PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN **49** (1980) SUPPL. A p. 1249–1252

ELECTRONIC AND VIBRATIONAL PROPERTIES OF GLOW-DISCHARGE AMORPHOUS Si:F:H

R. Tsu, M. Izu, V. Cannella and S. R. Ovshinsky
Energy Conversion Devices, Inc.
Troy, Michigan 48084

G-J. Jan and F. H. Pollak
Physics Department
Brooklyn College of CUNY
Brooklyn, N.Y. 11210

The electrolyte electroreflectance and Raman scattering spectra of several samples of glow-discharge amorphous Si:F:H films have been investigated. We have observed modulated optical spectroscopy structure at 3.4eV and 4.5eV, energies which correspond to peaks seen in crystalline silicon. In particular, the latter feature can be related to the degree of disorder in the material. Also we have seen peaks in the Raman spectra intermediate between amorphous and crystalline materials. These experimental results provide strong evidence that highly n-doped (P or As) a-Si:F:H possesses an intermediate range order (i.e., an improved connectivity between the elements of the random network).

A new type of amorphous semiconductor alloy has recently been reported [1] . This new material has silicon and fluorine as its main structural components. It is multi-elemental and includes hydrogen and can also include other elements. This Si:F:H alloy, prepared by the glow-discharge decomposition of SiF_4 mixed with hydrogen, has been reported to overcome a number of problems of a-Si and a-Si:H. In order to gain further information about the electronic and vibrational states of this amorphous semiconductor, we have investigated the electrolyte electroreflectance (EER) and Raman spectra of several samples of this material.

The Raman spectra of crystalline (c-Si) and amorphous silicon (a-Si) differ considerably. The former material exhibits a single, sharp line at 522 cm^{-1} while the latter shows a broad asymmetric peak around 475 cm^{-1}. To date, peak positions intermediate between these two have not been reported for disordered Si [2] except in ion-damaged amorphous material which has been partially annealed by pulsed laser radiation [3]. The presence of the sharp 522 cm^{-1} line can be used to identify crystallinity [4]. Recent experiments on annealed SiO_x films confirm the usefulness of Raman scattering as a method of detecting crystallinity [5].

We have observed in several samples of a-Si:F:H (a) structure in the EER spectra in the range 1-5eV and (b) Raman peaks intermediate between 475 cm^{-1} and 522 cm^{-1}. This is the first report of modulated optical structure above the fundamental amorphous gap [6,7] and intermediate Raman peaks in a disordered tetrahedral semiconductor. In all samples investigated, EER features were seen at 3.4eV and 4.5eV, energies which correspond to optical and modulated optical structure of crystalline silicon [8]. In particular, the 4.5eV feature can be related to the degree of local disorder in the material. The observations of the 3.4eV and 4.5eV EER structures (particularly the latter) as well as Raman peaks intermediate between 475 cm^{-1} and 522 cm^{-1} strongly indicated that highly n-doped (P or As) a-Si:F:H possesses an intermediate range order (IRO) i.e., an improved connectivity between the elements of the random network. Our work on As-doped material has been presented elsewhere [9] so that we will concentrate on the results for a-Si:F:H (P).

The samples for this investigation were prepared by the glow discharge process, using an RF power of ~30w to decompose SiF_4 gas with a gas mixture of SiF_4:H of ~5:1. The RF power used was capacitively coupled to the gas having a dc bias of approximately -100V on the sample electrode. Typically, a flow of 0.05 liter/min at 0.5 Torr was used. Doping was accomplished by the introduction of PH_3. The temperature of the substrate was typically 300°C.

Shown in Fig.(1) are the EER spectre of two a-Si:F:H (P) samples (GLAD 35-A-B and GLAD 35-B). Both have a room temperature conductivity of [10] (ohm-cm)$^{-1}$. The former sample is about 0.3 μm thick on a crystalline silicon substrate while the latter is about 0.15 μm thick on a SnO_2 substrate. The EER measurements were made using the electrolyte technique [8].

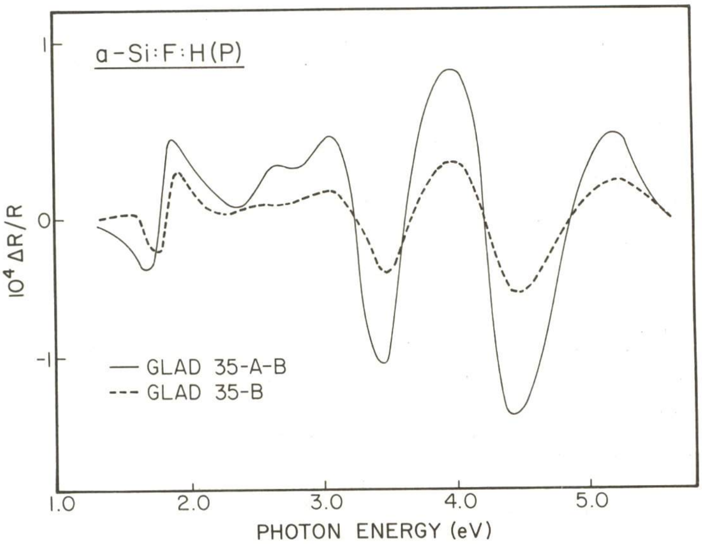

Fig.(1) Electrolyte electroreflectance spectra for a-Si:F:H doped with P(0.1% of PH_3 in SiF_4)

