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Optical Properties of Siloxene Films Prepared by High-Temperature Heat Treatment from Thin Films of Polysilane Containing Anthryl Groups

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We report the synthesis of linear and network polysilanes containing anthryl groups and the optical properties of the thin films by heat treatments. We observe the shift to a lower energy of the absorption edge in UV–visible absorption spectra of the thin films, when the polysilane films were heated at 500 °C. This behavior is interpreted in terms of the formation of network siloxene films by the dissociation of anthryl groups from silicon structures and the accompanying incorporation of oxygen into the silicon structures. The addition of UV irradiation before heating enhances the spectral changes caused by heat treatment. It is shown that a vacuum degree during heating and backbone structures of polysilanes affect the formation of the network siloxene structures by heat treatment. © 2011 The Japan Society of Applied Physics

1. Introduction

Polysilanes contain σ-conjugated silicon–silicon bonds in the polymer backbone. Interesting optical properties characteristic of σ-conjugated polysilanes have been known to change by the backbone structures.[1–5] Polysilanes with various substituent groups have been synthesized with advances in synthetic techniques.[6] The backbone structure can be controlled by choosing the monomer precursors at the synthetic stage. However, few studies have been carried out on the optical properties of polysilanes containing anthryl groups.[7–10]

Solution processes such as spin-coating and printing are promising because of the simple, easy, and large-area film preparation. The high performance of electroluminescence (EL)[11] and thin film transistors (TFTs)[12] has been demonstrated using solution-processed silicon films because of their high solubility in organic solvents and high carrier mobility.[13,14] Recently, several research groups have reported promising results for the formation of amorphous silicon films and siloxene-like multilayers by heat treatment of solution-processed thin films using silicon clusters[15,16] and network polysilyne[17] as a precursor. It has been reported that electronic structures and photoluminescence are varied by controlling heating temperature under vacuum. Several types of siloxene with different degrees of oxidation such as Weiss siloxene[18] have attracted attention owing to their remarkable electronic and optical structures.

In this study, we report the synthesis and optical properties of linear and network polysilanes containing anthryl groups. The effect of heat treatments of the thin films under vacuum was investigated using UV–visible spectroscopy. The marked changes in absorption spectra by heating at 500 °C were found to be a result of the formation of network siloxene structures. The structural changes accompanying heat treatment were analyzed with infrared absorption spectroscopy and atomic force microscopy (AFM). Their dependence on the vacuum degree during heating was observed and the effect of UV irradiation before heating was also investigated. The experimental results show that the addition of UV irradiation before heating markedly enhances the spectral changes caused by heat treatment.

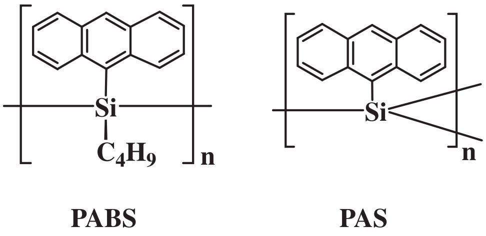

Fig. 1. Chemical structures of PABS and PAS.

2. Experimental Procedure

2.1 Materials

Poly(9-anthrylbutylsilane) (PABS) and poly(9-anthrylsilylene) (PAS) were polymerized from the corresponding dichlorosilane monomer using toluene solution by the Wurtz coupling method.[19] The respective dichlorosilane monomer was synthesized with slight modification from that described previously.[8] The structures of obtained monomers were confirmed by NMR analysis. The chemical structures of PABS and PAS are shown in Fig. 1. The molecular weights of the respective polysilanes relative to polystyrene standards were determined by gel permeation chromatography. The weight-average molecular weights (M_w) of PABS and PAS were 2.89×10^3 and 2.95×10^3, respectively.

2.2 Film preparation

Solid thin films of polysilanes were prepared by spin-coating 5% toluene solution onto quartz plates for UV–visible absorption measurements, onto Au-evaporated glass plates for IR reflection–absorption (RA) measurements, onto quartz plates for AFM measurements. Heat treatments were carried out by heating the films for given times under a constant vacuum degree. After the heat treatment, the thin films were cooled to room temperature prior to spectroscopic and microscopic measurements. The thin films were irradiated with a 500-W high-pressure mercury lamp in air at room temperature.

