JOURNAL OF MATERIALS SCIENCE 14 (1979) 1361–1369

Epitaxial growth of antimony electrodeposits on oriented single-crystal surfaces of copper

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The epitaxial growth of antimony electrodeposits obtained at 25 and 50° C from chloride and citrate baths on copper single-crystal cathodes orientated along (1 0 0), (1 1 0) and (1 1 1) crystallographic planes has been studied by electron diffraction. Current densities ranging from 10 to 1000 A m^{-2} and thicknesses between 0.2 and 10 μm have been investigated. Amorphous electrodeposits were usually obtained from the chloride bath at a temperature of 25° C. The monocrystalline deposits obtained from both baths on (1 0 0) and (1 1 1) copper planes were oriented with their (1 1 0) and ($\bar{1}$ 1 0) planes and with their (1 0 0) plane, respectively, parallel to the substrate. On the (1 1 0) copper substrate, monocrystalline deposits were only obtained from the citrate bath, their ($\bar{2}$ 2 1) plane being parallel to the substrate face. For the sake of completeness, some bismuth electrodeposits on the same copper substrate faces were also studied. The results are discussed in terms of work of nucleation, symmetry of the deposit–substrate interface region and mismatch along close packed directions. They are also discussed in connection with the results related to bismuth electrodeposits.

1. Introduction

The study of thin layers of metals epitaxially formed on monocrystalline metallic surfaces is of importance in connection with the development of solid state devices and microcircuits. In a previous work [1] the epitaxial growth of antimony electrodeposits obtained from a chloride bath on single-crystal substrates of gold and silver orientated along (1 0 0), (1 1 0) and (1 1 1) crystallographic planes was studied by high-energy electron diffraction (RHEED). The deposits were generally crystalline; only on the silver substrate were some deposits amorphous, especially at low temperature and current density (c.d.).

The epitaxial deposits showed the same planes and orientations on both substrates, but a wider range of growth conditions (i.e. c.d. and thickness) was observed with deposits on gold. To contribute to the knowledge of the antimony electrodeposition on single-crystal substrates, it would be of interest to extend the study to different metals; however, the number of substrates is limited by the high nobility of antimony and, therefore, by possible displacement reactions. Copper can be chosen, due to its high equilibrium voltage; furthermore, copper is a common substrate for the study of electrochemically and vacuum deposited metals having the same or different structure.

Several experiments on the electrodeposition of bismuth on copper were also performed. Literature data are very scarce. Rudoi *et al.* [2] studied the dependence of c.d. on overpotential during the formation from chloride solution of amorphous antimony on polycrystalline copper. The very early stages of the deposition of bismuth on (1 0 0) and (1 1 1) oriented copper substrates have been examined by low-energy electron diffraction (LEED) [3].

TABLE I Orientation of antimony deposits from chloride and citrate baths on (1 0 0), (1 1 0) and (1 1 1) faces of copper single-crystals

Bath	Temperature (° C)	Current density ($A\,m^{-2}$)	Thickness (μm)	Growth on		
				(1 0 0) face	(1 1 0) face	(1 1 1) face
Chloride	25	10	0.2	amorphous	amorphous	amorphous
		100	1.0	amorphous	amorphous	amorphous
		1000	10	–	–	amorphous, (1 0 0)
	50	10	0.5	(1 1 0)*, $(\bar{1}\,1\,0)$, $[3\,\bar{1}\,1]$†	$[\bar{2}\,2\,1]$, $[2\,\bar{1}\,1]$	(1 0 0)
		100	1.0	(1 1 0), $(\bar{1}\,1\,0)$, $[3\,\bar{1}\,1]$	$[\bar{2}\,2\,1]$, $[2\,\bar{1}\,1]$	R‡
Citrate	50	10	0.25	–	$(\bar{2}\,2\,1)$	(1 0 0), R
		10	0.5	–	$(\bar{2}\,2\,1)$	R
		25	0.2	–	$(\bar{2}\,2\,1)$	(1 0 0), R
		25	0.5	–	$(\bar{2}\,2\,1)$	(1 0 0), R
		25	1.0	–	–	(1 0 0), R
		50	0.5	–	–	R
		50	1.0	(1 1 0), $(\bar{1}\,1\,0)$	$[\bar{2}\,2\,1]$	(1 0 0), $[\bar{2}\,2\,1]$
		100	1.0	$[\bar{2}\,2\,1]$, $[2\,\bar{1}\,1]$	$[\bar{2}\,2\,1]$	–
		300	1.0	$[\bar{2}\,2\,1]$, $[2\,\bar{1}\,1]$	$[\bar{2}\,2\,1]$	–

*Plane of the deposit parallel to the substrate surface.

†Texture axis of the deposit.

‡Random deposit.

