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Electron beam induced optical and electronical properties of SiO_2

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Abstract

Ionizing radiation in dielectric and optically transparent silica as well as thin SiO_2 layers produces defect luminescence as well as charge storage. A comparison of different excitation–relaxation processes like cathodoluminescence, charge injection and trapping, secondary electron field emission, and exoelectron emission leads to a generally similar excitation dose behaviour described by an electron beam saturation dose of 0.01–0.1 C/cm^2. This suggests a correlation of these four electron excitation mechanisms likely related to the same kind of defect in glassy SiO_2, the 2-fold-coordinated silicon =Si: centre with typical electronic singlet–singlet and singlet–triplet transitions according the Skuja model. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Amorphous silicon dioxide is still of great importance in microelectronics and modern communication technology. Extrinsic and intrinsic defects have a decisive influence on the material efficiency and its application. Several defects in amorphous silica are optically active and can be studied by luminescence spectroscopy [1].

Cathodoluminescence (CL), the emission of light as a result of electron irradiation, is particularly suitable for investigation of thin films, whereas photoluminescence is rather difficult to measure because of the small efficiency in thin layers. By means of CL large excitation doses are obtained within a thin layer.

However, ionizing radiation in the dielectric and optically transparent material SiO_2 produces defects, charge trapping, luminescence as well as exoelectron postemission. All these phenomena have been investigated in context. Under cathodo-excitation, e.g. the main blue luminescence band at 460 nm (2.7 eV) is appearing and then strongly growing with an exponential saturation [2].

From the energy position of the luminescence bands and their behaviour with respect to the electron irradiation dose and the temperature we may expect new findings about the nature of defects and luminescence centres. Moreover a comparison of different excitation–relaxation processes like CL, charge injection (IV) and charge trapping, secondary electron field emission (SEFE), and exoelectron emission (EEE) will provide similarities and additional information of defects in glassy SiO_2.

2. Experimental

The electron beam irradiation experiments of crystalline and non-crystalline modifications of SiO_2 in view of the electron dose and temperature behaviour were performed an a scanning electron microscope (Zeiss DSM 960) additionally equipped with a cathodoluminescence parabolic mirror collector and sample temperature controller, Fig. 1. Electron energies of $E_0 = 0.5$–30 keV and the current densities $j_0 = 10^{-5}$–10^{-3} A/cm^2 have been used. Details of the experimental set up are given in [2].

Samples under investigation were crystalline quartz, thin amorphous SiO_2 layers, stoichiometric silica glass and oxygen deficiency silica glass. Quartz and silica are bulk samples, but the amorphous layers are thermally dry oxidized SiO_2 films with oxide thickness of 100–500 nm on silicon substrate, as usually used in microelec-

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tronics. The oxygen deficiency silica samples have a silicon excess of 0.015 wt.% produced by melting of SiO_2 cristobalite in Si vapour, see [3].

The change of optical properties were compared with corresponding alteration of the electronical behaviour. Electron beam charge injection into insulating layers is observed directly by means of SEFE. SEFE is based on extremely field-sensitive Fowler–Nordheim (FN) tunnelling of electrons from conducting substrates into and through insulating layers and indicating the charging-up state [4].

As an alternative method to record the release of trapped electrons we have used thermally stimulated exoelectron emission (TSEE) after electron beam excitation. Experimental details of TSEE are described more thoroughly in [5]. The instationary exoelectron emission during the thermal stimulated relaxation process is counted by means of a channeltron placed in front of the sample.

In order to get information on the structural changes of the SiO_2 network we have investigated the vibrational behaviour of amorphous SiO_2 films before and after electron irradiation. The IR measurements were performed by means of a Fourier-transform infrared (FTIR) spectrometer (Nicolet Magna IR 550) in transmission and in reference with blank Si substrates [6].