2.3 Characterization

UV–visible absorption spectra of the thin films were obtained using a Cary 500 UV–VIS–NIR spectrophotometer. Fourier RA spectra were obtained using a Perkin-Elmer

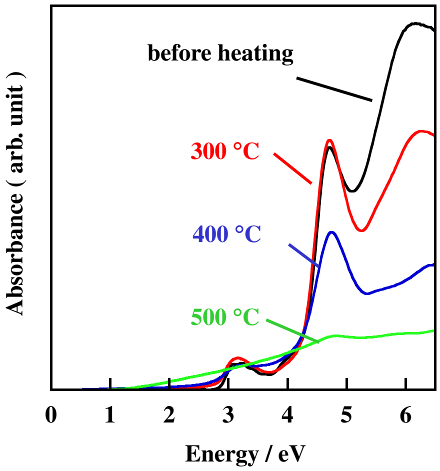

Fig. 2. (Color online) UV–visible absorption spectra of PABS thin films after heat treatment at a given temperature for 10 min under a reduced pressure of 7×10^3 Pa.

Spectrum 100 FT-IR spectrometer equipped with a liquid-nitrogen-cooled MCT detector. For RA measurements, the incident angle was 80°. AFM measurements were performed using a SEIKO SPA300 microscope operating in a noncontact mode using a silicon tip with a resonance frequency of 28 kHz and a spring constant of 1.9 Nm^{-1}. Film thickness was determined using a Veeco Dektak 8 surface profilometer with an accuracy of 1 nm. All the measurements were carried out in air at room temperature.

3. Results and Discussion

3.1 Heat treatment

Figure 2 shows the change in UV–visible absorption spectra after heating thin films of PABS at various temperatures for 10 min under a reduced pressure of 7×10^3 Pa. In the absorption spectra before heating, well-resolved peak structures and two absorption bands are observed at approximately 3.2, 4.8, and 6.0 eV, which can be assigned to π–π^* transitions of the anthryl groups, σ–σ^* transitions of polysilane chains, transitions of Si–C(butyl) bonds, respectively. The absorption peak at approximately 4.8 and 6.0 eV is gradually suppressed with increasing heating temperature. With heating at 500 °C, the absorption edge shifts to a lower energy. The absorption spectra show a broad absorption up to 1 eV, suggesting an electronic structure characteristic of amorphous semiconductors.[20] The color of the thin films changes from pale yellow to brown, indicating a decrease in the band gap. We estimated the band gap using Tauc's equation.[21,22] The estimated band gap is 1.5 eV. This behavior caused by heat treatment is characteristic of polysilanes with anthryl groups, because the absorption decreases gradually and disappears finally with increasing heating temperature in the absorption spectra of thin films of polysilanes with phenyl and naphthyl groups.

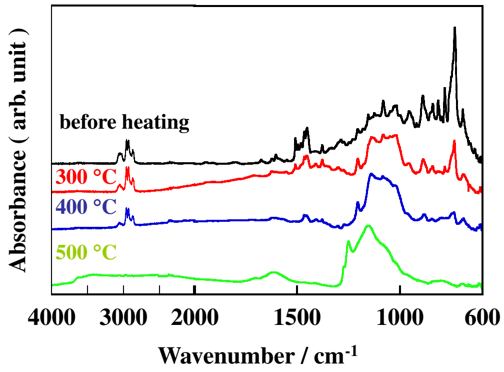

Fig. 3. (Color online) Infrared reflection–absorption (RA) spectra of PABS thin films after heat treatment at given temperatures for 10 min under a reduced pressure of 7×10^3 Pa.