TABLE II Orientation relationships, interatomic distances and corresponding mismatches between parallel directions

Substrate orientation	Antimony deposit orientation	Orientation relationship between parallel directions	Interatomic distances along the considered directions (Å)		Mismatch (%)
			Deposit	Substrate	
(1 0 0)	(1 1 0)	$[\bar{1}\,1\,\bar{1}]$ Sb* ∥ $[0\,1\,\bar{1}]$ Cu (chloride	10.63	2.55 × 4	4.2
		$[\bar{1}\,1\,0]$ Sb ∥ [0 1 0] Cu and citrate	4.31	3.61	19.4
		[0 0 1] Sb ∥ [0 0 1] Cu baths)	6.22	3.61 × 2	13.9
		$[\bar{1}\,1\,0]$ Sb ∥ $[0\,1\,\bar{1}]$ Cu (chloride	4.31	2.55 × 2	15.5
		$[\bar{1}\,1\,1]$ Sb* ∥ [0 1 0] Cu bath)	10.63	3.61 × 3	1.8
		$[\bar{1}\,1\,2]$ Sb* ∥ [0 1 0] Cu	7.57	3.61 × 2	4.8
		[0 0 1] Sb ∥ [0 1 1] Cu	6.22	2.55 × 2	22.0
	$(\bar{1}\,1\,0)$	$[1\,1\,\bar{1}]$ Sb* ∥ $[0\,1\,\bar{1}]$ Cu (chloride	11.20	2.55 × 4	9.8
		[1 1 0] Sb ∥ [0 1 0] Cu and citrate bath)	4.49	3.61	24.4
		[1 1 0] Sb ∥ $[0\,1\,\bar{1}]$ Cu (chloride bath)	4.49	2.55 × 2	12.0
		[1 1 1] Sb* ∥ [0 1 0] Cu	10.63	3.61 × 3	1.8
		[1 1 2] Sb* ∥ [0 1 0] Cu	7.46	3.61 × 2	3.3
		$[\bar{1}\,\bar{1}\,2]$ Sb* ∥ [0 0 1] Cu	7.87	3.61 × 2	9.0
		$[\bar{1}\,\bar{1}\,1]$ Sb* ∥ [0 0 1] Cu	11.20	3.61 × 3	3.4
(1 1 0)	$(\bar{2}\,2\,1)$	[1 1 0] Sb ∥ [0 0 1] Cu (citrate bath)	4.49	3.61	24.4
(1 1 1)	(1 0 0)	$[0\,1\,\bar{1}]$ Sb ∥ $[\bar{1}\,1\,0]$ Cu (chloride bath)	4.31	2.55 × 2	15.5
		[0 1 1] Sb ∥ $[\bar{1}\,\bar{1}\,2]$ Cu	4.49	4.42	1.0
		[0 1 0] Sb* ∥ $[\bar{1}\,1\,0]$ Cu (chloride and	6.22	2.55 × 2	22.0
		[0 0 1] Sb ∥ $[\bar{1}\,\bar{1}\,2]$ Cu citrate bath)	6.22	4.42	41.0

*Directions not strictly parallel to each other.

2. Experimental details

The copper monocrystalline cathodes prepared by a modified Bridgman technique [4] were orientated along the (1 0 0), (1 1 0) and (1 1 1) crystallographic planes. The electrolytic polishing of the cathodes, which is necessary to free the surfaces of work-hardened material, was performed in phosphoric acid solution (1:1 by volume), at a cell voltage of 2 V, for 10 min. The following electrodeposition solutions were employed:

