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The time-resolved photoluminescence (PL) decays are measured for transparent amorphous silica prepared from solid-phase sintering of nanometer-sized silica particles, which has recently been shown to exhibit a unique white PL emission under ultraviolet excitation [T. Uchino and T. Yamada, Appl. Phys. Lett. **85**, 1164 (2004)]. Unlike usual PL processes observed in normal silica glass, it is shown that the present PL results from trapping-controlled migration of photoexcited carriers and their radiative recombination. © *2005 American Institute of Physics.* [DOI: 10.1063/1.2034095]

The electronic excitation of amorphous silicon dioxide (a-SiO$_2$) and the consecutive trapping of an electron and a hole by a point defect have been a subject of continuous interest in the field of metal oxide semiconductor technologies and optical fiber communications. Since the optical and luminescence properties of a-SiO$_2$ depend strongly on the defect states, the electronic structure of point defects along with their electronic excitation processes has been extensively studied during the past decades.[1] It has been well recognized that in bulk a-SiO$_2$ there exit a large variety of intrinsic and extrinsic defects, creating midgap states that are responsible for the optical absorption and the related photoluminescence (PL).[1,2] In addition to bulk a-SiO$_2$, porous silica[3–7] and nanometer-sized silica particles[8,9] have attracted increasing interest in terms of their unique PL characteristics. In these materials, the ratio of surface atoms to bulk atoms are quite large, resulting in several potential light-emitting defect centers that are peculiar to the surface states. These surface-related defect sites strongly affect the dynamics of the electronic transitions and will, hence, influence the related optical and PL properties.

Recently, we have reported a new class of photoluminescent a-SiO$_2$ prepared from solid-phase sintering of nanometer-sized silica particles.[10] This material is optically transparent and nonporous at least on a macroscopic length scale, although it is synthesized by solid-phase sintering of nanometer-sized silica particles below ~1000 °C. The resulting transparent a-SiO$_2$ exhibits PL emission, which appears white to the naked eye, in the wavelength range from ~400–~700 nm at room temperature under the one-photon ultraviolet (UV) excitation. The observed PL decay-time constants (~100 μs) is rather long as compared with that reported previously for porous silica[3,4] (~10 ns) and unsintered silica nanoparticles[9] (~10 μs), and the observed PL decay has been found to be adequately modeled by a stretched exponential function,

$$I(t) = I_0 \exp[-(t/\tau)^{\beta}], \tag{1}$$

where $I(t)$ and I_0 are the PL intensity during the decay and $t=0$, respectively, τ a effective decay time, and β a dispersion factor. In general, $\beta<1$ represents a distribution of independent single exponentials with different lifetimes. This decay low is hardly observed in the PL process of silica-based amorphous materials through below the band gap excitation but is commonly observed in the band-to-band process of disordered and/or low-dimensional semiconductors;[11–15] the phenomenon is believed to result from the complicated diffusion dynamics of the photoexcited carriers produced by interband transitions.[16–20]

To get a better knowledge about the PL properties in the newly reported a-SiO$_2$ material, in this letter we present a detailed study of the PL decay shape evolution. In particular, we concentrate our interest on the temperature (T) dependence on the PL decay since T mainly determines the dominating PL dynamics. The inset of Fig. 1 shows a typical
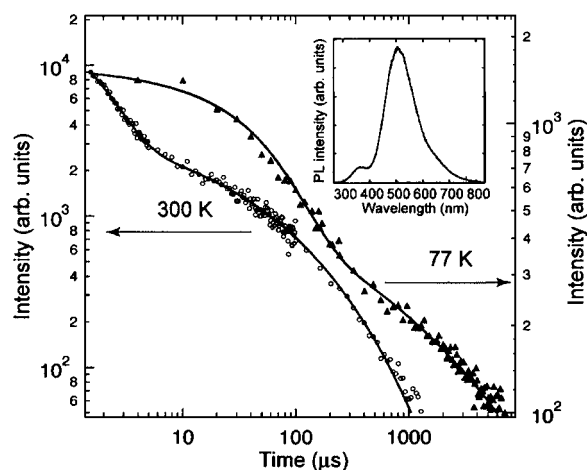

