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Visible photoluminescence from silicon-backbone polymers

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We have studied optical properties of Si-backbone polymers constructed by the organosilicon units having two or three Si—Si bonds in order to understand the mechanism of visible luminescence in silicon-based materials. The backbones of branch, ladder, and network polymers are constructed by the organosilicon units with three Si—Si bonds, and these polymers exhibit broad photoluminescence spectra in the visible spectral region. Sharp luminescence spectra are observed in quasi-one-dimensional chain and quasi-two-dimensional planar siloxene structures. The luminescence properties in branch, ladder, and network polymers are entirely different from those of one-dimensional or two-dimensional excitons in Si-backbone structures. Broad visible luminescence spectra with large Stokes shifts originate from the radiative recombination of excitons localized in disordered Si-backbone structures with three Si—Si bonds.

I. INTRODUCTION

In exploring optoelectronic materials and devices, a great deal of research effort is focused on reducing the dimensionality of the electronic structures in semiconductors. Very recently, Si low-dimensional nanostructures, such as porous Si and nanometer-size Si crystallites, have attracted intense interest from viewpoints of both fundamental physics and optical-device applications, because they exhibit strong visible luminescence even at room temperature.[1-3] Despite many theoretical and experimental work to clarify the mechanism of the strong visible luminescence from Si low-dimensional nanostructures, it still remains unclear.[1-3]

Natural analogs of Si low-dimensional structures, such as quantum wires and sheets, are chemically synthesized Si-backbond polymers. Modern organic synthesis techniques allow us to produce Si materials with controlled structures. The chainlike σ-conjugated Si polymers are well known as one-dimensional (1D) silicon-based materials that have alkyl or aryl groups in their side chains.[4] Their unique properties are primarily attributed to the quantum confinement effect on the conjugated electrons delocalized in polymer backbone chains.[5] Reflecting the 1D direct-gap nature, sharp optical absorption bands are observed at 3–4 eV in chainlike Si polymers. A sharp photoluminescence (PL) is observed near the absorption edge with a high quantum efficiency.

The highly hydrogenated amorphous silicon (a-Si:H, often called polysilane alloys) also contains Si chains.[6] However, there are many differences in optical properties between a-Si:H and chainlike Si polymers.[7] For example, the broad PL spectrum, due to the band tail emission, is observed in a-Si:H,[8] but a sharp PL band with a large quantum efficiency is observed in various chainlike Si polymers including disordered forms. Rather, the broad PL in polysilane alloys, a-Si:H, resembles that in network Si polymers.[9,10]

Theoretical calculations[11] suggest that two-dimensional (2D) Si-backbone polymers have intermediate electronic properties between 1D chainlike Si polymers of the direct-gap band structure and three-dimensional (3D) bulk Si of the indirect-gap band structure. An indirect-to-direct conversion of the optical transition in Si-based materials is considered to be related to the dimensionality of electronic structures. Although 2D crystalline polymers still a hypothetical polymer, network polymers[9,10] are of scientific importance because they serve as a conceptual bridge between the properties of 1D chains and fully coordinated 3D amorphous or crystalline silicon. Studies of optical properties of Si polymers with different backbone structures also help us to understand the microscopic PL mechanisms in a variety of Si-based materials, such as a-Si:H, porous Si, and Si nanocrystallites,[1-3,12-17] because the local Si structures can be controlled in chemically synthesized Si polymers.

In this work, we have studied the optical properties of Si-backbone polymers with different backbone structures. The backbones of branch, ladder, and network Si polymers are constructed by the oganosilicon units with three Si—Si bonds. Broad luminescence of network polymers is similar to those of branch and ladder structures. Sharp luminescence is observed in the quasi-one-dimensional chain and the quasi-two-dimensional siloxene structures. The luminescence properties of the branch, ladder, and network structures are entirely different from those of 1D excitons in chain and 2D excitons in planar Si structures. The disorder and strain induced by three Si—Si bonds in Si-backbone structures cause the exciton localization, and then the broad PL is observed in branch, ladder, and network polymers with three Si—Si bonds. We discuss the origin of the broad PL from Si-backbone polymers.

