Photoluminescent properties of hydrogenated amorphous silicon oxide powders

Wei-Fang Su[a] and Hong-Ru Guo
Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

(Received 31 July 2000; accepted 28 January 2002)

The photoluminescence properties of hydrogenated amorphous silicon oxide powder $SiO_{0.92}H_{0.53}$ were investigated. The powder was prepared by reacting lithium with trichlorosilane in tetrahydrofuran. The luminescence peak energy was located between 1.0 and 1.61 eV. The samples were treated under different conditions such as annealing, hydrolysis, and hydrolysis plus HF etching. The changes of the photoluminescent intensity and location on the treated powders can be explained by the electronic density of state model of amorphous semiconductors. The temperature dependence of luminescence properties of the powders can be described by the relationship of thermal quenching effect: $\ln[I_o/I(T) - 1] = E_D/E_o = T/T_o$ at temperatures between 100 and 300 K.

I. INTRODUCTION

The formation of hydrogenated amorphous silicon nanopowder involved in the plasma-enhanced chemical vapor deposition (PECVD) process has been reported.[1] This material is expected to be a good precursor in sintering ceramics and for catalytic surfaces. Similar to other silicon photoluminescent materials, such as amorphous silicon,[2] porous silicon,[3] and silicon nanocrystals,[4] silicon nanopowders formed by PECVD showed an intense photoluminescence (PL) emission. However, their photoluminescences were qualitatively different. When hydrogenated amorphous silicon was alloyed with oxygen, the original network changed from a dense homogeneous phase to a less dense inhomogeneous and strained phase.[5] Oxygen atom incorporation contributed to the changes of optical and electrical properties of those amorphous materials.[6] We synthesized a disordered, nonregular structure of silicon-based photoluminescent materials using a simple wet chemical method by reacting lithium with trichlorosilane in tetrahydrofuran. These materials have a composition of $SiO_{0.92}H_{0.53}$ and exhibit a heterogenous structure with a-Si dispersed in SiO_2 matrix.[7] The changes of their photoluminescence properties under annealing, hydrolysis, and hydrolysis plus HF treatments were investigated to determine the luminescence mechanisms of the material.

II. EXPERIMENTAL

Hydrogenated amorphous silicon oxide powders were synthesized by reacting lithium (99.9%, Aldrich Chemical Co., Milwaukee, WI) with trichlorosilane in tetrahydrofuran (THF; 99.9%, Fischer Chemical Co., Pittsburgh, PA) at room temperature under argon for 24 h with stirring.

The annealed samples were prepared by heating the samples in a tube furnace under Ar at 5 °C/min from room temperature to the desired temperature, then held at temperature for 60 min. The hydrolyzed samples were prepared by stirring the synthesized powder in distilled water for 24 h. The HF etching was performed on hydrolyzed samples by dipping the samples in a 10% HF solution (diluted from 49.5% HF solution, Aldrich Chemical Co.) for 10 s.

Photoluminescence measurements were performed in a vacuum chamber with the 488-nm line of an Ar ion laser as the excitation source.

III. RESULTS AND DISCUSSION

Figure 1 displays the PL spectra of our samples before and after annealing at 100 °C at various times. The PL spectrum of a-SiO_2 is also included in Fig. 1 for a comparison. The peak position shifted from 1.1 to 1.21 eV, and the PL intensity increased with increasing annealing time. When the annealing temperature was over 150 °C, the PL intensity obviously decreased with increasing annealing temperature, and the peak energy was shifted to a higher energy level, as shown in Fig. 2.

---

[a] e-mail: suwf@ccms.ntu.edu.tw

From the electronic density of state model of amorphous semiconductors, we know that the sample with the lowest deep defect density exhibits the highest PL intensity. For samples annealed at 100 °C, their PL intensities increased with increasing annealing time. The Raman spectra of 100 °C annealed samples indicated that the a-Si–Si band at 480 cm^{-1} was sharper than that of the sample without annealing. The peak position shifted a few cm^{-1} toward a c-Si–Si band at 521 cm^{-1}. The results implied that the microstructures and the electronic structures changed, especially in the localized states. At the same time, weak Si–O bonds (strain bonds or oxygen dangling bonds near or in the a-Si–a-SiO_x interface) diffused into the a-Si cluster region, saturated the silicon dangling bonds, and reduced the deep oxygen impurity levels. The gap between band edges became wider, and the PL peak energy shifted from 1.1 to 1.21 eV (Fig. 1).

