PHYSICAL REVIEW B VOLUME 51, NUMBER 16 15 APRIL 1995-II

Luminescence properties of a cubic silicon cluster octasilacubane

Yoshihiko Kanemitsu and Katsunori Suzuki
Institute of Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Michio Kondo
Electrotechnical Laboratory, Tsukuba, Ibaraki 305, Japan

Soichiro Kyushin and Hideyuki Matsumoto
Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan

(Received 9 May 1994; revised manuscript received 7 February 1995)

We have studied the luminescence properties of a Si_8 cubic cluster, octasilacubane. The photoluminescence (PL) is observed around 1.7 eV at low temperatures and the PL decay is a single exponential with a time constant of 3.1 ms. The PL intensity and the PL lifetime abruptly decrease with increasing temperature above 40 K. The PL properties are strongly affected by nonradiative recombination processes. The luminescence properties of the cubic Si_8 cluster are different from those of the chain and ladder Si_8 clusters. The optical properties of the cubic cluster are discussed.

I. INTRODUCTION

The study of the structure and properties of semiconductor clusters, particularly silicon clusters, has been an extremely active area of current research. Small Si clusters have usually been produced by pulsed-laser-evaporation methods.[1–5] Recent laser-evaporation methods combined with mass spectrometry produce size-selected Si clusters. However, since small clusters are short-lived intermediate species and there are few experimental studies of optical properties in small clusters, we have little information on the optical properties of vapor-phase small clusters.[1] We need to contrive experimental procedures for the study of the detailed structure and properties of Si clusters: For example, vapor-phase Si clusters deposited onto a solid matrix are prepared for the determination of the structure of small Si clusters.[6]

Modern organic synthesis and purification techniques can produce silicon materials with controlled molecular weight. These techniques have some advantages over the widely used laser-evaporation methods: For example, the size and shape of Si clusters can be exactly controlled, and the optical properties of Si clusters have been studied.[7,8] The study of the chemically synthesized Si clusters helps one understand the electronic properties of vapor-phase Si clusters.

Moreover, strong visible photoluminescence (PL) from nanometer-sized silicon materials such as porous Si,[9–12] nanometer-size Si crystallites,[13–15] and polysilanes[16–18] has recently attracted much attention both from the fundamental-physics viewpoint[19] and from the application interest to optical devices.[20] However, despite much work to clarify the mechanism of the PL in these Si materials, it still remains unclear. Since the local Si structure can be controlled in chemically synthesized Si clusters, the study of optical properties of chemically synthesized Si clusters also provides information for the ongoing discussion on the origin of the strong visible luminescence of nanometer-sized Si materials.

In this paper, we report the luminescence properties of a cubic Si_8 cluster, octasilacubane. The study of optical properties of a cubic Si_8 cluster becomes important for the understanding of the nature of the geometry and chemical bonding of small Si clusters[20,21] and the stability of magic-number Si_6 and Si_{10} clusters.[1–3] Broad PL with a peak of 1.7 eV was observed only at low temperatures. The PL intensity and PL lifetime decrease with increasing temperature above 40 K: The PL process is controlled by nonradiative recombination processes. The slow-decay and temperature-sensitive PL is attributed to "forbidden" radiative recombination. The optical properties of the cubic Si_8 cluster are quite different from those of chain and ladder Si_8 clusters. This is because the orbital hybridization and bonding in the cubic cluster are different from those in the other Si_8 clusters.

