CHEMISTRY LETTERS, pp. 1101－1104, 1991.

Electrical and Optical Properties of Heat-treated Silicon Network Polymers

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Conductive thin film was prepared by the heat-treatment of poly(phenylsilane) which has a silicon-silicon network structure. The decrease of optical band-gap $E_{g,opt}$ and the increase of spin concentration were observed with increasing heating temperature. The FT-IR spectra showed the formation of SiC structure at high temperature.

Polysilanes which have linear Si-Si backbone like a poly(dimethylsilane) are known as silicon carbide precursors. The SiC fiber of high tensile strength was first reported by Yajima et al. in 1975.1-3) In the process, the conversion of poly(dimethylsilane) to an intermediate polycarbosilane and curing in air are necessary because the weight loss of poly(dimethylsilane) is vigorous above 400 °C.4) Recently, the synthesis of a new class of silicon-silicon bonded network polymers which are soluble to common organic solvents has been reported.5) These network polysilanes have a high dimensionality which is close to that of a two-dimensional structure.6) The thermal stability due to the network structure should be expected.

The polysilanes also have attracted considerable attention as a new semiconducting polymer which shows unique electrical and optical properties due to delocalization of σ electrons along the silicon backbone. The semiconducting properties of polysilanes depend on the dimensional structure of the silicon backbone.6) In this paper we will report the change of electrical and optical properties of a silicon network polymer by heat-treatment. The purpose of our study is the preparation of a semiconducting thin film using organometallic polymer as a precursor. Usually, the SiC for a compound semiconductor has been prepared by CVD or plasma decomposition system.7) We expect the improvement of conductivity of polysilanes by the increase of the dimensionality of silicon backbone and the formation of SiC structure by heat-treatment.

A network poly(phenylsilane) was synthesized from trichlorophenylsilane by similar procedure to

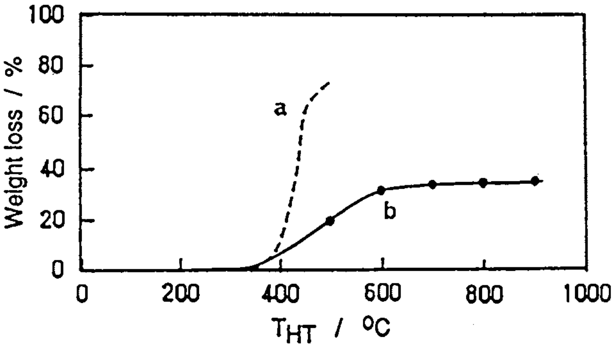

Fig. 1. Thermogarvimetric curves for (a) poly(methylphenylsilane) and (b) poly(phenylsilane).

Furukawa et al.[6)] The remaining Si-Cl end groups of poly(phenylsilane) were converted to Si-OMe using MeOH as a work up solvent. The molecular weight of poly(phenylsilane)was measured by GPC using monodispersed polystyrenes as standards; its Mw was 1090. Figure 1 shows the thermogravimetric curves of linear poly(methylphenylsilane) (Mw = 3120) and network poly(phenylsilane) under N_2 atmosphere. The weight loss of linear poly(methylphenylsilane) goes up to 80% above 500 °C accompanying the chain scission and the formation of volatile silicon compounds. On the other hand, network poly(phenylsilane) shows thermal stability. The increase of the weight loss of poly(phenylsilane) ceases above 600 °C and about 75% of poly(phenylsilane) remains up to 900 °C. This result suggests a possibility of one-step preparation of SiC using the silicon network polymer without the processes of conversion to polycarbosilane and curing in air.

A 5 wt% toluene solution of poly(phenylsilane) was spin-coated on a quartz plate. The spin-coated plate was heated in vacuo for 2 h. Figures 2 and 3 show the absorption spectra of heat-treated poly(phenylsilane) films. Before heating, the absorption edge of poly(phenylsilane) extends to 3.0 eV due to σ-conjugation along the Si-Si bonded network structure. The photon energy of absorption edge, that is, optical band-gap $E_{g,opt}$ increases with increasing heating temperature below 400 °C. The broadening of absorption spectra and the remarkable decrease of $E_{g,opt}$ appear above 600 °C.

Figure 4 shows optical band-gap $E_{g,opt}$ and electric conductivity of heat-treated films. The spin concentration and the peak-to-peak line-width ΔHpp determined by ESR measurements are also shown in Fig. 4. Electric conductivity increases suddenly above 600 °C and goes up to about 1 S/cm at 900 °C.

