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Fatigue Effect and Temperature Dependence in Luminescence of Disordered Silicide Layer Compound: Siloxene ($Si_6H_3(OH)_3$)

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Luminescence of disordered silicide layer compound, i.e., siloxene ($Si_6H_3(OH)_3$) is investigated at low temperatures. Fatigue in the luminescence is observed at 4.2 K and 77 K by prolonged irradiation of UV light. This fatigue is recovered by heating the sample at higher temperature. Inverse Arrhenius-type temperature dependence is also observed in the luminescence of siloxene. These results suggest that the electronic and structural properties of this material have a resemblance to some amorphous materials.

§1. Introduction

Siloxene is a disordered layer compound, which is composed of silicon, hydrogen and oxygen (Si: H: O = 6: 6: 3) and is prepared by the intercalation reaction from $CaSi_2$ crystal.[1)] Raw material $CaSi_2$ is a metallic layer compound and its silicon sublattice forms a layered structure similar to the group V materials.[2)] This crystal reacts with HCl under H_2O as

$$3CaSi_2 + 6HCl + 3H_2O \rightarrow Si_6O_3H_6 + 3CaCl_2 + 3H_2\uparrow, \quad (1)$$

where siloxene is produced. This material has been investigated by several inorganic chemists over 60 years.[3,4)] As to the structure of this material, one of the recent model proposed by Weiss *et al.* is shown in Fig. 1(a). It seems, however, too idealized for the actual structure of our siloxene. We characterized the obtained material by IR, ESR, microscopy and X-ray diffraction, and checked our material to be structurarally highly disordered and observed the existence of dangling bonds, bridging oxygen, the defect states relating to oxygen and microcrack within the layer structure. We believe that the actual structure is such as shown in Fig. 1(b): the small Si layer clusters are randomly and loosely connected by interlayer bridgings.

From the above consideration, siloxene is expected to have some properties similar to amorphous or glassy materials. Thus this material is related to the GD or sputtered amorphous Si: H or Si: O: H in its composition. On the other hand, siloxene has structurally the lower average coordination number and it reminds us of the model for the V group or chalcogenide glass recently proposed by Phillips.[5)]

From this point of view, we have made several measurements on this material. In this paper, we report the luminescence properties and discuss the points described above.

§2. Experimental

$CaSi_2$ crystal for the reaction (1) was prepared by the slow cooling from molten Ca and Si in Ta crusible at Ar atmosphere.[6)] Obtained crystals was easy to be cleavaged parallel to the Si layers. Cleavaged crystals were taken into a flask and after the reaction with 38% hydrosolution of HCl for 3 hours at room temperature, the remaining materials were washed by purified water to remove Ca and Cl ions, thereafter they were dried in vacuum of 10^{-5} Torr. Obtained siloxene was brillant pale yellow layer compound which was very easy to be peeled off.

Luminescence measurements were carried out at 1.8 K using UV lines (356 nm + 351 nm)

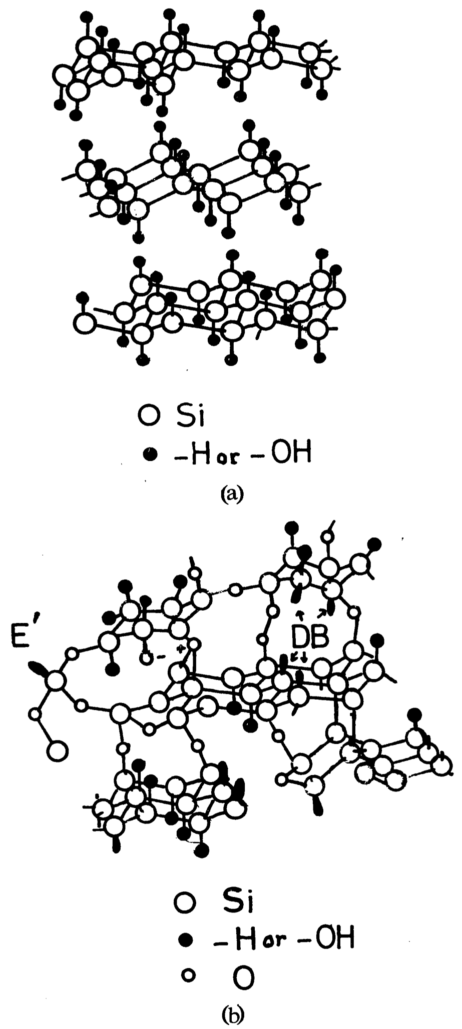

Fig. 1. Structual model for siloxene. (a) Ideal model after Weiss *et al.* (ref. 1) (b) Actual disordered structure expected from our characterization.