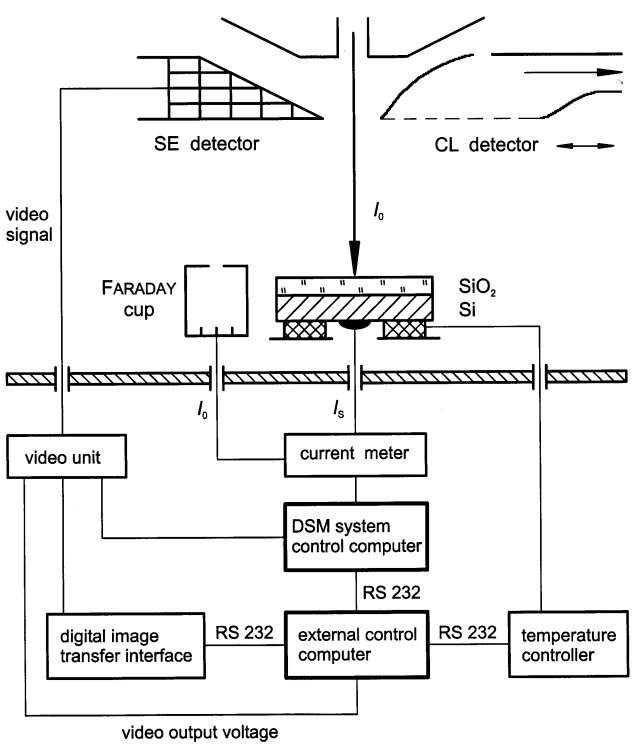

Fig. 1. Scheme of the charge injection system (SEFE) with CL installed in a digital scanning electron microscope DSM 960 (Zeiss).

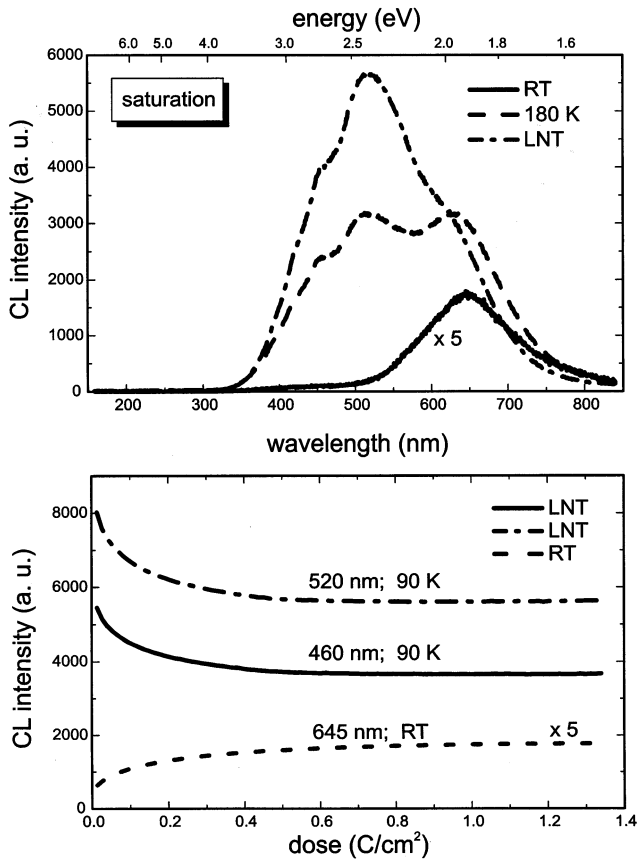

Fig. 2. (a) CL spectra of quartz crystal; (b) dose behaviour of selected bands; $E_0 = 15$ keV, $j_0 = 400$ nA.