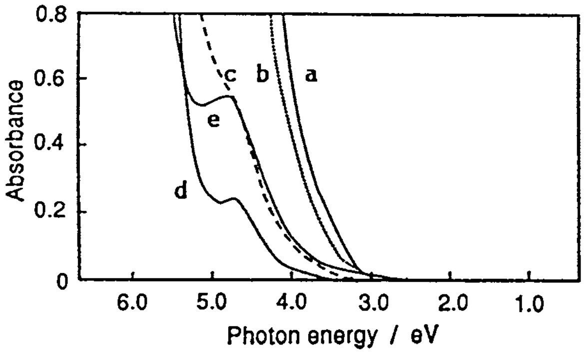

Fig. 2. Absorption spectra of heat-treated poly(phenylsilane). (a) before heating, (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C.

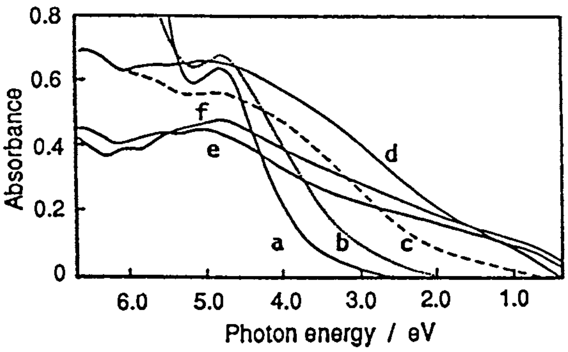

Fig. 3. Absorption spectra of heat-treated poly(phenylsilane). (a) 540 °C, (b) 570 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, (f) 900 °C.

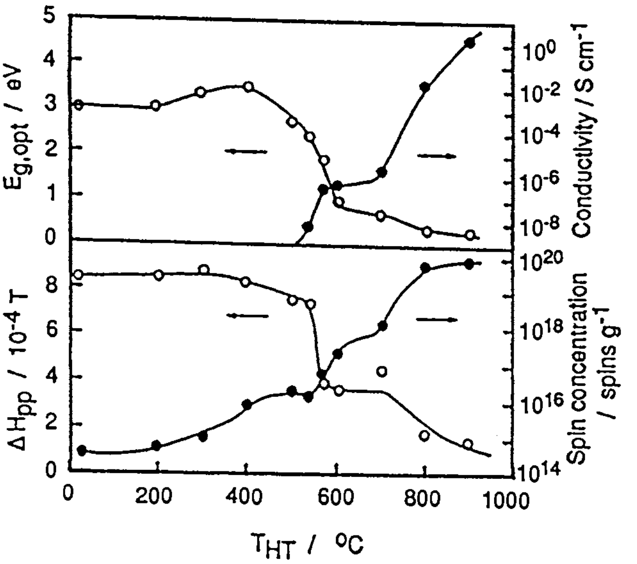

Fig. 4. Change of Eg,opt, electric conductivity, and ESR parameters of poly(phenylsilane) by heat-treatment.

The increase of spin concentration which is related to carrier concentration and the narrowing ESR signal which is related to carrier diffusion are observed with an increase of electric conductivity. The temperature dependence of these parameters is divided into three regions; the first, low temperature region below 400 °C in which the increase of the weight loss of poly(phenylsilane) is not significant, the second, medium temperature region in which the increase of the weigh loss is significant, and the third, high temperature region in which the increase of the weight loss ceases. The ESR line-shapes in the medium temperature region are inhomogeneous due to the overlapping of two components. The electric conductivity increases suddenly in the third region.

