Spectral Changes in Thin Films of Cyclicsilanes and Polysilanes by Heat Treatment

H Tachibana, T Mizuno and Y Akasaka

Electronics and Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, Higashi 1-1-1, Tsukuba 305-8565, Japan
E-mail: h-tachibana@aist.go.jp

Abstract. We report the optical properties of the thin films of cyclic and linear and polysilanes containing phenyl groups by heat treatments. We observe the shift to a longer wavelength of the absorption edge in UV-visible absorption spectra of the thin films, when the cyclic and linear polysilane films were heated at 500 °C after UV irradiation. This behavior is interpreted in terms of the formation of network siloxene films by the dissociation of phenyl groups from silicon structures and the accompanying incorporation of oxygen into the silicon structures. It is shown that UV irradiation before heating and substituent groups attached to cyclic and linear polysilanes affect the spectral changes by heat treatment.

1. Introduction
Polysilanes contains \(\sigma\)-conjugated silicon-silicon bonds in the polymer backbone. Interesting optical properties characteristic of \(\sigma\)-conjugated polysilanes have been known to change by the backbone structures [1, 2]. Polysilanes with various substituent groups have been synthesized as the advance in the synthetic technique. The backbone structure can be controlled by choosing the monomer precursors at the synthetic stage [3, 4]. Recently, we have reported promising results for formation of siloxene-like multilayer by heat treatment of solution-processed thin films using linear and network polysilanes containing anthryl groups as a precursor [5]. We investigate the effect of substituent and backbone structure on heat treatment of polysilane thin films. In this study, we report the optical properties of linear and cyclic polysilanes containing phenyl groups. The effect of UV irradiation before heating and heat treatments of the thin films under vacuum was investigated using UV-visible spectroscopy. The structural changes accompanying heat treatment were analyzed with infrared absorption spectroscopy and atomic force microscopy (AFM).

2. Experimental

2.1. Materials
Poly(methylphenylsilane) (PMPS) and poly[bis-(\(p\)-n-butylphenyl) silane] (PBPS) were polymerized from the corresponding dichlorosilane monomer using dodecane and toluene solution by the Wurtz coupling method, respectively [6, 7]. The decaphenylcyclopentasilane (DCPS) and respective dichlorosilane monomer and were available commercially.
2.2. Film preparation

Solid thin films of cyclic and linear polysilanes were prepared by spin-coating chlorobenzene and 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, respectively. Heat treatments were carried out by heating the films for given times under a reduced pressure of 200 Pa. 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 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. All the measurements were carried out in air at room temperature.

3. Results and discussions

3.1. Cyclic polysilanes

3.1.1. UV irradiation.

We investigated the effect of UV irradiation on DCPS thin films. Figure 1 shows spectral changes of DCPS thin film on irradiation of UV light. On irradiation with UV light, the absorption band decreases gradually. On UV irradiation more than 30 min, the intensity of the absorption band becomes constant. The structural changes were investigated using FT-IR absorption spectroscopy. Figure 2 shows the variation of the RA spectrum of the DCPS thin film on changing the UV irradiation time. In the RA spectra before irradiation, the absorption bands at approximately 1400 and 700 cm\(^{-1}\) are assigned to the phenyl C-Si stretching mode. After UV irradiation for 5 min, 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. On further irradiation with UV light, the intensities of the absorption

![Figure 1](image1.png)  
**Figure 1.** Change of absorption spectra of a DCPS thin film on irradiation with UV light.

![Figure 2](image2.png)  
**Figure 2.** Change of infrared reflection-absorption (RA) spectra of DCPS thin films on irradiation with UV light.
bands increase gradually. In addition, a broad structure appears at approximately 1800 cm\(^{-1}\), which is probably assigned to the phenyl C=C stretching mode. These results suggest that ring opening of DCPS on UV irradiation affords Si-O-Si structures in the thin films with the change in the orientation of phenyl group [8, 9].

3.1.2. Heat treatment.

The thin films after UV irradiation were subjected to heat treatment. The change in absorption spectrum with heating for 10 min under a reduced pressure of 200 Pa is shown Figure 3. The absorption peak at approximately 260 nm increases gradually with increasing heating temperature. With heating at 500 °C, the absorption edge shifts to a longer wavelength. The absorption spectra show a broad absorption up to 600 nm. In the RA spectra of DCPS thin films as shown in Figure 4, the intensities of absorption bands near 1100-1200 cm\(^{-1}\) assigned to Si-O-Si stretching band increase appreciably and become broader with increasing heating temperature. In addition, the absorption bands at 700 and 1400 cm\(^{-1}\) assigned to phenyl C-Si stretching band decrease at 500 °C. From comparison of two absorptions after irradiation (\(A_0\)) and after heating at 500 °C (\(A_1\)), the absorption ratio \(A_1/A_0\) of two peaks assigned Si-O-Si and phenyl C-Si stretching band is 1.60 and 0.67, respectively, indicating that the phenyl groups are removed from the thin film. This behavior caused by heat treatment is characteristic of DCPS after UV irradiation, because the absorption decreases gradually and disappears finally with increasing heating temperature in the absorption spectra of thin films of DCPS without irradiation. These results suggest that the shift to longer wavelength of absorption edge is achieved by the ring opening of DCPS, the incorporation of oxygen into silicon chains, elimination of phenyl groups, and the formation of network siloxene structures for the \(\sigma\)-n orbital mixing [5,10, 11].

