Intense ultraviolet and green photoluminescence from sol–gel derived silica containing hydrogenated carbon

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Abstract
Intense ultraviolet and green room-temperature photoluminescence (PL) at 335, 370 and 500 nm was observed in C-doped silica synthesized by a sol–gel process using tetraethoxysilane as the precursor and glucose as the carbon source, followed by thermal treatment at temperatures from 400 to 900 °C in air and ambient N_2. The 335 nm emission was accompanied by a shoulder at 325 nm which originated from nonbridging oxygen hole centres ($\equiv$Si–O•). The 370 nm emission may correlate with the Si–O–C species formed by $\equiv$Si–O• defects and carbon atoms. The 500 nm band results from hydrogenated carbon embedded in silica which mainly derived from the decomposition of glucose. Moreover, the green PL exhibited a vibrational structure with a peak spacing of about 1360 cm^{-1} when the sample was heated at 800 °C in N_2; this can be assigned to a vibronic coupling process involved in radiative electronic transitions in the hydrogenated carbon. Both the 370 and 500 nm PL emissions disappeared when the sample was heated above 600 °C in air, indicating oxidative decomposition of the light-emitting species in the material.

1. Introduction

The discovery of intense visible photoluminescence (PL) from porous silicon [1] has stimulated great interest in the study of Si-based light-emitting materials. In the past few years, SiO_2 materials synthesized by various techniques, such as the sol–gel process [2, 3], thermal oxidation of porous Si [4] and magnetron sputtering [5], have been extensively investigated. Ultraviolet (UV) and visible PL emissions have been observed from these materials. In order to utilize the emission from these materials as the light source for optical data storage it is desirable to have a shorter wavelength to realize a higher storage density [5]. Therefore, Si-based UV-emitting materials are of great importance.

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On the other hand, fabrication of semiconductor nanoclusters such as C [6] and Si [7] embedded in SiO$_2$ glass or film has also been reported. Visible PL has been observed from these systems. In the C-doped system, however, the origin of the visible emission was not certain. Green *et al* [8] reported that silicon oxycarbide was probably responsible for PL from tetraalkoxysilane sol–gel precursors containing a variety of organic carboxylic acids. Zhao *et al* [9] observed a broad PL band including peaks at 360 and 460 nm from C-implanted SiO$_2$ film. They attributed the emission to a complex of Si, C and O. In the experiment of Li *et al* [10], carbon was incorporated into silica glass during the sol–gel process. A complicated PL spectrum originating from SiC/C nanostructures was observed.

In this work we demonstrate intense room-temperature PL emissions over a wide band of wavelengths from the UV to the green region from thermally treated glucose-doped sol–gel silica at various temperatures. We suggest that the UV emission originates from nonbridging oxygen hole centres (NBOHC) in SiO$_2$, and the green emission is attributed to the formation of hydrogenated carbon. The present investigation may throw light upon the synthesis of SiO$_2$-based light-emitting materials.

1.1. Experiment

Tetraethoxysilane (TEOS), ethanol (EtOH), acid water (HNO$_3$) and glucose were mixed slowly in a 1:3:2:0.03 mol ratio at 25 °C. The mixture was stirred for 30 min and the clear liquid was allowed to gel at 60 °C. After 2 days, the container was opened to the air and the excess liquid was decanted. The remaining glass was then air dried at 25 °C for at least 1 day. The sol–gel was then heated to temperatures between 400 and 900 °C in air and ambient N$_2$ at a 2 °C min^{-1} ramp, followed by an isothermal hold for 2–4 h. This procedure produced a brown glass that underwent intense PL.

For comparison, pure TEOS-silica without glucose doping was synthesized under the same conditions as those mentioned above. It was then heated at 500 °C in air at a 2 °C min^{-1} ramp for 3 h for PL measurement.

PL and PLE spectra were measured on a Hitachi 850 fluorescence spectrophotometer at room temperature. The excitation light was produced by a xenon lamp. Fourier transform infrared (FTIR) spectra were measured with a MAGNA-750 spectrometer from 400 to 4000 cm^{-1}. The H and C content was investigated by an elemental analysis combustion experiment conducted using Vario EL-III equipment.

