Effects of iodine doping on electrical and optical properties of ternary Si:C:H films prepared by evaporation of organopolysilane

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Abstract. The effects of iodine doping on the electrical and optical properties of ternary Si:C:H films prepared by the evaporation of organopolysilane have been examined. The evaporated films contain a large number of one-dimensional silicon backbones, and their optical absorption spectra show a sharp peak at 300 nm. The 300 nm absorption peak shows a red shift due to the iodine doping, which clearly indicates the change in the electronic structure of the material. The vibrational frequencies for the $Si(CH_3)_2$ groups are also changed by the doping, and some new peaks are observed in the infrared absorption spectra. By changing the doping time, the conductivity can be controlled over the range from 10^{-14} to 10^{-9} S cm^{-1}. The doping mechanism is finally discussed on the basis of the obtained experimental data.

1. Introduction

The properties of organopolysilanes make them very versatile compounds and they are expected to be of use in various optical and electronic devices. One of the most important reasons is that the chemical backbones of these compounds are one-dimensional silicon chains having σ electrons. Up to the present, many kinds of organopolysilanes have been chemically synthesized, and their physical properties have been examined. With regards to their optical properties, they were transparent in the wavelength range above 400 nm, and had a sharp absorption peak at 300–350 nm (West 1988). Their conductivity was very small compared with that of conventional semiconductors with a value of about 10^{-12} S cm^{-1}. The AsF$_5$- or SbF$_5$-doped organopolysilanes having one-dimensional silicon backbones showed a high conductivity of up to about 10^{-5} S cm^{-1}. Those organopolysilanes, however, had side chains having π electrons.

In this paper, ternary Si:C:H films are prepared by evaporating dimethylpolysilane powder. The material obtained contains a large number of one-dimensional silicon backbones having σ electrons. In order to control the electrical conductivity, the interstitial doping is performed using iodine. As a result, it is found that the

conductivity can be controlled by about five orders of magnitude by iodine doping. The corresponding change due to the doping is observed in the x-ray diffraction pattern and the optical absorption spectrum, and the doping mechanism is discussed on the basis of those experimental data.

2. Experiment

The films used in this study have been fabricated by evaporating dimethylpolysilane powder, $[Si(CH_3)_2]_n$ with $n \sim 2000$, which was chemically synthesized (Furukawa *et al* 1992). First, the dimethylpolysilane powder and the various substrates were set on a molybdenum evaporator and a heated substrate holder, respectively, in a vacuum chamber. The substrates used were a single-crystal (100) silicon wafer, a quartz glass, and a slide glass. The distance between the source and the substrates was 10 cm. The chamber was then evacuated to $\sim 10^{-6}$ Torr by a rotary vacuum pump and a diffusion pump. After evacuation, the substrates were heated up to 470–670 K. Then, the powder was evaporated by applying an AC current of tens of ampere. The thickness of the films obtained was about 10–90 μm.

The film on a single-crystal silicon wafer substrate was examined by x-ray diffraction and infrared absorption (400–4600 cm^{-1}), and the film on a quartz glass substrate was examined by visible and ultra-violet absorption (200–800 nm). The conductivity was measured by evaporating an aluminium inter-digital electrode (planar type) onto the surface of the film. The doping was performed by enclosing the specimen and iodine in a box at 350 K.

3. Results and discussion

The current–voltage characteristics of the undoped and doped materials are shown in figure 1. The substrate temperature for these specimens was 470 K, and the doping time for the latter specimen was 20 h. The thicknesses were measured to be 42 and 59 μm for the undoped and doped specimens, respectively. In figure 1, both curves demonstrate ohmic character, so the conductivity value is deduced from the slope of those plots. The conductivity values obtained are about 1×10^{-12} and 2×10^{-10} S cm^{-1} for the undoped and doped specimens, respectively.