FIG. 1. The log–log representation of the PL decay at 510 nm measured at 77 and 300 K. A pulsed Nd:YAG laser (λ_{exc}=266 nm) were used for excitation. The decay data were obtained by combining several sets of decay signals collected with different delay sequences. Equation (2) was used to fit the decay data. The inset shows PL spectra taken at 300 K with a fixed gate width (20 ms).
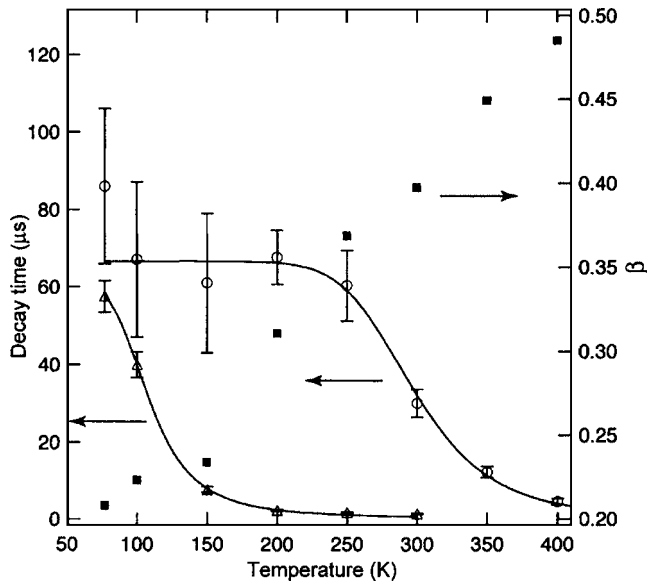
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FIG. 2. Temperature dependence of the decay time τ of the fast (open triangles) and slow (open circles) components and the dispersion factor β (filled squares) obtained through a least square fit of the PL decay data using Eq. (2). The solid lines through the τ data are least square fits with Eq. (3).

FIG. 3. Temperature dependence of the time-integrated PL intensity of the band at 510 nm. The solid line is a least square fit with Eq. (4).

example of the PL spectrum of the sample taken at 300 K. We see two major PL bands peaked at $\sim$360 and $\sim$510 nm. In this article, we focus only on the decay dynamics of the PL band at $\sim$510 nm since this broad visible emission represents more than 90% of the total emission from the sample and is especially interesting in terms of the broad visible light emission.

Transparent a-SiO$_2$ samples were prepared from nanometer-sized silica particles according to the procedure reported in our previous paper.[10] A pulsed Nd:YAG laser (8 ns pulse width, 10 Hz repetition rate, and $\sim$3 mJ/cm^2 per pulse) was used as excitation source for the PL measurements. The PL decay dynamics was analyzed by a monochromator (SpectraPro 300i; Acton Research) with a 150 lines/mm grating and a gated image intensifier CCD camera (PI·MAX:1024RB; Roper Scientific). The sample temperature was controlled between 77 and 400 K in a closed-cycle N$_2$ cryostat.

Figure 1 shows PL decays of the 510-nm band taken at 77 and 300 K. In Ref. 10, we presented a semilog plot of the PL decay measured at room temperature, but we here employ a log–log representation to represent the entire decay behavior acquired with sufficient accuracy. As a result of the log–log representation, we newly found that the decay signal consists of two components: a fast one, in the time range of $\sim$1–$\sim$100 μs, and a slow one, in the time range of $\sim$10–$\sim$1000 μs depending on temperature. We further found that the decay shape of the fast component was represented by a pure exponential function, whereas the decay shape of the slow component was still described by a stretched exponential function, Eq. (1), as reported in Ref. 10. Thus, the entire decay shape should be fitted by the following function rather than by Eq. (1),

$$I(t) = I_{0f} \exp(-t/\tau_f) + I_{0s} \exp[-(t/\tau_s)^\beta], \quad (2)$$

where subscripts f and s mean the values for the fast and slow components, respectively.

