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White light emission from transparent SiO_2 glass prepared from nanometer-sized silica particles

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We report that nanometer-sized silicon-dioxide particles are sintered to optical transparency at temperatures even below 1000 °C, forming nonporous bulk silica glass. The resultant silica glass exhibits visible emission, which appears white to the naked eye, in the wavelength range from ~400 to ~700 nm at room temperature under ultraviolet excitation. The observed emission is quite stable after prolonged exposure to the atmosphere and shows no appreciable light-induced degradation. The present photoluminescence characteristics are found to be basically different from those reported previously for silica nanoparticles and silica-based porous materials. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1782263]

The achievement of Si-based white light phosphors is one of the challenging goals in the field of display and lighting technologies. Recently, highly emissive white photoluminescent silica gels prepared from an alkoxysilane and a variety of organic carboxylic acids have been reported.[1] In these materials, intentionally doped carbonyl chromophores are believed be responsible for the white photoluminescence (PL). It has also been reported that some of the undoped silica gels display UV and/or blue PL emissions.[2–5] However, the PL properties of these porous materials depend on the ambient environment and storage condition.[2,4] Thus, poor stability and aging effects, which result basically from their porous nature, are a problem for a practical application. On the other hand, visible light emission from silicon nanocrystals embedded in silicon oxide thin films has received considerable attention owing to their chemical stability and robustness.[6–10] However, white light emission has not been reported from such Si/SiO_2 films. This is because main emission bands from the embedded Si nanocrystals are located mainly in blue ($<\sim 490$ nm) and red ($>\sim 600$ nm) regions, and the PL intensity of the green regions ($\sim 500 < \nu < \sim 550$ nm) from these materials is generally rather weak. To circumvent the above-mentioned problem, in this letter, we present a dense (not porous) transparent silica glass that emits not only white light but also highly stable PL upon UV irradiation.

We employed nanometer-sized silica particles, called fumed silica, as starting materials to prepare bulk silica glass. Fumed silica, which is a synthetic amorphous form of silicon dioxide, is produced by the hydrolysis of silicon tetrachloride vapor in a flame of hydrogen and oxygen at approximately 1800 °C.[11] Fumed silica is practically free of metal ions, and the residual hydrogen chloride is less than 60–200 ppm. Glinka *et al.*[12] previously reported that fumed silica exhibits some PL bands in the visible region under UV excitation. However, the obtained PL spectral features are strongly dependent on the amount and type of residual surface OH- and H-related species, and stability is still a problem as in the case of porous silica. In order to stabilize such surface-related species but to retain the emissive nature of the nanometer-sized silica particles, in this work fumed silica was calcinated at temperatures as low as possible, inducing solid-phase sintering as will be shown in the following.

As-received fumed silica obtained from Sigma (specific surface area is 390 ± 40 m^2/g and the particle size 7 nm) was compacted at 530 MPa into an opaque disk-shaped pellet of 19.3 mm in diameter and averaging 0.9 mm in thickness. When the pellet was heat-treated at 980 °C for more than ~100 h in air, it was found that as shown in Fig. 1(a), respective fine silica powders coalesced to form apparently transparent silica glass (the percent transmittance at 600 nm is ~80%), accompanied by significant shrinkage (15.5 nm in diameter and 0.7 mm in thickness). No sharp peaks were observed in the x-ray diffraction patterns of the transparent samples, confirming the absence of Si- and SiO_2-related crystalline phases. When the heating temperature exceeds more than ~1300 °C, however, crystalline phases, e.g.,

