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Nanostructures formed in pure quartz glass under irradiation in the reactor core

E.M. Ibragimova *, M.A. Mussaeva, M.U. Kalanov

Institute of Nuclear Physics Academy of Sciences, pos. Ulugbek, Tashkent 100214, Uzbekistan

HIGHLIGHTS

- Cristobalite and tridymite nanocrystals grow in SiO_2 glass at neutron irradiation.
- Oxygen vacancies and non-bridging atoms are accumulated in the nanocrystal shell.
- Splitting of absorption bands is due to formation of nanocrystal–glass interfaces.

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ABSTRACT

Optical spectroscopy and X-ray diffraction techniques were used for studying nanoscale particles grown in pure SiO_2 glass under irradiation with fast neutron fluencies within 6×10^{16}–$5\cdot10^{19}$ cm^{-2} and gamma-quanta $\sim1.8\times10^{20}$ cm^{-2} in the reactor core in water. The neutron irradiation results in destroying of the initial α- and β-quartz mesoscopic order of 1.7 and 1.2 nm sizes and growing of cristobalite and tridymite nanocrystals of 16 and 8 nm sizes in the thermal peaks of displacements reapectively. The point defects (oxygen deficient E'_s, E'_1, E'_2 and non-bridging oxygen centers) induced by the γ-irradiation are accumulated in the nanocrystals shell of 0.65–0.85 nm thickness. Interaction of close point defects at the nanocrystal–glass interface causes the splitting of optical absorption bands into the intensive ($D\sim2$–4) resonances characteristic for local interband electron transitions, having the width of 10–15 nm close to the nanocrystals' sizes and the energy depending on their structure.

1. Introduction

Radiation effects in SiO_2 materials have already been intensively investigated half a century ago as they are widely applied in space equipment and nuclear power (Clinard and Hobbs, 1986; Levin et al., 2003). Because of the mixed covalent and ion character of Si–O chemical bond, point defects can arise by the radiolysis mechanism at ionizing irradiation as a result of non-radiative recombination of bound electron–hole pairs (Griscom., 1985; Scuja., 1998; Trukhin., 2006). As shown in Griscom (1985), possible mechanism includes two stages: (a) self-localization of a hole just under the valence zone top at rupturing of Si–O–Si bond with simultaneous generation of oxygen deficient center (ODC) with the energy of 5.8 eV and O–O peroxy bond, and (b) localization of the second exciton at the same site, bringing to disintegration of the O–O-bond with formation of Si–Si center (5 and 7.2 eV) and interstitial molecular ion O_2^-.

Fast neutrons are known to create cascades of atom displacements and tracks with a high local temperature. Being exposed to fast neutron fluencies $>10^{19}$ cm^{-2}, the quartz lattice swells to 14 vol% and the SiO_2 glass network compacts to 3 vol% due to formation of the metamict phase with an intermediate density (Clinard and Hobbs, 1986). It was shown by Raman scattering spectroscopy that irradiation of KI-glass with fast neutron fluencies from $5\cdot\times10^{17}$ to 2.2×10^{20} cm^{-2} results in the density increase from 2.206 to 2.265 g/cm^3, and the characteristic size of mesoscopic order decreases from 2.5 to 1.9 nm (Malinovski et al., 2000). The authors suggested the model of irradiated glass structure containing clusters ordered like cristobalite and tridymite and separated by amorphous layers.

The point radiation centers (E and O_1^0) in the glass like and crystalline SiO_2 samples irradiated with 10 MeV-electrons were studied in Zatsepin et al. (2002, 2006). In the KV type glass E'_1-centers (5.78 eV) were found in the volume and E'_s-centers (6.3 eV) were in the superficial layer of 200 nm. The photoluminescence (PL) at 1.9 eV band occurred at exciting the O_1^0 centers at 4.75 eV. Two channels of non-radiative relaxation are possible, including intra center and external suppression of PL, both accompanied by generation of free electrons. The E' centers are

* Corresponding author. Tel.: +998 712893354; fax: +998 711503080.
E-mail addresses: ibragimova@inp.uz (E.M. Ibragimova), mussaeva_m@mail.ru (M.A. Mussaeva).