2. Results and discussion

The PL spectra (excited by 220 nm wavelength) of glucose-doped silica heated at various temperatures in air (400–800 °C) and in N$_2$ ambience (400–900 °C) are plotted in figures 1(a) and (b) respectively. The spectrum for the sample heated at 900 °C in air is not presented in figure 1(a) because it does not exhibit PL emission. The PL spectrum of pure TEOS-silica heated at 500 °C in air is also given as a reference. An intense UV PL emission at 335 nm (3.70 eV), with a shoulder at 325 nm (3.81 eV) (see inset of figure 1(a)), is observed in all of the spectra. The intensity of this peak increases steadily with heating temperature before a drastic decrease when the temperature reaches 800 °C (in air) or 900 °C (in N$_2$). When heated at 450–550 °C in air, two new bands emerge in the spectrum of glucose-doped silica: a weak peak at 370 nm (3.35 eV, UV) and a broad band around 500 nm (2.5 eV, green), as shown in figure 1(a). The intensity of the two bands maximized at 500 °C. Each band disappeared when the heating temperature reached 600 °C (in air). When heated in ambient N$_2$, however, the bands appeared at 500 °C and persisted up to 900 °C. At 800 °C, the intensity of the 500 nm band shows a
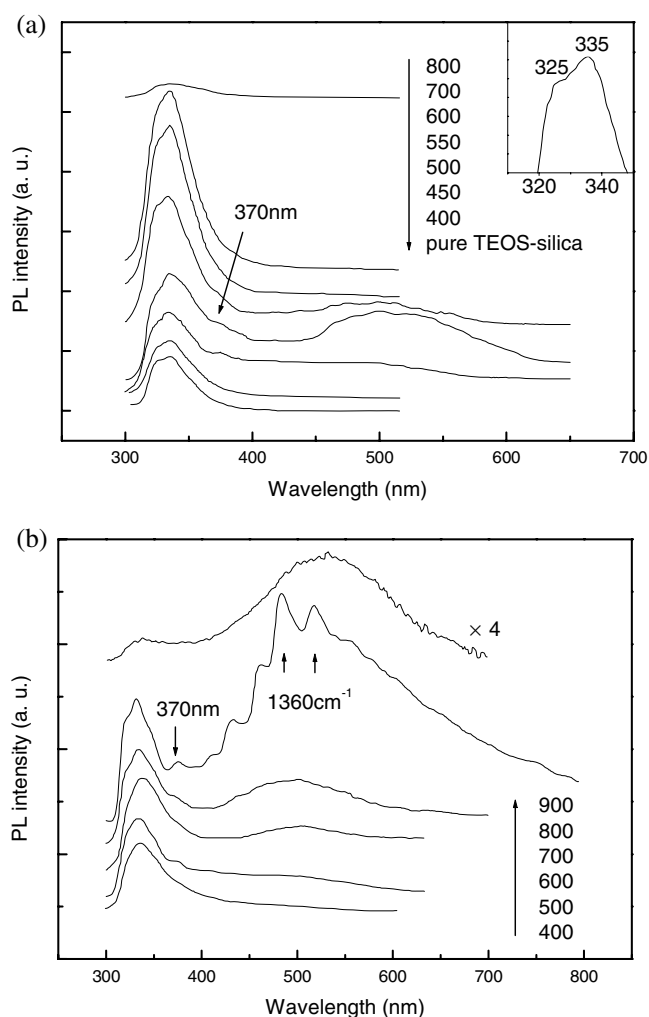
Figure 1. Room-temperature PL spectra from glucose-doped silica heated at (a) 400–800 °C in air and (b) 400–900 °C in ambient N_2. The PL measurement was excited with 220 nm UV light. A 290 nm short λ cutoff filter was used. The PL of pure TEOS-silica is plotted as a reference. The inset of (a) shows the magnified spectrum of double peaks at 325 and 335 nm. The intensity of the 900 °C spectrum was multiplied by 4.

significant increase and becomes stronger than that of the 335 nm band. More prominently, the spectrum exhibits a vibrational structure with a peak spacing of about 1360 cm^{-1} (0.17 eV). At 900 °C, the green PL band becomes much weaker with its position shifting to about 530 nm (2.35 eV).