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II. EXPERIMENT

Si-backbone polymers used in this work are (a) polymethylphenylsilylene (molecular weight $M_w = 1.2 \times 10^4$), (b) poly(dimethylphenylsilyl)phenylsilylene ($M_w = 8 \times 10^3$), (c) dodecaisopropyltetracyclodesilane,[18] (d) network polysilynes ($M_w = 7 \times 10^3$), and (e) planar siloxene. The synthesis procedures were described in the literature.[19–26] The Si-backbone structures of these polymers are illustrated in Fig. 1 and hereafter, we call these structures the chain [Fig. 1(a)], branch [Fig. 1(b)], ladder [Fig. 1(c)], network [Fig. 1(d)], and siloxene [Fig. 1(e)] structures. In the chain structure, the organosilicon units on the polymer backbone have two Si—Si bonds. In the other structures, the polymer backbones are constructed by the organosilicon units having three Si—Si bonds. Using these samples, we discuss the effects of the backbone geometry on the optical properties of Si polymers.

Absorption spectra of Si polymers dissolved in tetrahydrofuran (THF) were measured. For PL spectrum measurements, thin solid films were prepared on a quartz substrate from THF solution. The PL spectra were measured by using 325-nm excitation light from a He-Cd laser. Picosecond PL decay under a 1-ps and 300-nm laser excitation of ~1 pJ per pulse was measured using a monochromator of subtractive dispersion and a synchroscan streak camera. The calibration of the spectral sensitivity of the whole measuring systems was performed by using a tungsten standard lamp.

We measured the optical absorption spectrum of the sample before and after the laser irradiation. The shape, intensity, and peak energy of the optical-absorption spectrum were not changed by the laser irradiation. These results suggest that under our experimental conditions, no significant photo-oxidation and photochemical reactions occur.[4]

III. RESULTS AND DISCUSSION

A. Chain structure

We briefly describe the characteristics of the PL and absorption spectra of the chain, branch, and ladder structures at room temperature.[26] In the chain structure, sharp PL and sharp absorption bands are observed in a violet and ultraviolet spectral region. The Stokes shift between PL and lowest absorption peaks is relatively small. It is well accepted that the sharp absorption and PL bands are attributed to the quasi-one-dimensional excitons delocalized on the Si-backbone chain.[4,5] The structures of chainlike Si polymers take a variety of conformations such as *trans*-planar, *trans-gauche*, $\frac{7}{3}$ helical, and disordered forms, depending on organic substituents attached to the polymer backbones.[27] However, the PL band is very sharp in all conformations including disordered forms. Therefore, the sharp PL band is the most important feature of the optical properties of the chain structure.

On the other hand, in the chain structure, a very weak and broad PL band is also observed in the visible spectral region at room temperature. The intensity ratio of the broad visible PL to the sharp ultraviolet PL is less than $\frac{1}{50}$ at room temperature. In our samples, the intensity of the broad PL is very weak compared with previous reports.[28–32] The origin of the broad PL band is still controversial.[31,32] The study of the visible PL in Si-backbone polymers is also very important for understanding the mechanism of curious visible PL in silicon-based materials, such as porous Si and Si nanocrystallites.[1–3,12–17]

Figure 2 shows the temperature dependence of the PL spectra in the chain structure in the visible region. In the lower-energy region below the sharp PL band, two components are observed: a temperature-sensitive PL around 400 nm and a temperature-insensitive PL band around 500 nm. The peak near 400 nm is observed only at low

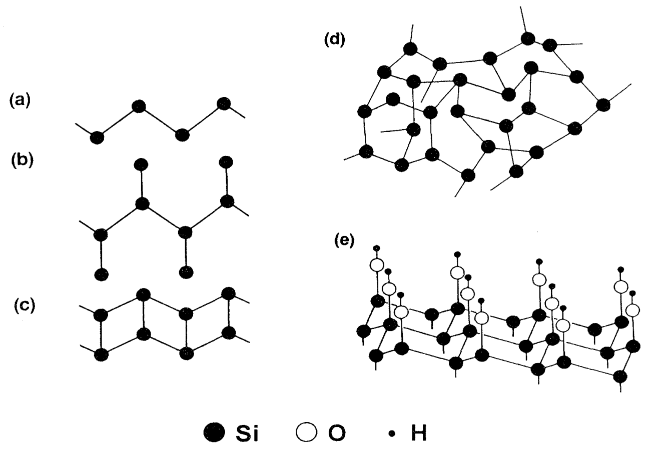

FIG. 1. Schematics of Si polymers with different backbones: (a) chain, (b) branch, (c) ladder, (d) network, and (e) planar siloxene structures. In planar siloxene, the open circles and the small dots mean oxygen and hydrogen atoms, respectively.