Figures 2(*a*), (*b*) and (*c*) show the x-ray diffraction patterns for the specimens prepared at 470 K, whose doping times are 0, 20 and 40 h, respectively. There are no strong diffraction peaks in the range $2\theta > 16°$. In figure 2(*a*), three diffraction peaks appear between $2\theta = 12°$ and $15°$. From the comparison of the experimental diffraction pattern with the theoretical one, it was found that the crystallographic structure of the dimethylpolysilane crystal is monoclinic ($a = 0.745$ nm, $b = 0.724$ nm, $c = 0.389$ nm, $\gamma = 67.1°$), and the diffraction peaks in figure 2 correspond to the (100), (010) and (110) reflections of the crystal (Furukawa and Takeuchi 1992). In this case, the silicon backbone (having an all-trans conformation) is parallel to the substrate surface. This highly oriented character causes the absence of strong diffraction peaks in the range of $2\theta > 16°$. Figure 2(*a*) indicates that the material contains a large amount of dimethylpolysilane crystal. The intensity of those three peaks, however, is reduced due to the 20 h doping cycle, as shown in figure 2(*b*), and becomes quite weak in figure 2(*c*). The results show that the crystalline part is reduced by iodine doping.
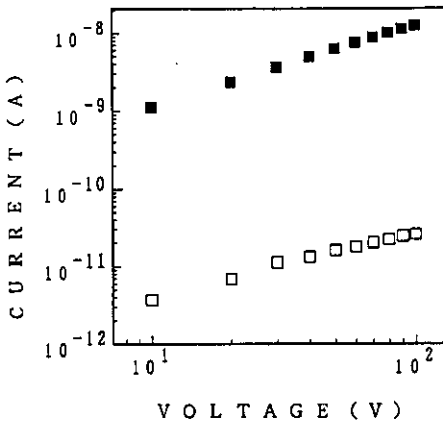
Figure 1. Current–voltage characteristic for the undoped (□) and doped (■) specimens. The doping time for the latter specimen was 20 h. These specimens were prepared at 470 K.
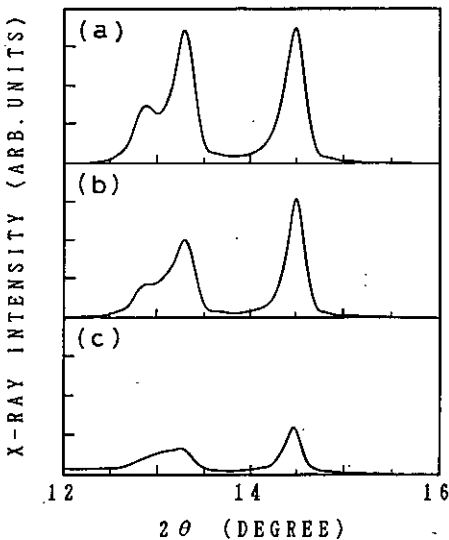

Figure 2. x-ray diffraction patterns for specimens with doping times of (a) 0, (b) 20, and (c) 40 hours. These specimens were prepared at 470 K. The horizontal axis shows 2θ, where θ is the diffraction angle.
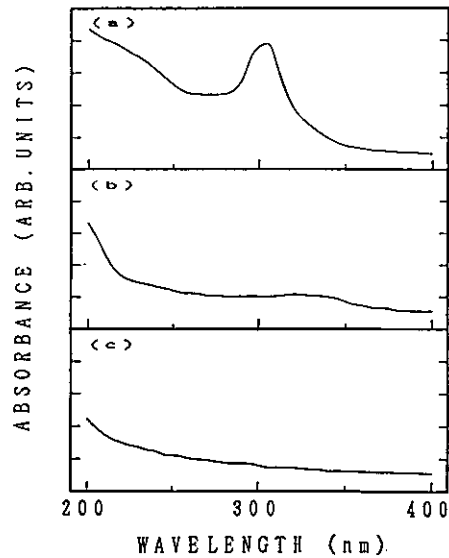
Figure 3. Optical absorption spectra for specimens with doping times of (a) 0, (b) 20, and (c) 40 hours. The specimens were prepared at 470 K.

The optical absorption spectra for the specimens corresponding to figure 2 are shown in figure 3. Figures 3(a), (b) and (c) represent specimens with doping times of 0, 20 and 40 hours, respectively. The undoped specimen shows a large peak at about 300 nm, which is due to the interband transition or exciton formation in one-dimensional silicon chains (Mintmire 1989, Moritomo *et al* 1991, Furukawa *et al* 1992). The strength of the absorption peak becomes considerably reduced by

the 20 h doping cycle, and the peak almost vanishes in figure 3(c). It should be noted that the peak wavelength in figure 3(b) is greater by about 30 nm than that in figure 3(a). These data clearly show that the electronic structure of the silicon backbones is changed due to the doping.

