

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 $c=3.03\text{\AA}$ 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 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 and their occurrence depended on the percentage misfit.

1. Introduction

So far cleavage surfaces of some minerals or salts¹⁾ 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 crystal²⁾. 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 $40\text{ m}\mu$ 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 $30\text{ m}\mu$ 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 A 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 $5 \times 10^{-5} \sim 5 \times 10^{-6}\text{ mmHg}$ before the sample was evaporated, and it became $5 \times 10^{-4}\text{ mmHg}$ or more after the evaporation was completed. The structure of bimetal film about $70\text{ m}\mu$ 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 $t_b^\circ\text{C}$ 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

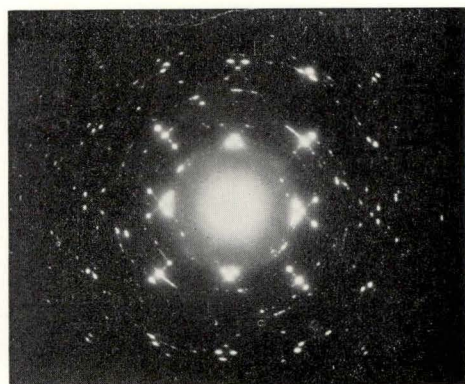


Fig. 1. Al on Ag. $t_b=400^\circ\text{C}$.

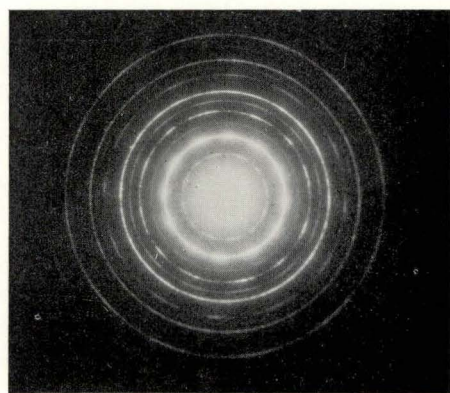


Fig. 2. Cu on Pd. $t_b=400^\circ\text{C}$.

Table I. The components of films as a function of the substrate temperature $t_b^\circ\text{C}$.

$t_b^\circ\text{C}$	-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	Al_2Pd_3
Pb on Pd	Pb_2Pd	Pb_2Pd	Pb_2Pd_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.

$\begin{matrix} b \\ a \end{matrix}$	Ag				Pd				Ni			
	$m\%$	$m'\%$	$t_{ep}^{\circ}\text{C}$	Or	$m\%$	$m'\%$	$t_{ep}^{\circ}\text{C}$	Or	$m\%$	$m'\%$	$t_{ep}^{\circ}\text{C}$	Or
Ni	-13.8	-25.4	100	$\square$	-9.4	-21.5	100	$\square$	0	-13.4	300	$\square$
Cu	-11.5	-23.4	0	$\square$	-7.1	-19.5	-100	$\square^*$	2.6	-11.1	200**	$\square$
Pd	-4.8	-17.6	< -196	$\square$	0	-13.4	100	$\square$	10.4	-4.4	300	$\square$
Al	-0.9	-14.2			4.1	-9.8			14.9	-0.5		
Au	-0.02	-13.4	-100	$\square$	4.9	-9.2	-100	$\square$	15.7	0.2	300	$\triangle$
Ag	0	-13.4	< -196	$\square$	5.0	-9.1	-100	$\square$	16.0	0.5	300	$\triangle$
Pb	21.1	4.9	-100	$\triangle$	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 $t_{ep}^{\circ}\text{C}$: epitaxial temperature

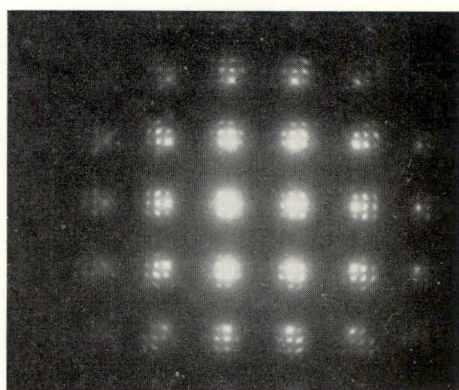
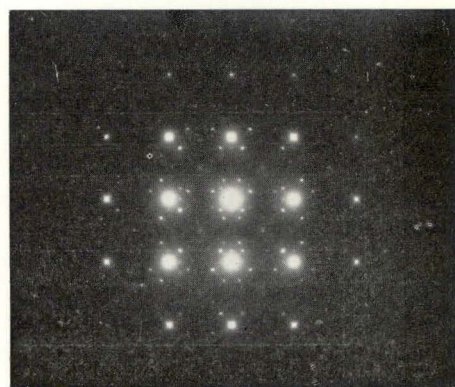
Or : orientation

