DISCUSSION

D.H. DONNAY: You seem to imply that twinning in (112) is common in body-centred tetragonal lattice. In order to get a row quasi-perpendicular to (112) the value of c/a should be critical.

A.L. MACKAY: The appropriate pseudo-cell is really cubic with $a'=3.47$ and $c=3.03$Å and hence closely recalls the situation in Mo and W.

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Structure of Thin Layers of Some F.C.C. Metals Deposited on Oriented Ag, Pd and Ni Films

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Some f.c.c. metals—Ni, Cu, Pd, Al, Au, Ag and Pb—were evaporated *in vacuo* on to oriented Ag, Pd and Ni films and the structure of these films were studied by the transmission method of electon diffraction. Some films were composed of intermetallic compounds of deposit and substrate metals. But some films were composed of two layers of deposit and substrate metals. In the latter case, the deposit metals grew in an oriented overgrowth on a substrate at a temperature higher than an epitaxial temperature. Two kinds of oriented overgrowth were observed and their occurrence depended on the percentage misfit.

1. Introduction

So far cleavage surfaces of some minerals or salts[1] have often been used as the substrates on which oriented overgrowths of some materials from the vapour phase were formed. But there are only a few investigations of the oriented overgrowth of metals deposited on the surface of metallic single crystal[2]. In order to obtain some informations concerning the mechanism of epitaxy, it seems to be very desirable to make further systematic studies on metal layers deposited on single crystal metal surfaces. In the present paper, an investigations will be described in which some f. c. c. metals–Ni, Cu, Pd, Al, Au, Ag and Pb–were deposited from the vapour *in vacuo* on to oriented Ag, Pd and Ni films and the structure of these films were examined by the transmission method of electron diffraction. Some films were composed of intermetallic compounds of deposit and substrate metals. But some films were composed of two layers of deposit and substrate metals. In the latter case the deposit metals grew in an oriented overgrowth on a substrate at a temperature higher than an epitaxial temperature. Two kinds of oriented overgrowth were observed. The occurrence of these kinds of oriented overgrowth depended mainly on the percentage misfit.

2. Experimental method

Oriented metal films about 40 mμ in thickness were deposited *in vacuo* on the cleavage surfaces of NaCl crystal heated to about 200°C (for Ag) or about 400°C (for Pd and Ni). After the dissolution of NaCl crystal in water, the oriented metal film was caught on a hole 0.1 mm in diameter perforated in a thin Ni plate. After it was ascertained by the method of electron diffraction that the metal film was a quasi-single crystal film having the (001) plane parallel to the film surface and the {111} twinning was comparatively less marked, it

was used as a substrate.

Ni, Cu, Pd, Al, Au, Ag and Pd metals generally about 30 mμ in thickness were evaporated *in vacuo* on to the oriented Ag, Pd or Ni films. When an oriented Ag or Pd film was used as a substrate, this was maintained at −196°C or temperatures ranging at an interval of 100°C between −100°C and 400°C during the evaporation of samples. When an oriented Ni film was used as a substrate, it was maintained at temperatures ranging at an interval of 100°C between 0°C and 400°C. A definite quantity of sample put in a small coil furnace made of tungsten wire 0.2 mm in diameter was evaporated by supplying a heating current 4.5 Å for 5 sec. The distance between the tungsten coil furnace and the substrate was about 3.5 cm.

In general, the pressure of residual gas was $5 \times 10^{-5} \sim 5 \times 10^{-6}$ mmHg before the sample was evaporated, and it became 5×10^{-4} mmHg or more after the evaporation was completed. The structure of bimetal film about 70 mμ in thickness prepared in this way, was examined by the transmission method of electrons of an accelerating potential about 40 kv.

3. Experimental results

The films are classified in the following two groups from the view point of their structure: (I) The films are composed of intermetallic compounds of deposit and substrate metals. (II) The films are composed of deposit and substrate metals.

(I) Al on Ag, Cu on Pd (in this case the substrate temperature was 400°C); Al on Pd; Pb on Pd and Al on Ni. The pairs of deposit and substrate metals belonging to this group are able to be alloyed in intermetallic compounds. The components of films as a function of substrate temperature t_b°C are summarized in Table I. In some films, crystallites of intermetallic compounds had certain orientations with respect to the substrate crystal. As an example in this case, a diffraction pattern due to an Al on Ag bimetal film is shown in Fig. 1. But in

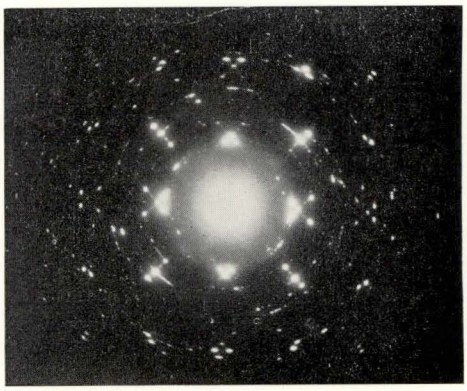

Fig. 1. Al on Ag. t_b=400°C.