As shown in Fig. 1, Eq. (2) gives us a good description of the PL decay in the entire time range. In Fig. 2, we present
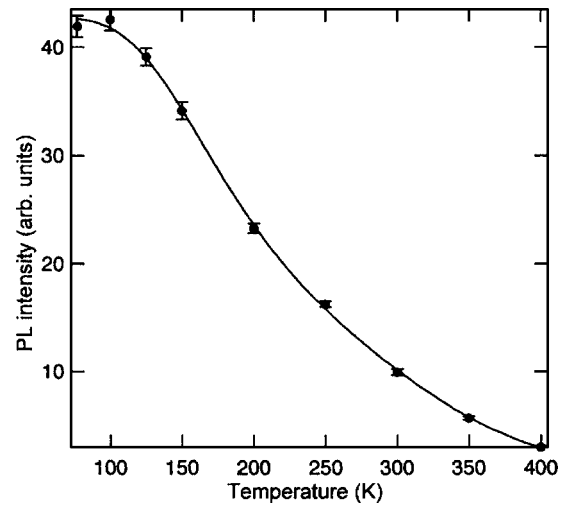
the temperature dependence of τ_f and τ_s. Since τ_f shows a rapid decrease with T and the PL intensity of this component decreases greatly with T as well, we cannot obtain the accurate value of τ_f for temperatures above $\sim$350 K. On the other hand, τ_s is almost constant from 77 to $\sim$250 K and shows a gradual decrease for higher temperatures. Assuming that the observed decrease of the respective decay times with T results from a competing nonradiative recombination process characterized by an activation energy E, we can obtain the values of E and a radiative decay time τ_R for the slow and fast components by fitting the respective data with the following function:[21]

$$\tau_{(f \text{ or } s)} = \frac{\tau_{R(f \text{ or } s)}}{1 + \tau_{R(f \text{ or } s)} \nu_{NR(f \text{ or } s)} \exp(-E_{(f \text{ or } s)}/kT)}, \quad (3)$$

where ν_{NR} is the nonradiative transition rate. From the least-squares fit of Eq. (3), the optimized parameters of τ_R and E for the fast and slow components were estimated to be 61 and 66 μs, and 0.065 and 0.27 eV, respectively. We should note that the radiative decay time of the fast component is almost comparable to that of the slow component. This suggests that as far as the radiative recombination process is concerned, the fast and slow components have a similar origin and, hence, can be characterized by a common radiative decay time τ_{RC}. It is hence probable that the apparent two-component PL decay behavior results from the two disparate nonradiative recombination processes having different activation energies E_f and E_s. Assuming that time-integrated PL intensity (I_{PL}) is proportional to the quantum efficiency η,[22] we can represent the I_{PL} as follows:

$$I_{PL} \propto \eta = \frac{\tau_{RC}^{-1}}{\tau_{RC}^{-1} + \tau_{NR(f)}^{-1} + \tau_{NR(s)}^{-1}}$$

$$= \frac{1}{1 + \tau_{RC} \nu_{NR(f)} \exp(-E_f/kT) + \tau_{RC} \nu_{NR(s)} \exp(-E_s/kT)}. \quad (4)$$

As shown in Fig. 3, the observed temperature dependence of I_{PL} is well-represented by Eq. (4), and the fitted values of E_f and E_s are 0.061 and 0.28 eV, respectively, which are in good

agreement with those obtained independently from Eq. (3) mentioned above.