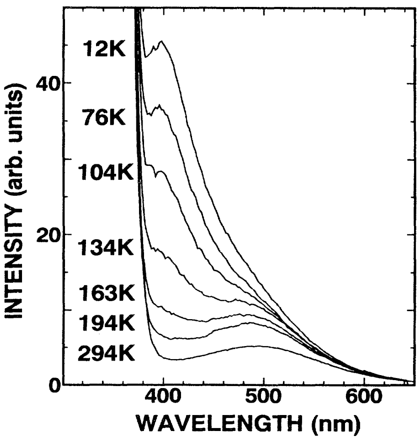

FIG. 2. Temperature dependence of PL spectra in the visible spectral region in the chain structure. A temperature-sensitive PL band appears near 400 nm at low temperature below 150 K. A broad PL band also appears near 500 nm even at room temperature.

temperatures less than 150 K. At low temperatures, the PL lifetime at 400 nm is very long (> 100 ns). In many chainlike Si polymers, a sharp and weak PL band is observed at the lower-energy side of strong PL band at low temperatures.[28–32] Since the excitation spectrum of the optical detection of magnetic-resonance signals is consistent with the long-lived PL spectrum at the lower-energy side of the strong PL band,[30] a weak and temperature-sensitive PL is interpreted as phosphorescence from the triple excited states.[32] Therefore, we speculate that the temperature-sensitive PL around 400 nm in the chain structure is phosphorescence from the triplet excitons. The phosphorescence is completely quenched at room temperature.

The broad PL around 500 nm is observed even at room temperature in the chain structure. There are two PL bands at room temperature: a sharp 360-nm PL band and a weak 500-nm PL band. Picosecond time-resolved PL decay measurements also show that the two different PL components exist in the visible region, as shown in Fig. 3. In this picosecond time region, the PL decay profiles at 360 nm in the strong and sharp PL and at 500 nm in the weak and broad PL band are given approximately by single-exponential functions with time constants of about 80 ps and about 1 ns, respectively. On the other hand, the PL decay profiles between 390 and 460 nm clearly show nonexponential. Here, we roughly fit the PL decays in the 390–460-nm region by using double-exponential functions: fast-decay and slow-decay components. The PL lifetime as a function of the PL wavelength is summarized in Fig. 4. There are two PL decay components: the fast component near 360 nm and the slow component near 500 nm. The fast and slow PL components in the 390–460-nm region are similar to the fast decay of the sharp PL at 360 nm and the slow decay of the broad PL at 500 nm, respectively. It is, therefore, considered that the fast and strong PL band around 360 nm and the broad visible PL band around 500 nm are overlapped in the 390–460-nm region at room temperature. At low temperatures, the PL decay in the initial 5-ns region cannot be observed around 400 nm, and this is because of the long-lived phosphorescence emission.

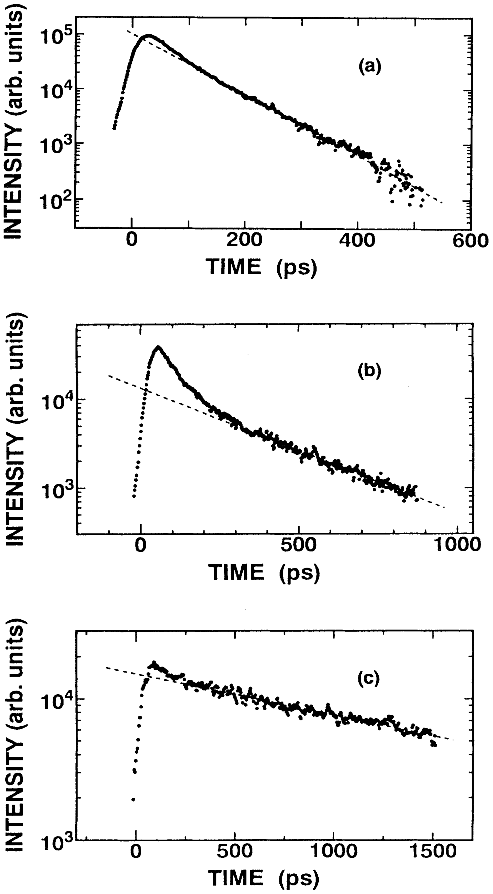

FIG. 3. Initial PL decay in the picosecond time region in the chain structure at different PL wavelengths: (a) 360, (b) 400, and (c) 500 nm. The decay of the 360-nm sharp PL band is exponential. The decay of the broad PL around 500 nm is slow. The PL decay profiles around 400 nm clearly exhibit nonexponential.