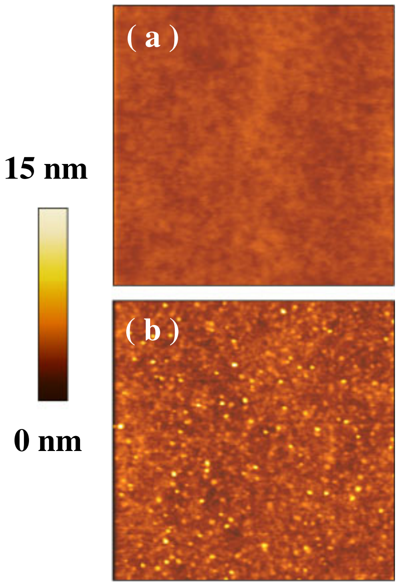

Fig. 4. (Color online) AFM images of a PABS thin film. The scanned areas are $20 \times 20\,\mu\mathrm{m}^2$: (a) before heating and (b) after heating at 500 °C for 10 min under a reduced pressure of 7×10^3 Pa.

The structural changes were investigated using FT-IR absorption spectroscopy. Figure 3 shows the variation of the RA spectrum of the PABS thin film on changing the heating temperature. In the RA spectra before heating, the absorption bands in the 3000–2800 cm^{-1} region are assigned to the CH_2 and CH_3 stretching modes, and those in the 3100–3000 cm^{-1} region are assigned to the stretching vibration modes of the anthryl C–H. The absorption bands at approximately 1400 and 700 cm^{-1} are assigned to the anthryl C–Si stretching mode. These absorptions disappear at 500 °C, indicating that the alkyl and anthryl groups are removed from the thin film. In addition, an intense absorption band with a broad structure appears at approximately 1100–1200 cm^{-1}, which is assigned to the Si–O–Si stretching mode. These band positions and the spectral profiles are known to be sensitive to the state of the siloxene structure.[23] In thin films after heating at 500 °C, several types of siloxene structure such as linear, branched, and cyclic ones are contained. These results suggest that Si–O–Si structures are formed by the elimination of alkyl and anthryl groups attached to polysilane chains from the thin films at 500 °C and reaction with a small amount of oxygen under a reduced pressure of 7×10^3 Pa.

The morphological changes before and after heating were observed by AFM. Figure 4 shows the AFM images of the PABS thin film before and after heating at 500 °C for 10 min

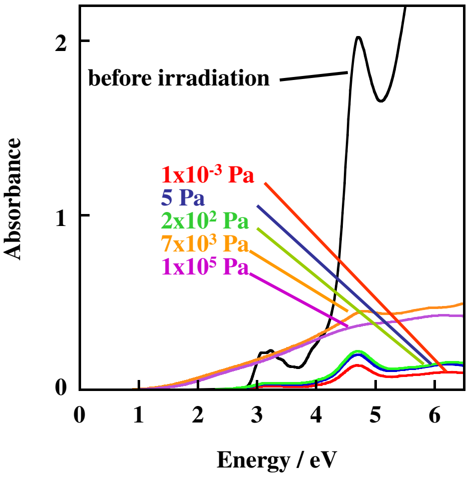

Fig. 5. (Color online) UV–visible absorption spectra of PABS thin films after heat treatment at 500 °C for 10 min under a given vacuum degree.

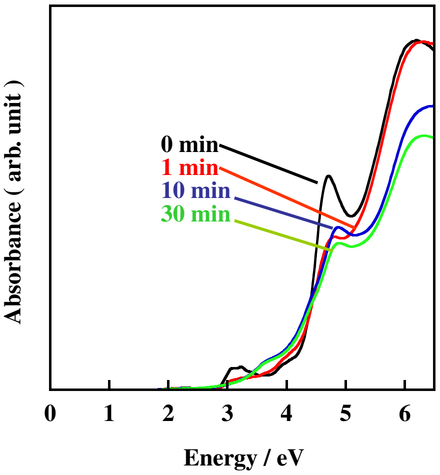

Fig. 6. (Color online) Change of absorption spectra of a PABS thin film on irradiation with UV light.

under a reduced pressure of 7×10^3 Pa. Before heating, the thin film surface is smooth with a surface undulation of less than 1 nm. The roughness of the film surface increases with heating at 500 °C, which is probably due to the elimination of alkyl and anthryl groups, and the resulting evaporation of PABS from the thin films. These behaviors are also supported by the film thickness measurements. The average thickness of the thin films decreases from 220 to 55 nm after heating at 500 °C. These films before and after heating exhibit rms roughness of <0.2 and ~ 3 nm, respectively.