Typical FTIR spectra for the light-emitting sol–gel silica heated in air (400–600 °C) and in N_2 (800 °C) are shown in figure 2. Absorption bands which appeared at 460, 800 and 1100 cm^{-1} in all of the spectra are characteristic vibrations of SiO_2. The absorption at about 1200 cm^{-1} is assigned to interstitial Si–O–Si vibration in silicon-based gels [2]. There are also three weak peaks corresponding to C–H stretching at 2800–3000 cm^{-1}. The 2960 cm^{-1} peak is assigned to an asymmetric mode of a saturated sp^3 CH$_3$ group and to an olefinic sp^2 CH$_2$
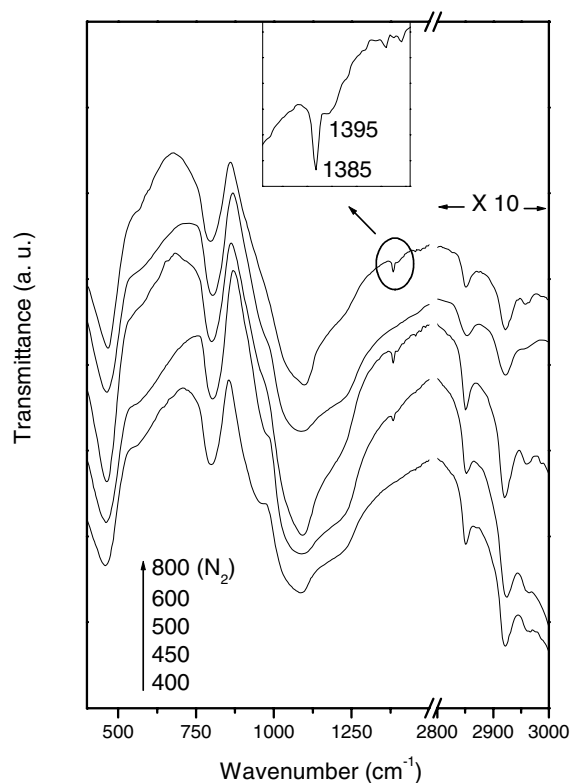
Figure 2. Typical FTIR spectra from glucose-doped silica heated at 400, 450, 500 and 600 °C in air, and at 800 °C in ambient N_2. The inset shows the detail of the 1385 cm^{-1} peak. The intensities in the region between 2800 and 3000 cm^{-1} are multiplied by 10.

group [11]. The 2920 and 2850 cm^{-1} peaks are attributed to a saturated sp^3 CH_2 group [11]. These CH_3 and CH_2 groups are derived from unhydrolysed alkoxy groups and undecomposed glucose. It should be noted that a peak at 1385 cm^{-1} is observed only in the samples that have the 500 nm PL band. The peak at 1385 cm^{-1} can be assigned to the bending mode of C–H monohydride [12, 13], and the small component at 1395 cm^{-1} is direct evidence for carbon atoms bonded to two or three methyl groups [14]. The result reveals the existence of hydrogenated carbon species [14] in the silica matrix.

The elemental H and C content for pure TEOS-silica and several typical glucose-doped samples is listed in table 1. The content of both H and C decreases with increasing temperature. The content of H and C in samples heated in N_2 is higher than that of samples heated in air, mainly due to the prevention of oxidation by N_2. The data reveal that the hydrogen and carbon present in the samples is not only due to the glucose but that some is due to the TEOS. However, it seems that the carbon derived from TEOS has nothing to do with the green PL because the pure TEOS-silica heated in air displays only one PL peak at 335 nm, different from the glucose-doped samples. Note that there is no simple correspondence between H (and also C) content and the green PL, because H (and also C) exists in several species according to FTIR spectra (see figure 2), among which only hydrogenated carbon is responsible for the green PL, as will be discussed later.

Figure 3 illustrates the PLE spectra monitored at 335, 370 and 500 nm. It is clear that each PLE spectrum is very different from the others. The present experimental results suggest that

Table 1. The content of H and C (wt%) in several typical samples.