3. Results and discussion

The cathodoluminescence experiments show that in all non-crystalline samples three characteristic luminescence bands are detected, Figs. 2–4: a red band at 650 nm (1.9 eV), a blue band at 460 nm (2.7 eV) and an ultraviolet band at 290 nm (4.3 eV), see also Refs. [1,2]. At low temperatures, the bands are increasing in intensity, and furthermore, a fourth band in the green area at 560 nm (2.2 eV) appears, Figs. 3 and 4. This band is attributed to the self-trapped exciton (STE) [4]. It is stable in the crystalline material quartz, see Fig. 2, but it decays in amorphous samples under electron irradiation doses already of about 0.01 C/cm^2 [7]. Obviously, the electron beam irradiation destroys quasi-crystalline short-range areas in the amorphous SiO_2. The CL dose behaviour indicates a causal relationship of the blue (B) and the UV luminescence band. This complex luminescence centre is associated with defect precursors like the single oxygen vacancy that may be transformed to the twofold coordinated silicon centre ≡Si: under electron beam irradiation [8], see also Fig. 8.

On the other hand, the red band shows a completely different dose behaviour. In all samples, we have observed an increase of its intensity with irradiation dose.

This luminescence centre is associated to the non-bridging oxygen hole centre (NBOHC) [1,2].

The cathodoluminescence dose behaviour of all samples investigated here is summarized in Table 1, detailed information is also given in [7].

In Fig. 5 a typical SEFE charge injection and thermal release cycle is presented. After very rapid positive charging-up and fixing the FN-field strength $F_0 \approx 7$ MV/cm, slower electron trapping over the whole injection time $t = 1000$ s is observed, indicated by decrease of the SE rate. During the following thermal stimulation, holes and electrons are detrapped, obviously from different centres at different temperatures. From the electron incorporation we may deduce an electron beam saturation dose of 0.03 C/cm^2 and an electron trapping cross section of about $\sigma = 9 \times 10^{-8}$ cm^2. This is close to the trapping cross section ($\approx 10^{-7}$ cm^2) of the non-bridging oxygen centre (NBO) found in [9].

However, since the electron incorporation and the blue (B) luminescence in stoichiometric SiO_2 layers show a very simultaneous dose behaviour, especially both are starting from zero (contrary to the red (R) luminescence of the NBO) we are inclined to associate the long term electron trapping with the twofold-coordinated silicon centre.

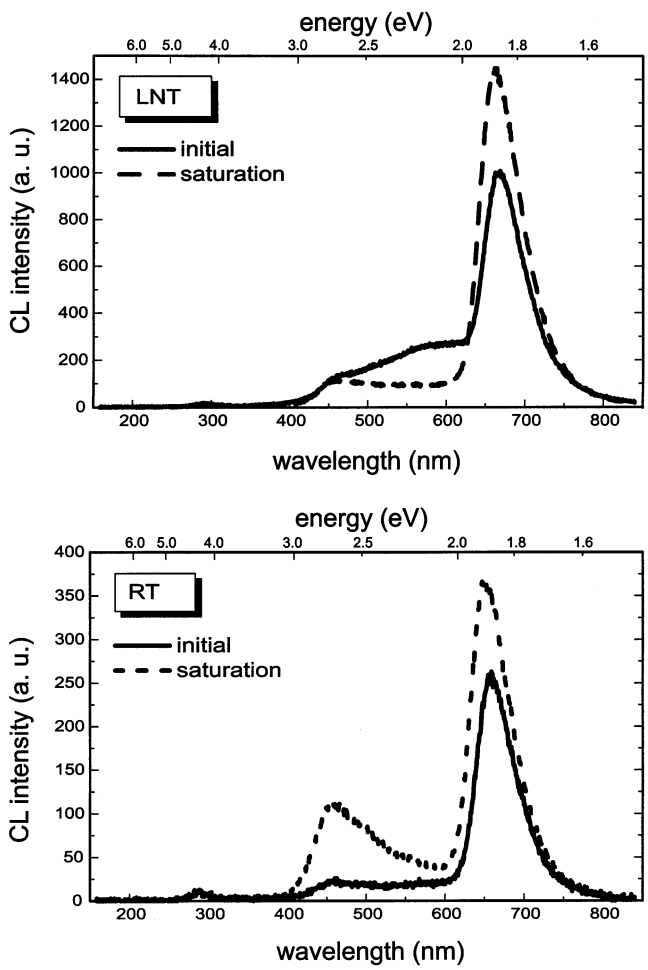

Fig. 3. CL spectra of a 500 nm thin SiO_2 layer; $E_0 = 10$ keV, $j_0 = 170$ nA (a) T, low temperature, (b) T, room temperature.