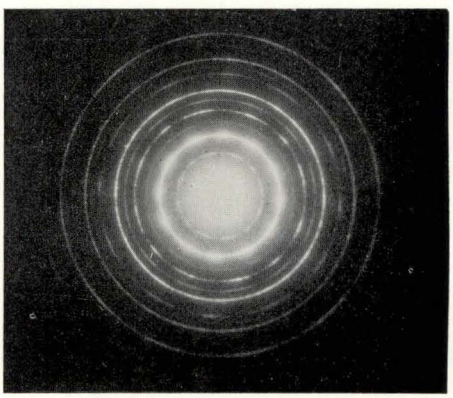

Fig. 2. Cu on Pd. t_b=400°C.

Table I. The components of films as a function of the substrate temperature t_b°C.

t_b°C	−196	−100	0	100	200	300	400
Al on Ag	Al	Ag_2Al	Ag_2Al	Ag_2Al	Ag_2Al	Ag_2Al Ag_3Al	Ag_2Al
Cu on Pb							CuPd
Al on Pd	Al	Al	Al	Al Pd_2Al_3	Al Pd_2Al_3	Pd_2Al_3	Ad_2Al_3
Pb on Pd	Pb_2Pd	Pb_2Pd	Pb_2Pb_3	Pb_2Pd_3 $PbPd_3$	Pb_2Pd_3 $PbPd_3$	$PbPd_3$	
Al on Ni			Al	Al	Al	AlNi Al_3Ni_2	AlNi Al_3Ni_2

Table II.

a \ b	Ag				Pd				Ni			
	m %	m' %	t_{ep} °C	Or	m %	m' %	t_{ep} °C	Or	m %	m' %	t_{ep} °C	Or
Ni	−13.8	−25.4	100	□	−9.4	−21.5	100	□	0	−13.4	300	□
Cu	−11.5	−23.4	0	□	−7.1	−19.5	−100	□*	2.6	−11.1	200**	□
Pd	− 4.8	−17.6	<−196	□	0	−13.4	100	□	10.4	− 4.4	300	□
Al	− 0.9	−14.2			4.1	− 9.8			14.9	− 0.5		
Au	− 0.02	−13.4	−100	□	4.9	− 9.2	−100	□	15.7	0.2	300	⧄
Ag	0	−13.4	<−196	□	5.0	− 9.1	−100	□	16.0	0.5	300	⧄
Pb	21.1	4.9	−100	△	27.3	10.2			40.5	21.7		

a : deposit metal
b : substrate metal
m % : percentage misfit for the parallel overgrowth
m' %: a percentage multiple misfit for the (111) oriented overgrowth on the (001) surface of substrate
t_{ep}°C : epitaxial temperature
Or : orientation
□ : $(001)_a \,||\, (001)_b$ and $[100]_a \,||\, [100]_b$
△ : $(111)_a \,||\, (001)_b$ and $[\bar{1}10]_a \,||\, [110]_b$ or $[\bar{1}10]_b$
⧄ : □ and △ occur simultaneously.
* : random orientation of CuPd in the ordered state at t_b=400°C
** : Weak D.S. rings due to deposit metal also appeared at a substrate temperature higher than t_{ep}°C.

some films, intermetallic compound crystal lites were randomly oriented. As an example in this case, a diffraction pattern due to a Cu-Pd bimetal film is shown in Fig. 2.

(II) Ni on Ag; Cu on Ag; Pd on Ag; Au on Ag; Ag on Ag; Pb on Ag; Ni on Pd; Cu on Pd (in the case where the substrate temperature was lower than 300°C); Pd on Pd; Au on Pd; Ag on Pd, Ni on Ni; Cu on Ni; Pd on Ni; Au on Ni and Ag on Ni. The pairs of deposit and substrate combinations belonging to the group (II) are able to form solid solutions over limited or whole ranges of solution[3]. The results in this case are summarized in Table II. The epitaxial temperature for each combination belonging to the gorup II is shown in the 4th, 8th and 12th columns in Table II. The orientation of crystallites in a deposit layer obtained at a substrate temperature higher than the epitaxial temperature is shown in the 5th, 9th and 13th columns.

Two kinds of oriented overgrowth were observed. One kind was such that the orientation of crystallites in a deposit layer was $(001)_a||(001)_b$ and $[100]_a||[100]_b$. This parallel overgrowth is quoted hereafter as the (001) orientation. As an example of this

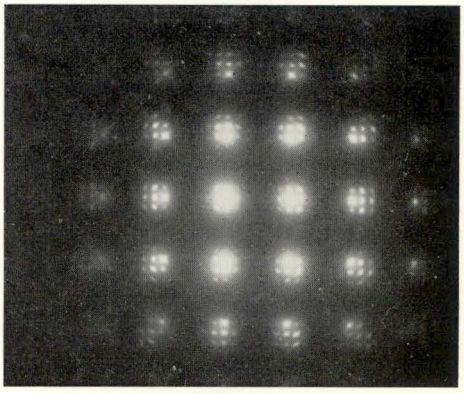

Fig. 3. Ni on Ag. t_b=400°C.

