Sub-band-gap-excited luminescence of localized states in SiO$_2$–Si and SiO$_2$–Al glasses

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ABSTRACT

Silica glass samples doped with extra silicon (SiO$_2$–Si: artificial oxygen deficiency) and with aluminum (SiO$_2$–Al: Al-doped without accompanying alkali ions) were studied. The luminescence properties of these two samples are compared in the range of temperature 15–290 K under excitation of ArF excimer laser (193 nm). In both samples the luminescence of oxygen deficient centers (ODCs) is detected, i.e., emission bands in the blue at 440 nm and the UV at 280 nm. Cooling of the both samples led to strong increases of luminescence intensity down to 80 K with much smaller increases for still lower temperatures. At 290 K in SiO$_2$–Si a luminescence similar to that of twofold-coordinated silicons in stoichiometric silica glasses was detected, i.e., displaying exponential decay of emission bands in the blue ($\tau = 10.3$ ms) and UV ($\tau = 4.5$ ns). In both samples emission at 440 nm occurs in times shorter that $\sim$400 µs, according to a non-exponential decay law. These decay times are much faster than the 10.3 ms *exponential* decay typical of the twofold-coordinated silicon center in pure *undoped* silica. Conversely, the decay of the UV band possesses an additional decay ranging from 2 to 5 µs, that is much slower than 4.5 ns typical of lone twofold-coordinated silicons in stoichiometric silica. Prolongation of the decay time of UV emission can only be explained in terms of electron–hole recombination processes. Moreover, the observed diminishing of the luminescence intensity concomitant with acceleration of decay times with increasing temperature above 90 K is found to be correlated with thermally activated recombination of self-trapped holes in pure silica [D.L. Griscom, J. Non-Cryst. Solids 149 (1992) 137]. It is concluded that the ArF-laser induced electronic processes of recombination luminescence in SiO$_2$–Si (and SiO$_2$–Al) are related to trapping of an electron on in a localized state related to oxygen deficiency (or to an Al in the SiO$_2$ network) and nearby trapping of a hole on a normal bridging oxygen, forming an STH.

1. Introduction

Localized states, by definition [1], are not point defect states in network of glasses that could conceivably appear in concentrations comparable with host material atoms. Rather, the bigger geometric dimensions of localized states in comparison with point defects makes them interesting as a spectroscopically identifiable subset of defect structures associated with range-III order in silica glasses (following the nomenclature of Wright [2]). It is presumed that there is no exciton-like transport between these localized states after excitation. This is a general approach, since concrete identification of the specific geometric and electronic structures of localized states remains an object of investigation of contemporary solid state physics of disordered materials.

Localized states in silica glass are interpreted through the luminescence of so-called modified oxygen deficient centers [3] – in contrast with the twofold-coordinated silicon centers, which are point defects in neutron-irradiated stoichiometric silica [4] and also in as-received pure non-stoichiometric silica glass [5]. The behaviors of these states in silica have also been extensively studied in samples with different levels of oxygen deficiency [6,7]. These studies have improved our understanding of the process. However, it was shown [6] that localized states are peculiar to all kinds of silica glass with approximately the same concentrations, even in oxygen surplus samples; and in order to observe them it has often been necessary to cool to sufficiently low temperatures [6,7]. By means of adding of extra silicon before fusion it has proved possible to increase the concentrations of oxygen deficient centers (ODCs) and reveal the properties of localized states associated with them [6,7]. Based on previous work [8], it is known that the optical absorption bands of aluminum-oxide localized states in silica containing alkali ions are situated above the optical gap of the host material (8.2 eV [9]), whereas aluminum impurities in

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silica not accompanied with alkali ions give rise to localized states in photon energy range below optical gap pure of silica [3].

