In-Situ Studies of Epitaxial Thin-Film Growth

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Early stages of oriented overgrowth of Ag, Au, and Pd on thin, single-crystal substrates of mica, molybdenite, Au and Pd were studied by high-resolution electron microscopy and diffraction. Cleaning of substrate surfaces and deposition of evaporated materials were conducted inside an electron microscope. High-magnification, continuous observation during growth permitted investigation of the kinetics of growth. A number of probably elementary epitaxial processes were studied in detail. Nucleation and growth behavior was examined for different supersaturations and free surface energies of substrate and overgrowth materials. The influence of alloying on growth and the spacing of parallel moiré structures was investigated.

The field of oriented overgrowth of a crystalline material on a crystalline substrate is of interest to various disciplines of science and technology. Although much experimental and theoretical work has beeen done since the early epitaxy experiments of Frankenheim [1], Royer [2], and Bruck [3], it is generally realized that no adequate quantitative theory of epitaxy yet exists. The state of the art therefore relies almost entirely upon empirical evidence whenever epitaxial concepts have to be employed for various applications.

Pashley [4] and Raether [5], reviewed the field of thin film epitaxy. Pashley attributed the failure to develop a practicable epitaxial theory primarily to the lack of knowledge of nucleation and growth mechanisms during the initial stages of overgrowth.

Since 1956, certain investigators (e. g. Bassett et al. [6], Newman [7], Göttsche [8], Haase [9]) have succeeded in collecting additional experimental information about the early stages of epitaxial thin film growth. Very significant results were obtained by in-situ electron diffraction experiments on layers that can be grown by evaporation in vacuum. The outstanding advantages of this technique are (1) high sensitivity in detection of minute quantities of deposits; and (2) capacity to investigate, for the first time in-situ, the kinetics of growth on an averaging basis. However, the information obtained by this technique on morphological and fine structural details of the deposits has been scarce.

Advanced replication and transmission electron-microscopy techniques (e. g. Bassett et al. [10], Matthews [11]) are clearly superior for this purpose although cognizance must be taken of replicating artifacts (Jacobs et al. [12]), or structural changes during transfer to the microscope, if the microscopy specimens are prepared outside the microscope vacuum. In order to prevent artifacts, and to follow morphological and structural changes by high-resolution microscopy and transmission electron diffraction, the growth experiments have to be conducted inside the electron microscope during observation at high magnifications. Bassett [13], was the first to employ this method in studying in-situ the growth of silver on molybdenite. Recently a similar but somewhat more sophisticated apparatus was used, and the procedure for in-situ growth studies was described in detail (Poppa [14]).

The potential advantages of high-resolution, in-situ studies of epitaxial thin-film growth on single-crystal, thin-film substrates are obvious. However, the complex nature of the experimental procedures

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[2] L. Royer, Bull. Soc. Franc. Mineral **51**, 7 [1928].
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[8] H. Göttsche, Z. Naturforschg. **11 a**, 55 [1956].
[9] O. Haase, Z. Naturforschg. **11 a**, 862 [1956].
[10] G. A. Bassett and D. W. Pashley, J. Inst. Met. **87**, 449 [1958].
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[12] M. H. Jacobs et al., Proc. 5th Int. Conf. El. Micro., Philadelphia 1962, DD-4.
[13] G. A. Bassett, Proc. Europ. Conf. El. Micr., Delft 1960, p. 270.
[14] H. Poppa, Phil. Mag. **7**, 1013 [1962]; Proc. 5th Int. Conf. El. Micro., Philadelphia, GG-14; Trans. 9th Nat. Vac. Symp., Los Angeles, p. 20.

limits the applicability of the method. In view of the probable interest to be aroused by any solution of various epitaxy problems, the limitations must be emphasized when discussing the results of this work. The most stringent restrictions are imposed by the relatively high background pressure, 1×10^{-5} Torr, of the microscope vacuum system. This factor influences not only the nucleation characteristics of substrate surfaces in general, but introduces specific contaminating reactions, known to electron microscopists, of the imaging electron beam with residual gas molecules. Although contamination by the electron beam can be drastically minimized it cannot be eliminated. The most convenient and appropriate way to reduce the beam influence during epitaxy experiments is by heating the substrate, but this severely limits the variability of important growth parameters like substrate temperature and condensation rates, and it does not eliminate the always present concern about negative ion or electron radiation damage.

Despite these experimental limitations, which appreciably restrict the scope of epitaxy studies by in-situ electron microscopy, a number of substrate overgrowth combinations were investigated. If the inherent limitations of this technique are kept in mind, the information obtained will contribute to an understanding of fundamental epitaxial processes. When it becomes possible to improve considerably the vacuum conditions at the site of the electron-microscope specimen, the importance of in-situ growth studies will greatly increase. Most of the present difficulties in the technique would then be eliminated.