Optical absorption and PL spectra, due to quasi-one-dimensional excitons, are also controlled by the geometry of the chain structure.[33] In some geometrical structures, it is expected that trapped states appear below the free-exciton state. The broadening and the Stokes shift of the "sharp" PL band in the *trans*-planar, *trans-gauche,* $\frac{7}{3}$ helical, and disordered forms can be explained by the geometrical effects on 1D excitons. However, the visible broad PL band is experimentally observed in all Si polymers and the intensity of the broad PL strongly depends on the sample preparation methods. It is pointed out that Si branching points (the organosilicon units with three Si—Si bonds) appear inevitably in the main chain during polymerization of silane monomers. We estimated the local structure near the branching point by using semiempirical PM3 molecular-orbital calculations on oligosilane methods.[34] All calculations were done by using the MOPAC version 6.0 program (QCPE #455).[35] The Si—Si bond length at the branch point becomes short compared with the Si—Si bonds in the main chain: The

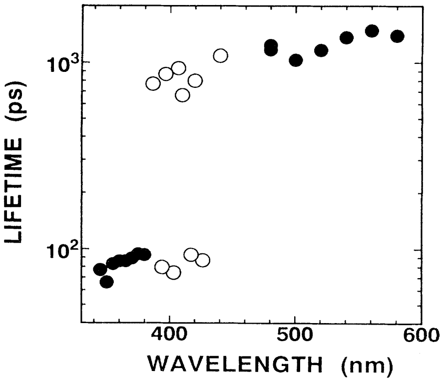

FIG. 4. The PL lifetime as a function of the PL wavelength. In the chain structure, there are two decay components: about 100-ps and about 1-ns components. In the range between 390 and 460 nm, the PL decay profiles is roughly described by two-exponential functions of 100-ps and 1-ns components (denoted by the open circles in the figure).

local strained structure is formed near the branch point. This calculation supports the prior conclusion in Ref. 9. The localized states exhibiting visible PL are considered to be formed by the local strained structures near the branch point. Therefore, the temperature-insensitive PL around 500 nm is the radiative recombination of excitons in localized states, reflecting the disordered nature such as structural defects in the "real" polymers[31] rather than geometrical effects of excitons in 1D quantum wires.[33] In the following section, we will discuss the origin of the broad PL in Si polymers.

B. Branch and ladder structures

In the branch and ladder structures, the broad PL is only observed in the visible region. A sharp and strong PL band, due to the quasi-one-dimensional excitons, is not observed in these structures. In the branch and ladder structures, the lowest absorption band was estimated by using Gaussian functions.[26] The intensities of the lowest absorption peak per organosilicon unit constructing the polymer backbones in the branch and ladder structures are very small compared with that in the chain structure. In the excitons delocalized in 1D geometry, theoretical studies predict the very strong concentration of the oscillator strength on the lowest exciton state.[36,37] In fact, the sharp absorption band is observed in the chain structure. However, the excitons do not show the 1D nature in the branch and ladder structures. Moreover, the Stokes shift between the PL and the lowest absorption peaks in the branch and ladder structures is large compared with that in the chain structure. A large Stokes shift indicates the formation of self-trapped excitons or the formation of the localized states controlling the luminescence properties.

Figure 5 shows the initial decay dynamics of luminescence at peak energies in the chain (~ 3.5 eV and ~ 2.4 eV), branch (~ 2.75 eV), and ladder (~ 2.3 eV) structures at room temperature. The initial PL decay profiles in the branch and ladder structures are similar to that of the weak visible PL at 500 nm in the chain structure, but different from that of the strong and sharp PL at 360 nm in the chain structure. Although the PL decay profiles are nonexponential, we roughly determine the effective decay time τ_{PL}, by using the single exponential function indicated by broken lines, in order to evaluate the radiative decay rate of excitons. In the branch and ladder structures, the quantum efficiency of PL, η, is very low ($\leq 10^{-3}$), but τ_{PL} is large (~ 0.8 ns), compared with those of the chain structure, where $\eta \sim 0.1$ in the chain structure (polymethylphenylsilylene) is used as a quantum yield standard.[5,38] Here, we can estimate the radiative decay rate of excitons τ_R^{-1} determined from the PL lifetime and the PL quantum yield, η/τ_{PL}. On the other hand, the radiative decay rate based on one unit in the polymer backbone τ_{abs}^{-1} can be evaluated from the integral of the lowest absorption band. The ratio $\tau_{\mathrm{abs}}/\tau_R$ roughly gives the delocalized region of excitons.[39,40] These calculations show that in the branch and ladder structures excitons are strongly localized on 2–3 Si atoms, but in the chain structure excitons are delocalized over 20–30 Si atoms.[38–40] Si-backbone polymers constructed by the units with three Si—Si bonds, the branch and ladder structures, have spectroscopic characteristics that excitons are strongly localized, the PL spectrum is broad, and the quantum efficiency is very low. The broad visible PL in Si polymers is caused by the introduction of Si units with three Si—Si bonds into the polymer backbone.

