α -Sn and β -Sn precipitates in annealed epitaxial $\text{Si}_{0.95}\text{Sn}_{0.05}$

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The structural properties of Sn precipitates in crystalline $\text{Si}_{0.95}\text{Sn}_{0.05}$ have been characterized by transmission electron microscopy and synchrotron x-ray diffraction. The Sn precipitates were produced by thermal annealing of epitaxial, single-crystalline $\text{Si}_{1-x}\text{Sn}_x$ layers grown by low-temperature molecular-beam epitaxy on Si (001) and relaxed $\text{Si}_{1-x}\text{Ge}_x$ substrates. Two different phases of solid Sn were identified in the annealed layers: the semiconductor phase, α -Sn, and the metallic phase β -Sn. The precipitates were found to consist of either only β -Sn or to contain crystallites of both solid Sn phases. The orientations, the sizes and the relative number densities of the α -Sn and β -Sn crystallites were investigated. *In situ* heating and cooling experiments were performed in the transmission electron microscope to study the melting and solidification characteristics of the α -Sn and β -Sn crystallites. The presence of α -Sn at temperatures far above the bulk $\alpha \leftrightarrow \beta$ transition temperature is explained by interface and pressure effects; the latter is likely to be due to the difference in thermal expansion of the precipitates and the matrix. [S0163-1829(99)00831-0]

I. INTRODUCTION

The production of metastable metal and semiconductor systems by, e.g., ion implantation or molecular-beam epitaxy (MBE) makes it relevant and feasible to study phase-separation effects (precipitation and segregation) in these materials. Investigations of precipitates in metal systems have been performed to reveal, e.g., the influence of the surface-volume ratio on melting characteristics.¹ In semiconductors, precipitates are mostly undesirable,² however, there are examples where device structures benefit from the presence of precipitates, e.g., as fast recombination centres [low-temperature GaAs (Ref. 3)] and as gettering centers for metallic impurities [oxide precipitates in Czochralski Si (Ref. 4)].

The group of IV-IV alloy layers (e.g., Si-Ge and Si-C) was recently extended by the production of single-crystalline layers of $\text{Si}_{1-x}\text{Sn}_x$ by MBE.⁵⁻⁸ An investigation of the thermal stability of strained $\text{Si}_{1-x}\text{Sn}_x$ layers grown on Si (001) substrates have shown that these layers relax by formation of interfacial misfit dislocations, dislocation loops, and precipitates.⁹ The threshold temperature, T_{ann} , for formation of misfit dislocations and that for precipitation were found to be identical; $T_{\text{ann}} = 500^\circ\text{C}$ for $\text{Si}_{0.95}\text{Sn}_{0.05}$ (alloy thickness: 1700 Å) and $T_{\text{ann}} = 700^\circ\text{C}$ for $\text{Si}_{0.975}\text{Sn}_{0.025}$ (thickness: 1700 Å).⁹ In the present study the precipitates generated in $\text{Si}_{0.95}\text{Sn}_{0.05}$ layers annealed at very high temperatures ($T \geq 900^\circ\text{C}$) are investigated. The large size of the precipitates (diameter: 100–300 Å) formed at these high annealing temperatures allows the observation of precipitate-related diffraction spots by transmission electron microscopy (TEM) and x-ray diffraction. The size distribution function of the

precipitates in strained $\text{Si}_{0.95}\text{Sn}_{0.05}$ annealed at 950°C are given in Ref. 9.

The precipitates were found to consist of two different phases, a semiconductor phase (α -Sn) and a metallic phase (β -Sn); α -Sn has the diamond structure whereas β -Sn has a bodycentered tetragonal unit cell with a basis; this unit cell can be described as a simple tetragonal unit cell with a basis consisting of four atoms: (0, 0, 0), (1/2, 0, 1/4), (0, 1/2, 3/4), and (1/2, 1/2, 1/2).¹⁰ The bulk $\alpha \leftrightarrow \beta$ phase transition temperature, $T_{\alpha-\beta}^0$, is 13.2°C ,¹¹ however, we find that α -Sn crystallites in the $\text{Si}_{0.95}\text{Sn}_{0.05}$ matrix persist up to about 200°C . The melting temperature for bulk β -Sn is 232°C and for β -Sn precipitates it is lower.¹²⁻¹⁴ The Sn precipitates are therefore melted during furnace annealing and the formation of the solid Sn phases takes place during the cooling sequence after annealing. *In situ* annealing studies in the transmission electron microscope confirm that the precipitates are melted above $\sim 210^\circ\text{C}$.