II. EXPERIMENT

Synthesis, purification, and characterization methods were described in Ref. 23. Here, we briefly describe the synthesis and characterization methods. The reductive coupling of (1,1,2-trimethylpropyl)trichlorosilane with sodium in toluene yielded octakis(1,1,2-trimethylpropyl)octasilacubane. All manipulations were carried out under argon atmosphere. Recrystallization from pentane solutions gave purified samples of octakis(1,1,2-trimethylpropyl)octasilacubane, as red-orange prisms. This cubic cluster was characterized by infrared and NMR spectroscopy, mass spectrometry, and x-ray crystallography. The crystal data were obtained using an Enraf-Nonius CAD4 diffractometer with Cu $K\alpha$ radiation. The determined structure is slightly distorted from an ideal cubic geometry. The Si-Si bond length ranges from 0.2398 to 0.2447 nm and the bond angle between two Si atoms varies from 87.2° to 92.6°. This distortion from an ideal cube may be due to the minimiza-

0163-1829/95/51(16)/10666(5)/$06.00

tion of the steric repulsion from 1,1,2-trimethylpropyl groups. Saturatedly bonded Si_8 clusters terminated by an organic substituent have no dangling bonds and become a model material for small silicon clusters.

The optical absorption spectrum was measured in tetrahydrofuran solution. The PL spectrum was measured by using 325- and 532-nm excitation laser light. The time-resolved PL spectrum was measured under 5-ns, 532-nm or 355-nm excitation (10 Hz repetition rate) using a boxcar signal averager. The calibration of the spectral sensitivity of the whole measuring system was performed by using a tungsten standard lamp. The temperature was varied from 10 to 300 K by controlling the flow rate of cold He gas in a cryostat.

III. RESULTS AND DISCUSSION

The optical absorption, PL, and PL excitation spectra of the cubic Si_8 cluster were briefly reported in our previous paper.[24] To discuss the details of the luminescence properties of the cubic Si_8 cluster, we compare the optical and PL spectra of chemically synthesized Si_8 clusters with different Si-skeleton structures. The optical absorption and PL spectra of Si_8 clusters with different structures are summarized in Fig. 1. The dangling bonds are terminated by the methyl and phenyl groups in the chain structure[7] [Fig. 1(b)] and by the isopropyl groups in the ladder structure[8] [Fig. 1(c)], respectively. In the chain and ladder Si_8 structures, the lowest absorption bands (the dashed lines in the figure) are observed in the ultraviolet spectral region. On the other hand, in the cubic cluster, a small absorption band around 2.4 eV and a large one around 3.5 eV are observed. The absorption-edge energy of the cubic structure is very small compared with those of the chain and ladder structures. The PL and PL excitation spectra were measured at 20 K. Similar PL and PL excitation spectra were reported in octasilacubanes with different organic terminations R (R = t-butyl or 1-ethyl-1-methylpropyl):[25,26] The organic termination groups do not play a dominant role in PL and absorption properties in octasilacubanes.[27] It is considered that the optical absorption and luminescence properties of a cubic cluster in the visible spectral region are determined by the electronic properties of the central Si_8 cubic skeleton.

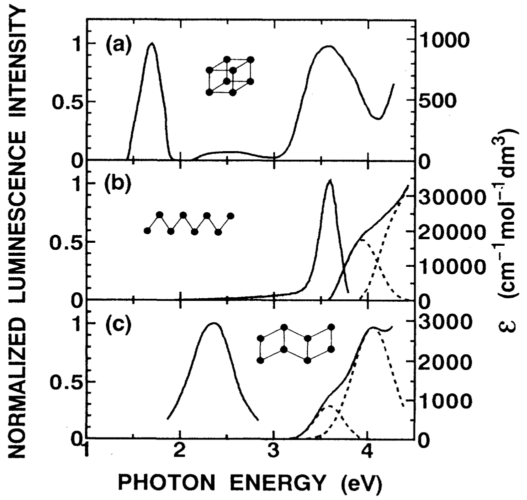

FIG. 1. Optical absorption and photoluminescence of chemically synthesized Si_8 clusters at room temperature: (a) cubic, (b) chain, and (c) ladder structures. The dashed lines in the absorption spectra are optimum tails of two Gaussian functions.