To clarify the spectral changes caused by heat treatment under vacuum, we investigated the vacuum degree dependence of absorption spectra in PABS thin films. Figure 5 shows the absorption spectra with heating at 500 °C for 10 min under various vacuum degrees. When heating under ambient pressure, similar spectral changes as that of 7×10^3 Pa are observed. Furthermore, the Si–O–Si stretching mode appears at approximately 1100 cm^{-1} in the FT-IR spectrum. Under a high vacuum of less than 200 Pa, the intensity of the absorption bands decreases rapidly, but no shift to a lower energy of the absorption edge is observed. This means that the evaporation of the thin films from a solid substrate occurs before the formation of Si–O–Si network structures. This is further supported by the decrease in the absorption bands in the FT-IR spectrum. These results indicate that the Si–O–Si formation plays an important role in the change in electronic structures caused by heat treatment. The amount of oxygen depends on the vacuum degree. The evaporation of PABS occurs in preference to siloxene formation by heat treatment under a high vacuum because of a trace amount of air, while the siloxene structures are formed with the evaporation of thin films under a low vacuum and an ambient pressure.

From these results, the observed spectral changes can be interpreted in terms of the theoretical results of band calculations for silicon–oxygen network polymers. The calculations have been performed by Takeda and Shiraishi[24] and by Brus.[25] In those studies, the calculations were carried out for three types of two-dimensional siloxene structure. The change in band gap results from the difference in σ–n orbital mixing of σ electrons of silicon with an oxygen atom's lone pair electrons. For the present heat treatment applied to PABS thin films, the decrease in band gap is achieved by the dissociation and elimination of substitution groups, the incorporation of oxygen into silicon chains, and the formation of network siloxene structures for the σ–n orbital mixing.

3.2 Effect of UV irradiation

To clarify the spectral changes accompanying the siloxene network formation, we investigated the effect of UV irradiation on heat treatment. Figure 6 shows spectral changes of PABS thin film on irradiation of UV light. After UV irradiation for 1 min, the intensities of the two absorption bands at approximately 3.2 and 4.8 eV decrease appreciably, which is related to the photodimerization of anthryl groups[26,27] and the photooxidation of polysilane chains containing Si–O–Si and Si–OH bonds,[28,29] respectively. These structural changes are further supported by the results of the FT-IR measurements. On further irradiation with UV light, the absorption band at approximately 4.8 eV is suppressed gradually and becomes broader. After UV irradiation for 30 min, the average thickness of the film decreases by 50 nm, which may be explained by volume shrinkage accompanying the photodimerization of anthryl groups.[24] The thin films after UV irradiation were subjected to heat treatment. The change in absorption spectrum with heating at 500 °C for 10 min under a reduced pressure of 7×10^3 Pa is shown Fig. 7. For comparison, the absorption spectra with heating without UV irradiation are also shown by dotted lines. Compared with the absorption spectra with heat treatment after UV irradiation and without irradiation, the spectral profile is almost the same, but the intensity of the absorption band is different. The intensity of the absorption bands when heated at 500 °C after UV irradiation is enhanced. This is due to the difference in the film thicknees, because the average thickness of the thin film with heat treatment after UV irradiation and without irradiation is 90 and 55 nm, respectively. In addition, the vacuum degree dependence of absorption spectra in PABS thin films shows different behaviors from that without irradiation, as shown

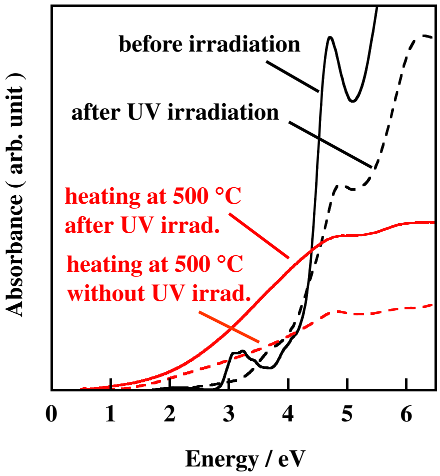

Fig. 7. (Color online) UV–visible absorption spectra of PABS thin films before UV irradiation, after irradiation for 30 min, and after heat treatment at 500 °C for 10 min under a reduced pressure of 7×10^3 Pa.