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supposed to result from the torn-off bonds in the glass phase, while oxygen vacancies are in the crystal phase and relax only non-radiatively with emission of electrons. Irradiation by 2.5 MeV electrons causes the luminescence at 185 nm (6.7 eV) (Griscom, 1985), apparently, related with the superficial centers.

Lately the great attention has been given to studies of silicon dioxide with nanosized inclusions influencing luminescence (Bogomolov et al., 2001; Bakaleynikov et al., 2004; Kortov et al., 2006; Zatsepin et al., 2008). The intensive catodoluminescence (CL) within 2–2.5 eV was excited at the interface of SiO_2 film and Si nanoclusters created by the electron beam due to overheat of microvolume to 1200 °C; the sizes of SiO_2 spheres of 250 nm and Si-nanoclusters of 4–5 nm were determined; the CL is caused by the ODC (Bogomolov et al., 2001; Bakaleynikov et al., 2004). Authors of (Kortov et al., 2006; Zatsepin et al., 2008) implemented the pyrolysis method for synthesizing the nanostructured SiO_2 ceramics, in which nanodimensional crystal-like inclusions were found, and the wide emission band in the visible range of spectrum was ascribed to fast radiating relaxation of superficial ODC.

Dielectric nanoparticles give nonlinear response to impact of nanosecond laser pulses, resulting either in restriction of the emission or increase in the transparency (Miheeva and Sidorov, 2004). The authors explain it by one-photon photogeneration of charge carriers from the deep impurity levels to defects near the nanoparticle surface. It should be noted that the boson peak of Raman scattering observed in the glass with the ordered clusters (Malinovski et al., 2000) also testifies to a nonlinear optical response.

The theoretical model of an optical transmission spectrum of dielectric liquid containing noninteracting dielectric nanoparticles of any form and small sizes, in the approach of effective mass was developed in Kulchin et al. (2009). According to the model and experiment, Al_2O_3 nanoparticles in the sizes of 40–50 nm have several discrete energy levels in the forbidden zone, which are widened to 0.4 eV and caused by defects on their surface, and quantum dimensional states (discrete levels) of charge carriers are formed in the conducting zone.

Analysis of the available literature shows that there are few data of meso-scopic structure of network of the pure silicate glass (Clinard and Hobbs, 1986; Malinovski et al., 2000), which may contain SiO_2 nanocrystals formed under the bombardment with high energy particles. Then the point defects described above, may accumulate at effective sinks, such as the interfaces between amorphous, metamict and crystal phases of different densities (cristobalite, tridymite, quartz). It is not established, where exactly (in volume or on surface of irradiated glasses) and how (randomly or arranged) the radiation induced structure defects are distributed, which are responsible for the abovementioned color and luminescence centers. Only E'_s-centers (6.3 eV) were identified in the superficial layer of 200 nm in KV glasses (Zatsepin et al., 2002, 2006). Interactions of nanoparticles among themselves and with point defects are of great scientific and practical interest for radiation material sciences and nanophysics.

This work was aimed at studying formation and interaction between radiation point and nano-dimensional (mesoscopic) defects of structure induced in high purity SiO_2 glass by intensive neutron and gamma irradiation in the nuclear reactor core.

2. Objects and experimental techniques

To reduce influence of impurity on mesostructure of glass and the radiation induced color centers, laser windows, made from the high purity quartz SiO_2 glass in the State Optical Institute (Russia), were chosen for experiments. Samples were optically polished plates with thickness of 1 mm and masses from 90 to 310 mg. The content of metal impurities (after potassium) determined with X-ray fluorescence techniques was $<10^{-4}$%, which is one order of magnitude less than that in KV type glass (Zatsepin et al., 2002; Zatsepin et al., 2006).