In the present paper, we perform comparative luminescence measurements of a sample containing extra silicon and a sample containing a comparable amount of aluminum without compensating alkalis. We choose temperature ranges ranging from liquid-helium temperatures to temperatures high enough to give rise to thermal quenching of the ODC luminescence. It has been shown experimentally that many types of glasses exhibit a particular temperature dependence of the luminescence that exponentially grows in intensity with cooling (see for example [10–12]). This was discovered for the case of chalcogenides glasses [10] and shown to be true also for luminescence centers induced by neutron irradiation in silica glasses. Later [11] this behavior was observed in the cases of localized states' luminescence in alkali silicate, alkali germanate, and phosphate glasses, as well as [12] for luminescence of self-trapped exciton in pure silica glass. Phenomenologically, the type of thermal quenching of luminescence in these cases has been explained (see for example [10]) as due to intra-center quenching with a distribution of activation energies having maximal density close to zero in the ensemble of structurally non-equivalent centers. However intra-center quenching of the point defects identified as the twofold-coordinated silicons does not begin taking place until temperatures much higher than room-temperature [4,5,8], a range that has not been measured in detail yet. Thus, one of the tasks of the present work was to carry out measurements at the highest possible temperatures.

Localized states of silica were previously studied with regard to the involvement of self-trapped holes (STHs) identified in pure silica glasses by ESR [13,14]. (In crystalline α-quartz, radiation-induced holes (heavy polarons) remain mobile even at 4.5 K [15–17].) A notable correspondence between luminescence of localized states in silica and STHs measured by ESR was found in [18], where it was determined that artificial oxygen deficiency increases the concentration of radiation-created STHs at 80 K. More recently, during studies of silica doped with Al (without charge-compensating alkali ions), it was found that ArF-laser irradiation (193 nm) at 80 K does not produce any hole centers other than STHs [3]. Similar irradiation of Al-doped glass with ArF laser at 290 K [3] generates aluminum–oxygen hole centers (Al–OHCs), Si E'centers, and an Al-related electron trap center of the type elucidated by Brower [19].

In the present paper we tacitly study STH participation in recombination processes in the range of temperatures where STHs are mobile, as well as below these temperatures down to LHeT. The chosen samples, SiO$_2$–Si and SiO$_2$–Al have been shown previously to provide both enhanced creation of STHs and enhanced luminescence of oxygen deficient centers [3,6,18,20].

2. Experimental

The high purity sample for this investigation was a Type IV silica known as KS-4 V [7,21]. The method of preparation was by electrofusion of cristobalitized synthetic silicon dioxide. The high level of oxygen deficit (about 10^{-2} wt%) was achieved by reaction of the cristobalite with silicon vapor [21]. Another sample of silica glass was doped with 0.025 wt% of Al$_2$O$_3$ by adding alumina to synthetic silicon dioxide powder before electrofusion.

The ArF laser (193 nm) and the KrF laser (248 nm), model PSX-100 were made by Neweks, Estonia; both had pulse energy of about 5 mJ with a duration of 5 ns. luminescence detection was realized by means of a grating monochromator (Bruker Optics, Chromax Spec 250) having both slits about 0.1 mm, corresponding to 0.16 nm resolution, with a photomultiplier tube (H6780-04) with 50 Ohm resistive load. An oscilloscope (Tektronic TDS

2022B) was exploited for decay curve registration. Each curve was averaged for 128 pulses. The time-resolved spectra were measured by registration of the decay curve for each point of the PL spectrum in two time ranges – one in the ns range another in the μs range. Measurements were realized with the use of helium refrigerator (Advanced Research System closed cycle with temperature controller LakeShore 325). The temperature range in this case was 12–300 K.

3. Results

In Fig. 1 time-resolved photoluminescence spectra of the studied samples excited with pulses of ArF laser (193 nm) at 12 K are presented. The spectra are very similar for SiO$_2$–Si and SiO$_2$–Al. There are two bands. A blue one at 2.8 eV (440 nm) with FWHM 0.8 eV is the principal band, which intensity is determined by integral under decay curve in the range 0–400 μs Fig. 1. Another band is the UV band at 4.4 eV (280 nm) with FWHM 0.5 eV, which is the principal band for the fast-decaying component in ns range (0–15 ns) Fig. 1. This UV band also has a slow component, but it is less expressive. The blue band is very similar in shape and intensity for both samples, whereas the fast component of the UV band is more intensive in SiO$_2$–Si sample Fig. 1. For SiO$_2$–Si the blue component with τ = 10.3 ms is well detectable at 285 K (Fig. 2). However, such a room-temperature component is practically absent in SiO$_2$–Al.

