STRUCTURAL CHANGE FROM CRYSTALLINE TO AMORPHOUS STATES IN SILOXENE BY THERMAL ANNEALING

H. UBARA, T. IMURA, A. HIRAKI, I. HIRABAYASHI^{**} AND K. MORIGAKI^{**}

Department of Electrical Engineering, Osaka University, Suita, Osaka 565, Japan

Institute for Solid State Physics, University of Tokyo, Roppongi, Tokyo 106, Japan

We have investigated structural change in crystalline silicide layer compound, siloxene by thermal annealing. When thermally annealed in vacuum at 300°C, the two-dimensionally ordered structure was destroyed to form the three-dimensionally disordered one. X-ray diffraction, Raman and IR analyses showed that the annealed siloxene was amorphous and might be described as a-Si:0:H. In annealing at the temperature higher than 350° C, dehydrogenation occurred. The composition of siloxene annealed at 600° C is similar to Si₂O.

1. INTRODUCTION

Siloxene $[Si_6H_3(OH)_3]$ consists of two-dimensional corrugated Si-layers with crystalline order as shown in Fig.1¹. On storage in the presence of water, siloxene is slowly changed into three-dimensional amorphous compound through oxidation and cross-linking, i.e.:

$$Si_{6}H_{3}(OH)_{3} + x.H_{2}O - Si_{6}H_{3-x}(OH)_{3+x} + x.H_{2}$$
 (1)
 $Si_{-}OH + H_{0}Si - Si_{-}OSi + H_{2}O$ (2)

In thermal annealing in vacuum, it is expected that siloxene will be finally transformed into a-Si₂O through destruction of layer structure with cross-linking and dehydrogenation. Therefore, it is significant for deeply understanding of formation process of amorphous structure to investigate the structural change from crystalline to amorphous states in siloxene.



EXPERIMENTS

Figure 1 Siloxene was synthesized according to The structural model for siloxene

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Weiss et al¹. CaSi₂ crystal was taken in a flask and treated with an aqueous HCl solution(38%) for 3 hr at room temperature. After filtration and drying on $P_{2}O_{5}$ in vacuum, brilliant yellow layer compound was obtained. Annealing of this compound was performed at temperatures (T_A) below 600°C for 10 min in vacuum (10⁻⁵ torr.).

3. RESULTS AND DISCUSSION

X-ray diffraction pattern of as-prepared siloxene and annealed samples are shown in Fig.2. The basal spacing in as-prepared siloxene is 6.23 Å and in good agreement with 6.33 Å of Weiss et al¹ and about ten layers are ordered in the direction of [001]. So, as-prepared siloxene is polycrystalline layer compound.



Figure 2 Change in X-ray diffraction pattern by thermal annealing

The peak intensity of the sample annealed at 200°C for 10 min decreased to a half of that in as-prepared siloxene. Since any difference in peak intensity between 10 min and 3 hrs' annealing was not observed, the essential destruction of Si-layers did not occurr even for 3 hrs' annealing at 200°C. At T_{Λ} =300°C the peak almost disappeared. Therefore, the annealed siloxene is amrphous in terms of X-ray diffraction. In Raman scattering of as-prepared siloxene a broad peak with FWHM of 24 $\rm cm^{-1}$ was observed at 495 cm^{-1} in comparison with the TO phonon at 520 cm^{-1} in c-Si. The peak decreased with T_{Δ} and disappeared at T_{A} =300 $^{\circ}$ C as observed in the X-ray diffraction pattern.

IR spectra were also changed by annealing (Fig.3). Fig.4 shows the change in each absorption peak with T_A . The assignment of the peaks are described in it. The peak at 640 cm⁻¹ assigned to Si-H wagging mode is also seen in the spectrum of a-Si:H. This peak increased with T_A up to 300°C and then decreased with T_A above 350°C. This behavior is quite similar to that of the peak at 870 cm⁻¹. The peak at 440 cm⁻¹ increased monotonously up to T_A =400°C and was saturated above T_A =400°C. Appearance of this peak means occurrence of the interlayer cross linking according to the reaction (2). On the other hand, the peak at 520 cm⁻¹ decreased rapidly with T_A and almost disappeared at T_A =300°C. In proportion to the decrease in the peak at 520 cm⁻¹, the peaks at 440, 640 and 870 cm⁻¹ increased with T_A up to 300°C. Since these three peaks are based on the three-di-



mensional structures, it is suggested that the structural change from two-dimensional crystalline to three-dimensional amorphous states in siloxene occurred through Si-layer destruction and interlayer cross-linking on annealing above 200°C. Above $T_A=350$ °C, the peak intensity at 640 and 870 cm⁻¹ decreased owing to dehydrogenation. The decreases in the intensity of other peaks above $T_A=350$ °C is also due to dehydrogenation from Si-H bonds in siloxene.

The formation of dangling bonds was quantatively followed by means of ESR analysis. The number of dangling bond centers in as-prepared siloxene was about 2x10¹⁴ per one gram. It increased gradually up to $2x10^{15}$ at $T_A=300^{\circ}$ C and then rapidly increased ($3x10^{17}$ at 350° C, $2.5x10^{18}$ at 400° C and $1x10^{19}$ at 450° C). Increasing in density of dangling bond centers became more sluggish from 450° C ($2x10^{19}$ at 500° C and $3x10^{19}$ at 600° C). Therefore, it seems that formation of dangling bonds is in competition with recombination of dangling bonds above $T_A=450^{\circ}$ C. In the ESR spectrum of the annealed siloxene ($T_A=400^{\circ}$ C), the two signals were apparently observed. The one signal (g=2.0043) is due to Si₃Si· dangling bond and the other (g=2.0004) is from 0_3 Si· or oxygen vacancy in Si0₂ structure².

Change in absorption edge of siloxene in visible light was observed by annealing(Fig.5). In annealing up to 200° C, absorption edge of annealed samples shifted to higher photon energy as compared to that of as-prepared siloxene. This hypsochromic shift of the absorption edge could be explained by the reaction of siloxene with adsorbed water according to the reaction (1). Above 200° C, the hypsochromic shift was stopped by interlayer cross-linking and destruction of Si-layers where high electronegative OH groups were eliminated through dehydration. Above $T_A=300^{\circ}C$ absorption edge red-shifted rapidly due to dehydrogenation in addition to dehydration. The rate of redshift became slower for siloxene annealed above 500°C, the structure of which is nealy related to a-Si₂0.

4. CONCLUSIONS

We performed annealing of siloxene at temperatures between 100°C and 600°C in high vacuum (10^{-5} torr.). Below T_A=200°C, the structural change in siloxene is due to the reaction of the Si-H group with adsorbed water forming Si-OH and H₂, but the essential destruction of Si-layers hardly occurrs. Above T_A=200°C two-dimen-





sional layer structure is destroyed to form three-dimensional amorphous structure through Si-layer destruction and cross-linking with dehydration, and siloxene annealed at 300°C is described as a-Si:0:H. Above 350° C dehydrogenation takes part in the structural change. Siloxene annealed at 600° C seems to be a-Si₂O.

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