We next turn to the temperature dependence of β obtained for the slow component. Figure 2 shows that β shows an almost linear increase with T in the whole range of temperature investigated. Theory predicts that a trap-controlled diffusion of photoexcited carriers, or a multiple trapping-detrapping mechanism,[16,17] results in a linear increase of β with T. As mentioned above, our data show that β increases almost linearly with T, implying that the trapping-detrapping process of photoexcited carriers and the resulting recombination process are responsible for the slow PL component.

The above experimental results allow us to assume that the observed two-component PL behavior is analogous to the one reported for semiconductor nanocrystals;[12,23] that is, the slow PL decay is related to recombinations of electron-hole pairs which originate from different spatial regions, whereas the fast PL decay results from recombinations of similar electron-hole pairs but created within the same spatial region. The difference in the PL decay dynamics can, hence, be ascribed to the difference in the carrier motions before they encounter. When the photoexcited electrons recombine with holes before experiencing diffusion, the resulting PL will show a simple exponential decay. However, the trap-controlled diffusion of carriers will modify the decay law to yield a slow component, resulting in a stretched exponential. We consider that this scenario is consistent with the observed difference in apparent activations energies of nonradiative recombination for the fast (E_f) and slow (E_s) components mentioned earlier. When the photoexcited electrons diffuse through a medium by the multiple trapping-detrapping mechanism, a variation in trap depth ε (measured from the band edge) will affect not only the encounter probability of electrons and holes, which is manifested as a dispersion factor β, but also the net activation energy of the nonradiative recombination. Since the release rate W from the trap is given by $W(\varepsilon) \propto \exp(-\varepsilon/kT)$,[16,17] the total rate of nonradiative recombination is expected to be proportional to $\exp[-(\varepsilon + E_{NR})/kT]$, where E_{NR} is the activation energy of nonradiative recombination without trap. Thus, we consider that the observed values of E_s corresponds to $\varepsilon + E_{NR}$, rationalizing the observed fact that E_s is larger than $E_f (= E_{NR})$.

Finally, we propose a possible structural model of the PL center that is responsible for the present broad visible emission. In bulk a-SiO$_2$, it has been demonstrated that band-to-band ($\geq \sim 9$ eV) excitation induces a broad self-trapped exciton (STE) emission band in the wavelength region from $\sim 450 - \sim 550$ nm.[24,25] Since the energy of the STE band is comparable to the 510-nm PL band observed here, we suggest that the present PL is related to a STE-like process. However, the excitation energy used in the this work (~ 5 eV) is well below the band gap energy and the resulting PL was achieved by one photon process. This indicates that the usual STE process associated with the band-to-band excitation cannot be applied to the present PL behavior as is, but the electronic transition from the midgap states will play a vital role in creating photoexcited carriers and the PL emission. Indeed, the present transparent a-SiO$_2$ sample has a

weak absorption feature below ~ 300 nm,[10] indicating the existence of the midgap absorption. At present, the definite defect structure creating the midgap absorption is unknown. However, we suggest that a highly strained $\equiv$Si–O–Si$\equiv$ linkage, accompanied by lengthening of the intervening Si–O bond, is responsible for the midgap states and the related PL phenomena. In the present consolidated sample, the atomic arrangements between the interface of the original nanometer-sized silica particles will not be fully relaxed because of the low-temperature solid-phase sintering, probably resulting in highly strained siloxane bonds and the relevant midgap absorption. Such a deformed siloxane linkage will be easy to capture an electron-hole pair to show STE-like relaxation since the accepted model of the STE in a-SiO$_2$ is a pair of a hole localized on an oxygen,[26,27] which is displaced substantially from the equilibrium position, and an electron localized on a neighboring silicon. We hence suggest that upon UV excitation the midgap states associated with the highly strained $\equiv$Si-O-Si$\equiv$ bonds contribute to the formation of photoexcited carriers, which can recombine immediately or can diffuse through the medium, exhibiting the fast and slow PL emissions.

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