The formation of α -Sn seems at first glance quite reasonable as this phase has the same crystal structure as the $\text{Si}_{1-x}\text{Sn}_x$ matrix. However, it has previously been demonstrated that thin substrate-stabilized α -Sn layers can only be grown in a very narrow temperature and thickness range on substrates that have a lattice constant close to that of α -Sn as misfit dislocations and other defects tend to trigger the transformation into β -Sn (see, e.g., Refs. 15 and 16). Hence, taking the low transition temperature, $T_{\alpha-\beta}^0$, and the 19.5% lattice mismatch between α -Sn and Si into account, it is less obvious that there are any α -Sn crystallites in the annealed layers at all. α -Sn has neither been found in sputtered, amorphous $\text{Si}_{1-x}\text{Sn}_x$ (Ref. 17) nor in Sn-implanted crystalline Si (Refs. 18–20) even though β -Sn precipitates were

identified in both cases. In contrast, we find that the α -Sn crystallites are the first to be formed during cooling from the liquid state and that the α phase is stable below the solidification temperature. Thus, α -Sn crystallites are always present in the $\text{Si}_{0.95}\text{Sn}_{0.05}$ layers.

The aim of the present paper is to study the structure and the orientation of the crystalline Sn precipitates embedded in a $\text{Si}_{0.95}\text{Sn}_{0.05}$ matrix. The investigation focuses on the presence of the two coexisting phases of solid Sn.

II. EXPERIMENTAL PROCEDURE

$\text{Si}_{0.95}\text{Sn}_{0.05}$ thin films were grown in a VG 80 Silicon MBE system; details about the growth procedure can be found in Ref. 5. Two types of $\text{Si}_{0.95}\text{Sn}_{0.05}$ layers were investigated: strained $\text{Si}_{0.95}\text{Sn}_{0.05}$ (thickness: 1700 Å) grown on a Si (001) substrate and strain-reduced $\text{Si}_{0.95}\text{Sn}_{0.05}$ (thickness: 1700 Å) grown on relaxed $\text{Si}_{0.80}\text{Ge}_{0.20}$ produced by compositional grading.²¹ The alloy compositions and thicknesses were determined by Rutherford backscattering spectrometry (RBS) using 2-MeV He^+ particles. The $\text{Si}_{0.95}\text{Sn}_{0.05}$ layer grown on relaxed $\text{Si}_{0.80}\text{Ge}_{0.20}$ is not completely strain free as it would necessitate a relaxed $\text{Si}_{1-x}\text{Sn}_x$ layer with $x=0.25$. However, the strain is considerably reduced compared to the layer grown on a Si substrate; the strain corresponds to an alloy layer containing about 1% Sn. An alloy composition of about 5% is close to the maximum Sn concentration where relatively thick (>1000 Å), single-crystalline $\text{Si}_{1-x}\text{Sn}_x$ layers can be produced using the present growth temperature (~ 300 °C) and rate (~ 0.3 Å/s).²²

The strained $\text{Si}_{0.95}\text{Sn}_{0.05}$ and the strain-reduced $\text{Si}_{0.95}\text{Sn}_{0.05}$ layers were annealed at 950 °C and 900 °C respectively, in a furnace in which a continuous flow of dry N_2 was maintained. The annealing time was always one hour. In the following the investigated layers are denoted “strained $\text{Si}_{0.95}\text{Sn}_{0.05}$ ” and “strain-reduced $\text{Si}_{0.95}\text{Sn}_{0.05}$ ” despite the change of the strain state caused by the annealing step.

The precipitates in the annealed layers were investigated by conventional transmission electron microscopy (TEM) using a Philips CM20 and by high-resolution (HR) TEM using a Philips CM200-UT-FEG, both microscopes were operated at 200 keV. Cross-section and plan-view analysis where done on samples prepared by standard preparation techniques. Controlled heating and cooling of two different specimens made of the annealed, strained $\text{Si}_{0.95}\text{Sn}_{0.05}$ sample were done *in situ* in the conventional transmission electron microscope to study the melting and solidification of the precipitates. These specimens were mounted in a heating stage and a good thermal contact was ensured between the specimen and the heating stage by either silver paste or a mixture of ceramic glue and copper powder. Identical results were obtained from the two samples with either type of thermal contact.

Synchrotron x-ray diffraction measurements were performed using the vertical scattering diffractometer at the BW2 wiggler beamline in HASYLAB (DESY, Hamburg).²³ The photon energy was 9.0 keV corresponding to a wavelength of 1.37761 Å. The x-ray diffraction measurements were performed in a grazing incidence geometry, where the momentum transfer is in the surface plane.²⁴ The angle of incidence was set to 0.2°. $\theta/2\theta$ scans as well as ω scans were

FIG. 1. TEM cross-section micrographs of strained (taken along the $\langle 110 \rangle$ direction) of $\text{Si}_{0.95}\text{Sn}_{0.05}$: (a) (111) two-beam, and (b) away from any Bragg conditions. The Moiré patterns seen in (a) originates from β -Sn (200) planes of the precipitates and (111) planes of the $\text{Si}_{0.95}\text{Sn}_{0.05}$ matrix.

performed; the former type of scan probes different planar spacings in a given direction whereas the latter type of scan is used to measure the variation in tilt of a given set of lattice planes.