Sample	H (%)	C (%)
A400[a]	1.19	4.86
A500	1.00	4.56
A600	0.79	2.63
A800	0.22	0.64
N500	1.82	7.38
N800	0.94	4.02
N900	0.38	1.98
Pure TEOS-silica	0.82	2.44
(500 °C, air)		

[a] 'A' and 'N' stand for heating in air and ambient N_2 respectively.

several types of luminescence centres (LC) contribute to the PL from glucose-doped silica. Yao *et al* [3] have observed similar double UV PL emissions at about 330 and 340 nm in thermally treated porous silica, using 220 nm light as the excitation source. They suggested that the double UV PL emissions originate from NBOHCs generated from surface-adjacent and isolated hydroxyls respectively. It is well known [15] that the heat treatment of the silica in air at moderate temperature gives rise to the formation of NBOHC by the following process:

$$2(\equiv\text{Si–OH}) \xrightarrow{heat} (\equiv\text{Si–O}\bullet) + (\equiv\text{Si}\bullet) + H_2O \uparrow .$$

Glinka and co-workers [16] proposed that the NBOHC (C_1^0) could be charge modified (C_1^+) by exciting one electron from C_1^0 to the conduction band (CB) of SiO_2. The energy separation between C_1^0 and the CB is 4.65 eV. Accordingly, the 274 nm (4.53 eV) peak in the PLE spectrum monitored at 335 nm (see figure 3) can be assigned to the $C_1^0 \rightarrow$ CB transition for NBOHCs generated from surface isolated hydroxyls by assuming that the corresponding energy separation is 4.54 eV [3] (the energy difference between the ground states of the two kinds of NBOHCs is 0.11 eV, as indicated in figure 1). The 274 nm peak is much weaker than the 220 nm one. This is reasonable because the photon involved in the transition may lose energy due to the interaction between the photon and the SiO_2 network before the optical transition occurs.

Based on the above results, the increase in the intensity of the UV band with heating temperature observed in figure 1 can then be attributed to nonbridging oxygen [15]. The drastic decrease in the intensity of the double peaks at high temperature (900 °C) may result from the annealing effect of the NBOHC defects.

Before discussing the origin of the green PL emission, we first draw attention to the fact that a wide variety of high surface area materials, including SiO_2 sol–gel, are known to photoluminesce to varying degrees in the blue–green spectral range [17]. However, pure TEOS-silica heated at temperatures from 400 to 900 °C in the present work does not exhibit PL at 370 and 500 nm. It is clear, therefore, that the incorporation of glucose plays an important role in the evolution of the luminescence species that are responsible for the two PL bands. It has been reported that C incorporating into SiO_2 followed by thermal treatment can produce an Si, O, C complex [9] or SiC/C nanostructure [10], which may act as an LC. Plasma-deposited amorphous carbon and diamond-like carbon films can also produce materials that exhibit room-temperature PL in a broad spectral range [11]. In our experiment, however, SiC is unlikely to be formed since the heating temperature is relatively low. The most important feature for the 500 nm PL band in the 800 °C (N_2)-heated sample is the appearance of a vibrational structure. The spacing between the most prominent peaks is about 1360 cm^{-1}. A similar PL structure has been reported previously [8, 18], but the source of emission was not positively identified.
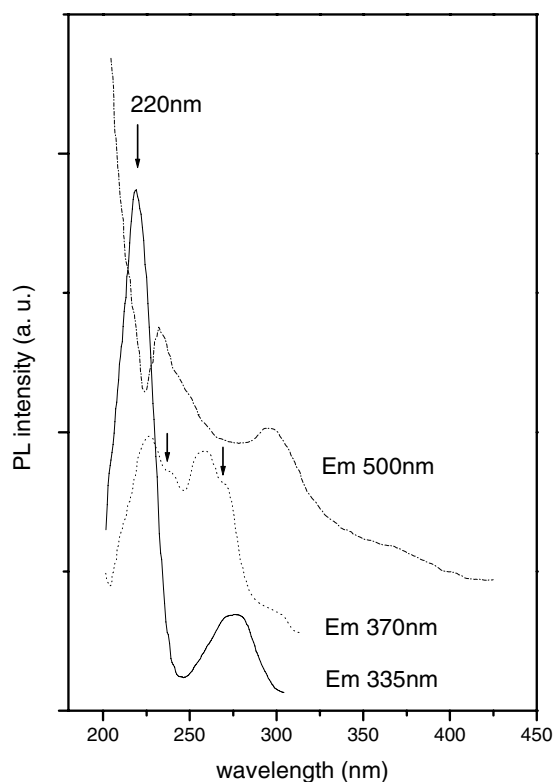
Figure 3. The PLE spectra from the thermally treated glucose-doped silica monitored at 335, 370 and 500 nm.

