Solid State Communications, Vol 62, No 4, pp 309–311, 1987.
Printed in Great Britain.

0038–1098/87 $3.00 + .00

FORMATION OF α-Sn BY CHEMICAL SPUTTERING OF β-Sn TARGET IN HYDROGEN PLASMA

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(*Received* 16 *September* 1986 *by* *H Kamimura*)

Microcrystals of α-Sn having averaged diameters of 10–20 nm grew when a target of β-Sn was chemically sputtered in atmosphere (0.2–1.0 torr) of hydrogen at substrate holder temperatures of 15–60°C, higher than the transition temperature (13°C) between α-Sn and β-Sn, although usual sputtering in Ar gas deposited only β-Sn phase.

THE GROWTH OF MICROCRYSTALS of Si and Ge is known in the chemical sputtering in hydrogen gas [1–3]. On the other hand, the usual sputtering in Ar or in H_2 diluted with Ar deposits amorphous films such as hydrogenated amorphous Si. Also graphite has been converted into diamond-like carbon by the sputtering in hydrogen [4, 5]. Generally, the chemical sputtering of group IV elements in pure hydrogen atmosphere shows a strong tendency to deposit microcrystalline films of sp^3 configuration. In expectation of getting α-Sn phase, we have carried out the chemical sputtering of metallic tin in hydrogen, and have studied the structure of the deposited films by means of X-ray diffraction and Mössbauer effect measurements.

The transition of β-Sn into α-Sn occurs below 13.2 ± 0.1°C [6]. Actually, the rate of this transition, however, is slow; it has been reported to take 300 h at −50°C in a study by means of Mössbauer effect measurements [7]. The presence of impurities (or catalysts) is believed to affect the rate. α-Sn is a tetrahedrally coordinated substance like Si and Ge, but it bears a character of direct optical transition with zero band gap. With a finite band gap by bonding of H on the microcrystal surface as observed for microcrystalline Si, or simply by doping of Ge, this material might have possibility for a high sensitive infrared sensor.

The samples were deposited in a conventional rf sputtering apparatus (ANELVA SPF-210H) set with a disc target of β-Sn (99.99%), on substrates of crystalline Si, slide glass or sapphire, which were water-cooled to a temperature of about 15°C or slightly heated to 40°C. The hydrogen (H_2) pressure (0.2–1.0 torr) and rf power (20–100 W) were altered. A deposition rate onto the crystalline Si substrate was 0.12 nm s^{-1} (±10%) when rf power was 100 W and H_2 pressure was 0.4 torr. A reference sample was also prepared by sputtering in pure Ar of 5×10^{-3} torr at 15°C. The crystalline structure of the films 0.2 to 2.5 μm thick which were deposited on slide glass was identified by X-ray diffraction (CuK_α, JEOL JDX-100PA diffractometer). The samples were stored at about 5°C in a refrigerator, X-ray diffraction was measured at a room temperature (about 20°C). Mossbauer effect was measured at about −180°C by transmission of 23.8 keV γ-ray from $Ca^{119m}SnO_3$ source (10 mCi) through the sample deposited on a sapphire plate. The electron microscopy was carried out at The University of Tokyo with an ultra high voltage microscope (JEOL 1250) operated at 1 MeV. A sample of 190 nm thick was prepared on a copper grid to which it was transferred from KBr substrate. Then, the copper grid was set on a cold stage cooled down by liquid nitrogen to −196°C. Reflectance measurements were carried out with Shimadzu UV-365 spectrometer.

Figure 1(a) shows the X-ray diffraction pattern for a typical example of the films deposited by the chemical sputtering of the tin target with hydrogen. Relatively broad diffraction lines from α-Sn (1 1 1), (2 2 0), (3 1 1) and (4 0 0) are clearly seen over 2θ angles below 60°. Sharp lines from β-Sn also appear with their line widths as narrow as the instrumental width of the diffractometer. The average grain size of α-Sn crystal is estimated from the (1 1 1) diffraction width and Scherrer's equation to be about 13 nm. The peak positions of 2θ angle for the α-Sn (1 1 1) diffraction for ten samples with various thicknesses prepared under the different rf powers and H_2 pressures give an av-