The chemical reaction of poly(phenysilane) by heat-treatment was investigated by diffuse reflectance FT-IR spectra. In Fig. 5, the diffuse reflectance spectrum before heating shows the existence of Si-O-CH_3 structure; absorption band **b** (2840 cm^{-1}) assigned to C-H stretch of Si-O-CH_3, band **d** (1481 cm^{-1}) to CH_3 deformation of Si-O-CH_3, and band **f** (1090 cm^{-1}) to Si-O-C stretch. The bands **a** (3049 cm^{-1}), **c** (1595 cm^{-1}), **e** (1427 cm^{-1}), and **g** (696 cm^{-1}) are assigned to aromatic C-H stretch, aromatic C-C stretch, aromatic C-Si stretch, and aromatic C-H bend, respectively. The absorption bands in the 450 - 500 cm^{-1} range are attributable to Si-Si bond stretch.[8] New bands **h** (854 cm^{-1}) and **i** (2173 cm^{-1}) are growing with increasing temperature as shown in Fig. 5. These are attributable to Si-H bend and Si-H stretch, respectively. The Si-H structure should be formed by the Si-Si band cleavage and the hydrogen abstraction of silyl radical. This explanation is consistent with the decrease of σ-conjugation which is suggested by the increase of $E_{g,opt}$ and the increase of spin concentration below 400 °C. The diffuse reflectance spectra show decrease of the intensity of absorption bands **b**, **d**, and **f** by the decomposition of methoxy end group above 300 °C, which is accompanied by the formation of Si-O-Si structure (band **j**, 1028 cm^{-1}). The decomposition of methoxy group proceeds up to 600 °C as shown in Fig. 6. This suggests that the weight loss of poly(phenylsilane) is caused mainly by the thermal decomposition of methoxy end group.

The absorption bands **a** and **e** due to aromatic C-H stretch and aromatic C-Si stretch, respectively, diminish above 600 °C as shown in Fig. 6. The formation of SiC structure is suggested by the band **k**

(800 cm^{-1}). The spectrum at 900 °C is similar to that reported by Yajima et al. for SiC.[2)] The increase of the absorption shoulder at higher wavenumber near 4000 cm^{-1} above 600 °C is consistent with the results of $E_{g,opt}$ determined by the electronic absorption spectra. The high conductivity shown in Fig. 4 above 600 °C is due to the formation of SiC structure. One-step preparations of a high conductive SiC film from spin-coated thin film was achieved by the heat-treatment of a silicon network polymer.

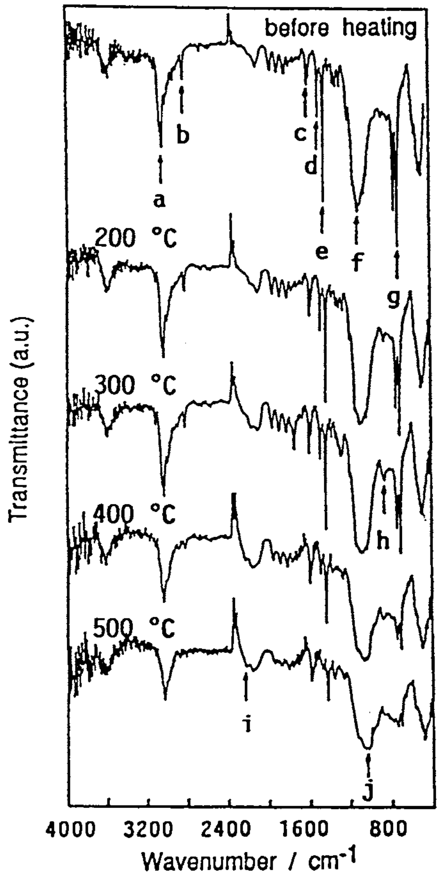

Fig. 5. Diffuse reflectance spectra of heat-treated poly(phenylsilane).

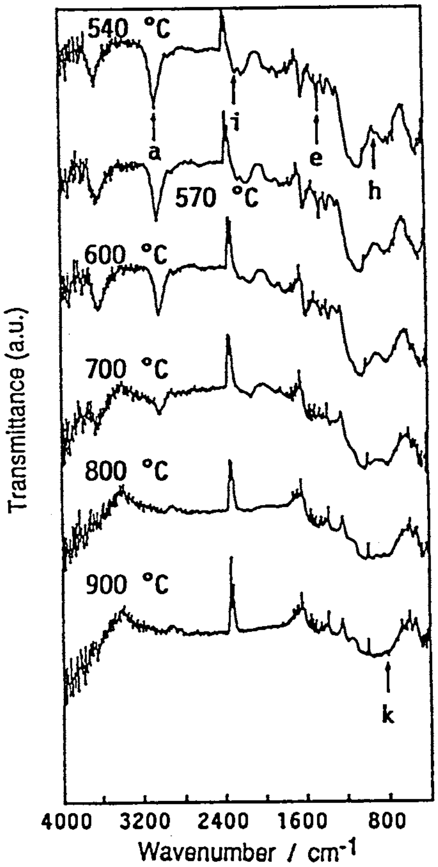

Fig. 6. Diffuse reflectance spectra of heat-treated poly(phenylsilane).

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(Received March 29, 1991)