III. RESULTS AND DISCUSSION

A. The shape of the precipitates

Precipitates in the annealed, strained $\text{Si}_{0.95}\text{Sn}_{0.05}$ layer are seen in the cross-section TEM micrographs in Fig. 1. Moiré-fringes are found in a fraction of the precipitates [Fig. 1(a)] when a (111) two-beam condition is fulfilled indicating that the precipitates are crystalline and that they have lattice planes that either are parallel to matrix planes or can become parallel to matrix planes when rotated about the $\langle 110 \rangle$ axis of the matrix (the direction almost orthogonal to the plane of the paper). In Fig. 1(b), which is obtained away from any Bragg conditions, the projections of the precipitates are seen more clearly. In plan view TEM micrographs the projection of the precipitates is squarelike.⁹ Most of the precipitates are formed like truncated octahedrons bounded by mainly $\{111\}$ planes as well as smaller $\{100\}$ planes of the matrix. The precipitates in the strain-reduced $\text{Si}_{0.95}\text{Sn}_{0.05}$ layer (not shown) are found to have similar shapes and sizes as those in the strained layer.

In general, the shape of a precipitate is determined by strain and interface energies.²⁵ The interface energy of a precipitate is related to the atomic bonding at the interface whereas the strain energy is caused by a difference in the (bulk) lattice constants of the precipitate material and the matrix. The Sn precipitates have an atomic density which is significantly smaller than that of the $\text{Si}_{0.95}\text{Sn}_{0.05}$ matrix (the density of α , β , and molten Sn is ~ 40 , 25, and 30% smaller than of $\text{Si}_{0.95}\text{Sn}_{0.05}$, respectively), however, as the diffusion of Sn is vacancy assisted,²⁶ the strain in the precipitates is

probably reduced by the vacancies accompanying the diffusing Sn atoms. Dislocation loops identified⁹ near the precipitates do also reduce the strain between the precipitates and the matrix. The shape of the Sn precipitates is therefore ruled by the interface energy between the $\text{Si}_{1-x}\text{Sn}_x$ matrix and the Sn precipitate and since the interface energy favors a high surface-volume ratio they are almost spherical: The anisotropy of the surface energies of the crystalline matrix makes an octahedral shape favourable. The Sn precipitates are found to be truncated octahedrons which are bounded by $\{111\}$ and $\{100\}$ planes of the matrix; these planes are known to be the low-energy planes of Si.²⁷ The shape of the Sn precipitates is determined by the surface energies of Si because the Sn precipitates are molten during furnace annealing (see below).

B. The crystalline phases, sizes, and orientations of the precipitates

TEM and x-ray diffraction studies reveal the presence of both α -Sn and β -Sn crystallites in the annealed, strained, and strain-reduced $\text{Si}_{0.95}\text{Sn}_{0.05}$ layers; the presence of both phases of solid Sn in annealed $\text{Si}_{1-x}\text{Sn}_x$ was confirmed recently by Mössbauer measurements.²⁸ In the TEM diffraction patterns corresponding to the $\langle 001 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions both phases can be identified (Fig. 2); Table I lists the TEM results concerning the orientation of the crystallites relative to the matrix. α -Sn and β -Sn peaks are also found in the x-ray diffraction spectra with the scattering vector along the $\langle 100 \rangle$ and $\langle 110 \rangle$ in-plane directions as indicated in Fig. 3. All the strong peaks found in these x-ray spectra are equivalent to spots in the TEM micrographs. The lattice constants determined from the x-ray spectra (Table II) are close to, but all larger than, tabulated values for α - and β -Sn (Ref. 29) (the errors on these measurements are expected to be less than 0.001 Å); thus, there is tensile strain in the precipitates. The average size d of the precipitates can be estimated using the formula $d = 2\pi/w$, where w is the full width half maximum of the gaussian profile fitted to the peaks in the $\theta/2\theta$ scans of Fig. 3. The widths of the peaks in the ω scans were found to be approximately three times larger than in the $\theta/2\theta$ scans probably due to a variation in the orientation of the crystallites. This mosaic structure indicates a slight variation in the tilt of the precipitate planes which are (almost) orthogonal to the surface plane of the $\text{Si}_{0.95}\text{Sn}_{0.05}$ layers. For both types of x-ray scans the widths of the α -Sn and β -Sn peaks were similar. The sizes of the precipitates in the strained $\text{Si}_{1-x}\text{Sn}_x$ layer estimated on the basis of the x-ray $\theta/2\theta$ spectra (given in Table II) are in good agreement with results from TEM investigations.⁹ As seen from Table II neither of the two types of crystallites (α - or β -Sn) are generally larger in one of the $\text{Si}_{0.95}\text{Sn}_{0.05}$ layers compared to the other. Thus, the difference in strain in the two $\text{Si}_{0.95}\text{Sn}_{0.05}$ layers (before annealing) does not significantly influence the sizes and the phases of the crystallites. This is likely to be due to the formation of interfacial misfit dislocations, which relieve most of the strain at an early stage during annealing whereas the formation and the coarsing of the precipitates takes place during the entire annealing time.

