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► To cite this version:

M. Vergnat, G. Marchal, Ph. Mangin. Preparation and structure of amorphous semiconductor hydrogenated tin. Applied Physics Letters, 1990, 57 (22), pp.2300-2301. 10.1063/1.103893 . hal-02113399

HAL Id: hal-02113399

<https://hal.science/hal-02113399>

Submitted on 28 Apr 2019

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Preparation and structure of amorphous semiconductor hydrogenated tin

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(Received 13 July 1990; accepted for publication 17 September 1990)

Evaporation on substrates maintained at 77 K under an atomic hydrogen flow allows us to prepare amorphous semiconductor tin. The resistivity is very high, $3 \times 10^3 \Omega \text{ cm}$ and the diffraction pattern is typical of the random continuous networks of amorphous germanium and silicon. This structure is stable up to 180 K.

Crystalline tin exhibits two allotropic phases with a transition temperature at 13.2 °C. The low-temperature α phase (grey tin) is a zero-gap semiconductor with the four-fold coordinated diamond structure. The interatomic distance is 2.81 Å. The high-temperature β phase (white tin) is metallic with a tetragonal structure, in which each atom is surrounded by four atoms at 3.02 Å and two atoms at 3.17 Å. This raises the question of the feasibility of preparing and of the stability of amorphous semiconductor α -Sn since previous attempts to obtain such a structure were not successful. Vapor deposition of tin on low-temperature substrates always leads to amorphous or microcrystalline metallic tin.¹

In this letter we show that semiconductor amorphous tin with fourfold coordination can be obtained if tin is deposited at low temperature under a flow of atomic hydrogen. To the best of our knowledge, it is the first time such a phase has been synthesized.

Tin was evaporated from a thermal cell on substrates kept at liquid-nitrogen temperature. The substrates were grids covered with carbon for electron diffraction and glass plates for electrical measurements. The tin deposition rate (2 Å/s) was controlled and monitored with a quartz crystal microbalance system. Hydrogen was introduced through a 1 mm tungsten tube pointing at the substrate. Atomic hydrogen was produced by thermal dissociation in a tungsten tube heated to 2500 K.² The hydrogen flow was regulated by maintaining the total pressure in the evaporation chamber at 10^{-5} Torr.

Transmission electron diffraction was performed *in situ* at low temperature and during the warming of the samples. The electron diffraction patterns were recorded using a scanning high-energy electron diffraction system (SHEED) operating at 45 kV. Electrical measurements were carried out simultaneously.

Three types of samples were fabricated:

- (a) nonhydrogenated samples: Sn;
- (b) samples hydrogenated with molecular hydrogen: Sn:H₂;
- (c) samples hydrogenated with atomic hydrogen: Sn:H.

As-quenched Sn and Sn:H₂ exhibit very similar resistivity behavior with a large relaxation process between 100 and 200 K (Fig. 1). After annealing at room temperature, the resistivity $\rho_{300 \text{ K}}$ is 14.4 $\mu\Omega \text{ cm}$ with a positive temperature coefficient $\alpha = 3 \times 10^{-3} \text{ K}^{-1}$. These values are close to that of crystalline β -tin ($\rho_{273 \text{ K}} = 11 \mu\Omega \text{ cm}$ and

$\alpha = 4.7 \times 10^{-3} \text{ K}^{-1}$).³ The as-quenched Sn:H films exhibit a completely different behavior with a low-temperature resistivity of $3 \times 10^3 \Omega \text{ cm}$ and a very sudden transition at 180 K (Fig. 2). At this temperature, the resistivity decreases by eight orders of magnitude in a few seconds. After this transition, the behavior of the resistivity is very similar to that observed in Sn and Sn:H₂ samples. The temperature dependence of the resistivity was studied between 77 and 180 K. Even for samples annealed just below the transition temperature, no thermally activated conductivity following an Arrhenius law has been observed but, as it is the case for pure amorphous silicon and germanium, the temperature dependence of the resistivity was better described by the variable range hopping formula (Mott's law)⁴:

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}],$$

with a value of T_0 equal to 10^7 .

Figure 3 shows the electron diffraction patterns collected at 77 K from (b) as-quenched Sn or Sn:H₂ samples, from (a) as-quenched Sn:H samples, and (c) from samples (Sn, Sn:H₂, or Sn:H) annealed at room temperature. The (c) diffraction pattern is clearly that of β -tin. The peaks are easily indexed. They are better resolved with some textural changes if an annealing is performed at higher temperature. At first glance, the (b) diffraction pattern could be considered as that of an amorphous material. The large

FIG. 1. Variation of the dc resistivity (linear scale) vs temperature for tin prepared without hydrogen or with molecular hydrogen.

FIG. 2. Variation of the dc resistivity (logarithmic scale) vs temperature for tin evaporated under an atomic hydrogen flow.

width of the peaks is a point in favor of an amorphous structure. However, the peak positions correspond neither to those of metallic glasses nor to those of amorphous semiconductors; if it is an amorphous structure, it is completely new with presumably a short-range order similar to that found in crystalline β -tin. On the other hand, the correspondence between the position of the first peak of (b) and the (200) and (101) peaks of β -tin and the lack of a sharp electrical transition characteristic of a crystallization process (Fig. 1) is in favor of a microcrystalline structure. The shift of the second peak of (b) compared to the (220) and (211) of (c) makes the conclusion uncertain.

Unlike (b), the (a) diffraction pattern is unambiguously that of a tetrahedrally bonded semiconductor with two intense peaks and a shoulder on the high scattering vector side of the third peak. The positions of the first two maxima $K_1(\text{Sn:H}) = 1.69 \text{ \AA}^{-1}$ and $K_2(\text{Sn:H}) = 3.00 \text{ \AA}^{-1}$ are in the ratio 1.78, which is precisely that found in amorphous silicon⁵ where the positions of the peaks are at $K_1(a\text{-Si}) = 2.00 \text{ \AA}^{-1}$ and $K_2(a\text{-Si}) = 3.60 \text{ \AA}^{-1}$. By considering the Si-Si interatomic distance $d_{\text{Si-Si}} = 2.35 \text{ \AA}$ given by the radial distribution function of amorphous silicon and by using simple relations of proportionality, $d_{\text{Si-Si}} K_{1,2}(\text{Si}) = d_{\text{Sn-Sn}} K_{1,2}(\text{Sn})$, we can estimate the interatomic distance in amorphous Sn:H as $2.80 \text{ \AA}$, which is very close to the interatomic distance found in crystalline

FIG. 3. Electron diffraction patterns of (a) hydrogenated tin at 77 K, (b) unhydrogenated tin at 77 K, and (c) crystallized tin.

α -Sn. Moreover, the resistivity transition observed at 180 K is very sharp (it happens in a few degrees), which is characteristic of crystallization of an amorphous structure.

In conclusion, tin deposited at 77 K with a flow of atomic hydrogen is an amorphous semiconductor, similar to amorphous silicon and amorphous germanium, stable up to 180 K. It remains to be explained why hydrogen stabilizes the tetrahedral symmetry of tin and to try to raise the stability of amorphous semiconductor tin. Multilayers of the type Si:H/Sn:H/Si:H/Sn:H could be a way.

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