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Photoluminescence and laser-irradiation effect of siloxene compound

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The electronic structure of siloxene has been suggested recently to be the origin of the visible luminescence of porous Si. We study photoluminescence characteristics from siloxene compound under different laser-irradiation, ambient-gas, temperature and vacuum conditions. We find that some spectral characteristics are different from those of porous Si. Especially, we observed a decrease in the luminescence intensity during laser irradiation and a partial recovery with annealing at proper temperatures, which is similar to the Staebler–Wronski effect involving dangling-bond generation in amorphous Si.

1. Introduction

Recently, the electronic structure of siloxene ($Si_6O_3H_6$) compound was suggested as a candidate for the origin of visible-light emission from porous Si, since it is reminiscent of porous Si in photoluminescence (PL) and Raman spectra [1]. Siloxene consists of hexagonal Si rings connected by oxygen atoms. The tetrahedral bonding of the Si on the rings is maintained by the attached hydrogen atoms [2–4]. The optical properties of siloxene compound alone are of interest due to its unique luminescence properties in the class of Si-related compounds, especially if a thin film with such structures can be obtained. However, the origin of the light emission from siloxene structures is also an open question. The stability of the light emission, which is the major concern for technological implications, has not yet been established.

In this Letter we report some unique luminescence properties of siloxene under laser irradiation and after thermal annealing at different temperatures. Our results show that the PL degradation involves dangling-bond generation, oxygen association, and switching between metastable states. More importantly, the process is partially reversible by annealing at the proper temperature. This is similar to the laser-induced effect in amorphous Si, the Staebler–Wronski effect [5].

2. Experimental results and discussion

Siloxene was chemically synthesized from the reaction of $CaSi_2$ powder with concentrated HCl acid by the method described earlier [2–4]. The product powder was compressed to a pellet at ambient temperature and ambient atmosphere. It has been known that the luminescence band can be tuned over a large spectral range by the chemical substitution of hydrogen, oxygen or monovalent ligands, such as halogens, OH^- or others. The appearance of this compound can be changed from green to yellow. The increase of oxygen and decrease of hydrogen correspond to an increase in the three-dimensional cross linkages between the adjacent Si hexagonal rings by oxygen bridges in this polymer-like material.

We found that a decrease in PL intensity is associated with laser irradiation. This phenomenon should be studied and clarified carefully, since without reaching a stabilized luminescence condition, experimental results from varying other parameters may not be reliable. A freshly-prepared compressed siloxene pellet was placed in an ultrahigh-vacuum (UHV) chamber and an Ar laser with a 458 nm line was used for both PL excitation and irradiation in the degradation study. The power density is 2–40 mW mm^{-2}. Luminescence is collected through a UHV chamber window, dispersed by a monochromator and detected by a GaAs cathode PMT. In the spectra shown the system response was not corrected for.

Fig. 1 shows the spectra from a siloxene sample before and after laser irradiation in air. Before the irradiation, the intense yellow luminescence was visible to the naked eye. The PL peak position is at 510 nm (2.43 eV) with a half width of 0.36 eV. Fig. 2 shows the peak intensities as functions of the duration of laser irradiation in different environments: ultrahigh vacuum of 6×10^{-9} Torr and ambient atmosphere of oxygen. The basic observations can be summarized as follows: (1) the stabilized intensity level in UHV depends on the laser-irradiation power; (2) the stabilized intensity level in ambient oxygen is about 3 times higher than in UHV with the same laser-irradiation power; and (3) the stabilization time takes about 2 h in all cases.

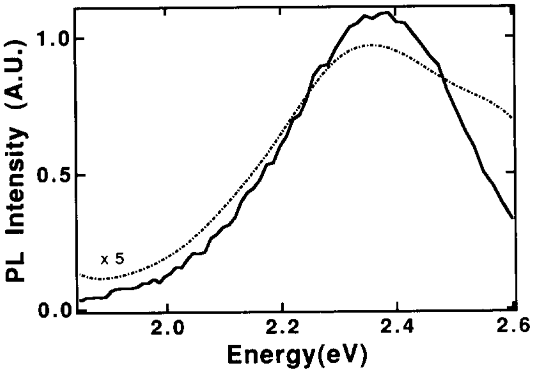

Fig. 1. Siloxene luminescence spectra before (—) and after (-··-) laser irradiation for 150 min in air. Power density 2 mW mm^{-2}.