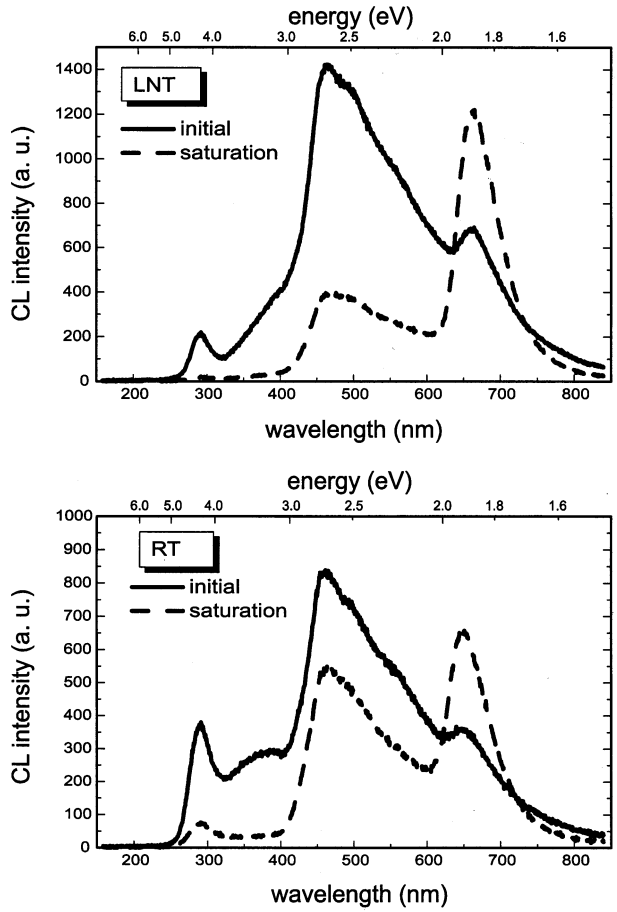

Fig. 4. CL spectra of silica with oxygen deficiency; $E_0 = 15$ keV, $j_0 = 400$ nA (a) T, low temperature, (b) T, room temperature.

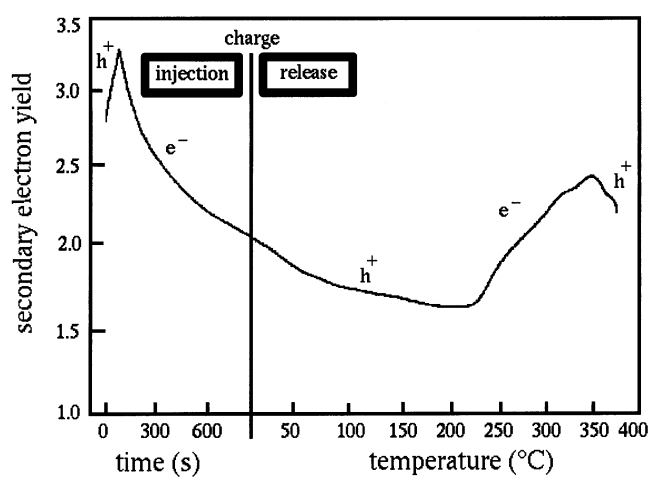

Fig. 5. Typical SEFE cycle with fast hole storage at the beginning, turnaround and long term electron incorporation with time; the thermal stimulation shows slight hole emission and then strong electron release between 250 and 350°C; sample: 30 nm SiO_2 on Si.

