Journal of Non-Crystalline Solids 59 & 60 (1983) 645-648
North-Holland Publishing Company

OPTICAL PROPERTIES OF DISORDERED SILICIDE LAYER COMPOUND: SILOXENE ($Si_6(OH)_3H_3$) - TIME RESOLVED LUMINESCENCE

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Time-resolved luminescence of a disordered layer compound, i.e., siloxene ($Si_6(OH)_3H_3$) was investigated at low temperatures. Two components of different decay times (fast component τ<100nS, and slow component 100nS<τ<50μS) were observed in as-grown samples. The polarization memory and excitation energy dependences of the luminescence were also investigated.
The results on the luminescence of this material have a resemblance to those of chalcogenide glasses. The mechanism of the luminescence and the recombination process are interpreted in terms of a molecular exciton model taking account of the structural properties of siloxene.

1. INTRODUCTION

Siloxene is a disordered layer compound, which is composed of silicon, hydrogen and oxygen (Si:H:O=6:6:3). We have investigated the luminescence by CW excitation in this material[1] and have observed (a) fatigue effect by intense laser light irradiation at low temperatures and its thermal recovery, (b) inverse Arrhenius type ($I \propto \exp(-T/T_0)$) anomalous temperature dependence. These properties have also been observed in the luminescence of a-Si:H and chalcogenide glass. The mechanism of such phenomena has not yet been well understood, but it is related to the flexibility of the structure of those materials.

It is important for discussing the electronic states to know structural information of the material. Recently, Ubara et.al. has carried out the characterization of the structure of siloxene by various measurements including X-ray diffraction,IR, Raman scattering, ESR, ESCA, DSC etc.[2] They found that the as-grown siloxene is a paracrystallite having a layered order, i.e., it is formed from small Si layered clusters with -OH and -H ligands coupled by the oxygen bridge or hydrogen bond with each other and that layered order breaks into amorphous phase by vacuum-annealing. Since each cluster size and strength of inter-cluster couplings are distributed, we suppose that this material is composed of a molecular aggregate having a complex diagonal and off-diagonal disorder.

2. EXPERIMENTAL

Time resolved luminescence measurements were carried out at 4.2K. The sample was excited by a dye laser of a pulse width of about 1nS with an appropriate band pass filters and the luminescence was detected by using a 25cm grating monochromator, a fast photomultiplier and a box-car integrator. Total time resolution of our system was less than 2nS. Correction for the optical system was carried out automatically by a microcomputer.

The sample was made from $CaSi_2$ crystal and 38% hydrosolution of HCl for 3 hours at room temperature. After reaction, the obtained siloxene was dried in vacuum of 10^{-5} Torr. Annealing was carried out in vacuum of 10^{-6} Torr for 15 minutes at 350°C.

3. RESULTS AND DISCUSSION

The luminescence spectra of siloxene exhibit a broad asymmetric Gaussian-like lineshape as shown in Fig.1. The luminescence peak of a typical as-grown sample is about 2.6eV at delay time t_d= 0nS. Spectral lineshape changes with time. For annealed samples, the emission band shifts to lower energy and is peaked at about 2eV.

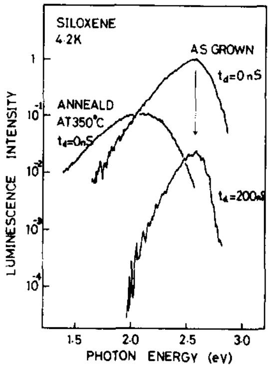

Fig.1 Time-resolved luminescence spectra for as-grown and vacuum-annealed samples. Excitation energy was 3.25 eV.

Fig.2 shows the results for an as-grown sample. The luminescence intensity decay curve consists of two component. The fast decay component (t_d<100nS) is well represented by t^{-1} time dependence. In the delay time t_d>100nS, the slow component becomes dominant and it spans to 50μS. The luminescence peak position $E_p(t)$ is also plotted as a function of t_d in Fig.2. The feature in $E_p(t)$ is characterized by a fast decrease with time for t_d<10nS, followed by an increase for 10nS<t_d<500nS. Similar behaviour in $E_p(t)$ has also been observed in a-Si:O:H[3] and sp-a-Si:H[4] and has been attributed to the Coulomb interaction between recombining electron-hole pairs. In siloxene, however, the behaviour in $E_p(t)$ could be interpreted by the overlapping of the fast and the slow decay components,since the lineshape is highly time-dependent, as shown in Fig.1. The above feature shows that the fast and the slow components originate with different mechanisms. This is supported by the fact that the polarization memory is observed in short t_d region less than 100nS, where the fast decay component is dominant.