Analysis of the TEM results as well as x-ray diffraction measurements along different scattering vectors (both in

FIG. 2. TEM diffraction patterns taken along the (a) $\langle 111 \rangle$, (b) $\langle 110 \rangle$, and (c) $\langle 001 \rangle$ directions of the $\text{Si}_{0.95}\text{Sn}_{0.05}$ matrix. To the right the diffraction patterns are sketched and the strong spots associated with the precipitates are numbered. The numbers corresponds to the following planes in solid Sn: (1) α -Sn (111), (2) β -Sn (200), (3) β -Sn (101), and (4) α -Sn (220). Note that the double diffraction is substantial in the diffraction micrographs; as an example some of the double diffraction spots are primed in (a).

plane and out of plane) reveal that (1) the spots denoted “1”, “2”, “3”, and “4” in the TEM diffraction micrographs (Fig. 2) do not originate from the same crystallite, and (2) most of the precipitates do not have a low-index axis parallel to the $\langle 001 \rangle$ direction of the $\text{Si}_{1-x}\text{Sn}_x$ matrix; the crystallites are rotated about the normals to the characteristic planes “1”, “2”, “3”, or “4”. Thus, the spots seen in Fig. 2 correspond only to two-fold symmetries. However, we did not observe additional spots (or rings) in the micrographs taken along the $\langle 110 \rangle$ and $\langle 111 \rangle$ axes indicating a “random” rotation of the crystallites. HRTEM investigations reveal that the precipitates are rotated differently about the surface

TABLE I. The orientation of the α -Sn and β -Sn crystallites relative to the $\text{Si}_{1-x}\text{Sn}_x$ matrix as determined from the TEM diffraction micrographs and the x-ray spectra.

Sn phase	Parallel planes
α -Sn (“4”)	α -Sn(220) $\parallel$ $\text{Si}_{1-x}\text{Sn}_x$ (400)
α -Sn (“1”)	α -Sn(111) $\parallel$ $\text{Si}_{1-x}\text{Sn}_x$ (220)
β -Sn (“2” + “7”)	β -Sn(200) $\parallel$ $\text{Si}_{1-x}\text{Sn}_x$ (220)
β -Sn (“3”)	β -Sn(101) $\parallel$ $\text{Si}_{1-x}\text{Sn}_x$ (220)

FIG. 3. X-ray diffraction spectra of annealed, strained $\text{Si}_{0.95}\text{Sn}_{0.05}$ measured along the (a) $\langle 110 \rangle$ and (b) $\langle 100 \rangle$ directions of the $\text{Si}_{0.95}\text{Sn}_{0.05}$ matrix. (c) and (d) are x-ray scans along $\langle 110 \rangle$ and $\langle 100 \rangle$ in annealed, strain-reduced $\text{Si}_{0.95}\text{Sn}_{0.05}$. q is the momentum transfer. The key for the peaks 1–4 is the same as in Fig. 2, the following assignment apply for the peaks 5–8: (5) β -Sn (200), (6) β -Sn (101), (7) β -Sn (220) and (8) α -Sn (220). Unidentified powder rings are denoted “p”.

normals to the characteristic planes mentioned above and also precipitates with no relation to the diffraction pattern in Fig. 2 are found. Different Moiré fringes are found in the precipitates (both in plan-view and cross-sectional TEM analysis) but some of the precipitates do not exhibit a Moiré pattern indicating that the phase and/or the orientation of the crystallites are different. Analysis of the Moiré fringes in Fig. 1(a) revealed that this pattern can only originate from (200) β -Sn planes that are parallel to (111) planes of the matrix. The lack of the corresponding β -Sn (200) spots in the direction of the Si(111) spots in diffraction mode [Fig. 2(b)] is probably due to the overlap of these spots ($\mathbf{k}_{\beta(200)}$ is only 8% longer than $\mathbf{k}_{\text{Si}(111)}$). Considering the variation in the orientation of the precipitates and the lattice mismatch between the precipitates and matrix, it is likely that most of the precipitate-matrix interfaces are incoherent.

