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Hydrogen effusion from evaporated $\text{Si}_{1-x}\text{Sn}_x\text{:H}$ ($0 \leq x \leq 0.2$) amorphous semiconductors

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The release of hydrogen from $\text{Si}_{1-x}\text{Sn}_x\text{:H}$ ($0 \leq x \leq 0.2$) amorphous semiconductors prepared by reactive evaporation on substrates maintained at 77 K is monitored by effusion experiments. The effusion peaks are associated with desorption from voids. The deconvolution of these peaks allows one to deduce the different atomic configurations containing hydrogen and to determine their stability and their Gibbs free energy of desorption. © 1995 American Institute of Physics.

Amorphous semiconductor alloys such as $\alpha\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ and $\alpha\text{-Si}_{1-x}\text{Sn}_x\text{:H}$ constitute an important class of materials which are attractive due to their potential applications in multiband-gap solar cells. The $\alpha\text{-Si}_{1-x}\text{Sn}_x\text{:H}$ alloys are generally prepared by reactive sputtering¹ or glow-discharge decomposition² but, in most cases, these alloys tend to become inhomogeneous as the Sn concentration increases because of the segregation of part of the Sn atoms which form $\beta\text{-Sn}$ precipitates.³ It has also been reported that even small amounts of Sn incorporated into $\alpha\text{-Si:H}$ result in the degradation of the photoconductive response, which has been attributed to an increase of structural defects or of the number of dangling bonds on the Sn atoms.

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 allowed us to elaborate homogeneous amorphous semiconductor alloys in the whole composition range from silicon to pure tin.⁴ The as-deposited films are void-rich and contain many $(\text{SiH}_2)_n$ groups.⁵ This letter reports a study of the stability of hydrogen in these amorphous semiconductors by the effusion method. This technique, previously used by our group in the study of TiH_2 ,⁶ of $\alpha\text{-GdFe:H}$ alloys⁷ and of porous silicon,⁸ allowed us to analyze the kinetics of the hydrogen release using a model of desorption from different atomic configurations and to determine the Gibbs free energy of desorption from these sites.

The elaboration conditions and the effusion technique were described in Ref. 5. The low temperature of the substrate was chosen to avoid $\beta\text{-Sn}$ precipitation, but we verified that effusion curves for pure silicon films evaporated at 77 and 300 K were identical. The results of this study can therefore be compared to those of samples deposited at room temperature.

Since the first effusion studies of $\alpha\text{-Si:H}$,^{9–11} numerous publications have appeared concerning hydrogenated amorphous silicon. They show that the hydrogen content increases with decreasing substrate temperature. While samples prepared at low substrate temperature generally show two effusion peaks, a low-temperature peak at 350–400 °C and a

high-temperature peak at 500–600 °C, only the high-temperature effusion peak remains at a substrate temperature of 200 °C and above. The low-temperature peak is usually associated with hydrogen desorption from voids and the high-temperature peak is associated with the diffusion of atomic hydrogen in the compact material. An easy discrimination whether the evolution rate is diffusion-limited or not is the measurement of the thickness dependence. If diffusion limits the evolution rate, the rising diffusion length with increasing film thickness will result in a shift of the evolution peak to higher temperatures. Such a shift was not observed between films with thicknesses of 200 and 3300 Å. Therefore, the effusion peaks observed in the evaporated films have been associated with hydrogen desorption from voids, which is in agreement with the low deposition temperature and with the low atomic density of these samples.⁵

The effusion spectra of $\alpha\text{-Si}$, $\alpha\text{-Si}_{90}\text{Sn}_{10}$ and $\alpha\text{-Si}_{80}\text{Sn}_{20}$ are represented in Figs. 1–3, respectively. The thickness of the samples was 3300 Å. The heating rate was 15 °C/min. As will be discussed below, each curve can be deconvoluted with several peaks, which must correspond to different sites of hydrogen in the material. In order to deter-

FIG. 1. Thermal effusion spectrum of amorphous silicon. The experimental points are represented by the symbol (+). The dotted lines represent the simulated individual and total effusion curves.