The two spectra are very similar with pronounced peaks around 2eV, 3.4eV and 4.5eV. Above 3eV the features in Fig. (1) correspond to those in Ref. [9]. The structure around 2eV is very similar to that reported by Okamoto et al. [6] and more recently by Al Jalali and Weiser [7]. This is the energy range of the fundamental absorption edge. The results of Fig. (1) and those reported in Ref. [9] are the first observation of modulated spectra above this region in a disordered semiconductor.

In Fig. (2) we have plotted the Raman spectra of several types of amorphous silicon. Experimental details are given in Ref. [9]. The a-Si:F:H (P), with a Raman peak at about 528 cm^{-1}, is the same material used to obtain the EER spectra of Fig. (1) (both GLAD samples gave essentially the same Raman spectra). The sample designated a-Si:F:H (As) in Fig. (2) is the same as sample 103 of Ref. [9]. The position of the c-Si peak is indicated by an arrow at 522 cm^{-1}.

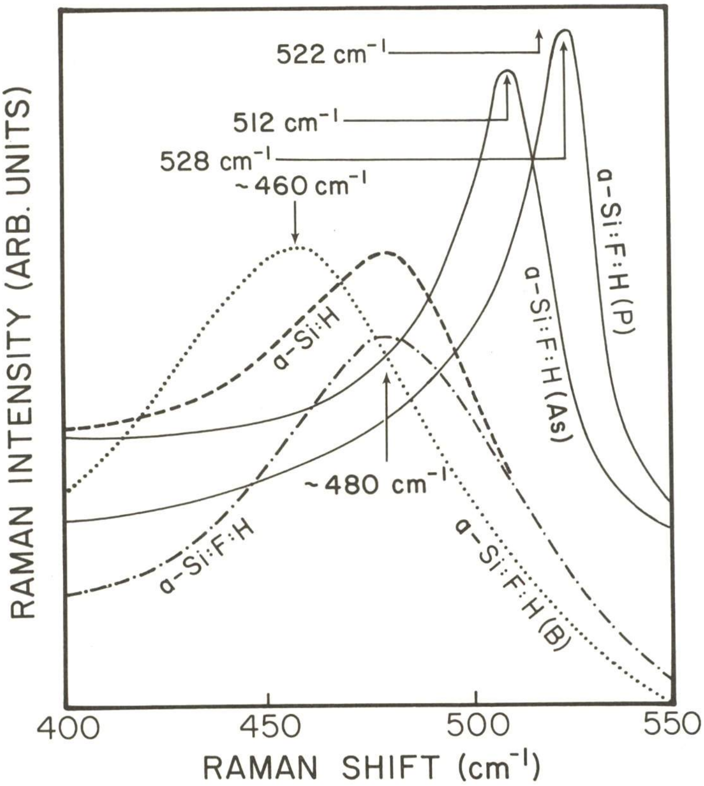

Fig.(2) Scattering intensity versus Raman shift: The n-doping for both a-Si:H and a-Si:F:H is introduced by 0.1% of PH_3 or AsH_3 in the gas mixture. The a-Si:F:H(B) sample has 1% B_2H_6 in SiF_4.

Although EER structure has been reported in the vicinity of the absorption edge for a-Si:H, ER response has not been obtained involving transitions above the absorption edge. The structures we observe at 3.4eV and 4.5eV correspond to the interband transitions in c-Si[8]. Regardless of the thicknesses of these samples, the peak energy positions were not changed. On this basis, together with the small depth of penetration of the light at these energies, we have ruled out any interference effects.