Fig. 3 zooms in on the "flaring up" of the intensity of ArF-laser-induced blue luminescence at times shorter that ∼400 μs. This short-lived component exhibits non-exponential decay; which is very similar for both SiO$_2$–Si and SiO$_2$–Al. The UV band corresponding to this fast blue luminescence possesses decay times in the μ-second range, Fig. 4. The decay kinetics curves are non-exponential with little changes in the shape of the curves in the temperature range 12–90 K. At higher range of temperature we observe acceleration of the decay. This acceleration correlates with changes of PL intensity presented in Fig. 5 being determined as integrals under the decay curves.

In Fig. 6, the concave-downward trend of the exponential decay time of the blue luminescence, under in-band KrF (248 nm) excitation, τ_{blue}, between 475 and 625 K and straight-line decrease above the latter temperature imply that thermal quenching of the excited triplet state in SiO$_2$–Si becomes increasingly important above 475 K.

As also seen in Fig. 6 the blue PL intensity, I_{blue} of SiO$_2$–Si increases with increasing of the temperature above room-temperature, with little change in decay time constant ($\tau_{\text{blue}} \approx 10$ ms) up
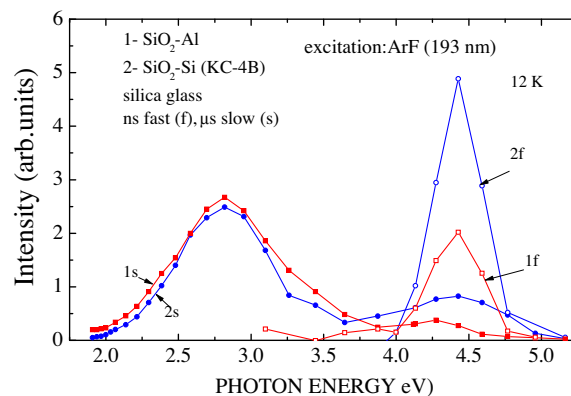

Fig. 1. Time-resolved photoluminescence spectra of silica samples with aluminum (1) and excess silicon (2). *f* – integral under decay curve of the 4.4-eV band in the temporal range 0 – 15 ns, *s* – integral under decay curve of the 2.8-eV band in the range 0–400 μs. *T* = 12 K. Excitation pulses: ArF laser (6.4 eV).
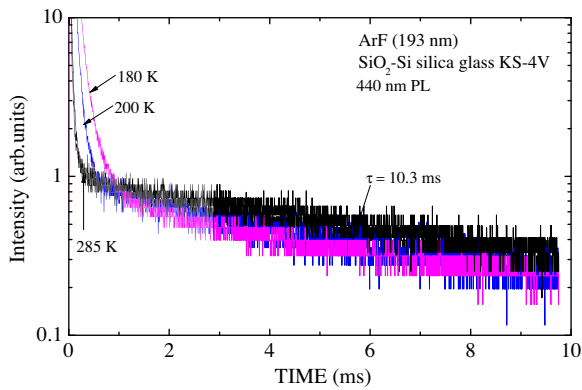
Fig. 2. Decay kinetics of blue PL at 440 nm (2.8 eV) of SiO₂–Si glass subjected to pulsed ArF-laser excitation at different temperatures. The most notable decay component in this time range at 285 K is an exponential decay with $\tau = 10.3$ ms. At 285 K the exponential part was determined by numerical integrations to be five times more intensive than the faster parts of the decay.
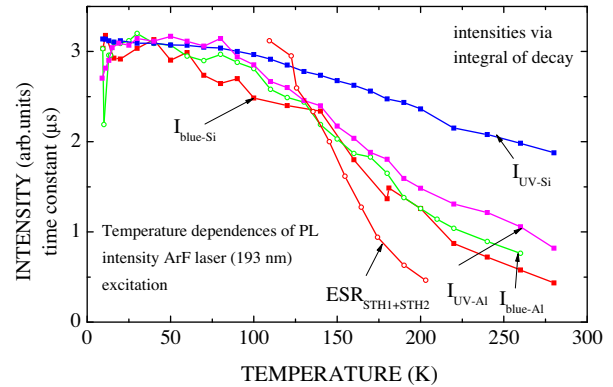