Experimental

A detailed account of the experimental techniques employed for in-situ studies of thin-film growth by high-resolution electron microscopy was published recently [14], and therefore only a description of the general procedure is necessary here. Deviations from it are mentioned when they become necessary in the course of individual growth experiments.

Electron-transparent- single-crystal, thin-film substrate specimens that had been prepared either by cleavage of layer-structured minerals or by vacuum evaporation onto heated bulk substrate materials (e. g. MAYER [15]) were mounted on titanium, or platinum, electron-microscope specimen grids. By employing a modified HITACHI HU-11 airlock-type heating stage, and a PENNING-type ion gun attached to the windows of the specimen exchange chamber of the HU-11, the thin-film specimen was bombarded with 500 – 800 eV argon ions prior to placing it in the microscopy position. Ion bombardment of the thin-film substrate was used to thin the specimen (if the sputtering yield of the film material was suitable) and to clean its surface (FARNSWORTH [16]). Usually the specimen was then heated to about 300 – 400 °C, and after thermal stabilization was reached and a substrate area of interest was selected, the deposition of overgrowth material was started. A one-loop tungsten filament, plated with the evaporant and contained in a special platinum specimen holder, served as evaporation source. The tungsten filament was shielded and arranged so that no vital parts of the microscope could be contaminated by the evaporating material.

During growth the microscope was usually operated at 40 000 X magnification. The image or diffraction pattern was recorded either by a 16 mm motion-picture camera located outside the microscope or by high-resolution series micrographs using the built-in plate camera of the HU-11, which provides 36 exposures. The growth rate had to be kept low because of insufficient image brightness at high magnifications. For series micrographs showing successive stages of film growth the condensation rates were generally of the order of 20 – 60 Å /min, whereas growth rates up to 500 Å/min were used for lower resolution motion pictures.

The Growth of Silver on Hexagonal or Pseudo-Hexagonal Layer Structures

Silver on mica

It has long been known (RÜDIGER [17]) that oriented silver deposits can be obtained by evaporation onto heated mica substrates. The epitaxial orientation is usually (111) silver parallel to (0001) mica and [110] silver parallel to [1200] mica; the related twin orientation also occurs occasionally. BASSETT et

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[17] O. RÜDIGER, Ann. Phys., Lpz. **30**, 505 [1937].

al.[6] determined the conditions under which smooth and excellent single-crystal films of silver can be produced on mica. MATTHEWS[11] examined epitaxial silver films on electron-transparent mica substrates in great detail by using the diffraction contrast (WHELAN et al.[18]) and moiré techniques (e. g. GEVERS[19]). His specimens were, however, prepared in a separate vacuum system, which made it impossible to study the kinetics of growth and nucleation. In-situ experiments were therefore conducted with this combination of materials under varying conditions of supersaturation.

According to theory (TURNBULL[20], VOLLMER[21], Bauer[22 a, b]) the nucleation probability W is given by an expression of the form

$$W = C \exp \{ - A_k/kT \}$$

where A_k is the nucleation energy, and A_k and the factor C are dependent upon supersaturation, free surface energy of nucleus, substrate and nucleus-substrate interface and free energies of surface diffusion and adsorption. For decreasing substrate temperatures the influence of supersaturation – which is determined mainly by evaporation rate and substrate temperature – becomes more and more pronounced and overrides in particular the orientation dependent effect of the interfacial free energy. One can therefore expect many small and less well oriented nuclei if film growth thakes place at lower substrate temperatures.

This is demonstrated in Fig. 1 *, which shows 3 out of 10 stages of growth at a substrate temperature of $T = 300°$. The small and thick nuclei appear first and the relatively large substrate area between the nuclei is filled in later. Differences in image contrast show that the filled in areas are considerably thinner than the original small nuclei and tend to develop defined crystallographic forms. In later growth stages the differences in image contrast decrease and the large silver islands merge to form a continuous film.

A somewhat surprising result of the combination silver-mica was the relatively rare appearance of 37 Å parallel moirés formed by epitaxial superposition of silver crystallites on mica substrates. These moirés were found only in about 10 percent of the overgrowth crystallites. It ist not known whether MATTHEWS[23], experienced similar difficulties, but the growth conditions he used were probably different with reference to the rate of deposition. According to the dynamical theory of moiré fringe patterns (GEVERS[19]), the contrast of moiré fringes is a sensitive function of superimposed-layer thickness and small local deformations in the composite foil. Series micrographs like Fig. 1 demonstrated this dependence qualitatively and thus provided a possible explanation for the rather rare occurrence of parallel moirés at certain growth stages.

At higher substrate temperatures the nucleation probability is lower. Fig. 2 a depicts one out of 12 less magnified series micrographs of silver growth on mica at lower supersaturations ($T = 450$ °C). There are fewer larger and much thicker crystallites, which are opaque almost from the time they are initially distinguished on the microscope screen. The thickness of silver crystallites precludes the observation of parallel silver-mica moirés. (The moiré pattern in the corner of the micrograph is a much wider-spaced mica rotation moiré.) Nevertheless a number of significant observations can be derived from micrographs of this kind.