In the absorption spectrum, a low peak and a high peak are observed at 2.4 and 3.5 eV, respectively. The observed peak energy of the strong absorption band is consistent with a theoretical calculation of the lowest optically allowed transition energy in a cubic Si_8H_8 cluster (3.4 eV).[28] On the other hand, two large peaks are observed at 2.4 and 3.5 eV in the PL excitation spectrum.[24] The intensity ratio of PL excitation to the absorption bands at 2.4 eV is much higher than that at 3.5 eV, implying a higher PL efficiency per photon absorbed at 2.4 eV. Although the peak height of the one-photon absorption spectrum at 2.4 eV is very low, the PL spectrum is efficiently observed under 2.4-eV excitation.

Figure 2 shows the temperature dependence of the PL intensity. A typical PL spectrum is illustrated in the inset of Fig. 2, and the shape of the PL spectrum is asymmetrical Gaussian. The PL intensity in this figure is the spectrally integrated PL intensity. The PL intensity is a constant at low temperatures and abruptly decreases with increasing temperature above 40 K. These results suggest that the PL properties are strongly affected by nonradiative recombination processes.

The PL decay profile is approximately described by a single-exponential function at the measurement temperatures. The temperature dependence of the PL lifetime is summarized in Fig. 3. The PL lifetime does not depend on the temperature below 40 K. However, at high temperatures above 40 K, the PL lifetime abruptly decreases with increasing temperature. The temperature dependence of the PL lifetime in Fig. 3 is very similar to that of the PL intensity in Fig. 2. At high temperatures, the PL efficiency and the PL lifetime are limited by nonradiative

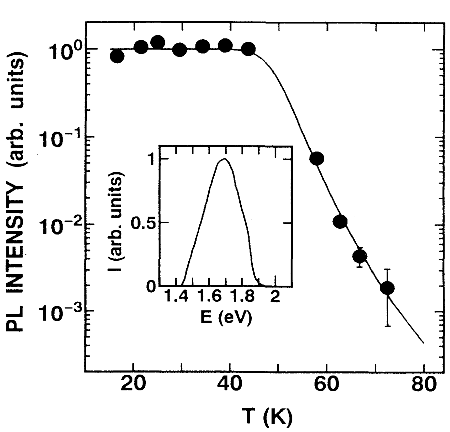

FIG. 2. Spectrally integrated intensity of photoluminescence from a cubic Si cluster as a function of temperature. The inset is the PL spectrum at 16 K. The solid line is the theoretical calculation based on a simple configuration coordinate model.

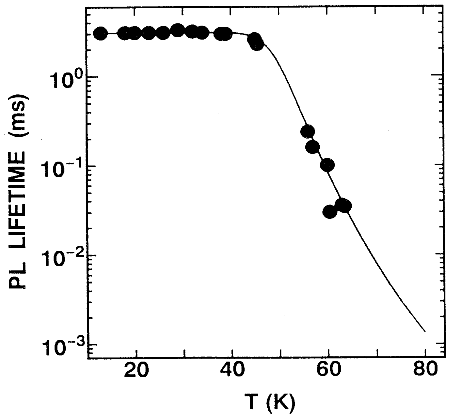

FIG. 3. The PL lifetime of a cubic Si cluster as a function of temperature. The solid line is the theoretical calculation based on a simple configuration coordinate model. The temperature dependence of the PL lifetime is very similar to that of the PL intensity.

recombination processes. Moreover, a light-induced electron-spin resonance (ESR) response implies the presence of a triple excited state.[24] The luminescence properties of the cubic Si cluster are consistent with the characteristics of those of the phosphorescence from the triplet state in chainlike polysilanes.[29] Therefore, it is considered that the slow-decay PL at low temperatures originates from the "forbidden" radiative recombination such as the singlet-triplet transition or the singlet-singlet transition having the same orbital symmetry.