(a) 0.5M $SbCl_3$ + 3M HCl

(b) 52.4 g $litre^{-1}$ Sb_2O_3 + 149.78 g $litre^{-1}$

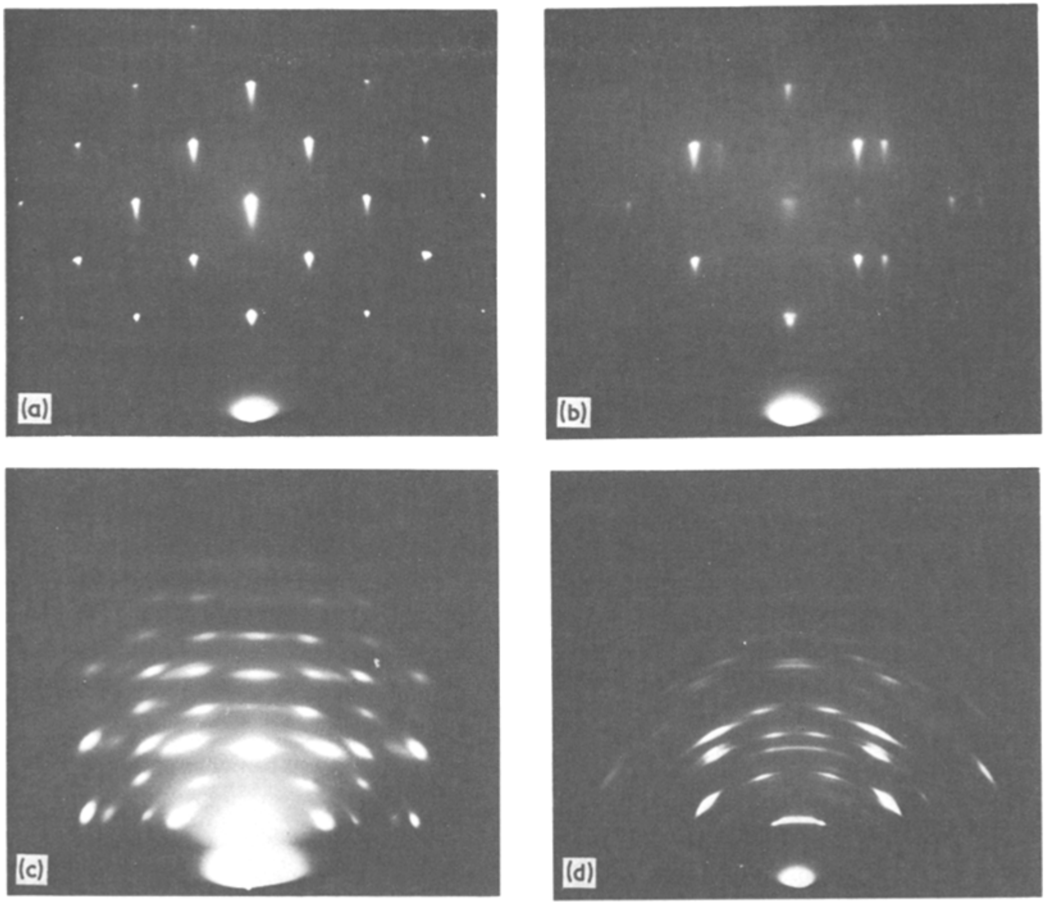

Figure 1 RHEED patterns of antimony deposits from the chloride bath: (a) (1 1 0) Sb || (1 0 0) Cu; (b) ($\bar{1}$ 1 0) Sb || (1 0 0) Cu; (c) (1 0 0) Sb || (1 1 1) Cu; (d) (1 1 0) copper substrate face; (50° C). (a) 100 A m^{-2}, 1 μm; beam along [0 0 1] Cu. (b) 100 A m^{-2}, 1 μm; beam along [0 1 0] Cu. (c) 10 A m^{-2}, 0.5 μm; beam along [$\bar{1}$ $\bar{1}$ 2] Cu. (d) 100 A m^{-2}, 1 μm.

potassium citrate + 179.7 g litre^{-1} citric acid
(c) 0.5M $Bi(ClO_4)_3$ + 2M $HClO_4$.

The solutions were prepared with reagent-grade chemicals and doubly distilled water and were further treated with activated carbon. In order to avoid displacement reactions in the absence of applied current, the electrodes were polarized as soon as they were dipped into the solution.

Cell, apparatus and techniques were the same as those used in the previous work [1].

3. Results

3.1. Antimony deposits

The results concerning the antimony deposits obtained on the various copper single-crystal substrates, under different conditions of temperature, c.d. and thickness are given in Table I. In Table II the orientation relationships between the parallel directions* of deposit and substrate, as well as the corresponding interatomic distances and mismatches, are given.

3.1.1. Deposits from chloride solution

The deposits from a chloride solution obtained at 25° C were generally amorphous. At 50° C, on the other hand, they were crystalline and showed significant differences on different substrates. In fact, while the epitaxial deposits on the (1 0 0) plane were orientated with the (1 1 0) and/or ($\bar{1}$ 1 0) planes parallel to the substrate (Fig. 1a and b), on the (1 1 1) plane they were orientated with the (1 0 0) plane parallel to the substrate (Fig. 1c). The deposits on the (1 1 0) substrate were polycrystalline under all conditions, with [$\bar{2}$ 2 1] and [2 $\bar{1}$ 1] texture axes (Fig. 1d).

The arched diffraction spots obtained from

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*Owing to the pseudo-cubic structure of antimony (D^5_{3d} space group, $a = 6.22$ Å, $\alpha = 87°\ 42'$), when the parallelism has been assigned to a pair of directions, there is not always strict parallelism for the other pairs of directions.