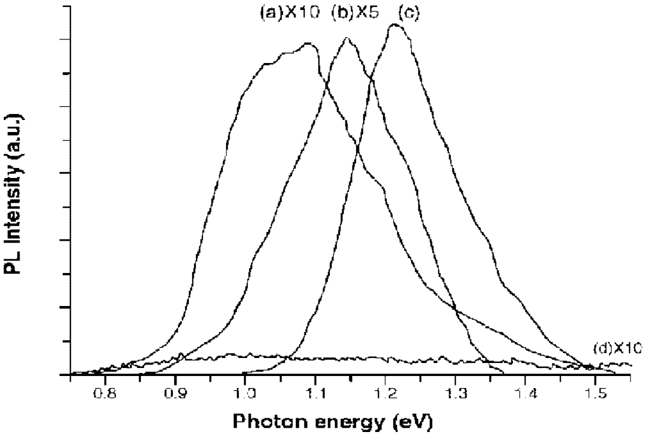

FIG. 1. PL spectra of hydrogenated silicon oxide powders annealed at 100 °C in argon for (a) 0 min, (b) 30 min, and (c) 60 min, and (d) SiO_2.

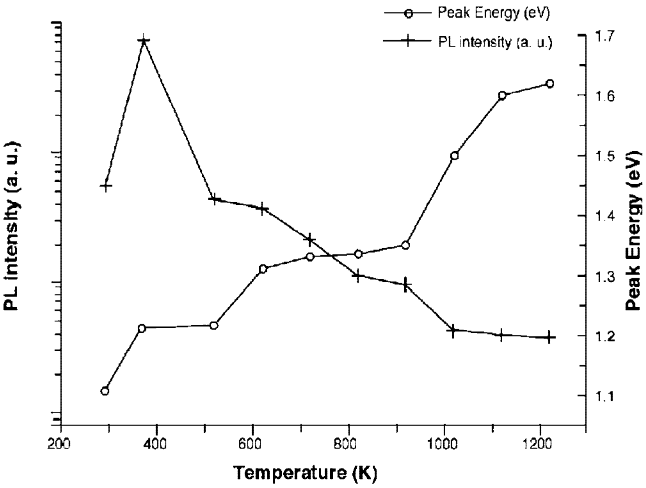

FIG. 2. Changes of the maximum PL intensity and PL peak energy versus annealing temperature of the hydrogenated silicon oxide powders.

Fourier transform infrared (FTIR) spectroscopy was used to investigate samples annealed at temperatures over 150 °C. The absorption peak intensity of the H_x–$Si(Si)_{3-x}$ band[8] near 2100 cm^{-1} decreased and shifted to H–$Si(OSi)_3$ band[9,10] at 2265 cm^{-1} with annealing temperature increasing up to 350 °C. However, the intensity of 2265 cm^{-1} peak decreased with increasing temperature up to 550 °C. Finally, at 600 °C, there is no absorption at 2265 cm^{-1}. These results indicated that Si–H bonds in a-Si cluster were broken by thermal annealing. In addition, oxygen atoms near the interface region diffused into the a-Si clusters, the optical gap became wider, and the PL peak energy shifted to a higher energy.[11]

Annealing (thermal energy) changed the physical and electronic structures of the samples. The H atom was diffused out of the samples during annealing. How can we reduce the incidence of the Si–H bonds without changing the physical structure of the samples? Okuda *et al.* reported that the H atom of Si–H bond can be broken by OH-containing molecules.[12] Therefore, we hydrolyzed the sample in water to break the Si–H bond according to the following reaction:

$$\mathrm{Si{-}H}_x + \mathrm{H_2O} \rightarrow \mathrm{Si{-}H}_{x-y}\mathrm{OH}_y + y\mathrm{H}_2 \quad .$$

For hydrolyzed sample, the infrared absorption peak of $Si_{3-x}Si$–H_x at 2000–2265 cm^{-1} was not observed, and the intensity of the Si–OH band at 3650 cm^{-1} increased. Two luminescence peaks were observed at 1.05 and 1.21 eV for the hydrolyzed sample (Fig. 3). The 1.05 eV peak may be due to a-Si, and the 1.21 eV peak may be from the oxygen-rich region. We dipped the hydrolyzed sample into a HF solution (10%) for 10 s. Figure 4 shows that the HF-etched sample exhibited a relatively larger PL intensity at lower energy peak (1.05 eV) than that of the hydrolyzed sample, and the high energy peak shifted to 1.3 eV. FTIR studies of the hydrolyzed sample with HF etching showed that the peak intensity of the Si–O–Si