 $\square$: $(001)_a || (001)_b$ and $[100]_a || [100]_b$ $\triangle$: $(111)_a || (001)_b$ and $[\bar{1}10]_a || [110]_b$ or $[\bar{1}10]_b$ $\triangle$: $\square$ and $\triangle$ occur simultaneously.* : random orientation of CuPd in the ordered state at $t_b=400^{\circ}\text{C}$ ** : Weak D.S. rings due to deposit metal also appeared at a substrate temperature higher than $t_{ep}^{\circ}\text{C}$.

some films, intermetallic compound crystallites 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 solution³⁾. The results in this case are summarized in Table II. The epitaxial temperature for each combination belonging to the group 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. $t_b=400^{\circ}\text{C}$.Fig. 4. Pb on Ag. $t_b=200^{\circ}\text{C}$.

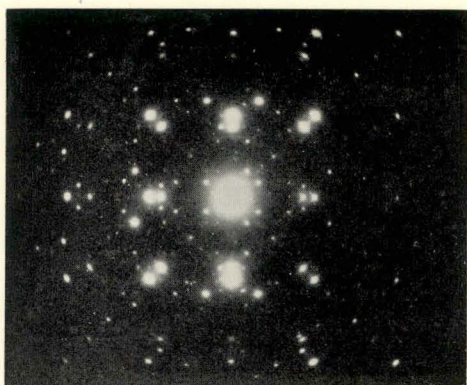


Fig. 5. Ag on Ni. $t_b=400^\circ\text{C}$.

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-

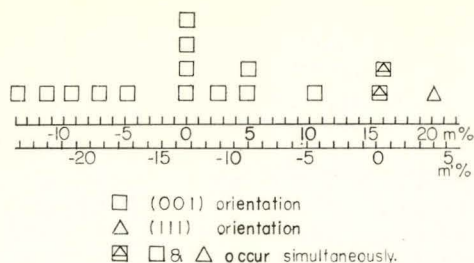


Fig. 6.

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 occasion, I should like to add another example of the application of electron diffraction 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.

Recent Progress in Neutron Diffraction

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Some of the recent advances in neutron diffraction techniques over the past five years are discussed, followed by an account of recent studies in neutron crystallography as illustrated on both magnetic and molecular structures.

Quite apart from their eventual development for recording complete diffraction patterns, these methods are now extremely useful and simple for testing beam shapes and intensities in the process of setting up spectrometers. The urge to get the most efficient use out of expensive high-flux reactors has led to a number of schemes which employ more than one spectrometer on a single reactor hole, using separate monochromating crystals, either in series or parallel, to serve, for example, both a single crystal and a powder instrument. Several careful studies of collimator and crystal holder designs (e.g. by S. S. Shull, J. Willis) have been made to arrive at the best possible compromise for any particular purpose—among the various experimental parameters. Where single crystals only are used it is useful to secure improved resolution at higher θ values by displacing the parallel focusing position in this direction by choosing a larger Bragg angle at the monochromator. On the other hand, when weak magnetic reflections are being sought at small angles, it can be preferable to retain a large interplanar spacing for the monochromator. The latter remains a not very satisfactory link in the chain from reactor to detector and it would be of great advantage if crystals in a wide range of spacings and with some choice of values of mosaic spread could be available to the experimenter. As a typical example of the improvement which can be made using the higher neutron flux we cite the combination of our work (Bacon and Street) on antiferromagnetic gold-manganese alloys close to the composi-

The past five years have seen considerable progress in the development of techniques for neutron diffraction studies, with the two-fold aim of increasing the speed and accuracy of data collection and of widening the range of materials which can be studied. Of prime importance has been the commissioning in many laboratories of reactors with a higher neutron flux, measured in units of 10^{16} neutrons per cm in the place of 10^5 . Advantage has been taken of the increased intensities of the neutron beams both for the study of polycrystalline samples and of single crystals, either to provide improved angular resolution or to reduce the size of crystal needed for an adequate examination. When the latter course has been followed it has become possible to use roughly equidimensional crystals, measuring a millimetre or two in each direction, leading directly to the opportunity of using 3-dimensional methods of Fourier synthesis in place of the previous virtual restriction to planar projections. A number of systems for automatic programming of single-crystal spectrometers have been designed and are being brought into operation. The attractive possibilities which have been shown to exist when polarised beams of neutrons are used are also now being pursued in several countries.

In spite of its cumbersome size the BF₃ counter remains in almost universal use for crystallographic studies, though its limitations, particularly at the earlier survey stages of an investigation, are increasingly realised. Advances in photographic techniques have been reported from several laboratories in the U.S.A. and are to be greatly encouraged.