Fig. 3. Decay kinetics of the blue PL at 440 nm (2.8 eV) of SiO₂–Si and SiO₂–Al glasses subjected to pulsed ArF-laser excitation at different temperatures.

Fig. 4. Decay kinetics of the UV PL at 280 nm (4.4 eV) of SiO₂–Si and SiO₂–Al glasses subjected to pulsed ArF-laser irradiation at different temperatures. The kinetic curves of SiO₂–Al more closely correspond to exponential approximation; however, the overall decays of these two very different samples are extraordinarily similar.

Fig. 5. Temperature dependencies of photoluminescence intensities of both SiO₂–Si and SiO₂–Al, obtained by integration of decay kinetics curves. The curve labeled as ESR(STH1 + STH2) is temperature dependence of annealing of ESR signal of the self-trapped hole (two different types) taken from Ref. [13].
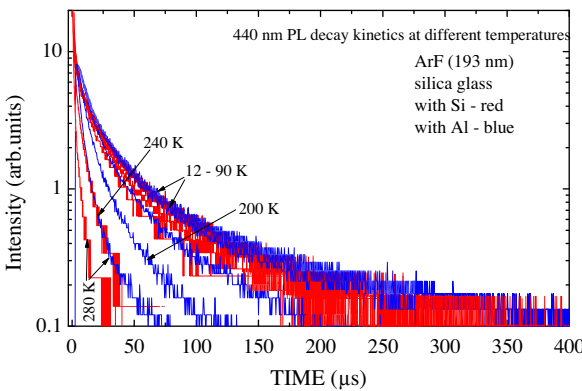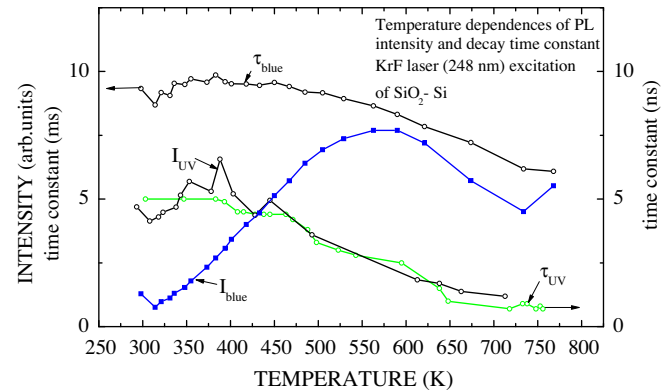

Fig. 6. Temperature dependencies of PL intensity (and decay time constant) during (and following) pulsed KrF-laser (248 nm) excitation of SiO₂–Si. Luminescence was detected through optical filters transmitting blue-band light in one case and UV band in another. In the sample SiO₂–Al (data not shown here), whatever blue luminescence there may have been with $\tau = 10$ ms was below detection sensitivity.
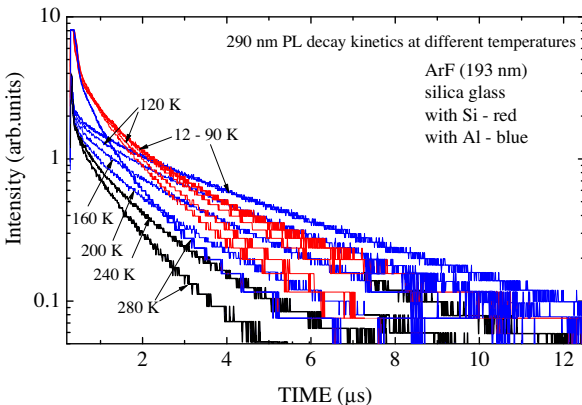
4. Discussion

