Luminescence and Si and Ge Nanocluster Formation in Silica

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Abstract

Cathodoluminescence (CL), high resolution transmission (HR-TEM) and scanning transmission electron microscopy (STEM), and energy dispersive X-ray analysis (EDX) have been used to investigate Si and Ge cluster formation in amorphous silicon dioxide layers and their respective luminescence behavior. In Ge+ ion implanted SiO2 an additional violet (V) Ge related emission band is identified at (410 nm). A post-implantation thermal annealing at temperatures Ta = 700, 900, 1100°C for 60 minutes in dry nitrogen or vacuum leads to a huge increase of the violet luminescence up to 900°C, followed by a decrease towards 1100°C. The strong increase of the violet luminescence is associated with formation of low-dimension Ge aggregates like dimers, trimers and higher formation; the following decay of luminescence is due to further growing to Ge nanoclusters.

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1. Introduction

Amorphous silicon dioxide (a-SiO₂) is an important dielectric material with diverse use in modern microelectronic devices [1] and optical fiber communications [2,3]. The optical properties of the glass, such as absorption [4], photoluminescence [5], and nonlinear optical properties [6], are significantly affected by the presence of dopants and nanoclusters.

In this context the physical properties of small nanometer-sized particles in the silica matrix have received considerable attention in recent years. Such structures are usually prepared by ion implantation which is a commonly used technique for the addition of dopants to thin layers and can effortlessly produce nanometer-sized clusters within the host material.

Hence silicon (Si) and germanium (Ge) are common dopants in silica technology. Ge implantation is frequently used in a variety of applications in communication and sensing technology such as photoinduced Bragg gratings in optical fibers. In this way Ge atoms can be located in the SiO₂ host network and give rise to the violet and UV cathodoluminescence emission at 3.1 and 4.2 eV, see [7,8].

In this article, we focus on the use of cathodoluminescence (CL) spectroscopy in combination with energy-dispersive X-ray analysis (EDX) hosted both in a scanning electron microscope (SEM) to understand the physical structure and formation mechanisms of Si and Ge nanoclusters and their influence on the luminescence defect centers. Moreover, the formation of Si and Ge nanoclusters in the amorphous silica matrix is demonstrated by high-resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (STEM).
2. **Experimental**

The cathodoluminescence (CL) measurements were performed in a digital scanning electron microscope (Zeiss DSM 960). The CL spectra over the wavelength 200-800 nm were detected via a parabolic mirror collector and analyzed with a Spex-270M spectrograph then registered by a charge coupled device (CCD) camera in single shot technique and with a spectral resolution of 4 nm. A cooling and heating temperature stage changed the sample temperatures between 80 and 670 K. In general, the CL excitation was performed with electron energies of 2-30 keV and beam currents of about 100 nA in TV scanning mode over an area of 2.9×10^{-5} cm². This corresponds to an electron beam current density \( j_e \approx 3.3 \text{ mA/cm}^2 \). With 512×512 pixels the scanning beam focus of a diameter \( \approx 1 \text{ µm} \) is strongly (\( \approx 90\% \)) overlapping from pixel to pixel and guarantees a homogeneous excitation over the excited area.

As samples we have used amorphous, thermally grown SiO₂ layers, 500 nm thick, wet oxidized at 1100 °C on a Si-substrate. The layers are of microelectronic quality and have been doped by ion implantation with Ge⁺ ions of an energy of 350 keV, with Si⁺ ions of 150 keV, and O⁺ ions of 100 keV, all with a uniform dose of 5×10^{16} ions/cm² leading to an atomic dopant fraction of about 4 at.% roughly in the half depth of the SiO₂ layer, see Fig.1.

Afterwards, a post-implantation thermal anneal was performed at temperature \( T_a = 900 - 1100 \) °C for 1 h in dry nitrogen. The growth of Si and Ge nanoclusters has been shown by means of a scanning transmission electron microscope STEM (200 keV FEI Tecnai F20) in cross section technique as demonstrated in Fig.1 (right). Si nanoclusters have been made visible by transmission electron microscopy (100 keV TEM, EM-420 Philips).
3. Results and Discussion

The main luminescent centers in pure, silicon, and oxygen implanted silica are the red luminescence λ=650 nm (1.9 eV) of NBOHC and the ODC centers with a blue λ=460 nm (2.7 eV) and ultraviolet luminescence λ=290 nm (4.2 eV), as to be seen in Fig. 2 where the spectra of pure SiO2 layers on a Si substrate as well as doped with Ge+, Si+, and O+ ions are compared. In Ge-doped amorphous SiO2 layers an additional luminescence band is detected at λ=410 nm (3.1 eV) and the red luminescence from the NBOHC center of the SiO2 matrix is conserved. In Fig. 2 we recognize a larger blue (B) emissivity of the Si+ implanted layer compared to the pure and the O+ implanted ones as well as a larger red (R) luminescence of the O+ implanted samples with respect to the Si+ implanted ones. Thus we state that a silicon surplus or, in other words, oxygen deficiency in SiO2 increases the blue luminescence, whereas an oxygen surplus does not affect the blue luminescence but increases the red luminescence.