Here, in order to discuss the temperature-sensitive PL in a cubic cluster, we consider a thermally activated nonradiative process. If we assume that the radiative rate from the lowest excited state is τ_R^{-1} and the nonradiative recombination rate is given by $\tau_{\mathrm{NR}}^{-1}=\nu\exp(-\Delta/kT)$, the PL intensity is given by $I_{\mathrm{PL}}=\tau_R^{-1}/(\tau_R^{-1}+\tau_{\mathrm{NR}}^{-1})$ and the PL decay rate is given by $\tau_{\mathrm{PL}}^{-1}=\tau_R^{-1}+\tau_{\mathrm{NR}}^{-1}$. The solid lines in Figs. 2 and 3 are calculated ones using the values of $\Delta=86.6$ meV, $\tau_R=3.1$ ms, and $\nu=2.1\times10^{11}\ \mathrm{s}^{-1}$. The temperature dependence of the PL intensity and the PL lifetime are well explained by a simple picture in which the photoluminescence decay rate τ_{PL}^{-1} is determined by two relaxation channels having the radiative decay rate τ_R^{-1} and the nonradiative decay rate τ_{NR}^{-1}. The luminescence dynamics is controlled by the nonradiative recombination process. However, the microscopic mechanism of the thermally activated process is not clear. A possible model is a configuration coordinate one illustrated in Fig. 4, where G is the ground state and E_1 and E_2 are the excited states. The temperature-sensitive luminescence originates from the radiative transition between the lowest excited E_1 and the ground G states. In this model, Δ is a barrier for nonradiative recombination. A large Stokes shift between the PL and absorption peak energies ($\sim$0.7 eV) and the PL process controlled by nonradiative recombination mean that the cubic Si cluster is a strong electron-phonon coupling system. Another model is a defect-controlled recombination process: The temperature-sensitive PL with a large Stokes shift might arise from a radiative recombination process via defect states. At the present stage, although the microscopic recombination mechanism is not clear, the thermally activated nonradiative recombination process controls the temperature-sensitive PL intensity and PL lifetime.

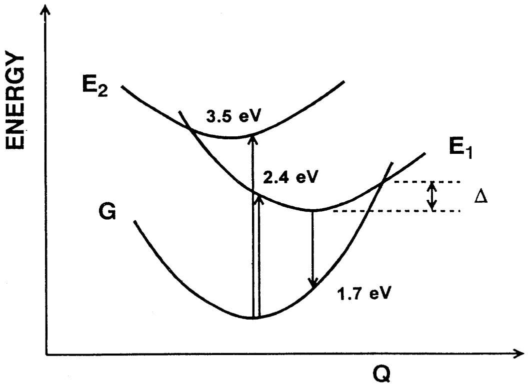

FIG. 4. Configuration coordinate diagram for recombination processes. The transition between the G and E_2 states is the optically allowed one, and the transition between the G and E_1 states is the optically forbidden one. The energy difference Δ is a barrier for nonradiative recombination. The large absorption band at $\sim$3.5 eV corresponds to the transition between the G and E_2 states. Since the peak energy of the excitation spectrum is equal to that of the weak absorption band, the weak absorption peak at $\sim$2.4 eV is due to the transition between G and E_1 states.