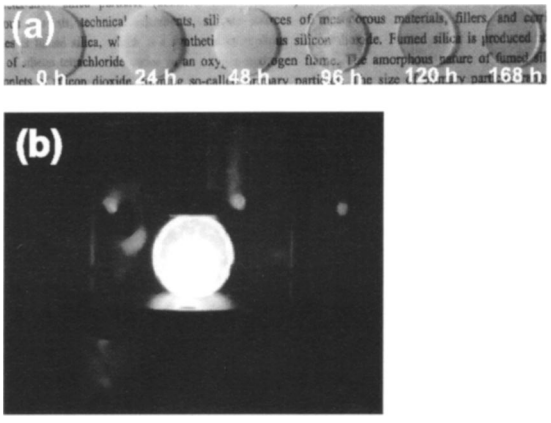

FIG. 1. (a) The sintering process for the disk shaped samples; heating times are indicated below the respective samples. (b) A photograph of photoluminescent silica glass, which was prepared by heating fumed silica at 980 °C for 168 h, excited with a pulsed Nd:YAG laser light ($\lambda_{exc}=266$ nm; ~3 mJ/cm^2 per pulse). A bright part corresponds to the irradiated area with the laser (beam diameter ~10 mm).

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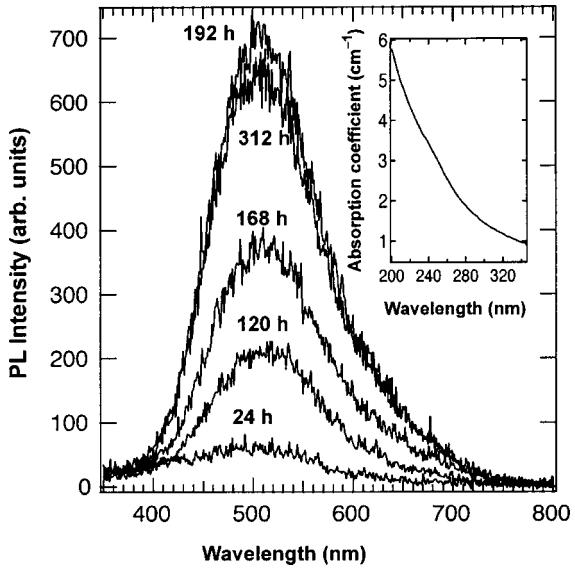

FIG. 2. PL spectra of the silica glass samples heat-treated at 980 °C for different hours excited with a xenon lamp (λ_{exc}=228 nm). The inset shows an absorption spectrum of the sample heat-treated at 980 °C for 168 h.

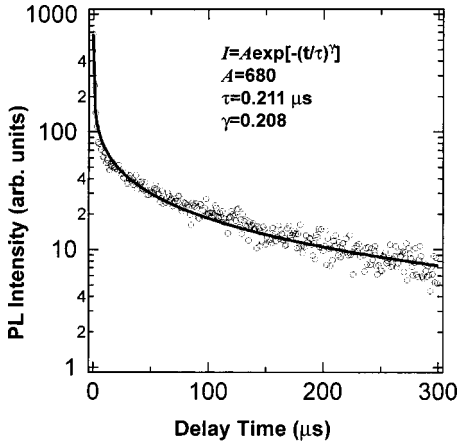

FIG. 3. A semilog plot of the PL decay signals for transparent silica glass prepared by heating fumed silica at 980 °C for 168 h. The time-resolved PL signal was detected at 510 nm using a pulsed Nd:YAG laser (λ_{exc} =266 nm) with a gate width of 0.5 μs. The solid line is the best-fit curve using a stretched exponential function.

α-cristobalite, appeared, and clear transparent samples were not obtained. We should also note that micrometer-sized silica glass powders compacted in the same manner as fumed silica were not sintered to transparency irrespective of a very long time ($>\sim$200 h) sintering at $\sim$1000 °C, indicating that the present solid-state reaction leading to transparent silica glass is attributed to a peculiar characteristic of nanometer-sized silica particles. We have recently discovered that fumed silica can be sintered to transparency even at room temperature when pressed under $\sim$6 GPa.[13] These unique sintering behaviors of fumed silica most likely result from its highly reactive nature and its inherent structural characteristics.[14] The concentration of the residual OH groups in the transparent silica glass was rather low ($\sim$200 to $\sim$400 ppm), which was determined by the infrared absorption of the OH stretching band.[15] This indicates that most of the OH groups at the surface of original fumed silica particles were dehydroxylated during the sintering process. The density of the transparent samples obtained after heating more than $\sim$100 h was found to be virtually identical to that of normal bulk silica glass (2.20 g/cm^3), implying that these samples are not porous in terms of the macroscopic length scale.

