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Study of the hydrogen stability in evaporated amorphous $\text{Si}_{1-x}\text{Sn}_x\text{:H}$ ($0 \leq x \leq 0.2$) alloys by neutron scattering and exodiffusion measurements

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Exodiffusion and low-angle neutron scattering experiments are used to investigate the influence of tin on the hydrogen stability in evaporated amorphous $\text{Si}_{1-x}\text{Sn}_x$ ($0 \leq x \leq 0.2$) alloys. The neutron diffraction experiments, which are performed on $\text{Si}_{1-x}\text{Sn}_x\text{:H}/\text{Si}_{1-x}\text{Sn}_x\text{:D}/\dots$ multilayers, consist in following the decay of the diffracted intensity during thermal treatments. Both studies give information on the structure of the alloys and show that the hydrogen stability decreases with increasing tin concentration.

Thin films of semiconductor alloys such as $\alpha\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ or $\alpha\text{-Si}_{1-x}\text{Sn}_x\text{:H}$ constitute an important class of materials that are attractive due to their potential applications in multiband-gap solar cells because relatively narrow gaps can be obtained with low germanium or tin content.

We have previously studied $\alpha\text{-Si}_{1-x}\text{Sn}_x\text{:H}$ alloys prepared by coevaporation of silicon and tin along with an atomic hydrogen flow on substrates kept at liquid-nitrogen temperature. These experimental conditions allow us to elaborate amorphous semiconductor alloys in the whole composition range from silicon to pure tin.¹

In this communication, we present a first study of the relative stability of hydrogen in different $\alpha\text{-Si}_{1-x}\text{Sn}_x\text{:H}$ alloys ($x=0, 0.1$, and 0.2). The chemical bonding and the microstructure were characterized respectively by infrared spectrometry and by low-angle x-ray scattering. Then, the stability of hydrogen was studied from two complementary points of view. We followed the diffusion of hydrogen over very short diffusion distances by performing low-angle neutron scattering experiments on multilayers.² Then, exodiffusion experiments allowed us to observe the release of hydrogen from the different samples.

Tin and silicon were evaporated from a thermal cell and from an electron beam gun, respectively, under a flow of atomic hydrogen on substrates maintained at liquid-nitrogen temperature. The deposition rates were controlled and monitored with a quartz microbalance system. Atomic hydrogen was produced by thermal dissociation of molecular hydrogen in a tungsten tube heated to 2400 K. The hydrogen flow was regulated by maintaining the total pressure in the evaporation chamber at 6×10^{-3} Torr.

The first characteristic of these samples is that they contain essentially SiH_2 bonds. Indeed, the infrared transmission spectrum of a hydrogenated silicon sample shows the polysilane features³ (Fig. 1): An intense absorption band at 2100 cm^{-1} (stretching modes), a doublet with relatively sharp features at 890 and 845 cm^{-1} [wagging and scissors modes of $(\text{SiH}_2)_n$ groups] and the band at 630 cm^{-1} (rocking modes). The band at 2000 cm^{-1} corre-

sponding to stretching modes of monohydride (SiH) groups is absent. Moreover, the absorption bands at 1050 and 980 cm^{-1} correspond to SiO_2 and SiO stretching modes arising from a weak oxygen contamination of the films. Peaks in absorption characteristic of Sn-H bonds were not observed in $\alpha\text{-Si}_{1-x}\text{Sn}_x$ alloys. This fact, which is an indication of the strong preference of hydrogen to bond to silicon rather than to tin, is in agreement with the results from other groups obtained on sputtered⁴⁻⁶ and evaporated⁷ samples.

The second feature is the low density of the alloys containing hydrogen, which was observed from x-ray scattering experiments performed on $\text{Si}_{1-x}\text{Sn}_x/\text{Si}_{1-x}\text{Sn}_x\text{:H}$ multilayers prepared by evaporation of the alloys alternately with and without hydrogen. Indeed, such multilayers, with a modulation wavelength in the $100 \text{ \AA}$ range, give rise to "Bragg" peaks in low-angle x-ray scattering, the intensity of which is a function of the contrast between the layers (Fig. 2). Such a diffraction pattern was obtained for each multilayer, the intensity of the peaks being practically constant versus tin concentration. As the x-ray scattering factor from hydrogen is very weak, the diffraction peaks show the difference between the high atomic density of the alloy evaporated under vacuum and the low atomic density of the hydrogenated alloy.