Figure 4 shows the infrared absorption spectra for the same specimens of figure 2. In figure 4(a), a peak appears at 830 cm^{-1} which is due to the vibration of the $Si(CH_3)_2$ rocking mode. As shown in figures 4(b) and (c), the peak is split into two peaks by the 20 h doping cycle, and the right hand peak (at 800 cm^{-1}) is increased by the 40 h doping.
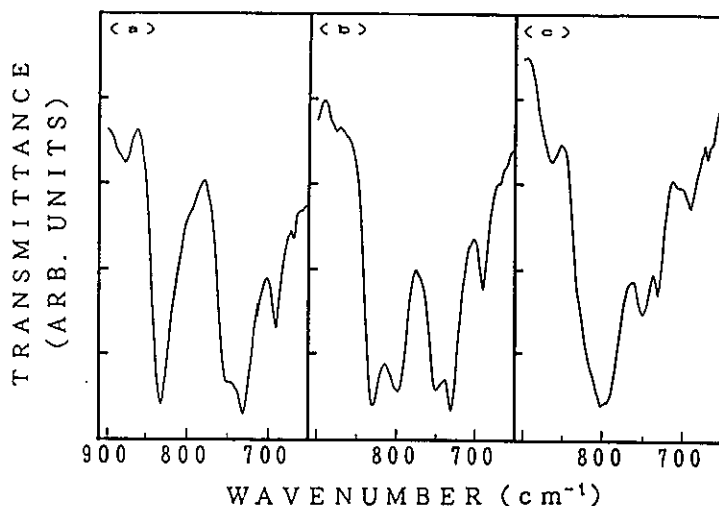

Figure 4. Infrared absorption spectra for the same specimens as those shown in figures 2(a), (b) and (c). The absorption band at 800–830 cm^{-1} corresponds to the $Si(CH_3)_2$ rocking mode.

Figure 5 shows the infrared absorption spectra in a higher frequency band for the same specimens as those shown in figures 2 and 4. In figure 5(a), a peak appears at 1250 cm^{-1} which is due to the vibration of the CH_3 rocking mode. This peak is also split into two peaks by the iodine doping, as shown in figures 5(b) and (c). In contrast to figure 4, the frequency of the new peak becomes greater than in the undoped specimen.

The frequency shifts apparent in figures 4 and 5 can be explained as follows. The electron transfer from the one-dimensional silicon chain to the iodine atom occurs in the doped material, because the electronegativity of iodine is very large. On the other hand, the electronegativity of carbon is also large, so the electron cloud is shifted from the silicon to the carbon even in the undoped material. This shift in the electron cloud is probably reduced, because of the large electronegativity of the doped iodine atom. In this case, the ionic component of the Si–C bond becomes reduced, causing a reduction in the vibrational frequency concerning the $Si(CH_3)_2$ group. In contrast to the Si–C bond, the shift in the electron cloud from the hydrogen to the carbon atom is enhanced, because the carbon atom does not receive a high enough proportion of the electron cloud from the silicon atom. This causes an increase in the
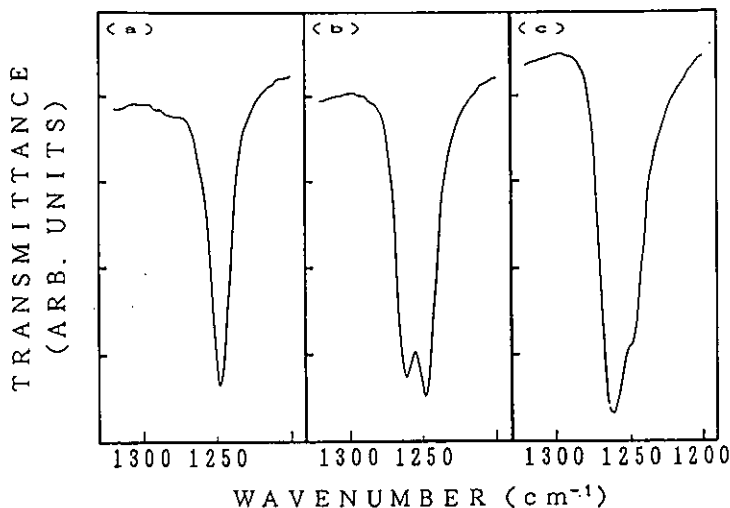
Figure 5. Infrared absorption spectra for the same specimens as those shown in figures 2(*a*), (*b*) and (*c*). The absorption band at 1250–1270 cm^{-1} corresponds to the CH$_3$ rocking mode.

vibrational frequency of the C–H bond. It should be noted that such a charge transfer is consistent with the experimental result shown in figure 3 since figure 3 indicates the change in the electronic structure of the one-dimensional silicon backbone.