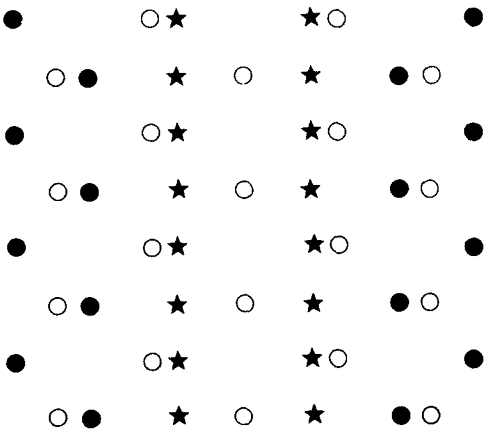

Figure 2 Interpretation of the diffraction pattern shown in Fig. 1b. ● [1 1 0] Sb ∥ [0 1 0] Cu (first orientation). ○ [1 1 1] Sb nearly ∥ [0 1 0] Cu (second orientation). ★ [1 1 2] Sb nearly ∥ [0 1 0] Cu (second orientation).

deposits on (1 0 0) indicate a tendency towards disorientation also at low c.d. and thickness. Furthermore, in some regions the deposits were polycrystalline with a $[3\bar{1}1]$ texture axis. The monocrystalline deposits showed two different orientation relationships, as reported in Table II: they were generally co-existent, but in some regions only the first one was found (Fig. 1a). When both orientations were present, the diffraction pattern of Fig. 1b was obtained, the interpretation of which is reported in Fig. 2.

The deposits obtained on (1 1 1) at low temperature showed in some cases faint reflections from the (1 0 0) plane: this indicates the existence of areas of monocrystalline antimony in deposits which were mainly amorphous. The monocrystalline deposits also showed in this case two orientation relationships (Table II): one corresponds to the parallelism between the closest packed directions of deposit and substrate (Fig. 1c)*. When the c.d. was increased, the deposits tended to become disoriented. The crystalline deposits were uniform and adherent; no growth figures were observed by metallographic microscopy. The amorphous deposits were uniformly bright and often showed poor adherence.

3.1.2. Deposits from citrate solution

The citric solution is commonly used as a technical plating solution. The deposits were obtained at 50° C and were generally crystalline (Table I).

On the copper (1 0 0) substrate, epitaxial deposits with the (1 1 0) and/or $(\bar{1}10)$ planes parallel to the substrate were obtained at low c.d.: the orientation was the same as the first orientation observed for deposits from the chloride solution (Fig. 3a and Table II). At higher c.d., however, polycrystalline deposits with $[\bar{2}21]$ and $[2\bar{1}1]$ texture axes were observed.

The deposits obtained at low c.d. on (1 1 0) were orientated with the $(\bar{2}21)$ plane parallel to the substrate; when c.d. and thickness were increased, a $[\bar{2}21]$ texture developed. In the diffraction patterns of the monocrystalline deposits (Fig. 3b and the corresponding interpretation diagram, Fig. 4) the spots were usually double-positioned and symmetrically arranged with respect to the [1 1 0] direction of the substrate.

In some regions, however, only one of the two orientations was present (Fig. 3c). Furthermore, the diffraction patterns show that the (0 0 1) and $(\bar{1}10)$ planes of the deposit are inclined about 71° and 19°, respectively, to the (1 1 0) plane of the substrate: this situation is represented in Fig. 5, where two antimony crystallites deposited on the copper surface are sketched. Considering the right-hand side crystallite, it may be observed that the [1 1 0] direction of antimony (which is parallel to the [0 0 1] direction of the substrate and therefore to the electron beam) is the zone axis of the (0 0 1) and $(\bar{1}10)$ planes of antimony. Thus, if the values of the angles formed by these planes with the substrate plane are also considered, the plane parallel to the substrate is $(\bar{2}21)$ (Table II). The diffraction spots showed a tendency to become arched. When c.d. and thickness were increased, the deposits were polycrystalline with a $[\bar{2}21]$ textures axis.

In the patterns obtained from deposits on (1 1 1), rings of polycrystalline material (Fig. 3d) and often faint reflections corresponding to the (1 0 0) plane parallel to the substrate were present (Table II). The deposits were generally uniform without growth figures.

3.2. Bismuth deposits

The narrow range of conditions in which epitaxial growth of antimony deposits has been obtained suggested a parallel study of bismuth electrodeposition, i.e. of a metal characterized by

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*The interpretation of Fig. 1c is not reported here, as it is analogous to that given for deposits on gold and silver substrates [1].