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FIG. 2. Thermal effusion spectrum of the Si₉₀Sn₁₀ amorphous alloy.

mine the rate constant and the energy associated with each site, the kinetics of the release of the dissolved hydrogen is analyzed using the surface desorption formula of the Eyring theory of the absolute rate processes.¹² The effusion rate R_p from each site can be assumed to follow the equation

$$R_p = \frac{d\left(\frac{c}{c_p}\right)}{dt} = \left(\frac{kT}{h}\right) \left(1 - \frac{c}{c_p}\right)^n \exp\left(\frac{\Delta S}{k}\right) \exp\left(-\frac{\Delta H}{kT}\right),$$

with c_p and c the original and evolved hydrogen concentrations, k and h the Boltzmann and Planck constants, respectively, and n the order of the reaction. The Gibbs free energy of desorption ΔG is equal to $\Delta H - T\Delta S$ where ΔH is the enthalpy and ΔS is the entropy of reaction. The total effusion rate R is the summation of the effusion rate of each peak. The Figs. 1–3 show the individual peaks and the total effusion rate. The effusion peak temperature T_p , the concentration c_p , and the free energy ΔG of each peak are listed in Table I.

FIG. 3. Thermal effusion spectrum of the Si₈₀Sn₂₀ amorphous alloy.

TABLE I. Values of the parameters T_p , c_p , and ΔG obtained from the simulation of the effusion spectra.

Alloy	Units	T_p (°C)	c_p (arb. units)	ΔG (eV)
Si	SiH ₂	408	9.5	2.0
	SiH	465	3.4	2.2
Si ₉₀ Sn ₁₀	Sn ₂ –SiH ₂	180	0.15	1.4
	SnSi–SiH ₂	310	1.4	1.8
	SiH ₂	408	6	2.0
	SiH	465	2.2	2.2
Si ₈₀ Sn ₂₀	Sn ₂ –SiH ₂	180	0.37	1.4
	SnSi–SiH ₂	295	1.4	1.7
	SiH ₂	360	3.4	1.9
	SiH	430	1.7	2.1

The effusion spectrum of hydrogen in pure silicon (Fig. 1) shows a low-temperature peak around 400 °C with a full width at half maximum of 80 °C. This spectrum differs strongly from the usual spectra which present two distinct peaks or only the high-temperature peak.^{9–11,13} However, it is very similar to the spectrum obtained by Kozłowski *et al.*¹⁴ for hydrogenated silicon prepared by sputtering on substrates maintained at liquid-nitrogen temperature. The structure of evaporated α -Si:H deposited at 77 and 300 K is therefore comparable to that of sputtered silicon deposited on substrates cooled at very low temperature. It is known that void-rich amorphous silicon alloys can contain trapped H₂,¹⁵ but the concentration of molecular hydrogen is expected to be less than a few percent of the total hydrogen content. Therefore, it is not likely that the principal effusion peak could be attributed to the release of unbound hydrogen. Moreover, it was verified that the gas evolution was correlated to the decrease of the infrared band absorption, and then to bound hydrogen. In fact, the effusion peak presents a slight shoulder on the high-temperature side and the curve has been deconvoluted in two effusion peaks. The first peak has a free energy $\Delta G = 2.0$ eV close to the value obtained for the low-temperature peak by Beyer¹³ (1.95 eV) or to the average values of Oguz *et al.*¹¹ (1.83 eV), and McMillan *et al.*¹⁰ (1.93 eV). This peak, which has an intensity much larger than the second, certainly corresponds to the SiH₂ units which are the dominant configurations, as shown by infrared spectrometry.⁵ The second peak is supposed to correspond to the Si–H configurations in the void-rich material. For these reasons, the first peak was simulated with first-order desorption kinetics, since it can be supposed that the desorbing H₂ molecule is formed by the association of two hydrogen atoms from the same dihydride species, and the second peak was simulated with a second-order kinetics since, when hydrogen desorbs from silicon monohydride species, two hydrogen atoms from two adjacent silicon monohydride species must recombine in order to form H₂.