Figure 6 shows the electrical conductivity of the evaporated film as a function of the doping time. The results for five series of doping experiments are indicated in figure 6. The conductivity of the undoped material is about 10^{-14}–10^{-10} S cm^{-1}. This large discrepancy between the values of the undoped specimens is considered to be caused by the difference in the crystallographic orientation of the dimethylpolysilane chains. That is, the direction of the chains is parallel to the substrate surface in the present film. Therefore, the conductivity may be very large when the direction of the chains is parallel to that of the current. Conversely, the conductivity may be small, when the direction of the chains is perpendicular to that of the current. As shown in figure 6, the conductivity is increased by the iodine doping, and the maximum value obtained is about 10^{-9} S cm^{-1}. Although all of the five series are not necessarily well controlled, one of them (the plot marked by open circles) shows the considerable change (by about five orders of magnitude) in the conductivity. Further experimental work should be performed in the future to investigate the relationship between the controllable range of the conductivity value and the chain direction.

The origin of the conductivity increase is discussed as follows. From figure 2, the material becomes non-crystalline by doping, so the effect of the crystallographic structure on the conductivity should be considered. However, the structural change from crystal to amorphous material normally causes a decrease in the electrical conductivity. Therefore, the increase in the conductivity shown in figure 6 cannot be explained by the structural change. The most plausible explanation is one where charge transfer from the one-dimensional silicon backbones to the iodine atoms occurs, which is partly explained by the discussion of figures 4 and 5. Figure 7 shows the schematic illustration of this charge transfer. The electron is transferred
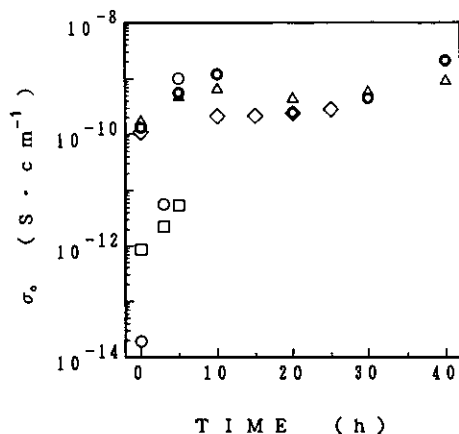
Figure 6. Electrical conductivity, σ_0, as a function of doping time. The specimens marked by ($\bigcirc$, $\odot$, $\triangle$), and ($\square$, $\diamond$) were prepared at 470 and 670 K, respectively.
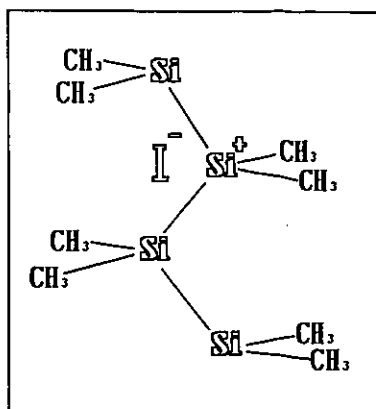

Figure 7. Schematic diagram of the doping mechanism.

from the silicon to the iodine atom, whose electronegativity is quite large. This creates a hole in the silicon backbone, and causes an increase in the electric conductivity.

4. Summary and conclusion

In summary, ternary Si:C:H films, which contain a large amount of one-dimensional silicon backbones, have been prepared by evaporating dimethylpolysilane powder, and the electrical and optical properties have been measured as a function of iodine-doping time. As a result, it is found that the conductivity can be controlled over the range from 10^{-14} to 10^{-9} S cm^{-1}, and the corresponding changes are observed in the optical absorption spectra. The doping mechanism is then discussed on the basis of x-ray and optical absorption data. Consequently, it is concluded that the operating mechanism is that of interstitial doping, in which the electron is transferred from the silicon atom in the backbone to the dopant-iodine atom.

Acknowledgments

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