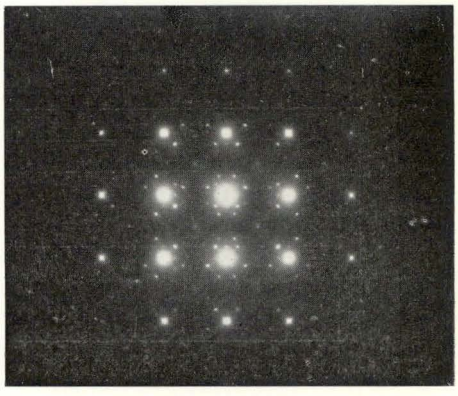

Fig. 4. Pb on Ag. t_b=200°C.

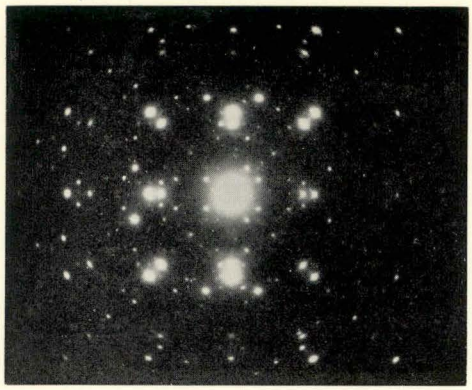

Fig. 5. Ag on Ni. t_b=400°C.

case, a diffraction pattern due to a Ni-Ag bimetal film is shown in Fig. 3. The other kind of oriented overgrowth was such that the orientation of crystallites in a deposit layer was $(111)_a||(001)_b$ and $[\bar{1}10]_a||[110]_b$ or $[\bar{1}10]_b$. This oriented overgrowth is quoted hereafter as the (111) orientation. As an example of this case, a diffraction pattern due to a Pb-Ag bimetal film is shown in Fig. 4. In the cases of Ag on Ni and Au on Ni, both the (001) and (111) orientations occurred simultaneously in the deposit layer (Fig. 5). In the case of Pb on Ni, diffraction pattern which was perfect enough to be analysed was not obtained.

4. The (001) and (111) orientations and the percentage misfits

It is assumed that the surface of the substrate is the (001) plane, and the kind of oriented overgrowth *versus* percentage misfits is plotted in Fig. 6. One of two percentage misfits in two orthogonal directions for the (111) oriented overgrowth on the (001) surface of substrate is equal to the percentage misfit $m\%$ for the parallel over-

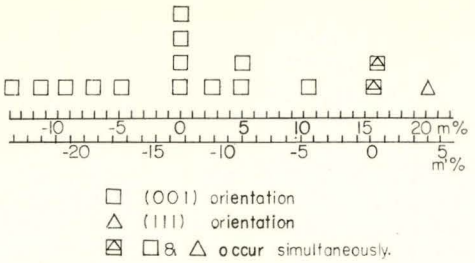

Fig. 6.

growth on the (001) surface of substrate. The other misfit $m'\%$ (a multiple misfit) is equal to $(0.866m - 13.4)\%$. $m'\%$ is tabulated in the 3rd, 7th and 11th columns in Table II. It will be seen from Fig. 6 that the (001) orientation occurs when $m\%$ is smaller than about 16%, and the (111) orientation occurs for low values of $m'\%$.

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DISCUSSION

M. BLACKMAN: How long the specimen is kept at a given temperature before it is concluded that there is no alloying? We have for instance found that tin on silver at room temperature gives the tin pattern if examined immediately; if the specimen is kept for twenty hours, there is definite sign of alloying.

S. SHIRAI: The film was warmed or cooled to the room temperature promptly after it was evaporated onto the substrate and kept at the room temperature for about 5 hours.

L. L. MARTON: On this occassion, I should like to add another example of the application of electron diffaction recently obtained in my laboratory. Dr. E. Hoerl has

just concluded a study of the structure and imperfections of solid β-oxygen, using electron diffraction techniques. The structure of β-oxygen was investigated and a rhombohedral structure was found. Its hexagonal cell has the dimensions $a=3.307\pm0.008$ Å, $c=11.256\pm0.015$ Å and contains three molecules parallel to the hexagonal axis at the positions: (1/3,1/3,0), (—1/3,0,1/3) and (0,-1/3,2/3). Faults in the stacking sequence of the (001) layers were observed with the Paterson treatment of growth faults in f. c. c. crystals.