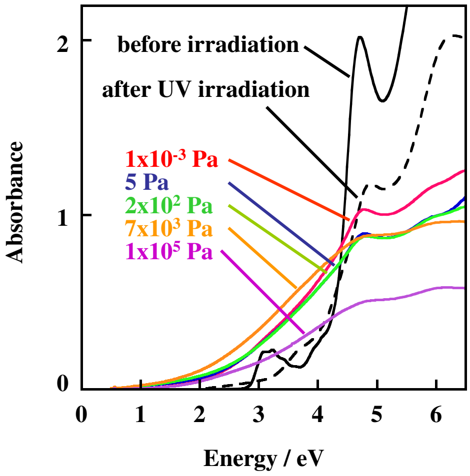

Fig. 8. (Color online) UV–visible absorption spectra of PABS thin films after heat treatment at 500 °C for 10 min under a given vacuum degree.

in Fig. 8. The absorption edge shifts to a lower energy, independent of vacuum degree, while the spectral profile and the intensity of the absorption band depend on vacuum degree. These results suggest that the evaporation of the thin film by heat treatment under a high vacuum is suppressed by the incorporation of oxygen into silicon network structures with UV irradiation. The amount of air depends on the vacuum degree. In thin films without irradiation, a certain oxygen content is necessary to form a siloxene network by heat treatment. When heating thin films under a high vacuum without UV irradiation, the evaporation of thin films occurs before the formation of a siloxene network, resulting in a decrease in the intensity of the absorption band. On the other hand, because a siloxene network is formed by UV irradiation before heating, the spectral changes by heat treatment of thin films after UV irradiation is probably due to the rearrangement, such as dissociation and rebonding, of the siloxene network bonds. Therefore, such structural changes are more conspicuous with a trace amount of oxygen at 1×10^{-3} Pa.

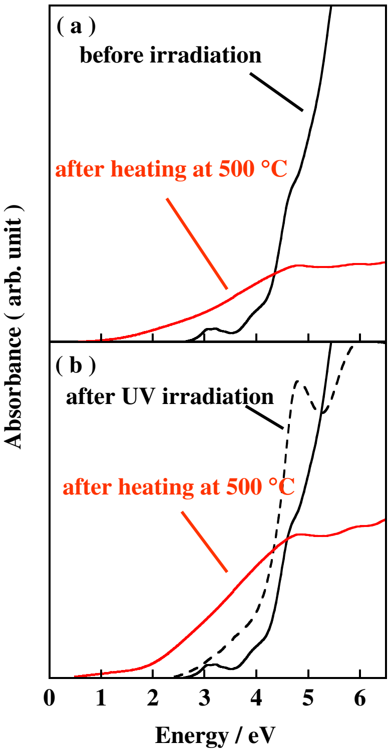

Fig. 9. (Color online) UV–visible absorption spectra of PAS thin films after heat treatment at 500 °C for 1 h under a reduced pressure of 7×10^3 Pa: (a) without UV irradiation and (b) after irradiation for 30 min.