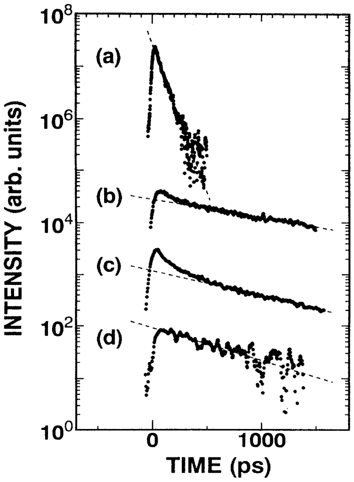

FIG. 5. Picosecond photoluminescence decay of three Si polymers: (a) chain (at 360 nm of strong and sharp PL band), (b) chain (at 500 nm of weak and broad PL band), (c) branch, and (d) ladder structures. We estimate the effective decay lifetime using the single exponential decay function. The broken lines indicate the effective decay time of (a) 80 ps, (b) 1 ns, (c) 0.8 ns, and (d) 0.7 ns.

Here, we consider the origin of the broad PL spectra in the branch and ladder structures from the electronic band structures of Si polymers. The band calculations were performed by Takeda and Shiraishi with the first-principle local-density-functional method.[11,41,42] In theoretical calculations, the organic substitutions without Si atoms in polymers are replaced by H atoms and the *trans*-planar form is considered as the chain structure and the branch and ladder structures are constructed using the chain structure of the *trans*-planar form. The band structures of the chain, branch, and ladder structures are shown in Fig. 6. The characteristic features of these band structures are summarized as follows.

(1) The band-gap energies of the branch and ladder structures are smaller than that of the chain structure.

(2) The E-k dispersion of the branch and ladder structures is flat compared with that of the chain structure.

(3) The density of states near the top of valence band and the bottom of the conduction band in the branch and ladder structures are larger than those of the chain structure.

(4) The energy of the indirect optical transition is close to that of the direct optical transition in the branch and ladder structure.

The above four characteristics of the band structure are possible origins of observed broad PL spectra at the visible region in the branch and ladder structures [(1) PL appears in the visible region, (2) and (3) the PL spectrum is broad, and (4) the PL lifetime is long]. A large part of

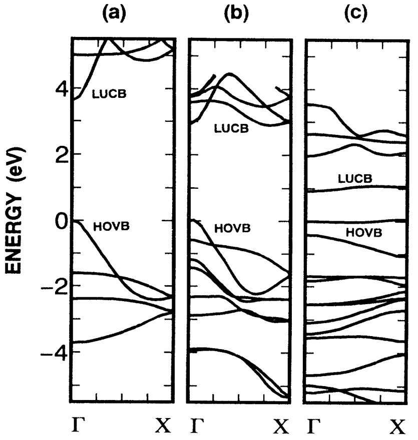

FIG. 6. Electronic structures of (a) chain, (b) branch, and (c) ladder structures. The energy scale is represented from the highest occupied valence-band state (HOVB) in electron volts. LUCB means the lowest unoccupied conduction band. The band-gap energy is the energy difference between LUCB and HOVB. These electronic structures are reproduced from Refs. 11 and 42.

experimental results can be explained by the above electronic band structures of polymers.