C. The thermal hysteresis of the α -Sn and β -Sn crystallites

The formation and the stability of the α -Sn and the β -Sn crystallites were investigated by *in situ* melting and solidification of the precipitates in the strained $\text{Si}_{0.95}\text{Sn}_{0.05}$ layer. Thermal cycling (heating followed by cooling) was done in the temperature range from 70 °C to 230 °C in steps of 5 °C or 10 °C and, for each temperature, thermal equilibrium was obtained by waiting at least 10 min. The fact that the precipitates are confined in the matrix makes it possible to repeat the thermal cycle many times without the risk of surface contamination or a change in the shape and size of the precipitates (the size does not increase as the diffusion is negligible at the temperatures used during the thermal cycling); irrespective of the number of heating cycles the same diffraction pattern was always found at room temperature. The phase transformation in the precipitates was investigated in diffraction mode; in this way the process of melting and solidification corresponds to the entire range of precipitate sizes.

TABLE II. The measured lattice constants, the corresponding table values (Ref. 29), the widths of the x-ray peaks, and the estimated size of the precipitates.

Material	Spot	Spot number	Measured lattice constant (Å)	Tabulated lattice constants (Å)	Relative change in lattice constant (%)	Width (Å ⁻¹)	Precipitate size (Å)
Strain-reduced 5%	α -Sn (220)	4	2.299	2.294	0.22	0.0337	186
	β -Sn (220)	7	2.070	2.062	0.39	0.0308	204
	α -Sn (111)	1	3.756	3.751	0.22	0.0257	211
	α -Sn (220)	8	2.294	2.294	0.00	0.0465	117
	β -Sn (200)	2	2.922	2.915	0.24	0.0255	213
	β -Sn (101)	3	2.798	2.793	0.18	0.0249	218
	β -Sn (101)	6	2.802	2.793	0.32		
Strained 5%	α -Sn (220)	4	2.298	2.294	0.17	0.0406	134
	β -Sn (220)	7	2.067	2.062	0.24	0.0270	187
	α -Sn (111)	1	3.764	3.751	0.35	0.0274	140
	β -Sn (200)	2	2.921	2.915	0.21	0.0246	156
	β -Sn (101)	3	2.803	2.793	0.36	0.0249	159
	β -Sn (200)	5	2.928	2.915	0.46		
	β -Sn (101)	6	2.804	2.793	0.40		

TABLE III. The temperatures where the diffraction spots either disappear or reappear during heating and cooling, respectively. ΔT is the thermal hysteresis. The bulk melting temperature of β -Sn is 232 °C.

Diffraction spot	Melting temperature (°C)	Solidification temperature (°C)	ΔT (°C)
α -Sn (220) (“4”)	~200	~180	20
α -Sn (111) (“1”)	~200	~160	40
β -Sn (200) (“2”)	~210	~93	117
β -Sn (101) (“3”)	~210	~93	117

The melting temperature of a given type and orientation of the crystallites is taken as the temperature where the diffraction spots disappear. Considerations of the Debye-Waller factor³⁰ reveal that the intensity of the α - and β -Sn spots in Table I are at maximum reduced by 4% and by 11%, respectively, when the temperature is increased from room temperature to 200 °C thus, the disappearance of the spots at elevated temperatures is not due to lattice vibrations. Furthermore, as no “twinkling”³¹ of the precipitates was observed in dark-field TEM investigations, the disappearance of the diffraction spots is not likely to be due to rotation of precipitates within their cavities. We cannot exclude that the disappearance of the α -Sn spots is due to a transformation of (parts of) the α -Sn crystallite into β -Sn, which is the last solid phase to melt during heating (see below).

The temperatures at which the α -Sn and β -Sn spots disappear or reappear during heating and cooling, respectively, are given in Table III. As indicated in this table the thermal hysteresis (the temperature difference between melting and solidification) of α -Sn is considerably smaller than for β -Sn. Furthermore, the α -Sn crystallites melt at a lower temperature than β -Sn, whereas, during the cooling sequence, the α -Sn crystallites are formed before any β -Sn solidifies. The observations that only a relatively small supercooling is required for the formation of α -Sn and that the solidification temperature of the α -Sn crystallites depends on the orientation of these, indicate that the formation of α -Sn is due to interaction with the surrounding matrix, i.e., the matrix induces the formation of α -Sn.

Several authors^{12–14} have demonstrated that the melting temperature of β -Sn precipitates on an inert substrate decreases following an $1/r$ law (r -radius of the precipitates); the change in melting temperature with radius is explained by a change in the surface/volume ratio. β -Sn precipitates, with a size in the range of 100–200 Å, melt at 10–20 °C below the bulk melting point.¹³ Precipitates confined to a matrix might have another melting temperature due to interface effects,³² however, the β -Sn crystallites in the present study exhibit a melting temperature suppression, ~22 °C like that of similarly sized Sn precipitates located on an inert surface.^{12–14} This indicates that the melting of the β -Sn crystallites are started at incoherent interfaces between the β -Sn crystallites and the surrounding matrix.