The effusion curves of the Si₉₀Sn₁₀ and Si₈₀Sn₂₀ alloys are represented in Figs. 2 and 3, respectively. With increasing tin concentration, the effusion curve shifts towards lower temperature and its width increases. Therefore, the average stability of hydrogen decreases and it appears to be a dispersion on the bond energies. This dispersion cannot be due to the existence of Sn–H bonds since their infrared absorption

TABLE II. Values of the experimental and theoretical contributions of the different $\text{Si}_{2-n}\text{Sn}_n\text{-SiH}_2$ sites for the $\text{Si}_{1-x}\text{Sn}_x$ alloys.

		$\text{Si}_2\text{-SiH}_2$	SiSn-SiH_2	$\text{Sn}_2\text{-SiH}_2$
$x=0.1$	th.	0.81	0.18	0.01
	exp.	0.80	0.18	0.02
$x=0.2$	th.	0.64	0.32	0.04
	exp.	0.66	0.27	0.07

bands are not observed in evaporated $\text{Si}_{1-x}\text{Sn}_x\text{:H}$ ($x \leq 0.2$) alloys.^{5,16} It must be assumed that hydrogen atoms are bonded to silicon atoms which have various local environments with a different number of tin and silicon atoms. As there are very few configurations containing only one hydrogen atom in pure silicon, they will be neglected for units containing backbonded tin atoms. Then, the effusion spectra have been deconvoluted by taking account units of type Si-H and units of type $\text{Si}_{2-n}\text{Sn}_n\text{-SiH}_2$ where the silicon central atom, which is bonded to two hydrogen atoms, is backbonded to a number n of tin neighbors. Therefore, in addition to the two peaks present for pure silicon, the curves have been deconvoluted with two supplementary peaks corresponding to the units SiSn-SiH_2 and $\text{Sn}_2\text{-SiH}_2$. For the above-mentioned reasons, the peak corresponding to the Si-H units is simulated with second-order kinetics and the other peaks are simulated with first-order kinetics. The ΔG values of the different units are displayed in Table I. As expected, the average ΔG decreases with the number of tin neighbors. For a given unit, ΔG remains nearly constant versus tin concentration. The small decrease of the T_p values for the $\text{Si}_{80}\text{Sn}_{20}$ alloys could be due to the second-neighbors influence.

This model must also allow one to determine the relative contribution of each $\text{Sn}_n\text{Si}_{2-n}\text{-SiH}_2$ site, which is supposed equal to $C_2^n x^n (1-x)^{2-n}$, the unit probability in a chemically disordered network. The relative contributions are displayed in Table II, with the simulation values. A very good agreement is observed between the theoretical and experimental values, which confirms the validity of this model.

In conclusion, the hydrogen effusion from evaporated $\alpha\text{-Si}_{1-x}\text{Sn}_x\text{:H}$ alloy ($0 \leq x \leq 0.2$) occurs at 400 °C and corresponds to desorption from voids. The deconvolution of the effusion curves shows that hydrogen occupies two sites in pure silicon with $\Delta G = 2.0$ and 2.2 eV, which corresponds to the SiH_2 and SiH configurations, respectively. In the Si-Sn alloys, the effusion curve shifts towards lower temperature and its width increases. By taking account of two other units where the silicon atom is backbonded to tin neighbors, it is possible to simulate the experimental data, the relative contribution of each peak being equal to the unit probability in a chemically disordered network. In these new configurations, the bonding between Si and H is weaker and it can break below 200 °C. Therefore, for samples prepared at the usual temperature of 200 °C, it can be expected that dangling bonds appear on the tin atoms and also on the silicon atoms backbonded to tin atoms.

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