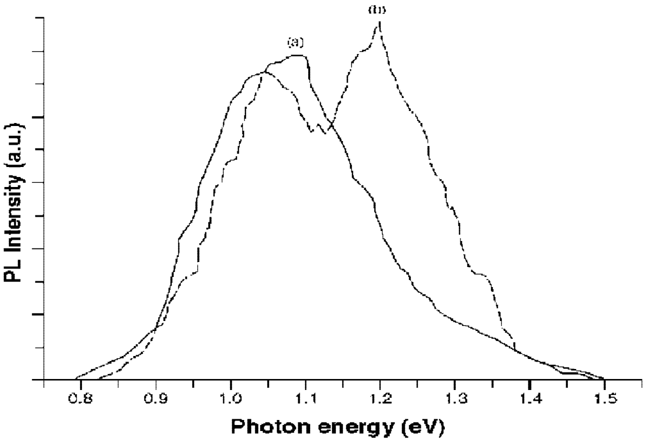

FIG. 3. PL spectra of hydrogenated amorphous silicon oxide powders: (a) as-synthesized sample and (b) hydrolyzed sample.

bond at 1000–1100 cm^{-1} decreased. There was a new peak at 800–900 cm^{-1} from the Si–F_x bond. Thus, the small blue shift (approximately 0.09 eV) in the high energy peak may be from the formation of Si–F bonds.

It is hard to obtain information about the energy distribution of recombination centers directly from the luminescence spectra. However, some conclusions can be drawn from the thermal quenching that occurs at temperatures above 50 K. At these temperatures, charge carriers are excited to the mobility edge; thus they can be diffused away to a nonradiative site. Thermal quenching is therefore a measure of the binding energy of the states in amorphous materials.

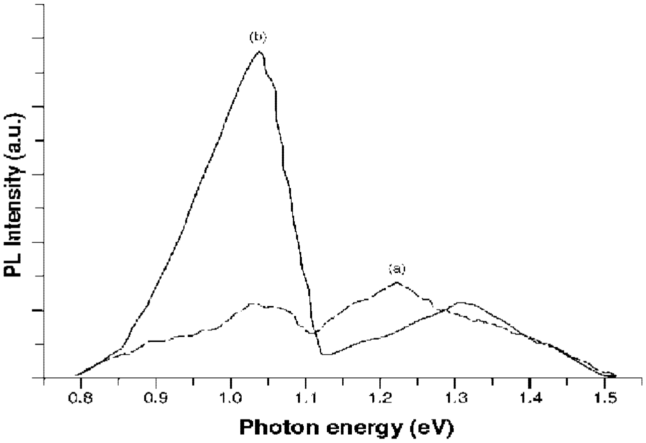

FIG. 4. PL spectra of hydrogenated amorphous silicon oxide powders: (a) hydrolyzed sample and (b) hydrolyzed plus HF etching.

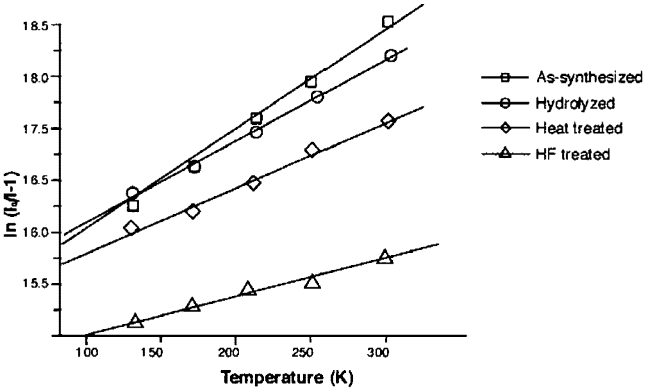

FIG. 5. Plot of $\ln[I_o/I(T) - 1]$ versus temperature of the hydrogenated amorphous silicon oxide powders with various treatments.

TABLE I. Calculated T_o and E_o values of hydrogenated amorphous silicon oxide with various treatments derived from thermal quenching effects.