However, it is considered that the band structure of the crystalline state is an oversimplified picture, because the polymers have local structural disorders in crystalline state or are noncrystalline materials. In particular, the backbone constructed by the units with three Si—Si bonds becomes rigid compared with that of two Si—Si bonds like the chain structure. The ladder structure is a highly strained one, because x-ray crystallography shows that two linear chains consisting of the ladder structures screw in one way and the Si—Si bonds in each chain repeat with alternating long and short distances.[19] Moreover, there are two types of backbone structures: *anti*- and *syn*-ladder structures. The PL spectrum is broad in both *syn*- and *anti*-ladder structures. The broad PL spectrum does not depend on the kind of organic substituents (isopropyl, neopentyl, or trimethylsilyl groups). The luminescence properties of the ladder structure are not sensitive to the geometry *(syn-* or *anti-structure)* of the ladder structure. These results imply that the local strain and the fluctuation of the Si—Si bond length in Si-backbone structures cause the exciton localization and control the luminescent properties. The broad PL spectra with large Stokes shifts are observed in the branch and ladder structures. Further theoretical studies are needed for the understanding of the mechanism of the exciton localization in silicon polymers. In particular, we need to clarify the geometrical dependence of the electron-phonon coupling strength theoretically and to develop the models for quantitative calculations on the effect of the disorder and strain on the electron-phonon coupling strength in polymer systems.

C. Network and planar structures

In the previous section, we reported that the broad PL at the visible region is observed in the branch and ladder structures, whose backbones are constructed by the organosilicon units with three Si—Si bonds. The branch and ladder structures are considered to be quasi-one-dimensional geometry, because the main chain of Si backbone is much longer than the other directions. However, the excitons are localized in a very small region on 2–3 Si atoms. In this section, we show the spectroscopic properties of "two-dimensional" network Si polymers constructed by the organosilicon units with three Si—Si bonds.

Figure 7 shows the optical absorption and PL spectra in network Si polymers $(R\mathrm{Si})_n$ with different organic substituents (R = phenyl, butyl, or propyl groups). The broad PL is observed around 2–3 eV. The absorption and PL spectra scarcely depend on the kind of the organic substituents. Moreover, the initial PL decay dynamics in network polymers are also shown in Fig. 8. The PL decay profiles are nonexponential. If we roughly estimate the PL decay time in the time region, using single-exponential functions denoted by the broken lines in the figure, it ranges 600 ps to 1 ns. The initial PL decay profiles in the picosecond time region scarcely depend on the kind of the organic substituents. These results indicate that the PL properties do not depend on the organic substituents and they reflect the electronic properties of the network silicon backbones. On the other hand, in the chain structure, the peak energies of the sharp absorption and PL bands depend on the kind of side-chain organic substituents, because the side-group substitution causes the backbone conformation changes varying electronic structures:[5,27] The backbone of the chain structures takes many crystalline conformation forms. In the network structures, the backbone takes the disordered form only, and the optical properties are determined by the random network structures.

In order to discuss the two dimensionality of disordered network backbone, we summarize the optical absorption and PL spectra in the ladder and network (R = butyl) structures and planar siloxene in Fig. 9. It is considered that the Si-backbone geometries of the ladder

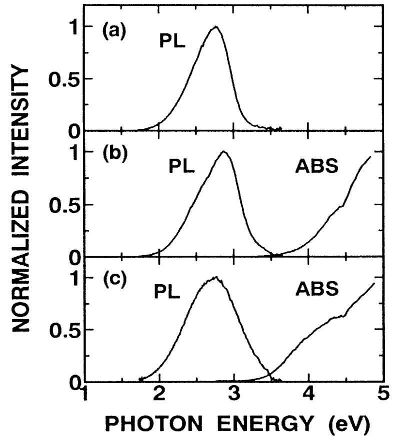

FIG. 7. Optical absorption and photoluminescence spectra in network structures with different organic substituents, $(R\mathrm{Si})_n$: (a) R = propyl, (b) butyl, and (c) phenyl. Photoluminescence spectra scarcely depend on the kind of the organic substituents.

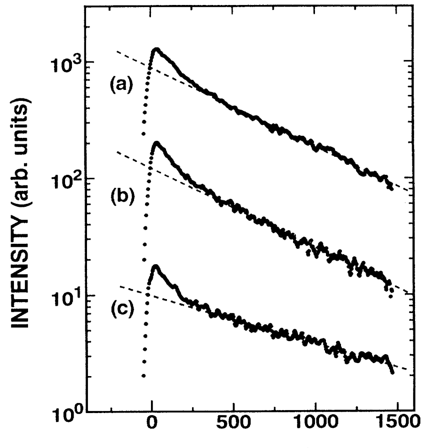

FIG. 8. Picosecond initial PL decay profiles in network structures with different organic substituents, $(R\mathrm{Si})_n$: (a) R = propyl, (b) butyl, and (c) phenyl. The PL decay profiles scarcely depend on the kind of the organic substituents. The PL decay profiles are nonexponential.