The PL intensity in the cubic cluster abruptly decreases with increasing temperature above 40 K, while the PL intensity in the chain and ladder clusters gradually decreases with increasing temperature. The PL spectra in the chain and ladder structures are clearly observed even at room temperature. The PL intensity in cubic Si_8 clusters is very sensitive to temperature compared with chain and ladder structures. Moreover, the PL decay properties of the cubic Si_8 cluster are entirely different from those of the Si_8 chain and Si_8 sheet: The lifetimes of the chain and ladder structures are 110 and 700 ps, respectively, at room temperature. The optical properties of the very small Si clusters are very sensitive to the Si-backbone structures. In particular, the PL characteristics (the slow-decay and temperature-sensitive PL) in the cubic structure are different from those in the chain and ladder structures. The optical absorption-edge energy (the lowest energy gap or the optical band gap) of the cubic cluster is very small compared with those of the chain and ladder clusters. Here, we comment on a possible origin for these significant differences of the optical properties. It is experimentally reported that the band gaps in small Si clusters in the laser-evaporation experiment (Si_4, Si_6, Si_7, and Si_{10}) are comparable to the band gap of bulk Si, 1.1 eV.[30] This seems somewhat surprising, because the band gaps in clusters are usually much larger than that of the bulk Si.[31,32] It is theoretically pointed out that the orbital hybridization and the bonding in small clusters are very sensitive to the size and shape of the clusters.[21,22] These experimental and theoretical studies strongly suggest that the relationship between the band gap and the size of the cluster is not simple in small Si clusters. In our experiments, the Si-Si bond angle in the cubic structure is about 90°, which is different from the bond angle of tetrahedral Si bonds (sp^3-hybridized orbital). On the other hand, the Si-Si bond angle in the chain and ladder structures is nearly equal to that of tetrahedral Si bonds. The molecular-orbital characteristics in the cubic cluster are different from those in the sp^3-hybridized chain and ladder structures. Therefore we speculate that the difference of the optical properties between the cubic and the other clusters is caused by the differences of the orbital hybridization and bonding in the clusters.

IV. CONCLUSIONS

We have studied the luminescence properties of a Si_8 cubic cluster, octasilacubane. Weak PL with a peak of 1.7 eV was observed at low temperatures. The PL decay was single exponential with a time constant of 3.1 ms at 40 K or less. The PL intensity and PL lifetime decreased with increasing temperature: The PL properties are controlled by a nonradiative recombination process. Spectroscopic analysis suggests that the slow-decay and temperature-sensitive PL is attributed to "forbidden" radiative recombination such as a single-singlet transition having the same orbital symmetry or a singlet-triplet transition. The luminescence properties of the cubic cluster are different from those of the chain and ladder clusters. The significant difference of the bonding between the cubic clusters and the others causes the difference of the optical properties. The study of the electronic properties of Si compounds with different geometry and different orbital hybridization becomes very important for the understanding of the structure and properties of small Si clusters.

ACKNOWLEDGMENTS

The authors would like to thank Dr. S. Yamasaki for fruitful discussions. One of the authors (Y.K.) is grateful to the Scientific Research Grant-in-Aid from the Ministry of Education, Science, and Culture of Japan for financial support.

---

[1] M. F. Jarrold, Science **252**, 1085 (1991).

[2] L. A. Bloomfield, R. R. Freeman, and W. L. Brown, Phys. Rev. Lett. **54**, 2246 (1985).

[3] T. P. Martin and H. Schaber, J. Chem. Phys. **83**, 855 (1985).

[4] M. F. Jarrold and V. A. Constant, Phys. Rev. Lett. **67**, 2994 (1991).

[5] K. D. Rinnen and M. L. Mandich, Phys. Rev. Lett. **69**, 1823 (1992).

[6] E. C. Honea, A. Ogura, C. A. Murray, K. Raghavachai, W. O. Sprenger, M. F. Jarrold, and W. L. Brown, Nature **366**, 42 (1993).

[7] Y, Kanemitsu, K. Suzuki, Y. Nakayoshi, and Y. Masumoto, Phys. Rev. B **46**, 3916 (1992).

[8] Y. Kanemitsu, K. Suzuki, Y. Masumoto, T. Komatsu, K. Sato, S. Kyushin, and H. Matsumoto, Solid State Commun. **86**, 545 (1993).

[9] A. G. Cullis and L. T. Canham, Nature **353**, 335 (1991).

[10] J. C. Vial, A. Bsiesy, F. Gaspard, R. Herino, M. Ligeon, F. Muller, R. Romestain, and R. M. Macfarlane, Phys. Rev. B **45**, 14 171 (1992).