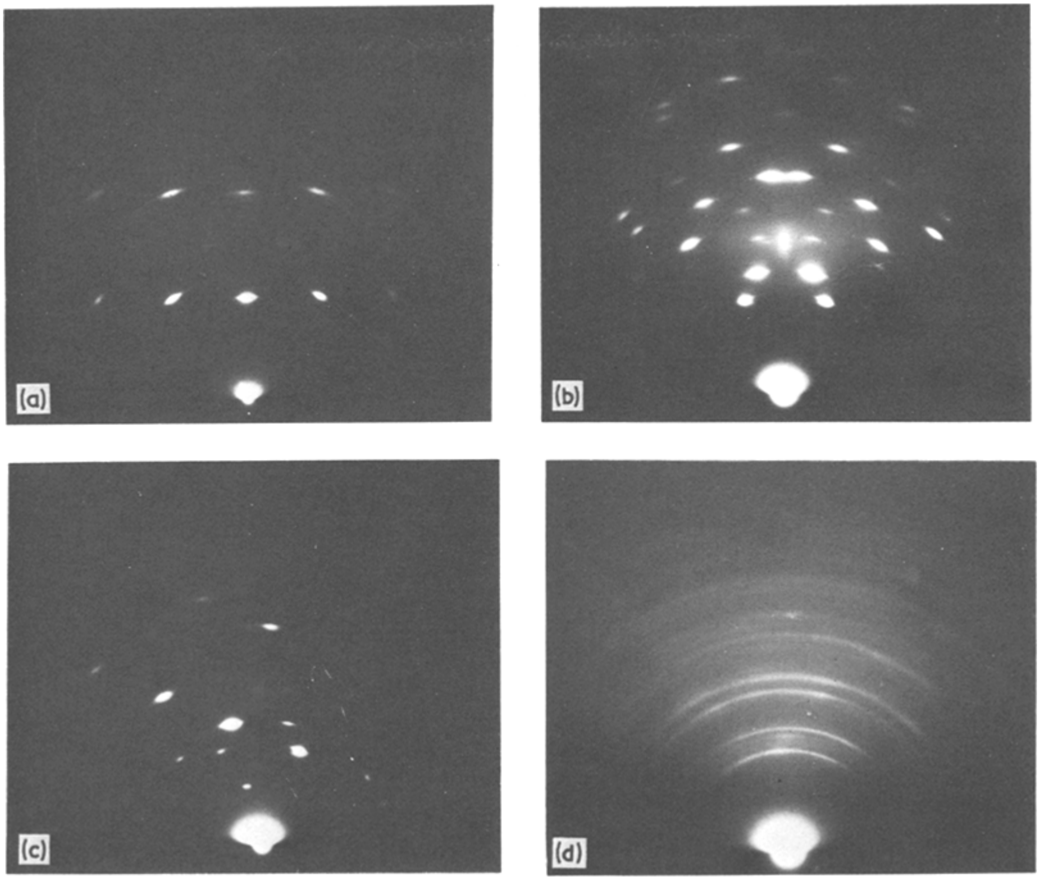

Figure 3 RHEED patterns of antimony deposits from the citrate bath: (a) ($\bar{1}$ 1 0) Sb‖(1 0 0) Cu; (b) (c) ($\bar{2}$ 2 1) Sb‖ (1 1 0) Cu; (d) (1 1 1) copper substrate face; (50° C). (a) 50 A m^{-2}, 1 μm; beam along [0 1 0] Cu. (b) 25 A m^{-2}, 0.5 μm; beam along [0 0 1] Cu. (c) 25 A m^{-2}, 0.5 μm; beam along [0 0 1] Cu. (d) 10 A m^{-2}, 0.5 μm.

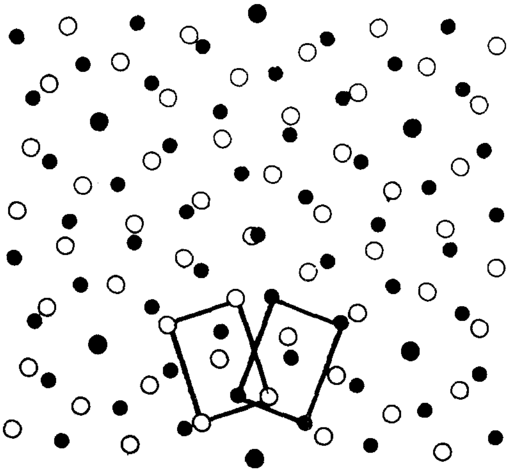

Figure 4 Interpretation of the diffraction pattern shown in Fig. 3b: ○ ● diffraction spots of double-positioned deposit.

chemical, electrochemical and structural properties closely similar to those of antimony.

Bismuth deposits on different substrates were studied from a somewhat different point of view in a previous work [5]. In the present research, deposition on copper single-crystal substrates has been studied in greater detail. In the range of conditions (10 to 300 A m^{-2}; 0.2 to 10 μm), in which the majority of antimony deposits have been obtained, the bismuth deposits were monocrystalline, orientated with the (1 0 0) plane parallel to the substrate, regardless of its orientation. Furthermore, the deposits obtained at 1000 A m^{-2} and a thickness of 1.0 μm were monocrystalline; however, when the thickness was further increased, they became progressively polycrystalline in character.