structure and planar siloxene are quasi-one-dimensional and quasi-two-dimensional, respectively. The planar siloxene $[(\mathrm{Si_6H_6O_3})_n]$ has a 2D Si-backbone layer, whose one-side is terminated OH groups, as shown in Fig. 1(e). Although the H-terminated 2D-Si layer is an indirect-gap semiconductor, the planar siloxene is a direct-gap semiconductor.[41] This difference is explained by the orbital mixing of delocalized σ electrons in a 2D-Si layer and nonbonding n electrons in O atoms in siloxene. In planar siloxene, the sharp PL and PL excitation spectra are observed. A Stokes shift between the PL and PL excitation spectra is small, as shown in Fig. 9(c). Sharp absorption and PL bands in siloxene are due to the excitons in quasi-two-dimensional Si backbone layers.[43] Figure 9 shows that the broad PL spectrum in the network structure is different from that of planar siloxene. Rather, the PL spectrum and initial PL decay dynamics in network are similar to those in the ladder structure. The absorption and PL spectra in the network structures appear at energies higher than those in planar siloxene. This blueshift of the absorption and PL bands and the broad PL spectrum can be explained by the localization of carriers and excitons in the disordered network structure.

The temperature dependence of the PL intensity at the peak energy in the ladder and network structures and planar siloxene is shown in Fig. 10. In these samples, the PL temperature dependence is described by the following inverse Arrhenius equation:

$$I_{\mathrm{PL}} = I_0 \exp\left[-\frac{T}{T_0}\right],$$

where I_0 and T_0 are constants. The values are T_0 are 120 K in the ladder structure, 95 K in the network structure, and 120 K in siloxene. The parameter T_0 is related to the degree of the structural disorder in noncrystalline materials.[44] In a wide temperature range, the above equation explains the temperature dependence of the PL intensity in the ladder and network structures, rather than siloxene. The above inverse Arrhenius equation is usually observed in the noncrystalline semiconductors with low coordination numbers; e.g., chalcogenide glasses.[45] In tetrahedrally coordinated amorphous silicon (low hydrogen concentration), the temperature dependence of the PL is expressed as a well-known relation observed in crystalline semiconductors.[46] On the other hand, in highly hydrogenated silicon alloy, so called polysilane alloy, the temperature dependence of the PL intensity is consistent with the above inverse Arrhenius relationship.[47] In our experiments, the inverse Arrhenius plot is clearly observed in the ladder and network struc-

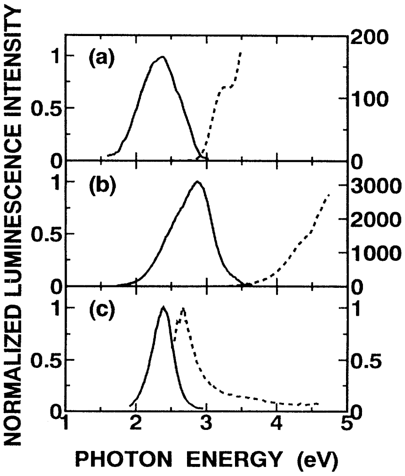

FIG. 9. Optical absorption and normalized photoluminescence spectra in Si polymers: (a) ladder, (b) network (R = butyl), and (c) siloxene structures. The broad PL spectrum in the network structure is similar to that in the ladder structure rather than the sharp PL spectrum in the quasi-two-dimensional siloxene.

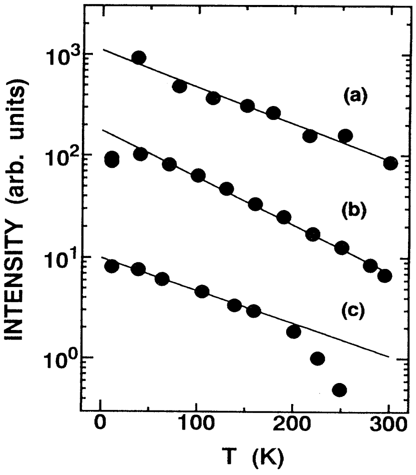

FIG. 10. Temperature dependence of the PL intensity at the peak photon energies: (a) ladder, (b) network (R = phenyl), and (c) siloxene structures. The solid lines indicate the inverse Arrhenius relationship. The data of siloxene are reproduced from Ref. 24.

tures, whose Si—Si coordination number is three. The broad PL and the temperature dependence of the PL intensity in network polymers are similar to those in highly hydrogenated polysilane alloys. Our experimental results suggest that the polymers with three Si—Si bonds exhibit the noncrystalline nature and there is a broad distribution of activation energies for nonradiative process. In Si-based materials, the Si—Si coordination numbers (or the number of Si—Si bonds in one unit) are very important for determining the electronic properties.