In Ge+ implanted samples, the common bands of pure SiO2 appears also but are not dominant ones. The violet luminescence (410 nm) is related to different states or phases of Ge, namely to GeO2 dissolved in the near SiO2 surface region and to Ge nanoclusters [9] even low dimensions aggregates like dimers Ge-Ge, trimers up to hexamer rings, [10] located deeper in the SiO2 layers which may be partially oxidized at their interface to the surrounding amorphous SiO2 matrix. Parallele to the increase of the annealing temperature $T_a$ the violet luminescence as well as the nanocluster size is growing from 2-4 nm at $T_a=900 \, ^\circ$C to 5-10 nm at $T_a=1100 \, ^\circ$C as shown in Fig. 3.

The formation of oxygen deficient centers (ODC) or even higher aggregates by means of electron beam irradiation has been manifested already earlier, see e.g. [10]. Even Auger electron spectroscopy (AES) has clearly evidenced that oxygen is dissociated from SiO2 due to electronic or thermal processes during electron beam excitation, see e.g. [11].
Thus we may assume electronic as well as thermal dissociation [12] of oxygen from the thin SiO$_2$ layers and more and more the appearance of under-stoichiometric SiO$_{x}$. This SiO$_{x}$ will undergo a phase separation described as below:

$$\text{SiO}_x \rightarrow \frac{x}{2}\text{SiO}_2 + (1-\frac{x}{2})\text{Si} \quad 1 < x < 2 \quad (1)$$

After heavy electron beam irradiation we observe Si cluster formation as presented already in [10] with a most probable cluster diameter of 4 nm and a maximum diameter of 10 nm. It can be expected that such clusters will be luminecent in the near IR region. Fig. 4 shows the CL spectra of pure crystalline Si and the spectra of Si nanoclusters embedded in the host silica. Luminescence bands are observed at around 1.1 eV and 1.3 eV assigned to crystalline and amorphous silicon phases, respectively. Another band at 1.6 eV is also to be seen after heavy electron beam bombardment in the SiO$_2$ structure.

Recently Si nanocrystals have been fabricated by thermal treatment of SiO-SiO$_2$ nanolattices, in a way which enables to control not only the size but also the density and the arrangements of the nanocrystals, [13,14]. In this method a strong photoluminescence (PL) and a size dependent shift of the PL position are shown as a proof for size control. A strong blueshift from 960 nm (1.3 ev) to 810 nm (1.5 eV) with decreasing nanocrystals size was observed with respective cluster sizes 3.8 nm and 2 nm, respectively.

4. Conclusions

Electron irradiation of $\alpha$-SiO$_2$ layers induces chemical defect reactions dependent on the sample oxidation, thermal annealing and CL measurement temperature. The red band R (1.9 eV ; 650 nm) is associated with the non-bridging oxygen hole center (NBOHC) whereas the blue band B (2.7 eV ; 460 nm) and the ultraviolet band UV (4.2 eV ; 295 nm) are attributed to the Si related oxygen deficient center (SiODC). In Ge$^+$-implanted SiO$_2$ a huge violet band V (3.1 eV ; 410 nm) associated with the Ge related oxygen...
deficient center (GeODC) dominates the CL spectra. After thermal annealing in dry nitrogen or in vacuum at temperature around $T_a=900 \, ^\circ\text{C}$ all luminescence bands grow. Thus the SiODC’s as well as the GeODC’s are formed by Si and Ge molecules clustering to dimers, trimers and higher aggregates. With further aggregation and growth to Si and Ge nanocrystals embedded in the SiO$_2$ matrix, the blue (SiODC) and the violet (GeODC) luminescence decreases again. The nanoclusters size are growing with annealing temperature from 2-4 nm at $T_a=900 \, ^\circ\text{C}$ to 5-10 nm at $T_a=1100 \, ^\circ\text{C}$. Further on, heavy electron beam bombardment of SiO$_2$ and associated oxygen dissociation creates Si nanoclusters in the size range of 2-10 nm with a most probable diameter of 4 nm giving rise to the luminescence in the near IR around 1.3 and 1.6 eV.
References

**Caption of figures**

**Fig. 1** Electron beam excitation densities in SiO$_2$ layers for different beam energies $E_0$. Here we show the Ge$^+$ implantation profile in the mean projected range $R_p=200$nm. On the right hand side a STEM micrograph of the sample is shown in cross section technique.

**Fig. 2** Typical CL-spectra of a pure SiO$_2$ layer in comparison to O$^+$, Si$^+$ and Ge$^+$ implanted layers recorded at room temperature (RT): Note the huge violet band in SiO$_2$:Ge; all after a post-implantation thermal annealing at $T_a=900\,^\circ$C.

**Fig. 3** CL intensities of Ge implanted SiO$_2$ layers passing a maximum at $T_a = 800 – 1000 \,^\circ$C (top) and the respective STEM cross section image showing the clusters growing by Ostwald ripening (middle) and the cluster size distributions (bottom).

**Fig. 4** CL spectra of electron beam modified SiO$_2$ showing in the near IR the fundamental transition of c-Si at $\hbar\nu=1.1$ eV, of a-Si at 1.3 eV and a probable transition in Si nanocrystal quantum dots at about 1.6 eV.
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Fig. 4 CL spectra of electron beam modified SiO\textsubscript{2} showing in the near IR the fundamental transition of c-Si at $h\nu=1.1$ eV, of a-Si at 1.3 eV and a probable transition in Si nanocrystal quantum dots at about 1.6 eV.