We observed ArF-laser-(6.4 eV)-induced luminescence in SiO₂–Si and SiO₂–Al silica glass samples, finding their intensities to increase with decreasing temperature in both cases below 290 K (Fig. 5). As seen in Fig. 1, the luminescence possesses two bands: a blue one at 2.8 eV (440 nm) and UV one at 4.4 eV (280 nm), which are usual [4–7,19] for oxygen deficient center (ODC) luminescence in a-SiO₂. In SiO₂–Si, oxygen deficiency is increased, so for that sample the mentioned luminescence is characteristic of $SiO_{(2-\delta)}$, where $\delta \approx 2 \times 10^{-4}$. Observation of these same luminescence bands in SiO₂–Al ($\sim 2.5 \times 10^{-4}$ Al₂O₃ by weight) with intensities comparable to those observed in SiO₂–Si shows that Al₂O₃ doping results in optical absorption properties practically indistinguishable from those of oxygen deficient centers in pure $SiO_{(2-\delta)}$, at least when excited by 6.4 eV ArF-laser photons. This confirms a tentative conclusion reached by two of us (A.N.T and D.L.G.) in an earlier paper [3].

However, a contrast between the two studied samples appears for excitation with KrF laser photons (248 nm), which is exactly in-band with the singlet–singlet absorption band of the twofold-coordinated silicon center [4,5]. For SiO₂–Si we indeed observe the luminescence of the lone twofold-coordinated silicon center (Fig. 6), since it is known [4] to be characterized by $\tau = 4.5$ ns for UV band and $\tau = 10.3$ ms for blue band. Thus, in the case of SiO₂–Si, we infer

to ~ 500 K. I_{blue} peaks near 575 K and then diminishes with further increase in temperature. Conversely, the KrF-laser-excited UV band exhibits thermal quenching above ~ 400 K characterized by an activation energy of about 0.07 eV, which controls both the intensity and decay time constant.

the UV and blue bands to be due to singlet–singlet and triplet-singlet transitions [4,5] of that center, respectively. By contrast, in SiO_2–Al, no luminescence with such parameters was observed under KrF-laser excitation at 290 K and higher temperature. There is observed only some visible luminescence without any UV band, as it is seen in SiO_2–Si for $T > 300$ K.

For SiO_2–Si we have measured the temperature dependencies of the blue and UV luminescences under in-band KrF excitation (248 nm). As seen in Fig. 6, the blue band increases in intensity up to 575 K with little change in decay time constant. This means that up to this temperature there is little or no direct thermal quenching of the excited triplet state. Rather, the increase in blue luminescence of SiO_2–Si with increasing temperature, coupled with the concomitant decrease in the UV band intensity and decay time under the condition of KrF-laser excitation implies thermal quenching of the excited *singlet* state – obviously by means of feeding the excited triplet state.

The photoluminescences we report here can be categorized as arising from two different mechanisms. One is intra-center luminescence that characterizes the twofold-coordinated silicons [4,5]. We believe that the other mechanism involves localized states more complex than the twofold-coordinated silicon, although these states must each include (possibly transient) twofold-coordinated silicon as part of their structure. The detailed structures of these localized states are still unknown, but whatever the correct model(s), it must be possible to construct it (them) from structural units associated with excess-Si (or doping with Al_2O_3).

