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

S. Houssaïni, M. Vergnat, A. Bruson, G. Marchal, C. Vettier

To cite this version:
S. Houssaïni, M. Vergnat, A. Bruson, G. Marchal, C. Vettier. Study of the hydrogen stability in evaporated amorphous Si$_{1-x}$Sn$_x$:H ($0 \leq x \leq 0.2$) alloys by neutron scattering and exodiffusion measurements. Journal of Applied Physics, American Institute of Physics, 1993, 73 (1), pp.483-485. 10.1063/1.353827. hal-02113403

HAL Id: hal-02113403
https://hal.archives-ouvertes.fr/hal-02113403
Submitted on 28 Apr 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Study of the hydrogen stability in evaporated amorphous $\text{Si}_{1-x}\text{Sn}_x: \text{H}$ ($0<x<0.2$) alloys by neutron scattering and exodiffusion measurements

S. Houssaïni, M. Vergnat, A. Bruson, and G. Marchal
Laboratoire de Métallurgie Physique et Sciences des Matériaux (U. R. A. au C. N. R. S. n° 155), Université de Nancy I, B. P. 239, 54506 Vandoeuvre-les-Nancy Cedex, France

C. Vettier
Institut Laue Langevin, B. P. 150X, 38042 Grenoble Cedex, France, and European Synchrotron Research Facility, B. P. 220, 38043 Grenoble Cedex, France

(Received 8 June 1992; accepted for publication 23 September 1992)

Exodiffusion and low-angle neutron scattering experiments are used to investigate the influence of tin on the hydrogen stability in evaporated amorphous $\text{Si}_{1-x}\text{Sn}_x$ ($0<x<0.2$) alloys. The neutron diffraction experiments, which are performed on $\text{Si}_{1-x}\text{Sn}_x: \text{H}/\text{Si}_{1-x}\text{Sn}_x: \text{D}$/... 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 $\text{a-Si}_{1-x}\text{Ge}_x: \text{H}$ or $\text{a-Si}_{1-x}\text{Sn}_x: \text{H}$ 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 $\text{a-Si}_{1-x}\text{Sn}_x: \text{H}$ 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.

In this communication, we present a first study of the relative stability of hydrogen in different $\text{a-Si}_{1-x}\text{Sn}_x: \text{H}$ 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.

The second feature is the low density of the alloys containing hydrogen, which was observed from x-ray scattering experiments performed on $\text{Si}_{1-x}\text{Sn}_x: \text{H}/\text{Si}_{1-x}\text{Sn}_x: \text{D}$/... multilayers prepared by evaporation of the alloys alternately with and without hydrogen. Indeed, such multilayers, with a modulation wavelength in the 100 Å 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 $\text{Si}_{1-x}\text{Sn}_x: \text{H}/\text{Si}_{1-x}\text{Sn}_x: \text{D}$/... 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 Å. The experiments were performed on the D10 instrument of the Institute Laue Langevin. The neutron wavelength was 2.36 Å. The nonmonochromator 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...
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 \( b_N = -0.374 \times 10^{-12} \text{ cm} \),
\( b_D = 0.667 \times 10^{-12} \text{ cm} \), low-angle scattering patterns of
\( \text{Si}_{1-x}\text{Sn}_x: \text{H}/\text{Si}_{1-x}\text{Sn}_x: \text{D}/... \) multilayers exhibit a peak that
originates in the isotopic modulation. The spectrum rep-
resented in Fig. 3 exhibits one diffraction peak at the scat-
tering vector \( q = 0.038 \text{ Å}^{-1} \) corresponding to a modulation
wavelength of hydrogen and deuterium equal to 160 Å. As
shown in a study of \( \text{a-Si}: \text{H} \), 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 concentra-
tions 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 \( \text{Si}_{1-x}\text{Sn}_x: \text{H}/\text{Si}_{1-x}\text{Sn}_x: \text{D}/... \) sample versus temper-
ature with a heating rate of 20 °C/h. The spectra were
fitted by Gaussian curves. The integrated intensity of the
diffract peaks is represented in Fig. 4. For pure silicon
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 intro-
duced 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 hy-
drogen increases with tin concentration and it can be as-
sumed 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. Deute-
rium was used to suppress background effects due to ad-
sorbed 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 par-
tial pressure was monitored by means of a quadrupole
mass analyzer. At a constant pumping speed, it is directly
proportional to the deuterium evolution rate.
Figure 5 represents the effusion spectrum for the $\text{Si}_{10}\text{Sn}_{20}:\text{D}$ 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 SiH$_2$ bonds in porous materials prepared at a low substrate temperature. 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-$\text{Si}_{10}\text{Sn}_{20}:\text{D}$, 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.\textsuperscript{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 $\text{Si}_{1-x}\text{Sn}_x:H$ (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 SiH$_2$ or (SiH$_2$)$_x$ bonds. Effusion experiments show that hydrogen desorbs 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-$\text{Si}_{10}\text{Sn}_{20}:\text{D}$. The hydrogen stability therefore decreases with increasing tin concentration. Low-angle neutron scattering experiments performed on $\text{Si}_{1-x}\text{Sn}_x:H/\text{Si}_{1-x}\text{Sn}_x:D/...$ multilayers confirm this result and show that hydrogen diffusivity at room temperature is low enough to maintain an isotopic modulation in the Si$_{10}$Sn$_{20}$ alloy with a period of 160 Å.

The authors are indebted to A. Burneau for his help in infrared spectrometry measurements and to Ph. Mangin for stimulating discussions.