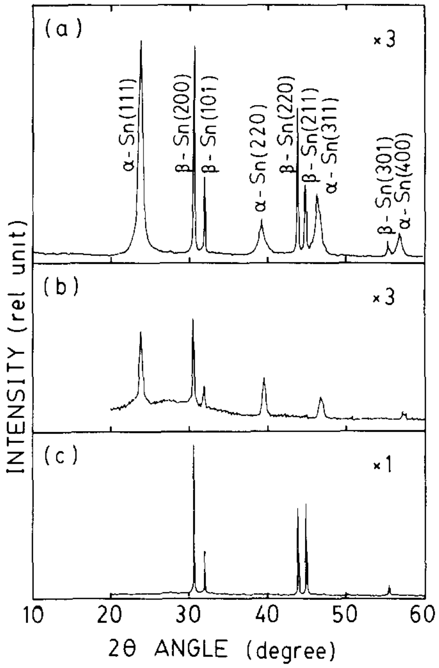

Fig. 1. X-ray diffraction patterns of films deposited on slide glass substrates by chemical sputtering of β-Sn target in H_2 and by usual sputtering in Ar (a) power. 20 W, H_2 pressure 0.2 torr, substrate temperature T_s 15 C, film thickness. 2.45 μm (b) power: 50 W, H_2 pressure 0.6 torr, T_s. 40 C, film thickness. 0.11 μm (c) power 20 W, Ar pressure. 5 × 10^{-3} torr, T_s: 15 C, film thickness: 0.85 μm

eraged plane distance of 3.74 ± 0.02 Å. The reported value is 3.75 Å in ASTM card 5-0390 Microcrystals of α-Sn can be deposited even on the substrate slightly heated at 40°C as shown in Fig 1(b). This substrate temperature is higher than the transition temperature from α-Sn to β-Sn (13.2 ± 0.1°C) Even at the substrate temperature of 60°C, microcrystals of α-Sn can be observed, but at 80 C only β-Sn is formed, under the optimum condition of power 50 W and H_2 pressure 0.6 torr. On the other hand, the usual sputtering in Ar gas produces the film consisting only of β-Sn crystal at the substrate temperature of 15°C, as shown in Fig 1(c)

Figure 2 shows a Mössbauer spectrum for the same film as in Fig. 1(a). The spectrum consists of the following three Lorentzian components: α-Sn component (isomer shift $\delta = 2.04 \pm 0.05\,\mathrm{mm\,s^{-1}}$, half width $\Gamma = 0.88\,\mathrm{mm\,s^{-1}}$) and β-Sn component ($\delta = 2.62 \pm 0.05\,\mathrm{mm\,s^{-1}}$, $\Gamma = 1.04\,\mathrm{mm\,s^{-1}}$) with a trace contamination of tin oxide component ($\delta = 0.01 \pm 0.05\,\mathrm{mm\,s^{-1}}$, $\Gamma = 1.08\,\mathrm{mm\,s^{-1}}$). The Γ values in the latter two might be influenced by quadrupole splitting The difference between the fitted curve and the data points is also shown in the lower part of Fig 2. These values of chemical shift are reasonable compared with

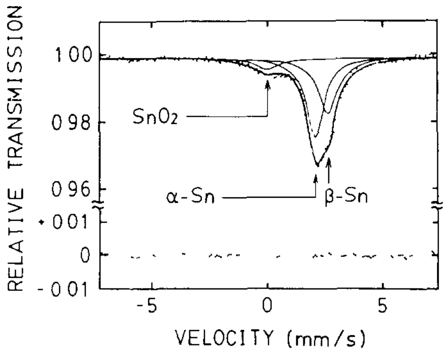

Fig 2. Mossbauer absorption spectrum of a film deposited at the same time as in Fig. 1(a) on a sapphire substrate The spectrum can be decomposed into three Lorentzian components α-Sn component ($\delta = 2.04 \pm 0.05\,\mathrm{mm\,s^{-1}}$, $\Gamma = 0.88\,\mathrm{mm\,s^{-1}}$) and β-Sn component ($\delta = 2.62 \pm 0.05\,\mathrm{mm\,s^{-1}}$, $\Gamma = 1.04\,\mathrm{mm\,s^{-1}}$) with trace contamination of tin oxide component ($\delta = 0.01 \pm 0.05\,\mathrm{mm\,s^{-1}}$, $\Gamma = 1.08\,\mathrm{mm\,s^{-1}}$). The measurement is carried out at about −180 C relative to $CaSnO_3$. The lower row of points shows the difference between a fit curve and observed data points

