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Recombination luminescence of oxygen-deficient centers in silica

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Abstract

The luminescence of silica glass, prepared by plasma chemical vapor deposition (PCVD) and quartz glass of type IV (trade mark KS-4V) methods, were studied while irradiated with pulses of ArF laser (193 nm) light in the range of sample temperatures between 10 and 300 K. The samples contain less than 0.1 ppm metallic and hydroxyl impurities. The samples synthesized by PCVD were of two kinds. The first one (amorphous) was as-deposited from plasma at a substrate tube temperature of ~1200 °C. The second one (fused) was prepared from the first by the tube collapsing with an external burner. In this process, a section of the substrate tube with the deposited glass was installed in a lathe and processed at a temperature of ~2100 °C during ~20 min until the tube was transformed to a rod. After such processing, the rod was cooled down to room temperature in air at an average rate of about 400 °C per min. The only observed luminescence possesses two broad bands, with not well defined position, one at 2.6–2.9 eV (a blue band) and another in the range of 4.4 eV (an UV band). There is a correspondence in luminescence properties between KS-4V silica and fused PCVD silica. Those bands have been attributed to oxygen deficient centers (ODC). No luminescence is observed in amorphous PCVD silica under irradiation with 193 nm laser light. So, formation of the sample by melting at least stimulates formation of ODCs at 193 nm. The blue band decays obeys to power law $\sim t^{-1}$ and is detected in the range of time 10 ns to 300 μs. The UV band possesses a fast, practically repeating excitation pulse, and a slow component (~30 μs). The obtained new kinetics data are compared with known in literature for lone twofold-coordinated silicon having exponential decay for the blue band equal to 10 ms and 4.5 ns for the UV band. That shows the blue band of new studied samples under ArF laser possesses decay component faster and the UV band slower than that of the twofold-coordinated silicon center. This corresponds to the recombination process of luminescence excitation by laser. We propose a model of the processes as charge separation under excitation with creation of a nearest self-trapped hole and electron trapped on the twofold-coordinated silicon, modified by its surrounding atoms or ions. This pair is recombining then with luminescence.

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1. Introduction

Intra-center photoluminescence (PL) of oxygen deficient center (ODC) is known through example of lone twofold-coordinated silicon center [1]. It is labeled as SiODC(II). Two luminescence bands at 2.7 eV (a blue band) and at 4.4 eV (a UV band) could be excited by excitation at 5 eV. The blue band belongs to triplet–singlet transition [1]. Corresponding absorption band is situated at 3.3 eV [2]. When excited at 5 eV, the blue band appears due to conversion from the singlet state to triplet state. The PL band at 4.4 eV is due to singlet–singlet transitions, $^1S_1$–$^1S_0$. The decay parameters of this luminescence are approximately fitted by an exponential function, with 10 ms time constant (τ) for the blue band and 4.5 ns for

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the PL band at 4.4 eV [1]. The center possesses excited states with larger energies [1], as well.

Luminescence could be excited in the range of ODC (I) band at 7.6 eV [3] however with decay times differing from the SiODC (II) case. The UV band is with a $\tau = 2$ ns at ~5 K [4,5]. We suggest that this difference is due to a change in the nearest neighbor ions perturbing the singlet state of the twofold-coordinated silicon.

Recombination luminescence of oxygen deficient center (ODC) was observed through thermally stimulated luminescence (TSL) with excitation at approximately of the 7.6 eV absorption band or ODC (I) in silica [3,6]. The efficiency of TSL peak creation decreases with cooling from 80 K to 10 K. Therefore e–h pair creation at ODC (I) sites was attributed to photodissociation of a complex defect with thermally stimulated removal of the dissociated particles and stabilization in the network of glass. We attribute the TSL to liberation of the trapped atomic (or ionic) particles and subsequent recombination providing ODC luminescence with a specific spectral shape differing from luminescence of lone twofold-coordinated silicon center (Si_2°) [3,6].