**Figure 3.** UV-visible absorption spectra of DCPS thin films after UV irradiation for 2 h and after heat treatment at given temperatures for 10 min under a reduced pressure of 200 Pa.

**Figure 4.** Infrared reflection-absorption (RA) spectra of DCPS thin films after UV irradiation for 2 h and heat treatment at given temperatures for 10 min under a reduced pressure of 200 Pa.
3.1.3. Morphology.

The morphological changes before UV irradiation, after irradiation, and after heating were observed by AFM. Figure 5 shows the AFM images of the DCPS thin film before UV irradiation, after irradiation for 2 h in air, and after heating at 500 °C for 10 min under a reduced pressure of 200 Pa. Before UV irradiation, the thin film exhibits rod-like structures. The average width and height of the rod-like structures are 50 nm and 2 nm, respectively. After UV irradiation, the rms surface roughness in the films decreases from 3.3 nm to 1.0 nm and smooth texture is observed. This suggests that the formation of the siloxene structures occurs by ring opening of the DCPS on UV irradiation. On further heating, the films become much smoother with a surface roughness of less than 1 nm, which is probably due to the rearrangement of the network siloxene structures. These behaviors are also supported by the film thickness measurements. The averaged thickness of the thin film decreases by 60 nm after UV irradiation, which may be explained by volume shrinkage accompanying the ring opening of DCPS. On further heating, the thickness decreases to one half after heating at 500 °C, which is probably due to the elimination of phenyl groups.

![Figure 5. AFM images of a DCPS thin film. The scanned areas of (a), (b), and (c) are 0.5x0.5, 1x1, and 1 x 1 μm², respectively: (a) before heating, (b) UV irradiation for 2 h in air and (c) after heating at 500 °C for 10 min under a reduced pressure of 200 Pa.](image)

3.2. Linear polysilanes

To clarify the spectral changes accompanying the siloxene network formation, we investigated the effect of UV irradiation of linear polysilanes on heat treatment. Figure 6 and 7 shows spectral changes of PMPS and PBPS thin film before UV irradiation, after irradiation, and after heating at 500 °C under a reduced pressure of 200 Pa, respectively. After UV irradiation, in both thin films the intensities of the absorption bands decrease appreciably, which is related to the photooxidation of polysilane chains containing Si-O-Si and Si-OH bonds [12, 13]. These structural changes are further supported by the results of the FT-IR measurements. When heating at 500 °C after UV irradiation, the absorption edge shifts to longer wavelength up to 600 nm in the PMPS thin films. On further heating at 500 °C, the intensity of the absorption band increases, but the absorption edge does not shift to longer wavelength. Compared with the absorption spectra with heat treatment after UV irradiation in the PMPS and PBPS thin films, the spectral profile is almost the same, but the absorption edge approaches to 1000 nm in the PBPS thin films, which is probably due to the difference in network siloxene structures formed by the dissociation of phenyl groups [10, 11]. Furthermore, such spectral changes are not observed in thin films of alkyl cyclicsilane and linear poly(di-alkylsilane) without phenyl groups by heat treatment after UV irradiation. These results suggest that The UV irradiation before heat treatment and substituent groups attached to polysilanes play an important role in the changes in electronic structures by heat treatment.
Figure 6. UV-visible absorption spectra of PMPS thin films before UV irradiation, after irradiation for 1 h, and after heat treatment at 500 °C for give times under a reduced pressure of 200 Pa.

Figure 7. UV-visible absorption spectra of PBPS thin films before UV irradiation, after irradiation for 2 h, and after heat treatment at 500 °C for 10 min under a reduced pressure of 200 Pa.

4. Conclusions

We have demonstrated that the absorption spectra change markedly with heating the thin films at 500 °C under vacuum after UV irradiation, resulting in a decrease in the band gap. The formation of network siloxene structures plays an important role in the decrease in the band gap. The spectral changes by heat treatment depend on UV irradiation before heating and substituent groups attached to cyclic and linear polysilanes.

Acknowledgments

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO).

References

[1] Miller R D and Michl J 1989 Chem. Rev. 89 1359
[2] Tachibana H, Matsumoto M, Tokura Y, Moritomo Y, Yamaguchi A, Koshihara S, Miller R D and Abe S 1993 Phys. Rev. B 47 4363
[3] Koshida N and Matsumoto N 2003 Mater. Sci. Eng. R 40 169
[4] Kyushin S and Matsumoto H 2003 Adv. Organomet. Chem. 49 153
[5] Tachibana H, Toya M, and Ishibe S 2011 Japan J. Appl. Phys. 50 04DK18-1
[6] Trujillo R E 1980 J. Organomet. Chem. 198 C27
[7] Acharya A, Seki S, Koizumi Y, Saeki A and Tagawa S 2005, J. Phys. Chem. B 109 20174
[8] Koe J R, Motonaga M, Fujiki and West R 2001 Macromolecules 34 706.
[9] Kusukawa T, Shike A and Ando W 1996 Tetrahedron 52 4995
[10] Takeda R and Shiraishi K 1993 Solid State Commun. 85 301
[11] Brus L 1994 J. Phys. Chem. 98 3573
[12] Nate K, Ishikawa M, Ni H, Watanabe H and Saheki Y 1987 Organometallic 6 1673
[13] Nespurek S, Zakrevskyy Y, Stumpe J, Saplich B and Kadashchuk A 2006 Macromolecules 39 690