The motion of hydrogen over very short diffusion distances was detected by performing low-angle neutron scattering on $\text{Si}_{1-x}\text{Sn}_x\text{:H}/\text{Si}_{1-x}\text{Sn}_x\text{:D}/\dots$ multilayers, which were prepared by coevaporation of the alloys under an alternated flow of hydrogen and deuterium atoms. The total number of bilayers was 50 and the theoretical bilayer thickness, calculated with the bulk densities of silicon and tin, was $120 \text{ \AA}$. The experiments were performed on the D10 instrument of the Institut Laue Langevin. The neutron wavelength was $2.36 \text{ \AA}$. The monochromator and analyzer crystal were (002) graphite and a pyrolytic graphite filter was used. The instrument was in the triple axis configuration set at zero energy with a graphite analyzer to reduce the background at low angles. The data presented

FIG. 1. Infrared transmission spectrum of a -Si:H evaporated at 77 K.

here were obtained with 10 min collimation on each side of the samples.

As the neutron coherent scattering amplitude of H and D are large and of opposite sign ($b_H = -0.374 \times 10^{-12}$ cm, $b_D = 0.667 \times 10^{-12}$ cm), low-angle scattering patterns of $\text{Si}_{1-x}\text{Sn}_x\text{:H/Si}_{1-x}\text{Sn}_x\text{:D/...}$ multilayers exhibit a peak that originates in the isotopic modulation. The spectrum represented in Fig. 3 exhibits one diffraction peak at the scattering vector $q = 0.038 \text{ \AA}^{-1}$ corresponding to a modulation wavelength of hydrogen and deuterium equal to $160 \text{ \AA}$. As shown in a study of a -Si:H,⁸ the modulation wavelength is larger than the theoretical thickness because of the smaller density of the hydrogenated and deuterated films. From the theoretical and experimental modulation values, the density deficit is estimated to be 25%–30%. Such spectra were obtained for $x = 0, 0.1$, and 0.2 , the intensity of the peak for the last sample being weaker than for the first ones. This weakening could be due to lower concentrations of isotopes or to a larger diffusion between the layers.

In order to study the hydrogen motion in the different alloys, we followed the evolution of the diffracted intensity of each $\text{Si}_{1-x}\text{Sn}_x\text{:H/Si}_{1-x}\text{Sn}_x\text{:D/...}$ sample versus temperature with a heating rate of 20°C/h . The spectra were fitted by Gaussian curves. The integrated intensity of the diffraction peaks is represented in Fig. 4. For pure silicon

FIG. 2. Low-angle x-ray scattering intensity vs glancing angle for $\text{Si}_{30}\text{Sn}_{20}/\text{Si}_{30}\text{Sn}_{20}\text{:H/...}$ multilayers.

FIG. 3. Low-angle neutron scattering intensity vs scattering vector for $\text{Si}_{90}\text{Sn}_{10}\text{:H/Si}_{90}\text{Sn}_{10}\text{:D/...}$ multilayers.

multilayers, the intensity remains nearly constant up to 300°C and then decreases rapidly due to the interdiffusion of hydrogen and deuterium in the different layers. The peak has almost disappeared at 400°C . When tin is introduced in the multilayers, the intensity $I(t)$ decreases as soon as the temperature increases and the curve is shifted towards lower temperatures. Therefore, the motion of hydrogen increases with tin concentration and it can be assumed that the hydrogen displacement is important enough at room temperature to weaken the diffraction peak intensity for $x = 0.2$.

For gas evolution experiments, deuterated films of $\text{Si}_{1-x}\text{Sn}_x$ were deposited on a float glass substrate. Deuterium was used to suppress background effects due to adsorbed water. Then the films were inserted into a quartz tube evacuated by an ionic pump and were heated at a constant rate of 15°C/min to 750°C . The deuterium partial pressure was monitored by means of a quadrupole mass analyzer. At a constant pumping speed, it is directly proportional to the deuterium evolution rate.

FIG. 4. Evolution vs temperature of the integrated intensity $I(t)$ (normalized to the initial intensity I_0) for $\text{Si}_{1-x}\text{Sn}_x\text{:H/Si}_{1-x}\text{Sn}_x\text{:D/...}$ multilayers.