On each substrate, a single orientation relation-

TABLE III Orientation relationships, interatomic distances and corresponding mismatches between parallel directions

Substrate orientation	Bismuth deposit orientation	Orientation relationship between parallel directions	Interatomic distances along the considered directions (Å)		Mismatch (%)
			Deposit	Substrate	
(1 0 0)	(1 0 0)	$[01\bar{1}]$ Bi ∥ $[01\bar{1}]$ Cu	4.52	2.55 × 2	11.5
		$[010]$ Bi* ∥ $[010]$ Cu	6.54	3.61 × 2	9.5
		$[011]$ Bi ∥ $[011]$ Cu	4.72	2.55 × 2	7.5
(1 1 0)	(1 0 0)	$[010]$ Bi ∥ $[\bar{1}10]$ Cu	6.54	2.55 × 2	28
		$[001]$ Bi* ∥ $[001]$ Cu	6.54	3.61 × 2	9.5
(1 1 1)	(1 0 0)	$[011]$ Bi ∥ $[\bar{1}10]$ Cu	4.72	2.55 × 2	7.5
		$[0\bar{1}1]$ Bi ∥ $[\bar{1}\bar{1}2]$ Cu	4.52	4.42	2.2

*Directions not strictly parallel to each other.

ship between copper and bismuth has been observed (Table III): this implies minimum mismatch along the parallel directions*. Comparison of the results reported in Tables II and III shows that only the bismuth deposits on (1 1 1) have the same type of orientation as that of antimony deposits. Surprisingly, in every other case the results for the two electrodeposited metals are different.

4. Discussion

Antimony deposits obtained at 25° C from the chloride solution were amorphous in every case; since this tendency was not observed for the deposits from the citrate solution, the hypothesis of a decisive role of antimony trichloride in inhibiting nucleation and growing of crystals seems to be confirmed.

By comparing the present results with those obtained with gold and silver substrates [1], it may be observed that the tendency to give amorphous deposits decreases as the nobility of the substrate increases: this can partly be related to the displacement reaction of the substrate metal. The formation of amorphous metal is much more pronounced on the (1 1 0) copper plane than on the other two substrates, in agreement with the results obtained during the deposition of antimony on antimony single-crystals [6] which showed that the tendency is stronger on the substrates which do not favour epitaxial growth. As the nobility, i.e. equilibrium potential, is identical for cathodes of the same metal having different orientations [7], a possible explanation may be based on a different influence of the crystallographic orientation on the kinetics of the displacement reaction.

As far as the crystalline deposits are concerned, though antimony may be considered a face centred pseudo-cubic metal, the strong difference in atomic radii of deposit and substrate (+ 27%) tends to exclude the possibility of iso-oriented growth since, owing to the unfavourable atomic-size factor, the influence of deposition conditions prevails on the influence of the substrate orientation. It is thus possible to expect for antimony (which is an intermediate metal in the kinetic

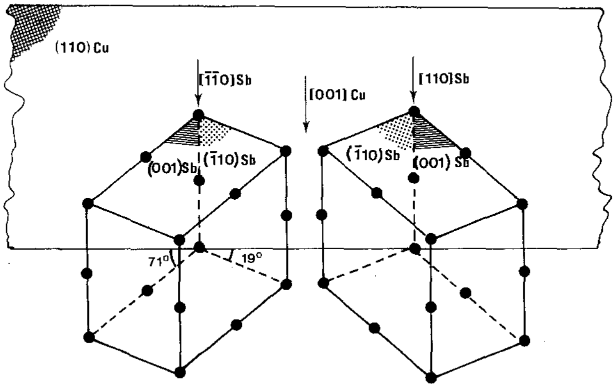

Figure 5 Double-positioned antimony crystallites from the citrate bath on a (1 1 0) copper substrate face.

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*In antimony, and also in bismuth (D^5_{3d} space-group; $a = 6.54$ Å, $d = 87°\ 34'$), when the parallelism is assigned to a pair of directions, there is not always strict parallelism for the other pairs of directions.