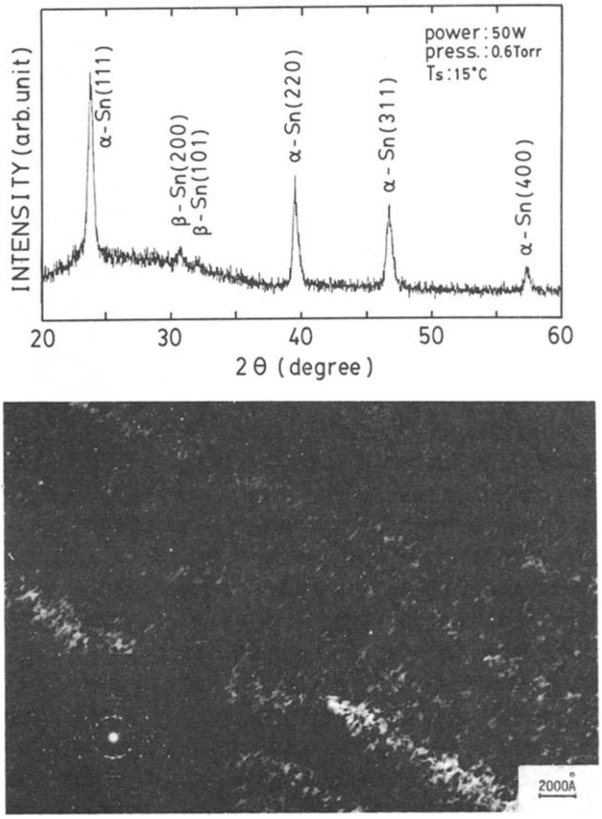

Fig. 3. X-ray diffraction pattern (a), and bright field image with the transmission electron diffraction pattern (b) for a film 190 nm thick that contains mainly α-Sn. To avoid heating by electron beam irradiation, the sample in the electron microscope is cooled down to −196°C.

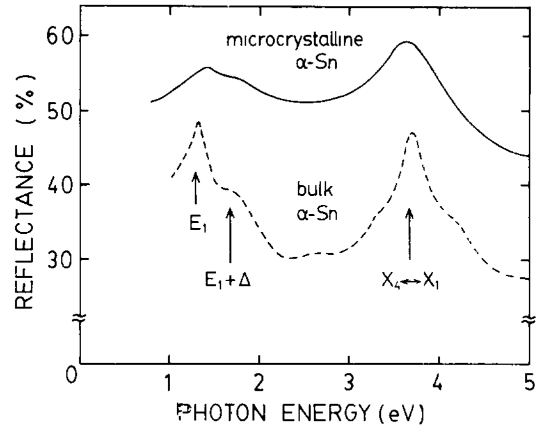

Fig. 4. Reflectance spectra of bulk α-Sn (after Cardona *et al.* [10]) and of microcrystalline α-Sn films with thickness ~0.3 μm.

those reported for both α and β form of tin [8]. In consideration of the recoilless fraction for both the forms of tin [7, 9], the volume fraction of α-Sn to α-Sn + β-Sn is estimated to be 0.44.

Figure 3 shows the X-ray diffraction pattern (a) and an electron microscope photo with the diffraction pattern (b) for an example that consists mainly of α-Sn with trace of β-Sn. The X-ray diffraction width gives an averaged diameter of about 18 nm; the electron microscope photo shows the grain size of a few tens of nm.

The reflectance of the film at 20°C with thickness ~0.3 μm consisting mainly of α-Sn (cf Fig. 3(a)) is shown in Fig. 4, where the reflectance of bulk α-Sn is also represented by a dashed curve [10]. Assignments of main structures in the reflectance spectrum of bulk α-Sn to the interband transition are indicated [11]. For microcrystalline (μc-)α-Sn films, the structure due to the transition ($X_1 \leftrightarrow X_4$) is broadened, but remains. However, the structure due to the transitions (E_1 and $E_1 + \Delta_1$) is observed very weakly. The result seems to be related to the fact that the lack of perfect long-range order in μc-α-Sn films influences strongly the transition (E_1 and $E_1 + \Delta_1$), but weakly the transition ($X_1 \leftrightarrow X_4$). The difference in the background of the reflectance between bulk α-Sn and μc-α-Sn may be due to the existence of β-Sn and amorphous Sn within ~10% volume fraction in μc-α-Sn films, which is concluded from Fig. 3.

In the chemical sputtering of β-Sn in pure H_2, hydrogen atoms (or ions) react with the target surface to generate tin hydride molecules (SnH_x), which evolve from the surface and are carried onto the substrate. Sn—H bonds break on the substrate surface and Sn atoms are deposited. It is necessary that the $5s5p^3$ bonding orbital becomes predominant in order to overcome metallic configuration in β-Sn and to generate α-Sn configuration. This process might be realized through the intermediate SnH_x molecules participating in the formation of the deposit. The process seems to be common to the formation of the sp^3 carbon from the graphite target with sp^2 configuration by the chemical sputtering in hydrogen [4]

Acknowledgements — We thank Prof. S. Ichiba in Faculty of Science, Hiroshima University for helpful discussion and measurements of Mössbauer effect.

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