The samples were irradiated in the research reactor WWR-SM (Tashkent) in two fuel channels cooled by water, at two fluxes of fast neutrons 0.66 and 1.4×10^{14} cm^{-2} s^{-1} (determined by Ni and Fe monitors with the threshold energies 1 and 3 MeV, respectively, which corresponds to the maximum in the reactor neutron spectrum (Clinard and Hobbs, 1986; Levin et al., 2003; Mussaeva et al., 2006, 2008)) to neutron fluencies of 6×10^{16}–5×10^{19} cm^{-2} and ionization doses 10^8–10^{11} R (determined with Si detector or two ionization chambers) (Clinard and Hobbs, 1986; Levin et al., 2003; Golant and Tugushev, 1999; Mussaeva et al., 2006). At such irradiation in water not only the mentioned point defects were expected to be generated, but also H- and OH-containing centers appear in the volume and on the surface due to water radiolysis that may increase the radiation optical hardness of silica glass that is important parameter for nuclear materials (Levin et al., 2003). Besides, nano-fragments of the glass network change and nano-phases of different densities may form in the thermal peaks of atom displacements (Clinard and Hobbs, 1986). Thermal neutron fluxes determined with Co monitor in these channels were $0.9–1.1\times10^{14}$ cm^{-2} (Mussaeva et al., 2006). Although thermal neutrons cannot knock-out atoms to produce Frenkel pairs, P cation impurity centers are generated by the nuclear reaction ^{31}Si(n, β)^{31}P with the low cross-section 0.13 mb. For assessing the contribution from gamma radiation component in the reactor into the defect production, we carried out gamma irradiations to the highest dose of 10^9 R both in the ^{60}Co isotope source of 520 R/s and in the shut-down reactor.

Optical absorption (OA) spectra were measured at 300 K using dual-beam spectrometer Specord M-40 (Carl Zeiss) in the wavelength range of 200–900 nm and optical density $D=\lg(I_0/I)$ to 2 and 4, and also one-beam spectrophotometer SF-56 A (LOMO) in the range of 190–1100 nm to $D=5$. Unlike the slow scan of spectra and narrow slits in M-40, the computer program for fast registration by photodiode array and processing of spectra in SF-56 A adjusts a digitization step within 0.1–10 nm and a slit width 0.3–6 nm, thus measurement time in each point varies within 0.02–0.6 s. Expecting intense wide UV-absorption bands after the irradiation, the maximal slit of 6 nm and scanning step of 5 nm were taken to detect optical density up to 5 with minimal instrumental error 0.25%. However, taking into account reproducibility of spectra, the actual experimental error was ~1%. The scanning steps are seen in the spectra below.

Concentrations of optical centers were calculated by the Smakula formula (Smakula, 1930; Dexter, 1956):

$$N = 1.28\times10^{17}\left[\frac{n}{(n^2+2)^2}\right]\frac{K_m H}{f},\quad \text{cm}^{-3} \tag{1}$$

where n – a refraction index for a wavelength λ corresponding to a maximum of a band or peak, for pure SiO_2 $n=1.46$ at the standard green line of mercury; f – an oscillator force close to 1 for hydrogen-like centers; H – a half width of a band, eV; K_m – an absorption coefficient in a band maximum, cm^{-1} which depends on D – optical density at a sample thickness of l (cm) as $K_m=D/l$ (here for 1 mm thick samples $K=10D$).

Spectra of photoluminescence (PL) and optical excitation in the range of 200–800 nm were measured at the set-up including a xenon lamp, two monochromators MDR-12 (LOMO) and SPM-2 (Carl Zeiss), the photo-electron-multiplier FEU-100 and the signal amplifier U5–11. The experimental error was ~5%. The PL intensity was corrected for a spectral sensitivity within 400–700 nm and sample mass.

Structural parameters, formation of dimensional defects and impurity phases, and also mechanical tensions were investigated