Spectrum of luminescence excited in recombination process differs from that excited in intra-center process[1] [3,6]. The singlet–singlet UV band with well defined maximum at 4.4 eV with FWHM about 0.7 eV, prevailing in the case of a lone ODC (II), decreases to favor of the triplet–singlet blue band, and the UV band becomes smeared [6] without well defined maximum.

The nature of luminescence appeared under ArF laser in silica samples obtained below and above glass transition temperature T_g is an object of the investigation. The task of this work is investigation of luminescence in silica irradiated with pulses 5 ns duration of light from an ArF laser. Luminescence decay kinetics was measured in samples of several types of silica. A silica type labeled KS-4V is silica produced by fusion in electrical furnace after cleaning with crystallization. The PCVD process provide another sample at temperatures less than the glass transition temperature, T_g, and a type produced by melting a sample of a PCVD silica.

2. Experimental

The samples for investigation were of three different types. One was a silica with a concentration of metallic impurities less than 0.1 ppm and content of OH group less than 0.1 ppm [3]. The samples were produced as KC-4B (or the same KS-4V) silica (see for example [3]). The method of preparation was based on electric melting of raw material cleaned by crystallization of synthetic silicon dioxide powder to cristobalite.

Another type of sample was amorphous silica deposited on the inner surface of a silica substrate tube by the surface plasma chemical vapor deposition (SPCVD) process. A setup designed for fiber preforms fabrication [7] is used for material synthesis. Layer-by-layer deposition is carried out by means of a vapor phase oxidation of a fiber optics grade [7] $SiCl_4$ in a microwave induced discharge sustained in oxygen, with the total pressure being several torr. The plasma column front is scanned back and forth along the substrate tube at a frequency of 0.5 Hz. 2.5 h deposition process on a 15 cm part of the tube's inner surface produces a deposited layer of about 5 mm thickness.

Third type of silica was fused material counterparts prepared from PCVD silica by collapsing the tube with the deposited layer by using an external propane touch used to produce fiber preforms. In this process, a section of the substrate tube with the deposited glass was installed in a lathe and processed at a temperature of ~2100 °C during ~20 min until the tube was transformed to a rod. After such processing, the rod was cooled down to room temperature in air at an average rate of about 400 °C per min.

The ArF laser (model PSX-100, made by Neweks, Estonia) has pulse energy of about 5 mJ with duration of 5 ns and a repetition rate up to 100 Hz. the light beam was passed through a lens used for alignment. The power delivered to the sample was ~1 GW/cm^2 in a spot 2 mm in diameter.

A liquid helium cryostat was used to maintain the temperature in the range 10–290 K. luminescence was detected by means of a grating monochromator with a photomultiplier tube possessing S20 photocathode, 50 Ohm impedance. An oscilloscope (Tectronic TDS 380) was used to observe the luminescence decay. The measured decays are presented in figures as recorded. The scatter in the data is an indication of the error in the measurements.

3. Results

In Fig. 1, the PL spectra typical for three classes of samples are presented. Two broad luminescence bands are observed in the spectra. One is at 2.6–2.9 eV and the other,

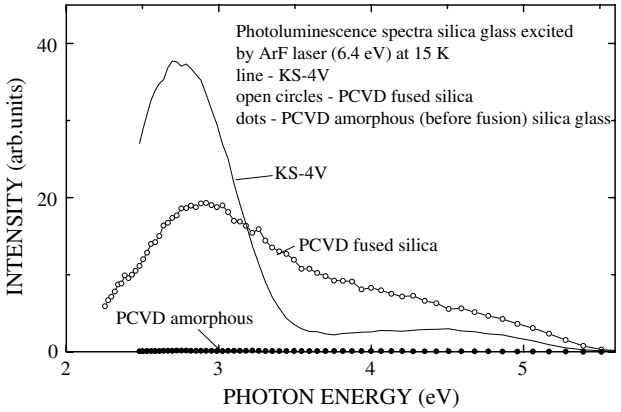

Fig. 1. PL spectra silica glass excited by ArF laser (6.4 eV) at 15 K line – KS-4V, open circles – PCVD fused silica, dots – PCVD amorphous (before fusion) silica glass.

[1] Intra-center process – process of excitation and emission related to transition between ground and excited states of a center.