In the present work, we note that the peak spacing of $1360 \, \text{cm}^{-1}$ is in good agreement with the bending mode of C–H monohydride at $1385 \, \text{cm}^{-1}$ (see figure 2). Moreover, the green PL band and the $1385 \, \text{cm}^{-1}$ IR peak appear and disappear simultaneously as the heating temperature increases from 450 to 600 °C (in air), as mentioned earlier. From this we suggest that the 500 nm PL is correlated with hydrogenated carbon and the vibrational structure observed for this band result from the vibronic coupling involving bending vibrations in the ground electronic state of the hydrocarbon. A similar vibrational structure with a peak spacing of $630 \, \text{cm}^{-1}$ correlating with hydrogenated species (Si–H) has been observed in nanoscale silica [15, 19]. The PLE spectrum monitored at 500 nm in figure 3 shows excitation in a broad energy range from 3.1 to 6.2 eV (200–400 nm), with two peaks at 230 nm (5.39 eV) and 295 nm (4.20 eV). A similar broad PLE spectrum has been observed from a-C:H material with a PL band at 530 nm [20], which supports the assignment in the present work of the green PL to hydrogenated carbon. The heat treatment above 900 °C dramatically reduces the intensity of the green PL band, which may due to the removal of hydrogenated carbon.

The PLE spectrum for 370 nm emission shows double peaks at 225 and 258 nm. Each peak has a shoulder (235 and 270 nm respectively) on the lower energy side. It seems that the 370 nm emission is correlated with NBOHCs since the energies of the 258 and 270 nm PLE peaks, 4.80 and 4.59 eV respectively, are very close to the energy separation of 4.65 eV between C_1^0 and CB of SiO_2, as mentioned earlier. On the other hand, the 370 and 500 nm bands appeared at 450 °C and disappeared at 600 °C when the sample was heated in air. Their

appearance at $450\,^\circ$C could be explained by the formation of carbon-related LCs in silica, while their disappearance at $600\,^\circ$C is probably due to oxidative decomposition of the light-emitting species in the material. Taking the oxidation effect into account, we propose that the LC responsible for the 370 nm band may correlate with Si–O–C species formed by $\equiv$Si–O$\bullet$ defects and carbon atoms during the thermal treatment. Similar PL emission originating from Si–O–C complex has previously been observed in C$^+$-implanted SiO$_2$ film [9] and amorphous Si:O:C film [21]. However, further investigations should be conducted to clarify this.

The luminescence of carbon impurities in silica has been extensively studied both in the past and more recently. Luminescent peaks originating from carbon-related species with positions from 415 to 600 nm, depending on the preparation conditions, have been reported [8–10, 22, 23]. Several C-related LCs, such as silicon oxycarbide and SiC/C nanostructures, have been proposed to explain the experimental results. However, green PL emission originating from hydrogenated carbon embedded in silica has seldom been reported. In our experiment, glucose doping at the stage of sol–gel synthesis and the subsequent annealing process gave rise to the formation of hydrogenated carbon species in the silica matrix; these were responsible for the green PL as demonstrated by FTIR and PL analyses.

3. Conclusion

In summary, three PL bands at 335, 370 and 500 nm were observed in glucose-doped sol–gel silica heated at temperatures of 400 to $900\,^\circ$C in air and ambient N$_2$. We suggest that the LC responsible for the three bands are NBOHC, Si–O–C species and hydrogenated carbon respectively. Moreover, vibrational structure was observed for the 500 nm band, which suggests that a vibronic coupling process takes place in radiative electronic transitions in the hydrogenated carbon.

Acknowledgment

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