The supercooling of β -Sn particles has been determined by Turnbull to be about 100–115 °C (Ref. 33) (the size of the precipitates was not given) and this relatively large supercooling was attributed to a homogenous nucleation mecha-

nism. Homogeneously nucleated solidification is characterized by the spontaneous formation of a solid nucleus in the molten precipitate which is not mediated by an interface or lattice imperfections.²⁵ In the present study the supercooling of the β -Sn crystallites was found to be 117 °C (Table III). As shown by the following analysis it is likely that the solidification of β -Sn crystallites is homogeneously nucleated.

Homogeneously nucleated solidification is characterized by a temperature-dependent critical diameter (of the solid nuclei mentioned above), d_c , below which the precipitates cannot solidify.²⁵ d_c and the supercooling ΔT is related by²⁵ $d_c = 4T_m\gamma_{sl}/(L\Delta T)$, where γ_{sl} is the interface energy between the solid and molten Sn, T_m is the bulk melting temperature, and L is the heat of fusion. Using³⁴ $L = 4.32 \times 10^8$ J/m³, $T_m = 505$ K, and²⁵ $\gamma_{sl} = 54.5 \times 10^{-3}$ mJ/m², we get $d_c \sim 2600$ K/ ΔT Å. With a supercooling of the order of 100 K $d_c \sim 26$ Å, which is much smaller than the precipitate sizes found by TEM. The nuclei starting the solidification of the β -Sn crystallites is therefore much smaller than the molten volume. However, the crystallites do not solidify at a smaller supercooling, equivalent to a larger critical radius, due to the small probability for forming large nuclei. The effective supercooling, ΔT , needed to start the solidification can be estimated following the analysis in Ref. 25; the number of nuclei N_{hom} , formed per time unit in a (spherical) volume, V , equal to the size of a precipitate (diameter ~150 Å) is given by

$$N_{\text{Hom}} = f_0 V \exp\left(\frac{-A}{T \cdot \Delta T^2}\right), \quad (1)$$

where $A = 16\pi\gamma_{sl}^3 T_m^2 / (3L^2 k_B)$ and f_0 is the frequency by which one atom is added to a cluster of the critical size. f_0 is function of the vibration frequency and the activation energy for diffusion of the Sn atoms. Assuming²⁵ $f_0 \sim 10^{11}$ s⁻¹ and a formation rate, N_{hom} , of 1 s⁻¹, the effective supercooling becomes ~140 K. Thus, this rough estimate is in good agreement with the supercooling we find experimentally. Furthermore, as a interface-nucleated (heterogeneous) solidification process is expected to have a considerably smaller supercooling it is most likely that the β -Sn crystallites are homogeneously nucleated; this is in agreement with the lack of interface effects changing the melting temperature as mentioned above.

D. The location and number density of the α and β -Sn crystallites

Figure 4 shows cross-section HRTEM micrographs of two Sn precipitates: (a) β -Sn precipitate and (b) a precipitate consisting of an α -Sn and a β -Sn crystallite. Also plan-view HRTEM investigations revealed precipitates consisting of both α - and β -Sn crystallites (not shown). The precipitates investigated by HRTEM were found to consist of one or two crystallites: the precipitates containing one crystallite were made of only β -Sn whereas the precipitates containing two crystallites contained both α -Sn and β -Sn. Most of the precipitates were found to consist of only β -Sn. To investigate whether α -Sn generally is found in two-phase precipitates consisting of more than one crystallite and to get an idea about the number density of α -Sn crystallites, we performed TEM investigations at elevated temperatures where only

FIG. 4. Cross-sectional micrographs of precipitates in annealed, strained $\text{Si}_{0.95}\text{Sn}_{0.05}$ taken along the $\langle 110 \rangle$ axis of the matrix. (a) β -Sn precipitate in which the β -Sn (101) planes (the almost vertical lines) are parallel to the (200) planes of the matrix, (b) a precipitate consisting of an α -Sn crystallite (upper part) and a β -Sn crystallite (lower part). In (b) the α -Sn (111) planes (horizontal lines) are parallel to the (200) planes of the matrix. In the β -Sn crystallite in (b) the β -Sn (200) planes are parallel to the (200) planes of the matrix.

α -Sn crystallites have solidified (temperature range: 100–160 °C during the cooling sequence, see Table III). Dark field analysis using the α -Sn (220) spots (“4” in Fig. 2) show the presence of a large number of α -Sn crystallites [Fig. 5(a)] and a comparison with the corresponding bright-field micrograph [Fig. 5(b)] shows that the α -Sn crystallite takes up only a fraction of the total volume of the precipitates containing α -Sn; the remaining part is still melted. As explained in subsection E, the difference in the density of α -Sn, β -Sn, and molten Sn makes it likely that the molten fraction becomes β -Sn during cooling.