By annealing in vacuum at 350°C, the layered order of as-grown siloxene

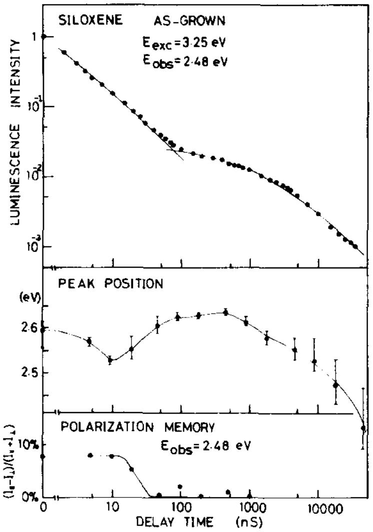

Fig.2 Luminescence decay, peak position and polarization memory with time delay for as-grown sample.

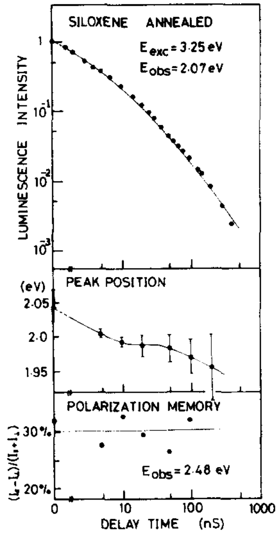

Fig.3 Luminescence decay, peak position and polarization memory for annealed sample.

breaks down due to the oxygen interlayer bridgings and effusion of H. The luminescence spectrum changes as shown in Fig.1. Time-resolved data are shown in Fig.3. Characteristics of the annealed samples are (1) red shift of the luminescence peak and (2) vanishing of slow decay component. The latter fact is evident from intensity decay, peak shift and polarization memory as a function of t_d.

Fig.4 is a plot of the observed peak positions versus excitation energies at zero delay time. The energies of the luminescence peak increase with excitation energies from low energy to a certain one (2.79eV for as-grown samples and 2.72eV for annealed samples) and remain constant by the excitation whose energy is higher than these values. Such threshold energy has also been observed in chalcogenide glass[5] and a-Si:H[6] and discussed in terms of mobility edge (or thermalization edge).

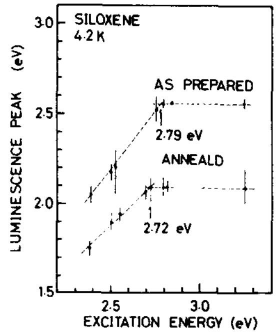

Fig.4 Luminescence peak energy vs. excitation energy plot for as grown sample and anneald sample, respectively.

Another important feature is a difference in the exciting energy dependence of the luminescence efficiency between the fast and slow decay. The fast component can easily be excited by the light whose energy is less than band gap energy, but the slow component cannot be excited. These results also suggest that different mechanisms operate for two components.

As regards the mechanism for the luminescence, two types of excitations can be considered. The one is that the excitation is restricted within one molecular unit. If it is transfered, it behaves as an ordinary Frenkel exciton, if it is localized, it is like an isolated molecular excitation. The other is a charge transfer excitation including polaron pairs. Since in such case the electrons and holes relax at different molecular units, it is expected that the radiative recombination , if exists, is slow as compared to the intra-molecule excitation and the nonradiative decay is also expected. If we attribute the fast decay component to the former and the slow component to the latter, the feature of the experimental results is well explained. For more precise understanding of the luminescence mechanism, other experiments, for instance, photoconductivity, photoinduced absorption etc. are required.

ACKNOWLEDGEMENT

We wish to thank Dr. H. Ubara and Dr. T. Imura for informing us of their results on structural properties on siloxene and also for helpful discussions.

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