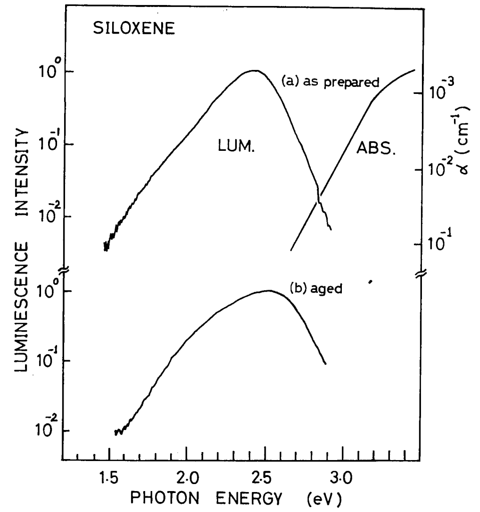

Fig. 2. Luminescence and optical absorption spectra of siloxene. (a) As prepared; (b) Aged after keeping in dry air for 3 weeks.

of Kr^+ laser. Avoiding the luminescence fatigue, exciting laser power was weakened below 0.1 mW. All the luminescence spectra were corrected for spectral response of optical system, i.e., the 25 cm single grating type monochromator and the GaAs photomultiplier. For luminescence fatigue, the sample was irradiated by Kr^+ laser of 100 mW for 45 min (1.7×10^{22} photons/cm^2) at 1.8 K. Annealing of the samples was carried out in the He atmosphere at the upper part of the cryostat. Annealing temperature was below 180°C.

§3. Results

Optical absorption spectra of siloxene exhibit the square dependence on photon energy, $\hbar\omega$, and the temperature independent Urbach (exponential) tail at the absorption edge, which are common features for amorphous materials. The optical gap, $E_{\rm opt}$, estimated from the $(\alpha\hbar\omega)^{1/2}$ vs $\hbar\omega$ plot was 2.9 eV for as prepared samples.

The luminescence spectra of an as prepared siloxene sample exhibit a broad asymmetric Gaussian like lineshape centered at 2.5 ± 0.1 eV, as seen in Fig. 2(a). As prepared siloxene is highly reducible and unstable, so that the composition was varied after keeping it in dry air atmosphere for several days. At the same time the luminescence spectrum changed a little as shown in Fig. 2(b). The luminescence intensity at energies lower than 2 eV increased and its peak position shifted to higher energy. The samples showing the spectra like Fig. 2(b) were stable by keeping in dry air for several months.

The optical properties can also be changed by annealing in vacuum. We performed annealing in vacuum of 10^{-5} Torr upto annealing temperature $T_A = 720$°C, and characterized annealed samples by optical absorption, IR, ESR and photoluminescence.

Optical absorption edge started to shift to lower energy by annealing above $T_A = 250$°C, the color of samples became from pale yellow

($E_{\rm opt} = 2.7$ eV) to dark brown ($E_{\rm opt} = 1.9$ eV by $T_{\rm A} = 550$°C).

Luminescence spectra were measured for annealed samples, which are shown in Fig. 3. By annealing below 100°C, the spectra did not varied, but above 200°C, the lineshape, the peak position and the intensity greatly changed. At $T_{\rm A} = 250$°C the line was broadened and the intensity of the lower energy region increased. As $T_{\rm A}$ became higher, the luminescence peak shifted to lower energy and the intensity decreased. For the sample of $T_{\rm A} >$ 350°C, the luminescence was not observed between 0.5 eV and 3.0 eV. This corresponded to creation of a large density (about 10^{18} spins/cm^3) of the dangling bond centers at high $T_{\rm A}$ region. This correlation between the dangling bond density and the luminescence intensity has also been observed in a-Si: H.

IR spectra were also changed by annealing. By annealing at $T_{\rm A} > 350$°C, the intensity of the stretching mode of Si–H around 2100 cm^{-1} and O–H around 3500 cm^{-1} began to decrease and at $T_{\rm A} = 720$°C they are almost quenched. The Si–O lines, however, did not decrease but remained after annealing of $T_{\rm A} =$ 720°C. These results show evidence for the effusion of –H and –OH as well as the bridging by oxygen. Such effusion resulted in an increase of the dangling bond spins.