As none of the crystallite orientations mentioned in Table I correspond to the same precipitate, we can compare the relative probability of the different orientations of the α and β -Sn crystallites from the area of the x-ray diffraction peaks. As the crystallites are of approximately the same size, the intensity I of the diffraction peaks is given by³⁵

FIG. 5. Plan-view TEM micrographs taken along the $\langle 001 \rangle$ axis at elevated temperature (111 °C) of annealed, strained $\text{Si}_{0.95}\text{Sn}_{0.05}$. The corresponding diffraction pattern shows no indication of β -Sn (a) Dark-field using the α -Sn (220) spot (4), and (b) the corresponding bright field. The same precipitate is marked by an arrow in (a) and (b).

$$I \propto \left[\frac{F}{v \cos(\theta_B)} \right]^2, \quad (2)$$

where F is the structure factor of the unit cell, θ_B the Bragg angle, and v the volume of the unit cell. F^2 is $32f_{\text{Sn}}^2$, $64f_{\text{Sn}}^2$, $16f_{\text{Sn}}^2$, and $8f_{\text{Sn}}^2$ (f_{Sn} is the atomic structure factor) for α -Sn (111), α -Sn (220), β -Sn (200), and β -Sn (101), respectively. The Bragg angle can be calculated from Bragg's law. The ratio of two diffraction peaks with areas A_1 and A_2 must be scaled with the intensities in the following way:

$$R = \frac{A_1 I_2}{A_2 I_1}. \quad (3)$$

For the β -Sn (200) and β -Sn (101) peaks in Table I R is very close to unity and this is also the case for α -Sn (111) and α -Sn (220); thus, based on the assumption that the crystallites are of similar size we get that, for each of the solid Sn phases, the number of precipitates is roughly equally distributed among the two orientations of each phase in Table I. We note that there are β -Sn crystallites with a different orientation (like spots “5” and “6”) which are not included in this analysis. If the sum of the scaled α -Sn intensities is divided by the sum of the scaled β -Sn intensities of the diffraction spots in Table I a value about close to unity is found. Thus, within this crude estimate the crystallites are equally distributed among the two solid Sn phases included in Table I. The HRTEM investigations reveal that the ratio of the volume occupied by α -Sn relative to that of β -Sn is much

smaller than unity (roughly of the order of 10%); this discrepancy is probably due to the fact that a large number of β -Sn precipitates does not contribute to the diffraction spots in Table I whereas precipitates of any orientation is observed by HRTEM.

E. The origin of the α - and β -Sn crystallites

The observations that α -Sn crystallites persist (during heating) and are formed (during cooling from the melted phase) at temperatures high above the bulk $\alpha \leftrightarrow \beta$ -Sn transition temperature, $T_{\alpha-\beta}^0$, indicates that the thermodynamical properties of the crystallites are changed compared to the bulk phase. Alloying and pressure effects are among the candidates responsible for the shift in the transition temperature. It has been demonstrated that $T_{\alpha-\beta}$ increases to 55 °C and 90 °C by a Si concentration in a Sn matrix of 0.4% and 2.5%, respectively.³⁶ The observation of tensile strain in the precipitates is, however, not compatible with a high Si concentration (Si lowers the average lattice constant) and furthermore, the eutectic concentration of Si in β -Sn is only about 10^{-5} %.³⁷ Thus, if there is any Si in the Sn precipitates the concentration must be very small, which means that the change of $T_{\alpha-\beta}$ due to alloying must be small.

The $\alpha \leftrightarrow \beta$ transition temperature changes as the external pressure is varied. This effect originates from the large change in the density (27%) associated with the $\alpha \rightarrow \beta$ transition; intuitively a phase transformation towards a more dense phase (β -Sn) is postponed by tensile strain. The phase diagram of bulk Sn is only well known for pressures higher than atmospheric pressure.³⁶ By extrapolation of high-pressure data, Vnuk, De Monte, and Smith³⁶ estimated the $\alpha \leftrightarrow \beta$ transition temperature to follow $T_{\alpha-\beta} = 13 \text{ K} - 50p \text{ K/kbar}$ below atmospheric pressure. Similarly these authors extrapolated the melting temperature of β -Sn to follow $T_{\text{melt}} = 232 \text{ K} + 3p \text{ K/kbar}$ below atmospheric pressure. The curves for $T_{\alpha-\beta}$ and T_{melt} intercept at -4.8 kbar (0.48 GPa) at a temperature of 215 °C; at this so-called triple point the molten Sn can solidify directly into α -Sn.