3.3 Effect of silicon backbone structure

We investigated the effect of heat treatment on the backbone structure of polysilanes on heat treatment. Figure 9(a) shows the change in the absorption spectrum of PAS thin films with network silicon structures with heating at 500 °C for 1 h under a reduced pressure of 7×10^3 Pa without irradiation. In the absorption spectra after heat treatment, the absorption edge shifts to a lower energy similar to that of PABS thin films with linear silicon structures, although both spectral profiles are different. The spectral changes after UV irradiation and the accompanying heat treatment are shown in Fig. 9(b). After irradiation with UV light for 30 min, a more distinct absorption band appears at approximately 4.8 eV with the increase in the intensity, which is probably due to dianthracene formed by the photodimerization of anthryl groups.[27] In addition, the absorption edge shifts to a lower energy. The color of the thin film changes from pale yellow to orange. Network silicon structures are bridged by oxygen with UV irradiation and the resulting formation of two-dimensional siloxene structures decreases the band gap energy. When heating after UV irradiation, the absorption edge shifts to a lower energy up to 1 eV. This suggests that the rearrangement of network siloxene structures occurs by heat treatment.

The change in the absorption spectrum in PAS thin film was investigated by varying the vacuum degree during heating. The spectral changes caused by heat treatment without and after UV irradiation are shown in Figs. 10(a) and 10(b), respectively. When heating PAS thin film without UV irradiation, the absorption edge shifts to a lower energy, independent of the vacuum degree during heating. In the absorption spectra of the thin film by heat treatment under a

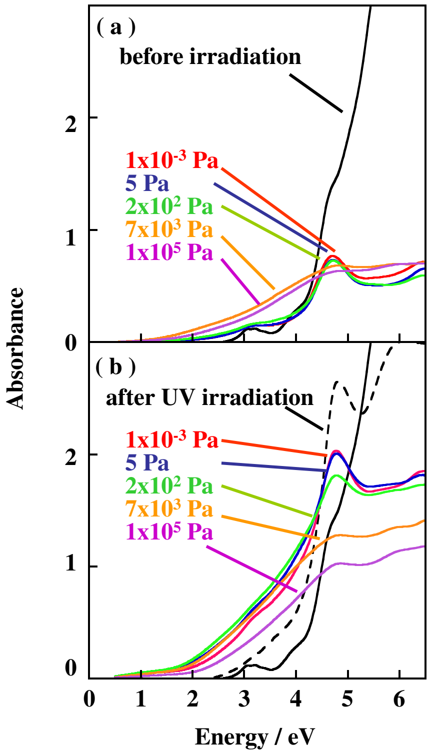

Fig. 10. (Color online) UV–visible absorption spectra of PAS thin films after heat treatment at 500 °C for 1 h under a given vacuum degree: (a) without UV irradiation and (b) after irradiation for 30 min.

low vacuum, the absorption band becomes broader and the absorption edge shifts to a lower energy, compared with that under a high vacuum, reflecting the difference in network siloxene structures. On the other hand, the spectral changes caused by heat treatment after UV irradiation are independent of vacuum degree. The spectral profile is almost the same although the intensity of the absorption band decreases with the increase of vacuum degree. Both a broad absorption band and the shift to a lower energy of the absorption edge are observed in all the absorption spectra after heating. Because oxygen is incorporated into network silicon structures with UV irradiation and the accompanying network siloxene structures are formed before heating, the spectral changes caused by the heat treatment of thin films after UV irradiation is probably due to the rearrangement of network siloxene structures. Therefore, the change in electronic structure occurs even with a trace amount of air at 1×10^{-3} Pa. The amount of air increases with the increase of vacuum degree. Because the decomposition due to oxidation occurs by heat treatment, the intensities of the absorption bands decrease with the increase of vacuum degree.

4. Conclusions

Linear and network polysilanes containing anthryl groups were synthesized. We have demonstrated that the absorption spectra change markedly with heating the thin films at 500 °C under vacuum, resulting in a decrease in the band gap. The anthryl groups are dissociated at 500 °C, followed by the incorporation of oxygen into linear and network silicon structures in the thin films. The formation of network siloxene structures plays an important role in the decrease in the band gap. This method provides a new way of fabricating thin films of solution-processed amorphous siloxene semiconductors. With an appropriate choice of the substitution groups attached to polysilane structures, backbone structures of polysilanes, a vacuum degree during heating, and UV irradiation before heating, the band gap of the thin films can be controlled by heat treatment.

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