[11] P. D. J. Calcott, K. J. Nash, L. T. Canham, M. J. Kane, and D. Brumhead, J. Phys. Condens. Matter **5**, L91 (1993).

[12] Y. Kanemitsu, H. Uto, Y. Masumoto, T. Matsumoto, T. Futagi, and H. Mimura, Phys. Rev. B **48**, 2827 (1993).

[13] H. Takagi, H. Ogawa, Y. Yamazaki, A. Ishizaki, and T. Nakagiri, Appl. Phys. Lett. **56**, 2349 (1990).

[14] Y. Kanemitsu, T. Ogawa, K. Shiraishi, and K. Takeda, Phys. Rev. B **48**, 4883 (1993).

[15] W. L. Wilson, P. F. Szajowski, and L. E. Brus, Science **262**, 1242 (1993).

[16] R. D. Miller and J. Michl, Chem. Rev. **89**, 1359 (1989).

[17] T. Hasegawa, Y. Iwasa, H. Sunamura, T. Koda, Y. Tokura, H. Tachibana, and M. Matsumoto, Phys. Rev. Lett. **69**, 668 (1992).

[18] W. L. Wilson and T. W. Weidman, Phys. Rev. B **48**, 2169 (1993).

[19] See, for example, *Light Emission from Novel Silicon Materials*, edited by Y. Kanemitsu, M. Kondo, and K. Takeda (Physical Society of Japan, Tokyo, 1994).

[20] See, for example, *Silicon-Based Optoelectronic Materials*, edited by M. A. Tischler, R. T. Collins, M. L. W. Thewalt, and G. Abstreiter, MRS Symposia Proceedings No. 298 (Materials Research Society, Pittsburgh, 1993).

[21] K. Raghavachari and V. Logovinsky, Phys. Rev. Lett. **55**, 2853 (1985).

[22] K. Raghavachari and C. M. Rohlfing, J. Chem. Phys. **89**, 2219 (1988).

[23] H. Matsumoto, K. Higuchi, S. Kyushin, and M. Goto, Angew. Chem. Int. Ed. Engl. **31**, 1354 (1992); S. Kyushin, H. Matsumoto, Y. Kanemitsu, and M. Goto, in *Light Emission from Novel Silicon Materials* (Ref. 19), p. 46.

[24] Y. Kanemitsu, K. Suzuki, K. Kondo, and H. Matsumoto, Solid State Commun. **89**, 619 (1994).

[25] K. Furukawa, M. Fujino, and N. Matsumoto, Appl. Phys. Lett. **60**, 2744 (1992).

[26] A. Sekiguchi, T. Yatabe, H. Kamatani, C. Kabuto, and H. Sakurai, J. Am. Chem. Soc. **114**, 6260 (1992).

[27] In our previous paper [Y. Kanemitsu *et al.*, Appl. Phys. Lett. **61**, 2446 (1992)], the ligand R is t-butyldimethlsilyl and the total number of Si atoms in the clusters is 16, where each R has one Si atom. The octasilacubane (Si_8) used in the present work is different from that in the previous cluster (Si_{16}). The absorption and PL spectra in the present cluster Si_8 are different from those in the previous cluster Si_{16}. However, the absorption and PL spectra in the present work are similar those in other Si_8 clusters (Ref. 25).

[28] T. Takagahara and K. Takeda (unpublished).
[29] T. Azumi, in *Light Emission from Novel Silicon Materials* (Ref. 19), p. 82.
[30] O. Cheshnovsky, S. H. Yang, C. L. Pettiette, M. J. Crsycrft, Y. Liu, and R. E. Smalley, Chem. Phys. Lett. **138**, 119 (1987).
[31] S. Y. Ren and J. D. Dow, Phys. Rev. B **45**, 6492 (1992).
[32] T. Takagahara and K. Takeda, Phys. Rev. B **46**, 15 578 (1992).