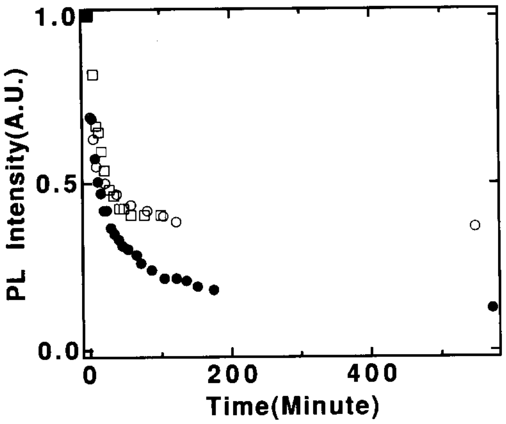

Fig. 2. Peak intensities as functions of laser-irradiation duration in ultrahigh vacuum of 6×10^{-9} Torr and ambient atmosphere of oxygen. (●) UHV, P=44 mW mm^{-2}; (□) UHV, P=14 mW mm^{-2}; (○) O_2, P=44 mW mm^{-2}.

The comparison of the laser-irradiation results between siloxene and porous Si is summarized in table 1. For porous Si, it was established that the laser-induced degradation is related to the participation of oxygen and the large surface area exposed. Since there is an abundant supply of oxygen in air or in a pure oxygen environment, but not in UHV, the stabilizing time for porous Si is much longer in UHV [6–8]. However, for siloxene compound the intense luminescence comes from the bulk, and the laser-induced degradation occurs within the laser penetration depth.

Our observations on the PL degradation due to laser irradiation are similar to the light-induced effect or light-soaking effect in amorphous silicon [9]. In amorphous silicon the recombination of the photoexcited carrier breaks the Si–Si weak bond, generates a defect state (most likely the dangling bond), changes the local configuration, and reaches a metastable state at higher energy. The defect generation by non-radiative recombination is a self-limiting process, since most of the non-radiative recombinations proceed with the existing defect states. In all previous studies of amorphous Si, the role of impurities was not found to be essential in such defect formation. For siloxene compound, this light-induced defect formation mechanism can also partially explain the experimental results: the generation of the dangling bond determines the PL intensity decrease; the relative composition of silicon, hydrogen and oxygen determines the emission energy.

The results from the subsequent annealing should provide a confirmation and verification of this light-induced mechanism. As in the case of amorphous Si, annealing provides thermal excitation to restore an original quasi-equilibrium state with a low defect density, which is in the reverse direction from the laser-irradiation process. Usually annealing at about 150°C for an hour can reduce the defect density substantially in amorphous Si. We applied a similar annealing treatment to siloxene after 10 h pre-irradia-

Table 1
Comparison of the laser-irradiation effect between porous Si and siloxene in three different environments: UHV (background pressure of 6×10^{-9} Torr), ambient atmosphere air and ambient atmosphere oxygen

	UHV			Air			Oxygen		
	power density (mW mm^{-2})	stabilization time (min)	I_f/I_i	power density (mW mm^{-2})	stabilization time (min)	I_f/I_i	power density (mW mm^{-2})	stabilization time (min)	I_f/I_i
porous Si	15.4	>700	>0.8	2.8	90	0.4	0.88	70	<0.01
siloxene	44	150	0.13	2	200	0.2	44	120	0.37
	14	50	0.4						

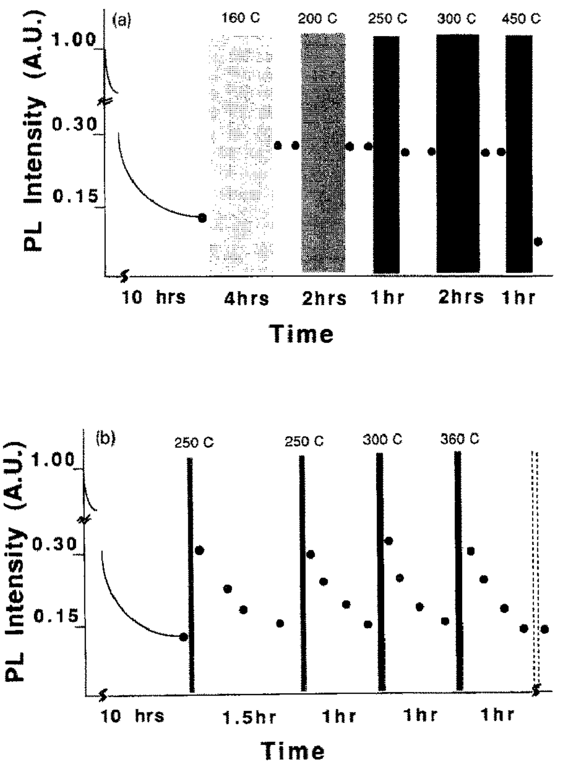

Fig. 3. Siloxene luminescence intensity changes with different annealing temperatures. (a) No laser irradiations between annealings; (b) laser irradiations were also applied between annealings, each annealing lasts for 1 h.