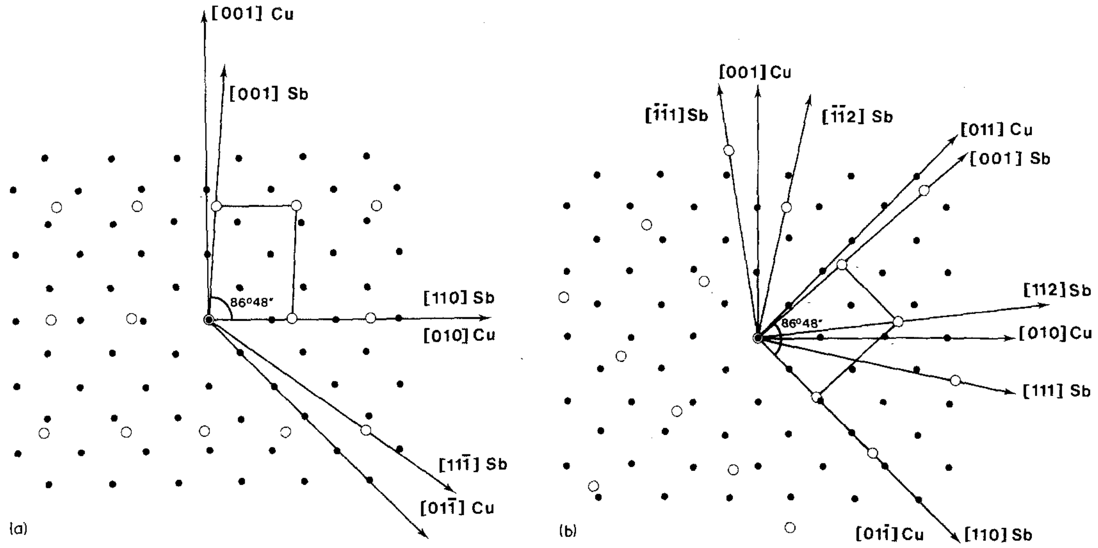

Figure 6 Positions of the antimony atoms of the ($\bar{1}$ 1 0) plane superimposed on the atoms of the (1 0 0) plane of the substrate face: ○ Sb; ● Cu. (a) [1 1 0] Sb‖[0 1 0] Cu. (b) [1 1 0] Sb‖[0 1 $\bar{1}$] Cu.

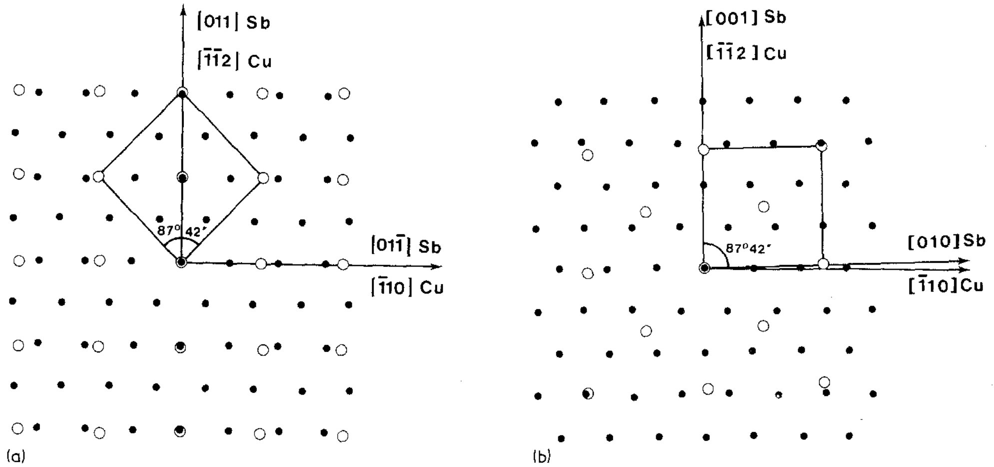

Figure 7 Positions of the antimony atoms of the (1 0 0) plane superimposed on the atoms of the (1 1 1) plane of the substrate face: ○ Sb; ● Cu. (a) [0 1 1] Sb‖[$\bar{1}$ $\bar{1}$ 2] Cu. (b) [0 0 1] Sb‖[$\bar{1}$ $\bar{1}$ 2] Cu.

electrochemical sense) the formation of nuclei orientated along the (1 0 0) plane (which is characterized by a lower nucleation work*) or the (1 1 0) plane (which is characterized by a slightly higher nucleation work [9]), as already observed for deposits on gold and silver substrates†.

The experimental results agree with the predictions: epitaxial antimony deposits orientated with the planes (1 1 0) and/or ($\bar{1}$ 1 0) and respectively (1 0 0) parallel to (1 0 0) and (1 1 1) copper substrates have been obtained from both solutions. The behaviour of the (1 1 0) substrate does not fit easily into this line of thought, since according to it, the (1 1 0) and/or ($\bar{1}$ 1 0) planes should be parallel to the substrate, instead of ($\bar{2}$ 2 1) found experimentally for deposits from the citrate solution. However, it may be recalled that when the last orientation is formed, the (1 1 0) planes of the deposit make a relatively low angle (19°) with respect to the substrate, as shown in Fig. 5. Crystalline deposits obtained from the chloride solution are in every case disoriented: this is possibly related, as already pointed out, to the tendency to form amorphous metal.

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*Thin antimony films on glass substrates have been recently found to have a cubic texture axis [8].