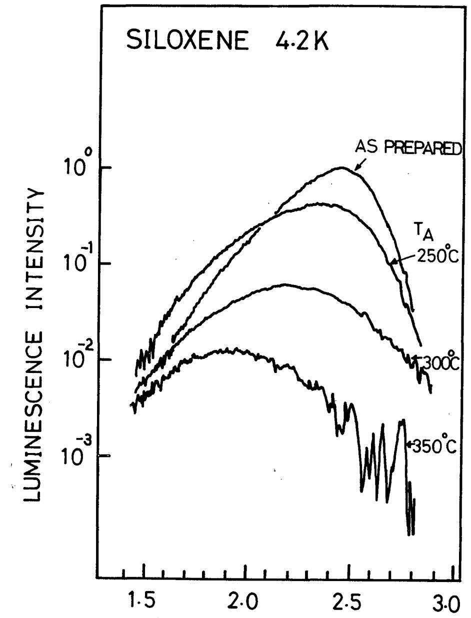

Fig. 3. Anealing effect on luminescence in vacuum of 10^{-5} Torr.

One of the most remarkable properties of siloxene is luminescence fatigue, which has been observed in several amorphous materials: a-Si: H[7] and chalcogenide glass.[8] The luminescence intensity of siloxene decreased by prolonged irradiation at low temperatures. This fatigue did not recover as far as keeping the samples at low temperatures. It suggests that the new states created by irradiation remain as a metastable state. This fatigue, however, recovered by thermal annealing below room temperatures. The detail of recovery depends on the samples: the lineshape of as prepared samples did not recover even after annealing at 300 K, and changed by annealing above 300 K. On the other hand, for the samples being subjected to many cycles of irradiation-annealing or the samples thermally annealed in vacuum at higher than 200°C, the recovery was almost 100%.

Figure 4 shows decrease of the luminescence

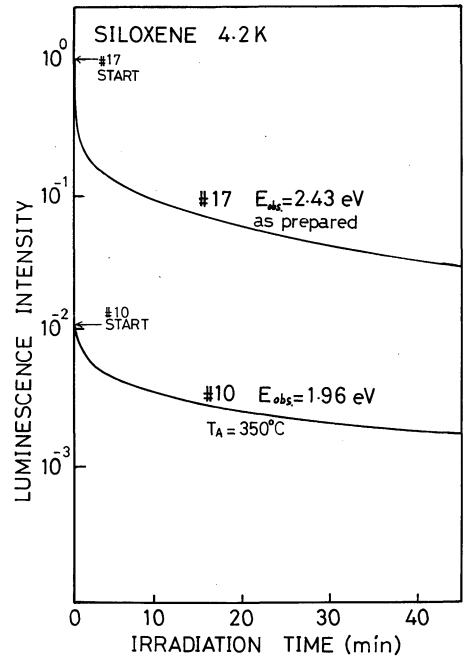

Fig. 4. Luminescence fatigue observed at the peak energy: $E_{\rm obs}$ during irradiation of intense UV light from Kr$^+$ laser. Samples No. 17 and No. 10 were as prepared and vacuum annealed at 350 °C, respectively.

intensity monitored during irradiation for the as prepared and annealed in vacuum (T_A = 350°C) samples. Monitored photon energy was the peak of the spectrum taken before irradiation. The lineshape of the luminescence spectra was almost unchanged and also did not show the peak shift by irradiation. The degree of fatigue in the lower energy region was little smaller than in the main peak and the higher energy regions, but the difference was small so that the monitored peak intensity in Fig. 4 also represents the total intensity within the error of 5%. The degree of fatigue for the as prepared sample is large compared to annealed samples, in particular for short exposure. The luminescence intensity was quenched by the total dose of 1.7×10^{22} photons/cm^2 to 1/20 of the value taken before irradiation. Decrease in the luminescence intensity by irradiation of unit photon/cm^2 is large compared to the case of a-Si: H prepared at 120°C–300°C.7)*