It has been established that the main contribution to the 3.4eV peak in Si is due to transitions along the <111> regions ($L'_3 - L_1$) of the Brillouin Zone (BZ) [10]. Hence it is the same as the E_1 peak in other diamond- and zinc-blend type materials. The <111> directions are precisely the directions of the bonds in the unit tetrahedron. Therefore, any feature related to them is expected to be retained as long as the short range order is preserved. For example, the large asymmetric single bump ϵ_2 (imaginary part of complex dielectric constant) of amorphous tetrahedrally bonded semiconductors coincides with the E_1 feature of the crystalline material. Several theoretical works have also demonstrated this relationship. On the other hand, the 4.5eV feature (E_2) in c-Si is due to transitions at the X point (X_4-X_1) and Σ regions (Σ_2- Σ_3) of the BZ. The E_2 feature in ϵ_2 is washed out in going from the crystalline to amorphous material. Based on this fact, as well as on theoretical calculations, the E_2 feature is to be associated with an ordering which is longer range than that related to E_1. For example, theoretical investigations of the polymorphs of Ge and Si show that the E_2 peak is selectively lowered with respect to the E_1

structure when the local disorder is increased [11]. Thus the observation of the E_2 structure in our EER experiment strongly suggests for IRO in our highly n-doped a-Si:F:H samples. (No EER has been found for low to moderate doping).

In the region slightly below 2eV our EER spectra (see Fig. 1) is similar to that observed by Okamoto [6] and calculated by Al Jalali and Weiser [7] based on a Kramers-Kronig analysis of their electroabsorption spectrum for a-Si:H. They interpret the electroabsorption effect as resulting from the influence of the external field on the localized states only. It is interesting to note that in c-Si the Γ_{25}' -L_1 gap is at 1.7eV [12]. Thus it may be that the features slightly below 2eV is related to this transition. It is possible that the <111> nature of the Γ_{25}' -L_1 gap, i.e. the tetrahedral bonding symmetry, is related to short range order[1].

The Raman spectra of a number of doped and undoped Si:F:H samples are compared with a-Si:H sample in Fig. (2). The Raman spectra of undoped a-Si:F:H is much more symmetrical (lower Raman intensity at lower frequencies) in comparison to the undoped a-Si:H. Generally there is a noticeable increase in the peak position from 475 cm^{-1} for a-Si:H to 480 cm^{-1} for a-Si:F:H, while a dramatic up-shift from 475 cm^{-1} for highly n-doped a-Si:H to the neighborhood of 520 cm^{-1} for highly n-doped a-Si:F:H. The peak position for the highly doped (1% B) a-Si:F:H significantly shifts down from 480 cm^{-1}. While the addition of fluorine may increase the range of order, high concentration of P- and As-doping results in a definite IRO. To date, of all the samples studied, the observations of EER and dramatic up-shift in the Raman peak position are well correlated. Since these effects are not found in a-Si:H (doped or undoped) we conclude that fluorine is responsible for promoting IRO in our highly n-doped a-Si:F:H samples.

1) See, for example, A. Madan, S.R. Ovshinsky and E. Benn: Phil. Mag B 40 (1979) 259 and references therein.
2) M.H. Brodsky, M. Cardona and J.J. Cuomo: Phys. Rev. B16 (1977) 3556.
3) See, for example, R. Tsu, J.E. Baglin, T.Y. Tan and R.J. Von Gutfeld: Proc. Vol. 80-1, Elect. Chem. Soc. (1980) 382, ed. by C.L. Anderson, G.K. Celler, and G.A. Rosgonyi and references therein; R. Tsu and S.S. Jha: Supplement Journal de Physique (Paris), Colloque C4 (1980) 25.
4) See, for example, M.H. Brodsky: Light Scattering in Solids, ed. by M. Cardona, Springer-Verlay, N.Y. (1975) 208 and references therein.
5) A. Hartstein, J.C. Tsang, D.J. Di Maria, D.W. Dong: Appl. Phys. Lett. 36, 836 (1980)
6) H. Okamato, Y. Nitta, T. Adachi and Y. Hamakawa: Surface Science 86 (1979) to be published.
7) See, for example, S. Al Jalali and G. Weiser: J. Non-Cryst. Solids, and references there, to be published.
8) See, for example, Y. Hamakawa and T. Nishino: Optical Properties of Solids: New Developments, ed. B.O. Seraphin North Holland, N.Y.(1979)and ref therein.
9) R. Tsu, M. Izu, S.R. Ovshinsky and F.H. Pollak: Bull. Am. Phys. Soc. 25 (1980) 295 and to be published in Solid State Comm.
10) F.H. Pollak and G.W. Rubloff: Phys. Rev. Letter 29 (1972) 789; K. Kondo and A. Moritani: Phys. Rev. B14 (1976) 1577.
11) B. Kramer: Phys. Stat. Sol.: (b) 47 (1971) 501; J.D. Joannopoulous and M.L. Cohen: Phys. Rev. 88 (1973) 2733; I.B. Ortenberger and D. Henderson: Proc. Eleventh Interm. Conf. on Physics of Semiconductors, Polish Scientific Publishers, Warsaw, (1972) 465.
12) R.A. Forman, W.R. Thurber and D.E. Aspnes: Solid State Comm 14 (1974) 1007.

We are grateful to Ralph Mohr for his assistance in the preparation of samples. F.H. Pollak wishes to acknowledge the support of PSC/BHE grant 13106.