In the chain structures, the disorder does not critically affect the observed PL spectrum, because the sharp PL band is dominantly observed in the chain structures of several conformations including the disorder forms. The inverse Arrhenium behavior and the broad PL spectrum observed in noncrystalline semiconductors appear in the ladder and network polymers. Wilson and Weidman[9,10] pointed out that in the network polymers, the random network structures give rise to localized electronic states known as the band tail of both the conduction and valence bands. Our study shows that the introduction of Si atoms with three Si—Si bonds into polymer backbone plays a primary role in causing the broad PL spectrum in Si polymers. Our conclusion supports the above conclusion by Wilson and Weidman. Therefore, we consider that broad PL bands observed in many Si-based materials, such as the branch, ladder, and network Si polymers and *a*-Si:H are closely related to the existence of Si atoms having three or four Si—Si bonds.

In amorphous semiconductors and semiconducting glasses, the coordination number is a very important factor for the structure and electronic properties.[44,48–50] In Si-based noncrystalline materials, the flexibility of covalent bonds is largest for the twofold coordinated group and least for the tetrahedral coordinated group. In SiO_2 glasses, the oxygen atoms bridging the tetrahedral Si atoms provide the essential flexibility, which is needed to form a random covalent network without much strain. Tetrahedrally coordinated amorphous silicon without the flexing bridges (the units having four Si—Si bonds) is highly overconstrained.[50] Therefore, it is considered that Si polymers, with the three Si—Si coordination numbers, are slightly strained materials and are intermediate strain state between SiO_2 glasses having two Si—Si bonds and fully coordinated amorphous Si having four Si—Si bonds. Molecular-orbital calculations also support the ladder and network structures are strained Si polymers.[51] The disorder and local strain of Si-backbone structures constructed by Si units with three Si—Si bonds (high Si—Si coordination numbers) causes the formation of the localized states in Si polymers, like amorphous semiconductors and semiconducting glasses. Consequently, the broad PL spectra and the temperature dependence of the PL intensity in the ladder and network polymers are similar to those of highly hydrogenated amorphous silicon.

IV. SUMMARY

We have studied the luminescence properties of Si polymers with different backbone structures. The branch, ladder, and network Si polymers constructed by the organosilicon units with three Si—Si bonds exhibit broad PL spectra with long-decay times in the visible region. The broad PL properties of these structures are entirely different from the sharp PL properties of the chain structure constructed by two Si—Si bonds.

In the chain structure, the sharp absorption and PL bands are observed in the ultraviolet spectral region. These sharp bands, due to the quasi-one-dimensional excitons, are observed even in disordered form, but a very weak PL appears at the visible region. This broad PL comes from the radiative recombination of excitons localized at branching points, which are inevitably induced during polymerization.

In the branch and ladder structures, the broad PL is only observed. The first-principle electronic structure calculations suggest that polymers consisting of Si atoms with three Si—Si bonds have electronic band structures causing broad PL spectra in the visible region. Moreover, the strain of the backbone structure and the fluctuation of the Si—Si bonds cause the exciton localization on 2–3 Si atoms.

In the disordered network structures, the excitons are strongly localized and the noncrystalline nature dominates the optical properties. The luminescence properties of branch, ladder, and network Si polymers are similar to those in amorphous semiconductors and semiconducting glasses. The disorder and local strain of Si-backbone structures with Si units of three or four Si—Si bonds bring about the formation of localized states and the exciton localization, which control the luminescence properties of Si polymers.

In the Si backbone polymers, the broad PL originates from the radiative recombination of excitons localized in the disordered backbone structures with three Si—Si bonds. Synthesis of the crystalline 2D polymers and the control of the 2D delocalization of excitons would realize wavelength-tunable PL with high quantum efficiency in the visible region. Studies of the structure-controlled Si polymers would help us to understand the microscopic PL mechanism in Si materials such as *a*-Si:H, porous Si, and Si nanocrystallites, and the formation mechanism of the localized states in amorphous silicon materials.

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