This fatigue was not recovered by the IR irradiation (Xe lamp 500W+IRD1A 1h 30 min) at low temperatures, but by heating the samples. Figure 5 shows the recovery curve by isochronal annealing for the annealed sample. The sample was heated at T_a for 5 minutes. The recovery was observed above 50 K and below room temperature. The intensity almost recovered to that taken before fatigue at room temperature. The fact that the recovery began at comparably low temperature and finished at room temperature, namely that the temperature region for recovery was wide, means that the activation energy for recovery process is distributed. This feature is similar to the case of chalcogenide glass,8) not to the case of a-Si: H.7)

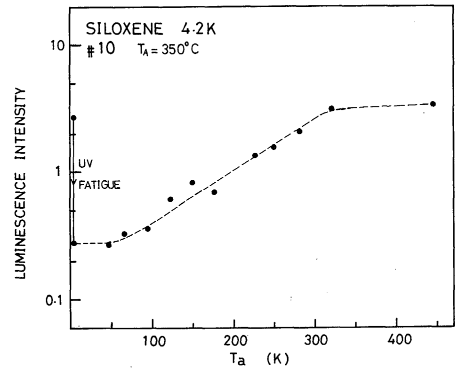

Fig. 5. Recovery of peak luminescence intensity (1.96 eV) vs annealing temperature for vacuum-annealed sample.

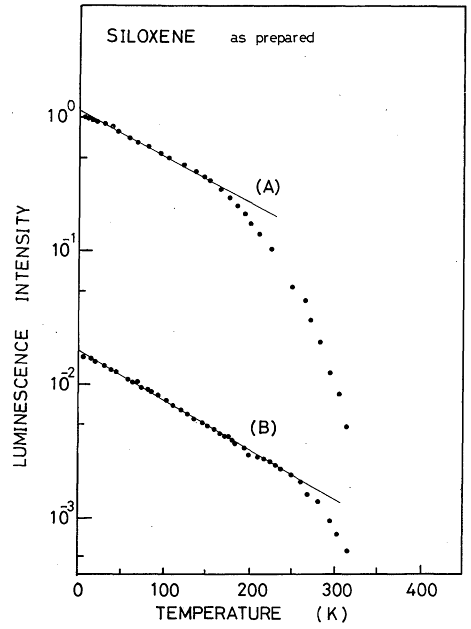

Fig. 6. Inverse Arrhenius plot for the temperature dependences of luminescence intensity for as prepared sample. (A) and (B) show the results taken before and after fatigue, respectively.

Temperature dependence of the luminescence and its change by photo-irradiation are interesting because they contain some information of the recombination process of this material. Figure 6 shows the temperature dependences of the luminescence intensities for the as prepared sample before and after irradiation. Inverse Arrhenius-type temperature dependence, i.e.,

$$I = I_0 \exp(-T/T_0), \tag{2}$$

was observed for the both cases. This temperature dependence has been reported on the luminescence of chalcogenide glasses (g-As_2S_3, g-Se17)) and silica glasses.12) The

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* Very recently, it was found that a GD a-Si: H sample with high hydrogen content such as 33 at.% preprared at low substrate temperature (T_s=75°C) exhibited large fatigue in the luminescence at low temperatures, *e.g.*, the luminescence intensity was decreased to 27% of the initial value after prolonged irradiation (total photon number: 1.2×10^{21} photons/cm^2)20,21)

characteristic temperature, T_0, is obtained from the slope in Fig. 6. It is about 120 K for both cases.

As was previously investigated, the correlation between the luminescence intensity and the paramagnetic centers in a-Si: H suggested that the dangling bond centers act as nonradiative centers.[9] Dangling bond centers are also created by prolonged light irradiation at low temperatures and they reduce the luminescence intensity.[10,11] Similar phenomenon was also observed in siloxene. The measurements were performed at 77 K and the sample was irradiated by UV light of 365 nm which was obtained from 500W Hg lamp through UV band-pass filter (UVD1A). Used sample was as prepared one whose spin density was about 10^{15} spins/cm^3 before irradiation. With the irradiation, the ESR signal intensity gradually increased. After irradiation for 45 minutes, the spin density became about 2.5 times before irradiation. This photo-created spin remained in the dark. This suggests that the created defect states are metastable states. This enhanced signal was stable so far as the sample was held at low temperatures, but the spin density decreased to the value taken before irradiation by thermal annealing at room temperature.