We have shown here that the recombination processes of localized states created by 6.4-eV photons at their respective excess-Si or Al-dopant precursor sites give rise to blue-band kinetics faster than 10 ms (i.e., ~400 μs, Fig. 3) and UV band kinetics slower 4.5 ns (i.e., ~4 μs, Fig. 4) in the temperature range 12–100 K. The slow kinetics of the UV band directly indicates that a recombination process now dominates over the intra-center process having the 4.5 ns time constant that characterizes lone twofold-coordinated-silicon centers. Thus, this luminescence grows in intensity with cooling below 290 K down to 100 K (Fig. 5) due to freezing out the diffusing species responsible for the recombination quenching. By contrast, intra-center quenching of luminescence excited at 248 nm is seen to take place at higher temperatures (Fig. 6). So, there are other mechanisms of luminescence quenching of the present localized states, even given that luminescence excited at 194 nm is quenched by a recombination process.

We have found little change in intensity with cooling below 100 K in our experiments with ArF (193 nm) excitation. So the usual model of thermal quenching for disordered materials [10] does not work here as well. Rather, the observed devolution of the decay process into a nearly temperature-independent mode below 100 K directly indicates some other process, which is temperature dependent in the range 290–100 K and independent below 100 K.

A recombination process in the present case can be due to charge separation during laser irradiation. So the intra-center, fast singlet–singlet transition for the UV band characteristic of the twofold-coordinated silicon center does not control the decay of the predominant defects that give rise the spectroscopically identical blue and UV bands in the SiO_2–Si and SiO_2–Al glasses. Rather, the decay kinetics of the UV band in these Si-excess and Al-doped samples directly reveals the recombination rate of electrons and holes that are *not initially trapped on the same point defect*. Trapping of an electron and a hole on the *same* defect means defect in an excited state.

So where *are* they trapped? Well, when we compare our temperature dependences with that of self-trapped holes (STHs) in pure SiO_2 glasses measured with ESR [13,14], we find the similarity illustrated in Fig. 5. Thus, it strongly appears that the observed luminescence intensity decrease with heating the SiO_2–Si and SiO_2–Al samples is related to e–h recombinations within localized states, each of which has trapped an electron together with an STH, the latter of which is thermally mobilized in the temperature range ~100–250 K [13,14]. This insight allows modeling of the processes that occur under irradiation with ArF-laser photons. These photons surely excite both localized states and point defects, which may or may not be parts of the localized states. The isolated, or "lone," point defect luminescence is manifested here through the fast-decaying UV band, previously associated with the twofold-coordinated silicons [4,5], which is very intensive in SiO_2–Si and neutron-irradiated pure silica, as compared with stoichiometric silica glass not subject to nuclear-particle irradiation. The ArF-laser excited intra-center blue luminescence is strongly overlapping with the spectroscopically similar recombination luminescence at low temperatures. The process of recombination luminescence we consider is charge separation within an excited localized state that results in the creation of an electron trapped on an ODC and an STH very close to that defect[1]. In such a way an excimer-like quasimolecule is created, which supports radiative transitions that in some ways resemble intra-center transitions and in other ways electron–hole recombinations. The rapidity of the recombination process must depend on the distance between the electron trap and the STH (as well as temperature). We suppose that most of the STHs induced by ArF-laser excitation are within the first coordination spheres of the co-excited trapped electron.

5. Conclusions

Luminescence of the present SiO_2–Si and SiO_2–Al glasses under excitation of ArF laser (193 nm) exhibits spectral properties similar to those previously observed [4] in neutron-irradiated pure stoichiometric silica. ArF laser excites recombination luminescence in both samples similarly. Electron–hole recombination process takes place within an as-yet-unspecified localized state – which depends on thermally stimulated motion of self-trapped holes. The main electronic process is thus creation of electron–hole pairs on localized states that comprise either oxygen deficient centers or cryptically analogous structures resulting from Al doping.

Acknowledgment

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[1] The recombination of pairs separated in longer distances (presumably some STHs could move farther from initial excitation point during action of excitation pulse), if present, is of lower intensity and could not be detected in the current PM measurement regime. For that purpose, photon counting methods should be used; and that was done for 80 K previously [2]. The decay in such detection regime was found to be of a power-law nature and its duration is hundreds of milliseconds [3,13].

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