples, in Ge-doped silica samples the luminescence efficiency changes during the annealing process with temperature T_A and time, Fig. 7. This process is comprehensively described in [1], where Ge diffusion processes, precipitation and finally nanocluster formation by Ostwald ripening have been investigated by Rutherford backscattering (RBS), transmission electron microscopy (TEM) in cross-section techniques and X-ray photoelectron spectroscopy (XPS). There the huge violet luminescence is related to different states (or phases) of Ge, namely to GeO₂ dissolved in the near SiO₂ surface region and to Ge nanocrystals located deeper in the SiO₂ layer which may be (partially) oxidized at their interface to the surrounding amorphous SiO₂ matrix.

5. Conclusions

Whereas in SiO₂ we find the three well-known bands R, B, UV as well as the STE luminescence, in GeO₂ there are two luminescence bands: a green–yellow one at 550 nm and a violet band at 400 nm with slow ($\tau = 130\text{--}250 \mu\text{s}$) and fast ($\tau < 20 \text{ ns}$)

decay, respectively. The luminescence can be excited either in inner-centre and electron–hole recombination processes. An analogous luminescence, however with strong non-exponential decay, is observed in glassy materials. The luminescence is ascribed to oxygen deficient luminescence centres, especially two-fold coordinated $=\text{Si}\cdot$ and $=\text{Ge}\cdot$ centres, respectively. The existence of such centres in SiO_2 and GeO_2 crystals with tetragonal rutile structure and the lack of those ones in hexagonal quartz-like structure are a proof for the existence of these ODC in structural elements with six-fold coordinated silicon or germanium, found in crystals with rutile structure as well as in silica and germanate glasses. In Ge-doped SiO_2 layers the red (R) luminescence due to NBOHC of the silica matrix is preserved, but the huge violet (V) band at 400 nm is attributed to two-fold coordinated $=\text{Ge}\cdot$ centres as observed in rutile-like GeO_2 crystals. These centres in Ge^+ implanted silica layers are especially developed during thermal annealing accompanied by Ge nano-cluster formation, probably embedded in a GeO_2 (or GeO_x) surroundings within the silica matrix.

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