The change of the $\alpha \leftrightarrow \beta$ transition temperature induced by the tensile strain in the precipitates can be estimated using the lattice constants found by x-ray diffraction. The pressure in the precipitates relative to atmospheric pressure is given by $\Delta p = B(a^3 - a_0^3)/a_0^3$, where B is the bulk modulus [42.6 GPa for α -Sn and 57 GPa for β -Sn (Ref. 34)] a_0 is the bulk lattice constant, and “ a ” is the lattice constants which have been determined experimentally. We find Δp in the range of 0.3–0.8 GPa; this is in the range of the triple point as given by Vnuk, De Monte, and Smith.³⁶ The pressure-induced change in the transition temperature can be estimated by the Clausius-Clapeyron equation:²⁵ $dp/dT = L/(T\Delta V)$, where p is pressure, T is the bulk transition temperature (286 K), $L_{\alpha-\beta}$ the specific heat of the transformation [2.12 kJ/mole (Ref. 34)] and ΔV is the change in volume per mole (4.32 cm³/mole). This equation gives $dp/dT = 0.00171 \text{ GPa/K}$ and using the above value for Δp an $\alpha \leftrightarrow \beta$ transition temperature in the range of 175–466 °C is calculated. Thus, a calculation based on the Clausius-Clapeyron equation as well as the extrapolation done by Vnuk, De Monte, and Smith³⁶ show that the tensile strain in the precipitates might increase the $\alpha \leftrightarrow \beta$ transition temperature to a value which is as high

as the melting point. Such a high value for $T_{\alpha-\beta}$ explains why the α -Sn crystallites are stable as observed in the present investigation where the α -Sn crystallites do not transform into β -Sn even at very slow cooling rates.

The tensile strain will induce an increase in the $\alpha \leftrightarrow \beta$ transition temperature, however, the origin of the tensile strain has not been considered. The tensile strain is likely to be due to the difference in thermal expansion of the matrix and the precipitate.³⁸ The thermal expansion is higher for liquid Sn and β -Sn than for Si (the thermal expansion of the Si_{0.95}Sn_{0.05} matrix is approximated by that of Si). At the high annealing temperatures where the Sn precipitates are formed, the strain in the precipitates is relaxed by vacancies as discussed in Sec. A, thus, the precipitate and the cavity containing the precipitate have the same size. However, when the temperature is lowered tensile strain starts to accumulate in the precipitates due to the difference in thermal expansion of the precipitate and the matrix. The local strain caused by the difference in thermal expansion cannot relax in the TEM specimen because relatively thick parts of the specimen are used in the diffraction studies.

We suggest that the formation of α -Sn is described by the following scenario: first, during cooling, a part of the molten precipitate solidifies into α -Sn. The solidification of α -Sn is presumably mediated by the matrix and the stability of this phase is a consequence of the tensile strain which shifts the $\alpha \leftrightarrow \beta$ transition temperature. Due to the low density of the α -Sn phase (α -Sn: $2.92 \times 10^{22} \text{ cm}^{-3}$, molten Sn: $3.50 \times 10^{22} \text{ cm}^{-3}$) a given number of atoms occupies a larger volume in the α -Sn phase than in the liquid phase and, therefore, the expanding solidification of α -Sn is stopped by a pressure increase in the remaining melt in the precipitate. The tensile strain in the α -Sn crystallite is lowered during this process, but anyway it does not transform into β -Sn. As the temperature is lowered the remaining melt solidifies into β -Sn phase, which has a density above that of molten Sn (β -Sn: $3.70 \times 10^{22} \text{ cm}^{-3}$). Tensile strain further accumulates when the temperature is lowered from the solidification temperature of the precipitates to room temperature. Using the thermal expansion of β -Sn the volume misfit, due to the temperature decrease from ~ 200 °C to 20 °C is about $\sim 0.9\%$, i.e., the cavity containing the precipitate is 0.9% larger than the volume of the precipitate. This volume mismatch corresponds to about 0.3% mismatch along each of the Cartesian directions and this is similar to the deviation from the bulk lattice constants found by x-ray diffraction measurements (Table II). Thus, the difference in thermal expansion (between the precipitates and the matrix) assists the formation of α -Sn and leads to tensile strain in both α and β -Sn precipitates.

CONCLUSION

The octahedral Sn precipitates found in annealed, epitaxial Si_{0.95}Sn_{0.05} alloy layers were investigated. Diffraction studies revealed the presence of both α -Sn and β -Sn crystallites and showed that low-index planes of the crystallites are typically parallel to planes of the surrounding matrix. HRTEM and dark-field TEM studies were used to locate the α -Sn and the β -Sn phases; precipitates of only β -Sn as well as mixed-phase precipitates were identified. The formation

and the stability of α -Sn crystallites were explained to be due to pressure and interface effects. The sizes of the α -Sn and β -Sn crystallites were found to be similar but the total volume occupied by α -Sn is smaller than that of β -Sn. A study of the melting and the solidification temperatures of the α -Sn and β -Sn crystallites revealed that the α -Sn phase is the first to disappear (during heating) and also the first phase to solidify (during cooling). The large thermal hysteresis of β -Sn indicates that the solidification of this phase is homoge-

neously nucleated whereas the α -Sn crystallites are likely to be induced by the surrounding matrix.

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