Table 1
Evaluation of the intensity of detected cathodoluminescence bands with increasing electron irratiation dose at low temperature and room temperature

Band (nm)	UV (290)		Violet (380)		Blue (460)		Green (560)[a]		Red (660)[b]	
	Low temperature	Room temperature	Low temperature	Room temperature	Low temperature	Room temperature	Low temperature	Room temperature	Low temperature	Room temperature
Quartz					↘		↘			↗
SiO_2-layer	↷	↷			↷	↗	↗		↷	↗
Silica stoich.	↷	↷			→	↗	↗		↗	↗
Silica O-def.	↘	↘	↘	↘	↘	↘	↗	↘	↗	↗
TEOS								↗[c]	↷	↷

[a] Quartz (520).
[b] Quartz (645).
[c] $T = 500$ K.

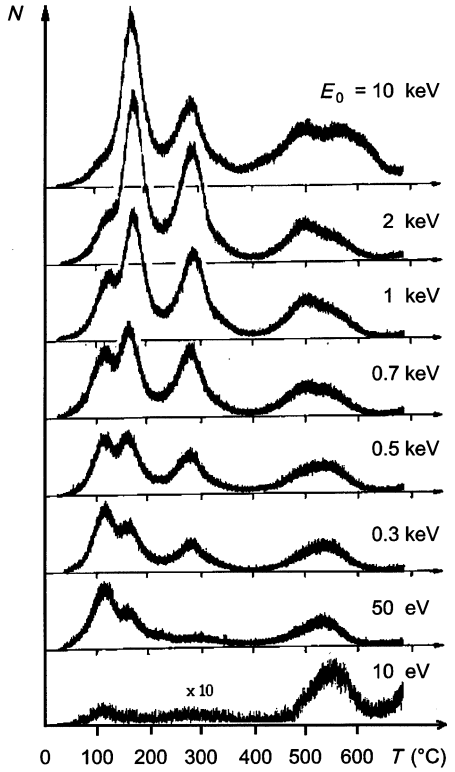

Fig. 6. Thermally stimulated exoelectron emission (TSEE) from a 300 nm SiO_2 layer after electron bombardment with energy E_0 and saturation doses 0.01 C/cm^2; heating rate $\approx$0.3 K/s.

In Fig. 6 TSEE curves from a SiO_2 layer after electron irradiation are presented. The electron beam energy $E_0 = (10–10\,000)$ eV has been varied in order to distinguish between volume and surface excitation. Both of the main TSEE peaks at 170 and 280°C vanish at low-energy electron excitation, i.e. they should be associated with volume centres. Their excitation dose behaviour with a saturation of nearly 0.01 C/cm^2 is similar to that of CL and SEFE discussed above.

From FTIR spectra, Fig. 7, we have recognized a softening of the TO-stretching mode at 1090 cm^{-1} by about 10 cm^{-1} towards lower wave numbers associated with an increase of the FWHM by 15 cm^{-1} and a lowering of the vibrational strength. After a thermal treatment of the irradiated samples, we detect a partial annealing of irradiation structural defects. The related structural models are discussed in Fig. 8.

4. Conclusions

We may realize an important difference of the luminescence spectra of amorphous and crystalline samples. In quartz samples at room temperature, we detect only the red luminescence, but this band, Fig. 2, is spread widely, much more than in amorphous samples. At low temperatures, the red band is almost covered by the stable blue and green luminescence bands. The intensity of the quartz bands is about 100 times higher than of those in amorphous materials.

A comparison of different excitation–relaxation processes like CL, IV and charge trapping, SEFE, Fig. 5, and EEE, Fig. 6, leads to a generally similar excitation–dose behaviour described by an electron beam saturation dose of about 0.01–0.1 C/cm^2, see also [6]. This suggests itself a correlation of these four excitation mechanisms likely related to the same kind of defect in glassy SiO_2, the 2-fold coordinated silicon centre ≡Si: of the Skuja model [8].

