EXISTENCE OF A UNIVERSAL LOW-ENERGY TAIL IN THE PHOTOLUMINESCENCE OF a -SiC:H ALLOYS

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(Received 4 December 1990 by J. Tauc)

Photoluminescence measurements have been performed in a -SiC:H alloys prepared by the plasma decomposition of SiH_4 and C_2H_4 gas mixture. It is found that the shift of the peak of the photoluminescence spectrum with increasing the gas flow ratio x ($= 2[\text{C}_2\text{H}_4]/(2[\text{C}_2\text{H}_4] + [\text{SiH}_4])$) parallels the widening of the optical gap. For $x \leq 0.6$ the samples show that the photoluminescence efficiency in the low-energy tail is insensitive to the gas flow ratio. Together with the similar results observed in a -SiGe:H and a -Si:H alloys by Gal *et al.* [*Phys. Rev.* **B31**, 4060 (1985)], it calls for re-examination of the currently accepted model for the dominant-photoluminescence process in good quality a -Si:H. The explanation adapted from the Brodsky's quantum well model is consistent with the experimental facts.

THE HYDROGENATED amorphous silicon (a -Si:H) has received extensive interest since 1976 when Carlson and Wronski successfully fabricated the a -Si:H solar cell by glow discharge method [1]. The attraction of this material is not only due to its low cost and easy fabrication, but also due to its impact to the traditional solid state theory based on the periodic arrangement of atoms. Despite extensive study, uncertainties still exist in the microscopic origins of many commonly observed effects [2]. In this paper we report the existence of a universal tail on the low-energy side of the photoluminescence (PL) spectra in a -SiC:H alloys. Similar results in a -SiGe:H and a -Si:H alloys have been reported earlier [3, 4]. This property calls for the re-examination of the currently accepted model of PL processes in a -Si:H.

Samples were made on 7059 glass substrates in a glow-discharge system. The deposition parameters are as follows: r.f. frequency 10 MHz, r.f. power density $\sim 0.3 \text{ W cm}^{-2}$, substrate temperature $\sim 200^\circ\text{C}$, chamber pressure ~ 1 torr, electrode spacing ~ 2 cm. The gas sources used for depositions are SiH_4 (50% in H_2) and C_2H_4 (50% in H_2). The composition x is defined to be the gas phase flow ratio of $2[\text{C}_2\text{H}_4]$ to $[\text{SiH}_4] + 2[\text{C}_2\text{H}_4]$.

The optical gap is obtained according to Tauc's plot [5]. The PL spectra were measured at 17 K using a 4880 Å line of an argon laser as the excitation source.

The spectra were taken using lock-in detection and a photomultiplier tube.

Figure 1 shows the optical gap and the PL peak position as a function of the gas flow ratio x . It can be seen that the optical gap increases linearly as the gas flow ratio increases. This suggests that the incorporation of carbon atom gradually widens the optical gap and the trend is almost linear. We can also see that the shift of the PL peak position with increasing the gas flow ratio parallels the widening of the optical gap.

Figure 2 shows the PL spectra for a -SiC:H alloys prepared by different gas flow ratio. The striking feature about the figure is the insensitivity of the low-energy tail of the PL spectra to x for $0 \leq x \leq 0.6$. This behavior has been observed in previous measurements of a -SiGe:H³ and a -Si:H⁴ with different H content.

Several models have been proposed to explain the dominant PL process which peaks near 1.4 eV in a -Si:H. The most commonly accepted model proposed by Street [6] is so-called band-tail to band-tail recombination. Harvard group [7] has also proposed an interesting model which claims that the emission is due to the recombination between localized electrons of energy just below the conduction-band edge and localized holes trapped by defects of the a -Si network stabilized by an unknown impurity. Even though these models can account for many experimental facts,

Fig. 1. Room-temperature optical gap and photoluminescence-peak position of a -SiC:H alloys measured at 17 K as a function of the gas flow ratio x . Open circles and solid circles represent optical gap and luminescence data, respectively. The solid lines are a guide to the eye.

there are several questions exist in the explanation of the PL spectra observed in a -Si:H based alloys. These questions have been pointed out by Gal *et al.* [3] after the observation of the existence of a universal tail to the low-energy PL spectra in a -SiGe:H alloys. Basically, they pointed out that in addition to the difficulty of the explanation of the universal tail, the above models also can not explain the narrowing of the emission line shape with increasing germanium content. Additional question is raised according to our measurement of a -SiC:H alloys. It is known that in the films the dangling bonds increase with increasing carbon content [8]. Since dangling bonds act as nonradiative centers, the PL intensity should decrease with increasing carbon content. However, in Fig. 2 we observe an opposite trend. Thus it seems clearly that

Fig. 2. Photoluminescence intensities at 17 K as functions of energy for alloys in the system a -SiC:H. The numbers denote the gas flow ratio in percent ($100 \times$).

a search of the mechanism to explain the dominant PL process in a -Si:H based alloys is still needed.