FIG. 5. Deuterium effusion spectra for Si:D and Si₈₀Sn₂₀:D films.

Figure 5 represents the effusion spectrum for the Si₈₀Sn₂₀:D alloy compared to that of deuterated silicon. The experimental spectra show only a low-temperature peak near 400 °C, which is generally attributed to the desorption of molecular hydrogen from SiH₂ bonds in porous materials prepared at a low substrate temperature.⁹ The high temperature peak at 500–600 °C, which corresponds to a diffusion process from Si—H bonds in compact films prepared at a high substrate temperature, was not observed. This is in agreement with the preparation conditions, since the substrate is at liquid-nitrogen temperature, and with the characterization (chemical bonds, porosity) described in the first sections.

When the tin concentration increases, the effusion peak shifts towards lower temperatures, from 420 °C for *a*-Si:D to 380 °C for *a*-Si₈₀Sn₂₀:D, and the width increases. On account of the much greater heating rate, the shift is smaller than that observed in neutron experiments. The areas of the effusion curves are nearly equal, therefore the alloys contain as much deuterium as pure silicon. In fact, Williamson *et al.*⁴ have made relative estimates of the H concentration for similar *a*-SiSn:H alloys using infrared spectroscopy. They showed that the same fraction of Si remains bonded to H as Sn is added. Due to the presence of Sn atoms, the H bonding might be significantly different

and yield to a higher H mobility. The peak displacement from 420 to 380 °C corresponds to the increase of the deuterium motion in the amorphous structure. The width increase certainly corresponds to a dispersion in the deuterium bond energies owing to the fact that deuterium atoms are bonded to silicon atoms that have various local environments with a different number of tin and silicon atoms.

From these results, it can be concluded that Si_{1-x}Sn_x:H (0 < *x* < 0.2) alloys coevaporated on a substrate maintained at liquid-nitrogen temperature under a flow of atomic hydrogen are porous, as shown by low-angle x-ray scattering experiments, and contain essentially SiH₂ or (SiH₂)_n bonds. Effusion experiments show that hydrogen desorb at low temperatures. For a heating rate of 15 K/min, the effusion peak decreases from 420 °C for *a*-Si:H to 380 °C for *a*-Si₈₀Sn₂₀:H. The hydrogen stability therefore decreases with increasing tin concentration. Low-angle neutron scattering experiments performed on Si_{1-x}Sn_x:H/Si_{1-x}Sn_x:D/... multilayers confirm this result and show that hydrogen diffusivity at room temperature is low enough to maintain an isotopic modulation in the Si₈₀Sn₂₀ alloy with a period of 160 Å.

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¹M. Vergnat, G. Marchal, and Ph. Mangin, *J. Non-Cryst. Solids* **137&138**, 907 (1991).

²M. Vergnat, S. Houssaini, C. Dufour, A. Bruson, G. Marchal, Ph. Mangin, R. Erwin, J. J. Rhyne, and C. Vettier, *Europhys. Lett.* **14**, 457 (1991).

³G. Lucovsky, *J. Non-Cryst. Solids* **76**, 173 (1985).

⁴D. L. Williamson, R. C. Kerns, and S. K. Deb, *J. Appl. Phys.* **55**, 2816 (1984).

⁵G. N. Parsons, J. W. Cook, J. G. Lucovsky, S. Y. Lin, and M. J. Mantini, *J. Vac. Sci. Technol. A* **4**, 470 (1986).

⁶A. M. Edwards, M. C. Fairbanks, and R. J. Newport, *Physica B* **167**, 247 (1990).

⁷D. Girginoudi, A. Thanailakis, and A. Christou, in *Interfaces, Superlattices and Thin Films*, edited by J. D. Dow and I. K. Schüller (Materials Research Society, Pittsburgh, 1987), Vol. 77, p. 603.

⁸M. Vergnat, S. Houssaini, C. Dufour, A. Bruson, G. Marchal, Ph. Mangin, R. Erwin, J. J. Rhyne, and C. Vettier, *Phys. Rev. B* **40**, 1418 (1989).

⁹W. Beyer, *J. Non-Cryst. Solids* **97&98**, 1027 (1987).