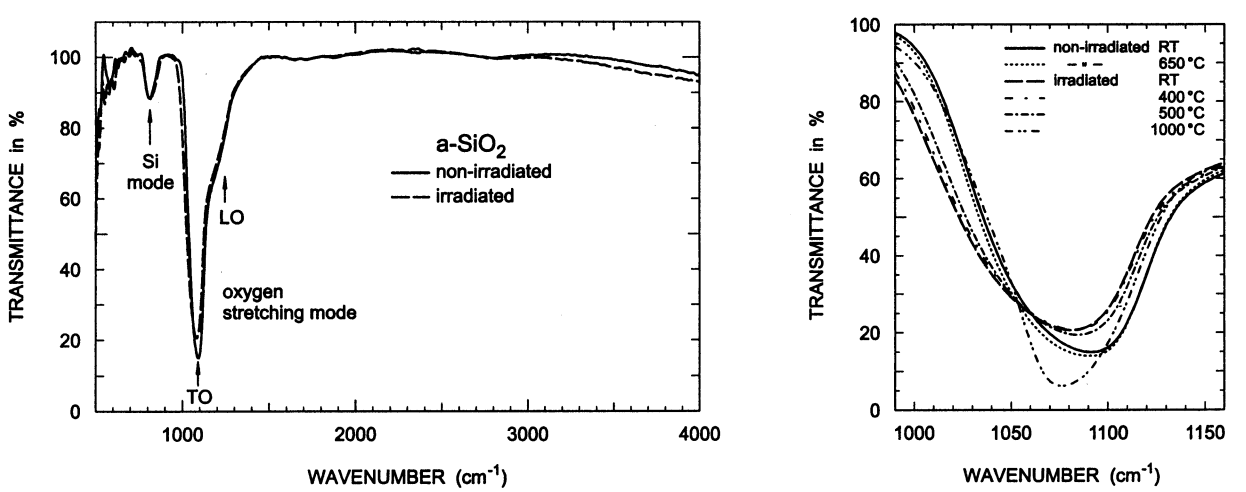

Fig. 7. IR spectra of non-irradiated SiO_2 on n-Si in order to indicate the mode softening due to electron irradiation as well as the partial thermal annealing.

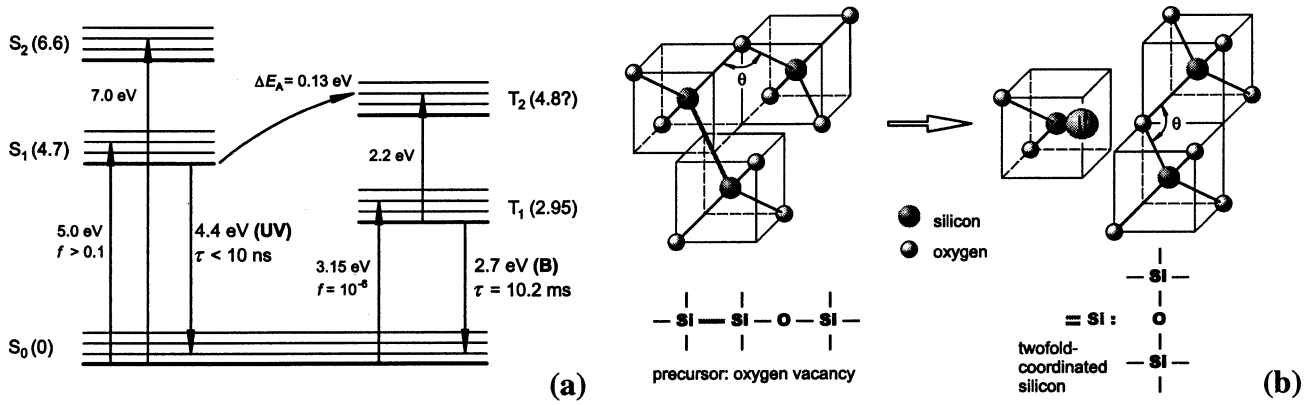

Fig. 8. (a) Extended energy scheme of the =Si: centre by Skuja [8]; (b) transformation of a simple oxygen vacancy as a precursur for the optical active twofold-coordinated silicon defect within the SiO_2 network.

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