Above results can be understood if one takes it account that the photo-created dangling bond centers act as the nonradiative center and make the luminescence intensity decrease. These results are similar to the case of a-Si: H.[10]

§4. Discussion

First, we discuss the electronic states involved in the radiative and nonradiative recombinations. Most of our experimental results show that the siloxene sample is a highly disordered material just like amorphous materials. As shown in Fig. 2, temperature independent Urbach tail in absorption and broad luminescence with slight Stokes shift may be caused by the distribution of localized states and it seems reasonable to consider that the electronic structure in siloxene is related to those of amorphous or glassy materials. Structural disorder can be imagined as the cause of above properties, for example, the size of the Si layered cluster, the randomness of interlayer bridging, the site disorder of ligands etc., which cause the fluctuation of the interlayer and inter-cluster interaction. By vacuum annealing, such interaction and its spatial fluctuation are modified and become intense so that the absorption edge shifts to lower energy and tailing becomes larger.

The origin of the electronic states for the radiative recombination is not yet well understood but the exciton mechanism recombination is more likely than the trapped electron-hole pair recombination.. The reason is that the decay time in siloxene is shorter than 20 ns and that there is no long decay luminescence.

Stokes shift of the luminescence in siloxene is not so large as in g-SiO$_2$ or chalcogenide glass,[12] and is zero or small, if any, just like a-Si: H.[13] This fact shows that the lattice relaxation is not so large and that the width of the luminescence spectra is determined mainly by the distribution of the localized states.

As to the nonradiative process, we can have more definite picture. The correlation between the ESR signals and the luminescence suggests that the dangling bond centers act as the nonradiative centers. The observed g value of 2.0043 deviates from the Si dangling bond ($g=2.0055$) at the cleavaged surface of crystal silicon[14] or in amorphous silicon.[15] The observed g shift is caused by the existence of one oxygen atom bonded to the Si atom which has the dangling bond. This is understood from the result of the a-Si: O$_x$ by Holzaenkamper *et al.*[16] It is reasonable if we consider that such defects exist at the outer region of the Si layer cluster and not at the internal part of the cluster.

Next, we consider the anomalous temperature dependence of the luminescence, i.e., inverse Arrhenius character.[17-19] As the mechanism of radiative recombination is due to the interaction between the radiation field and the electronic system, it is little dependent on the temperature even if the recombination mechanism is excitonic or distant electron hole pair. On the contrary, the nonradiative process is assisted by phonon, so that it is highly temperature dependent. Therefore, for the discussion of the above feature the details of the nonradiative process must be considered. There have not yet been definitive interpretation of it, but the reasonable one by Kastner[18] takes into account the distribution of the activation energies for nonradiative process. From ref. 18, inverse Arrhenius character is deduced from the exponential distribution for the activation energy: as

$$g(\Delta)=1/k\tilde{T}\exp(-\Delta/k\tilde{T}), \qquad (3)$$

where $\tilde{T}$ gives the limit of the distribution of Δ, and related to T_0 in eq. (2) as follows;

$$\tilde{T}=T_0\ln(\nu_0/\bar{\nu}_r), \qquad (4)$$

where ν_0 is the escape frequency to the nonradiative centers and $\bar{\nu}_r$ is the averaged radiative recombination frequency. For siloxene, a rough estimate with $\nu_0=10^{12}$ sec^{-1} and $\bar{\nu}_r=10^8$ sec^{-1} gives $\tilde{T}=1100$ K, which corresponds to about 95 meV. $\tilde{T}$ is the measure of potential fluctuation for electronic excited states and at the same time the frozen-in temperature like the glass transition temperature.[22] In this case, this temperature may be determined by the initial environment when siloxene is prepared in the reaction of (1).

As was mentioned before, inverse Arrhenius-type temperature dependence has been reported on the luminescence of chalcogenide glasses and silica glasses. Such temperature variation seems universal for glassy materials. This suggests that disordered siloxene has similar propertes to glassy materials in some sense. Indeed, siloxene has low average coordination number such as 2.40. This coordination number belongs to the category of glassy materials according to Phillips.[23,24]

§5. Concluding Remarks

The fatigue effect in the luminescence was observed in disordered silicide layer compound, i.e., siloxene at low temperatures. This fatigue can be recovered by annealing the sample at higher temperatures. It was confirmed that this fatigue was caused by an increase in the number of the dangling bond centers which act as the nonradiative centers. Temperature dependence of the luminescence was also investigated and inverse Arrhenius character was observed. These results suggest that this material has similar electronic and structural properties to amorphous or glassy materials such as a-Si: H and chalcogenide glass.

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