Samples	T_o (K)	E_o (meV)
As-synthesized	95	169
Annealed at 100 °C	145	259
Hydrolyzed	112	112
HF-treated	125	125

We investigated the temperature dependence on the luminescence properties of various samples (as-synthesized, annealed at 100 °C, hydrolyzed, and hydrolyzed plus HF etching). The samples showed a monotonically increasing PL intensity with decreasing temperature between 100 and 300 K. A straight line with a slope of $1/T_o$ was obtained by plotting $\ln[I_o/I(T) - 1]$ versus T as shown in Fig. 5, where I_o is the zero temperature extrapolation of the data in the saturation regime. Thus, the PL intensity is a function of temperature, and the carriers are within the exponential band tails. The linear relationship data can be fitted into the following equations[2,13]:

$$\ln[I_O/I(T) - 1] = E_D/E_O = T/T_O \quad , \tag{1}$$

where E_D is radiative decay energy for a particular value of radiative time τ_R and is given by[2]

$$\tau_R^{-1} = \omega_O e\,(-E_D/kT) \quad . \tag{2}$$

The F_o can be calculated from T_o by using the usual value of $\tau_R = 10^{-3}$ s and the phonon frequency $\omega \sim 10^{12}\ \text{s}^{-1}$. Table I summarizes the T_o and E_o values for each sample with different treatments. T_o and E_o are related to the density of localized states in the tail region. The sample annealed at 100 °C has the largest value of T_o (145 K) and E_o (259 meV) among the tested samples. That indicates the sample has a high quantum efficiency.

IV. CONCLUSIONS

Photoluminescence studies of the hydrogenated amorphous silicon oxide powders indicated that their structures were inhomogeneous and contained silicon dangling bonds in the SiO_2 matrix. The luminescence peak energy was located between 1.0 to 1.61 eV. The PL intensity of prepared samples achieved maximum efficiency at a low-temperature annealing (100 °C/60 min) due to the changes of microstructure and the reduction of defect density. However, the PL intensity decreased with increasing temperature (above 150 °C) due to the breaking of Si–H bonds, the formation of Si–O bonds, and nonradiative carriers recombination. The sample had defect states from Si–H bonds breaking. The blueshift of the PL peak energy at high annealing temperature was due to oxygen atoms near the interface region diffusing into the a-Si clusters. The optical gap became wider. The hydrolyzed samples exhibited two luminescence peaks at 1.05 and 1.21 eV from the a-Si and oxygen-rich region respectively. The HF-etching process removed Si–O bonds in the hydrolyzed sample and formed Si–H bonds that resulted in increasing peak intensity at 1.05 eV. The thermal quenching effect was used to explain the observed temperature dependence of the luminescence properties of the hydrogenated amorphous silicon oxide powders.

ACKNOWLEDGMENTS

The National Science Council of Republic of China (NSC-88-2216-E-002-006) and the Industrial Technology Research Institute, Electronics Research and Service Organization (1997–1998) supported this work.

REFERENCES

1. J. Costa, P. Roura, G. Sardin, J.R. Morante, and E. Bertan, Appl. Phys. Lett. **64,** 463 (1994).
2. R.A. Street, Adv. Phys. **30,** 593 (1981).
3. L.T. Canham, Appl. Phys. Lett. **57,** 1046 (1990).
4. S. Furukawa and T. Hiyasato, Phys. Rev. **B36,** 5726 (1988).
5. A. Morimoto, N. Noriyama, and T. Shimizu, Jpn. J. Appl. Phys. **26,** 22 (1987).
6. H. Watanabe, K. Haga, and T. Lohmer, J. Non-Cryst Solids **164–166,** 1085 (1993).
7. W-F. Su and H-R. Guo, Mater. Chem. Phys. **74,** 239 (2002).
8. G. Lucosvky and R.A. Rudder, Tetrahedrally Bonded Amorphous Semiconductor (Am. Inst. Phys., New York, 1981), pp. 95–99.
9. D.V. Tsu, G. Lucosky, and B.N. Davidson, Phys. Rev. **B40,** 1795 (1989).
10. L. He, T. Inokuma, Y. Kurata, and S. Hasegawa, J. Non-Cryst. Solids **185,** 249 (1995).
11. R. Carius, R. Fischer, E. Hozenkampfer, and J. Stuke, J. Appl. Phys. **52,** 4241 (1981).
12. S. Okuda, Y. Shioya, and H. Kashimada, J. Electrochem. Soc. **145,** 1338 (1998).
13. R.W. Collins, M.A. Paesler, and W. Paul, Solid State Comm. **34,** 833 (1980).