†On these metals the formation of nuclei orientated along (1 0 0) on the (1 0 0) and (1 1 1) planes and along (1 1 0) and ($\bar{1}$ 1 0) on the (1 1 0) plane has been observed [1].

To clarify the relative orientation between the epitaxial deposit and the substrate in Figs. 6a and b and 7a and b, the positions of antimony and copper atoms in the two orientations on the (1 0 0)* and (1 1 1) substrates are reported: for each pair of orientations on both substrates, the deposit–substrate interphase planes show a symmetry characterized by the highest number of symmetry elements (*p2mm* and *c2mm* two-dimensional space group for the (1 0 0) and (1 1 1) substrate, respectively). This is in agreement with the condition of maximum possible symmetry of the interphase plane, which is fulfilled by almost all the relatively thick expitaxial deposits [10], such as the antimony deposits studied in the present and previous work [1]. Furthermore, Figs. 6 and 7 show that the matching along certain parallel directions is very good (see also Table III).

Epitaxial deposits of bismuth are always orientated with the (1 0 0) plane parallel to the substrate. The results may be interpreted assuming that in the case of bismuth deposition the influence of deposition conditions prevails (very unfavourable atomic size-factor, i.e. +43%) and the formation of (1 0 0) nuclei is favoured during the nucleation process. In fact, the preferentially orientated polycrystalline bismuth deposits have a [1 0 0] texture axis, while the single-crystal bismuth electrodes orientated along the (1 0 0) plane show a parallel growth under a wider range of conditions than those orientated along (1 1 0) and (1 1 1) [6].

In Figs. 8 and 9 the distribution of the atoms of bismuth on the (1 0 0) and (1 1 0) copper substrates, respectively, are shown; the situation on the (1 1 1) plane was omitted, since it is similar to that reported in Fig. 7a for the antimony deposit. In each case the condition of maximum symmetry of the interphase plane is followed: *p4mm* and *p2mm* two-dimensional space group for the (1 0 0) and (1 1 0) substrate, respectively.

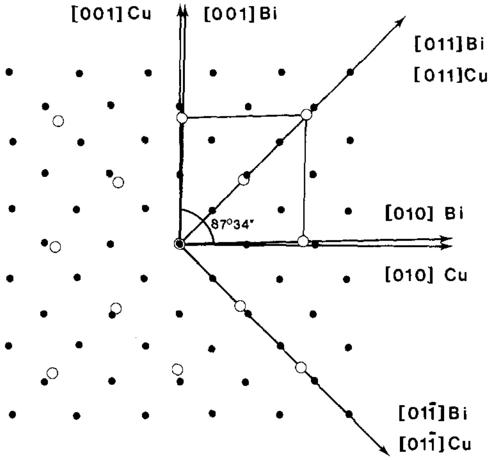

Figure 8 Positions of the bismuth atoms of the (1 0 0) plane superimposed on the atoms of the (1 0 0) plane of the substrate face: ○ Bi; ● Cu.

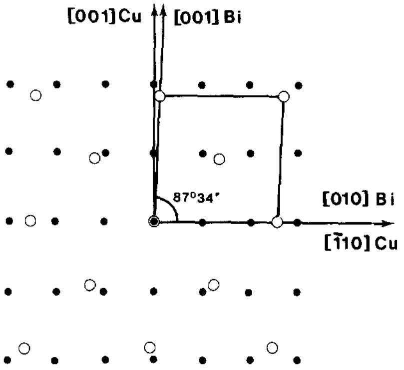

Figure 9 Positions of the bismuth atoms of the (1 0 0) plane superimposed on the atoms of the (1 1 0) plane of the substrate face: ○ Bi; ● Cu.

Comparison between antimony and bismuth electrodeposits show that the former has a stronger tendency towards the disorientation and the formation of amorphous metal. As the calculations by Pangarov [9] show, the work of formation of two-dimensional nuclei orientated along various crystallographic planes depends on the electrodeposition overvoltage; furthermore, for metals which are intermediate in the kinetic-electrochemical sense, such as antimony and bismuth, the work of nucleation is the least for the (1 0 0) plane. However, when overvoltage increases, the work of nucleation tends to become the least for (1 1 0). Since antimony [11] is characterized in electrodeposition by a kinetics of ion exchange slower than that of bismuth [12] and, therefore, by a higher overvoltage at the same c.d., one may understand why antimony deposits show the (1 1 0) plane parallel to the substrate, while this orientation is never observed for bismuth deposits.

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*For this substrate only the distribution corresponding to the ($\bar{1}$ 1 0) plane of antimony parallel to the substrate has been reported; indeed the situation when the (1 1 0) plane is parallel to the substrate is closely similar.

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Received 31 May and accepted 18 September 1978.