tion. Fig. 3 shows two annealing sequences for siloxene and the resulting PL intensity. In each sequence, a siloxene pellet was placed in the UHV chamber at room temperature and was irradiated by a laser beam until it reached a low but stabilized luminescence level. The ratio of the stabilized luminescence intensity to the initial intensity depends on the laser power density. For a laser power density of 14 mW mm^{-2}, this ratio is about 40%; for a laser power of 44 mW mm^{-2}, it is about 13%. All the luminescence data were acquired after the sample was cooled down to room temperature in UHV, which usually took about 10 h. In sequence (a) no further laser irradiation was applied after each annealing. In sequence (b) laser irradiation was applied after each annealing. Both show a partial recovery of the degraded luminescence intensity to about 30% of the fresh sample intensity level by a thermal annealing.

In sequence (a), several different temperatures, 160, 200, 250, 300 and 450°C were applied sequentially to anneal the sample which experienced the initial laser irradiation. Between annealings, luminescence was measured in the UHV at room temperature. Each annealing took 1 to 4 h. The first annealing of 160°C for 4 h doubled the intensity. The subsequent annealings at higher temperatures (200, 250 and 300°C) did not change the intensity and could not bring the intensity back to the original fresh sample level. Increasing the annealing temperature to above 450°C in UHV can be destructive, since the luminescence intensity is reduced substantially to below one tenth of the fresh sample intensity level. More evidently, there is no difference in the luminescence intensities between different sampling points with and without laser pre-irradiation after the annealing at 450°C. This destruction may be due to the desorption of hydrogen atoms at such a high temperature. In sequence (b), several different temperature annealings were also applied sequentially to the sample which experienced the initial laser irradiation. In contrast to (a), laser irradiation is applied after each annealing, and luminescence data were collected during the irradiation. We observed an intensity decrease in this process during the irradiation. The intensity decreases to about the same level as the previously stabilized level following the irradiation. Finally, the last step in sequence (b) shows no intensity change for the sample kept in the UHV for overnight at ambient temperature without laser irradiation.

From both figs. 3a and 3b, it appears that there are two quasi-stable states corresponding to the luminescence. The lower intensity one responds to the laser irradiation and the higher intensity one responds to the annealing. The latter has an intensity level of 30–40% in this case, and annealing in any temperature cannot bring it to the original level. We suggest that the mechanism in the laser-induced PL degradation for siloxene is similar to that of the light-induced effect in amorphous Si, i.e. the Staebler–Wronski effect. The dangling-bond generation has a major effect on the PL degradation, which is a partially reversible process. The hydrogen and oxygen could passivate the dangling bond in the proper temperature range.

Results from the temperature variation of the PL are shown in fig. 4. The sampling point was pre-exposed to the laser irradiation and the intensity was stabilized. The PL intensity increases monotonically upon lowering the temperature down to 20 K, and the effect is reversible. In porous Si, the relation is different: the intensity peaks in the range of 100–200 K, and it drops at lower temperature [10].

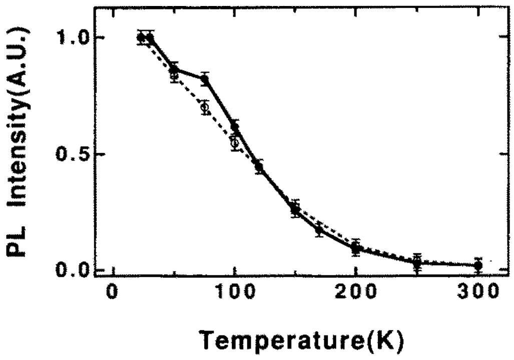

Fig. 4. Photoluminescence peak intensity with variable temperature for siloxene compound. (-●-) *T* decrease; (--O--) *T* increase.

3. Conclusions

In summary, PL from siloxene compound with light and temperature effects has been studied experimentally. The Staebler–Wronski effect was observed during laser irradiation and annealing. The different responses to light and temperature in comparison with porous Si indicate that the two have somewhat different origins for the light emission.

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