Based on the existence of a universal tail to the low-energy PL spectra, Gal *et al.* [3] have suggested an alternative explanation for the PL process in a -SiGe:H alloys. They assume that the emission is associated with the recombination between the excited and ground states of an ensemble of specific silicon and/or hydrogen related defect states. The constant low-energy tail results from the constant density of the defect states. The shift of the PL peak with increasing Ge content results from the removal of excited states of the defect which become resonant with extended states as the gap is reduced. This interpretation suggests that the change in PL intensity with alloy composition is an unavoidable property of the alloy system and not necessarily an indication of the quality of material.

Even though this model can be extended to explain our PL spectra observed in a -SiC:H alloys very well, it is very difficult for us to visualize a specific defect which has the properties independent of alloy composition and the energy separation between its excited state and ground state can vary continuously at least from 0.8 eV to more than 2.0 eV. In addition, the distribution of the excited states of the specific defect across the optical gap acting as deep defect states should affect not only PL spectra but also the other properties of a -Si:H and should be observable in other measurements. However, it is found that the dominant defects in good quality a -Si:H are dangling bonds not the other some kinds of unknown defects [2].

As an alternative explanation we adapt the Brodsky's quantum well model [9]. Figure 3 shows the one dimensional schematic energy diagram of a -SiC:H alloys with the carbon content in Fig. 3(b) being than that in Fig. 3(a). The low band gap a -Si region forms the valley (well) and the microvoids containing SiH, SiH₂, CH₂, and CH₃ from the mountains (barriers). The PL is believed to be the recombination of the electron and hole pairs in the well, and the optical gap is determined by the electronic transition involving one of the delocalized bands. The continuous blue shift of PL peak with increasing carbon content corresponds to the enhancement of the size and number of CH_x mountains. Thus, the confined carriers thermalizing into wells with smaller width can emit photons of larger energy. The same argument can be applied if carbon is replaced by germanium. In this case, the continuous redshift of PL peak corresponds to the shrinkage of the size and number of SiH_x mountains, and the confined carriers thermalizing into wells with larger width emit photons

Fig. 3. One-dimensional schematic energy diagram of the Brodsky's quantum well model for a -SiC:H alloys with the carbon content in (b) being larger than that in (a). E_{OP} and E_{PL} represent the energies of optical absorption and photoluminescence, respectively.

of smaller energy. The insensitivity of the low-energy tail of the PL spectra results naturally from the same emission origin, which is the low band gap a -Si region, for different alloy composition. The same as the model proposed by Gal *et al.* [3], the present interpretation also suggests that PL intensity cannot be used as a monitor for electronic states near midgap. The PL intensity not only depends on electronic states near midgap, but also depends on the number of electron-hole pairs confined in the well region. For instance, if we replace SiH_x barrier by CH_x barrier, there will be more carriers confined in the well since the barrier height of CH_x mountain is larger than that of SiH_x mountain. Thus, the present model can explain the experimental fact that PL intensity in a -SiC:H alloys can be larger than that in a -Si:H even though a -SiC:H contains high dangling bonds. We therefore can see

that the Brodsky's quantum well model is consistent with all the experimental facts. In addition, it has the advantage that we do not need assume the existence of an unknown defect with peculiar properties.

In summary, a -Si:H based alloys, including a -SiGe:H, a -SiC:H and a -Si:H with different H content, exhibit insensitivity of the low-energy tail in PL spectra to alloy composition. This property raises several questions concerning an appropriate model for the dominant PL process in good quality a -Si:H. It calls for the re-examination of the currently accepted model proposed by Street [6]. The explanation adapted from the Brodsky's quantum well model is consistent with all the experimental facts. It is very interesting to see whether the properties observed in the present study exist in other a -Si:H based alloys, such as a -SiO:H, and a -SiN:H. Thus, we can conclude that the insensitivity of the low-energy tail in PL spectra to alloy composition is a common property for all a -Si:H based alloys or even for all amorphous semiconductors with tetrahedral bonding.

Acknowledgements — This work is supported by National Science Council of the Republic of China.

REFERENCES

1. D.E. Carlson & C.R. Wronski, *Appl. Phys. Lett.* **28**, 671 (1976).
2. P.K. Willardson & A.C. Beer, (Editors), *Semiconductors and Semimetals*, Vol 21, Academic Press, New York (1984).
3. M. Gal, J.M. Viner, P.C. Taylor & R.D. Wieting, *Phys. Rev.* **B31**, 4060 (1985).
4. B.A. Wilson, A.M. Sargent, K.W. Wecht, A.J. Williams, T.P. Kerwin, C.M. Taylor & J.P. Harbison, *Phys. Rev.* **B30**, 3320 (1984).
5. J. Tauc, *Optical Properties of Solids*, (Edited by F. Abeles), North-Holland, Amsterdam (1970).
6. R.A. Street, *Adv. Phys.* **30**, 593 (1981).
7. D.A. Anderson, G. Moddel & W. Paul, *J. Non-Cryst. Solids* **35 & 36**, 345 (1980).
8. M. Kumeda, S. Nakanishi & T. Shimizu, *Jpn. J. Appl. Phys.* **26**, L1915 (1987).
9. M.H. Brodsky, *Solid State Commun.* **36**, 55 (1980).