The PL spectra were measured at room temperature with a spectrofluorometer (a Photon Technology International, QM-2000-3) using a pulsed xenon source for excitation. In addition, time-resolved PL measurements were performed using the fourth-harmonic (266 nm) of a Nd:YAG pulsed laser (8 ns pulse, $\sim$3 mJ/cm^2 per pulse) with a repetition rate of 10 Hz. The time-resolved PL was collected with a monochromator (SpectraPro 300i; Acton Research) with a 150 lines/mm grating and a gated image intensifier CCD camera (PI·MAX:1024RB; Roper Scientific).

We have found that the present optically transparent samples exhibit white light emission, which is quite visible to the naked eye [see Fig. 1(b)], under UV excitation. The present white PL was quite stable within the given time of UV irradiation and shows no aging effects after exposure to the ambient environment for more than 12 months. Figure 2 shows a series of PL spectra of the fumed silica samples calcinated at 980 °C for various heating times. It is clear from Fig. 2 that the UV excitation results in a broad PL band at $\sim$510 nm, ranging from $\sim$400 to $\sim$700 nm. We should note that the intensity of the $\sim$510 nm PL band increases with increasing heating time until it reaches a maximum after 192 h. It has also been found that the observed PL spectral feature is hardly dependent on the wavelength of the UV (200–300 nm) excitation. Since the present transparent silica glass has a weak absorption feature below $\sim$300 nm (see the inset of Fig. 2), it is quite likely that the observed PL is attributed to the one-photon excitation process from the mid-gap states associated with the absorption, which is supposed to be created during the calcination process. From the time-resolved PL measurements (see Fig. 3), the decay process of the $\sim$510 nm band is not described by a pure exponential function but is tentatively represented by a stretched exponential function: $I \propto \exp[-(t/\tau)^{\gamma}]$, where I is the PL amplitude, τ is a characteristic decay time, and γ is a stretching parameter that represents the degree of deviation from a single exponential decay. We found that the value of γ is rather small (0.21, see Fig. 3), indicating a very broad distribution of actual lifetimes.

As mentioned earlier, Glinka *et al.*[12] have shown that fumed silica itself also exhibits visible PL emission under UV excitation; when excited by the fourth harmonic (266 nm) of a Nd:YAG pulsed laser, red and green PL bands located at 652 and 523 nm are observed. Glinka *et al.*[12,16] suggested that the PL bands at 652 and 523 nm are ascribed to nonbridging oxygen hole centers and hydrogen-related species on the surface of silica nanoparticles, respectively. Glinka *et al.*[12,16] have also shown that the PL intensity of the band at 652 nm increases with increasing heating temperature up to 900 °C, whereas the PL signal at 523 nm remains almost unchanged irrespective of the heating treatment. In contrast to the results observed for unconsolidated fumed silica, the present silica glass samples exhibit only one broad PL band at $\sim$510 nm, and the PL intensity increases with increasing heating time. In our samples, the heating treatment was carried out at 980 °C for more than 100 h to induce solid-state sintering; on the other hand, Glinka *et al.*[12,16] heated the samples at 900 °C for 2 h to retain the basic morphology of the original silica nanoparticles. We thus consider that the origin of the PL emission from the present

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silica samples is different from that from unconsolidated silica nanoparticles. It should also be noted that in unconsolidated silica nanoparticles, the PL band at 523 nm measured with 266 nm pulsed laser light decays with a time constant of $\sim 3-4\ \mu s$,[17] whereas the decay process of the present ~ 510 nm PL band measured with the same pulsed laser light has much shorter and longer components, as demonstrated by a small value of γ (see Fig. 3). This result also implies that these two PL bands are attributed to different microscopic origins.

In summary, we have shown that transparent silica glass prepared from nanometer-sized silica particles exhibits robust white-light PL emission under UV excitation. Although the physical origin of the white PL emission is yet unknown at present, the transparent silica glass obtained in this work will open up a new practical application in the field of lighting products and related optoelectronic and display technologies. Further analysis to get a detailed picture of the white PL emission along with its emission quantum yield is under way.

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