First, evidence exists of some preferred nucleation along a cleavage step on the mica substrate that runs diagonally through the picture. It is then obvious that in many instances the crystallites show well-developed crystallographic shapes that are useful in judging rotational misalignments of the crystallites with reference to the mica substrate.

With the help of the selected area diffraction pattern, which is purely single crystalline, the ⟨110⟩ silver directions or the ⟨1200⟩ mica directions in the basal plane can be projected into the micrograph, and the alignment of the ⟨110⟩ crystallite edges relative to the substrate can be judged. It can be seen that the coincidence of directions is not very satisfying. With silver on MoS_2, which will be discussed later, the alignment is much better.

In this connection the questions arise as to how the edges of crystallites form (so that this can be used as a measure for rotational alignment), and why some crystallites have completely irregular

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* Figs. 1 – 16 see Table p. 840 a – d.
[23] J. W. MATTHEWS, Proc. Europ. Conf. El. Micro., Delft 1960, p. 276.

shapes. The answers can be found by comparing successive stages of growth. A way of accomplishing this is to compare Fig. 2 a, picture by picture, with other micrographs of the same series (POPPA [14]). But this is a tedious process. A more convenient method of evaluating series micrographs is demonstrated in Fig. 2b. For this picture only the outlines of the silver crystallites were reproduced by the photographic technique of acquidensitometry (KRUG [24]), and copies of three different growth stages so obtained were superimposed. It could then be readily seen, for example, that many silver crystallites grow faster in certain preferred directions of the substrate and that well-developed crystallites lose their shape when coalescing with others. The latter phenomenon was reported by PASHLEY [4] for the growth of silver on molybdenite, and can be observed on normal series micrographs. The changes in silver-covered substrate areas during coalescence, and the growth of crystallites as a function of preferred direction, however, were followed more clearly on combined micrographs like Fig. 2 b.

Motion-picture observations, which included higher rates of growth, supported the previous results, but this voluminous source of data on kinetic details of growth cannot be presented conveniently in publications. Of particular interest in this connection is the phenomenon of mass transfer shortly before, and during, the merger period of two overgrowth crystallites. Here the so-called "bridging effect" should be described. This was first observed during the growth of silver on amorphous carbon substrates and represents the formation of small, interconnecting bridges between islands before merger. From sometimes vivid contract fluctuations within the two participating islands and small changes in shape, it is deduced that a mass transfer precedes the actual merger. During coalescence itself the combined mass of the participants is distributed over a larger substrate area before contraction to a smaller and more opaque island takes place. An over-all picture of liquid-like behavior of the overgrowing material is forcibly impressed upon the observer.

Detailed observations of coalescence processes are scarce because of the speed of these processes contrasted to the time-resolution capabilities of the motion-picture technique. Much more sensitive and faster recording methods with good spatial resolution are needed before further progress can be made. This will be accomplished eventually by the use of an image intensifier or a vacuum motion-picture camera.

Silver on Molybdenite (MoS_2)

BASSETT's original in-situ growth studies (BASSETT [25]) were performed with this combination of materials. The epitaxial orientation is {111} silver parallel to (0001) molybdenite and ⟨110⟩ silver parallel to the ⟨1100⟩ basal plane directions of molybdenite. For reasons not fully understood, but probably attributable to quite different interfacial energies, the combination silver-MoS_2 is much better suited for in-situ transmission microscopy than the pair silver-mica. This is due to three-dimensional silver overgrowth crystallites on MoS_2 being much thinner and thus more electron-transparent than for mica substrates.

Fig. 3 is similar in character to Fig. 2 a but here 4 out of 28 stages of growth are shown to mediate a picture of the growth process in general at a substrate temperature of $T = 450$ °C. In contrast to Fig. 2 a a large amount of internal structure can be seen in individual nuclei, and it ist obvious that the ⟨110⟩ edges of the growing crystallites are much better aligned with the ⟨1100⟩ basal plane directions of the MoS_2 substrate than in the mica case.

NEWMAN [7] found that during the growth of Ni, Au, and Cu on silver substrates the number of nuclei increased constantly. This result could not be verified. As long as the evaporation rate was kept constant the number of silver nuclei did not increase; instead the individual nuclei grew in size. Each time the evaporation rate was increased, however, new and smaller crystallites appeared (Fig. 4) and grew from then on until the number of crystallites was decreased by merger processes during later stages of growth.

Of continuing interest is the development of internal structures of growing nuclei. Some of these structures are twins or stacking faults; the nature of others is not yet fully understood (BASSETT et al. [10]; PASHLEY et al. [4]). These internal structures are often held partially responsible for the high concentration of lattice defects in thin films grown by evaporation. High-resolution sequential photography can shed

[24] W. KRUG and E. LAU, Feingerätetech. **9**, 1 [1952].

[25] G. A. BASSETT, Prgc. Europ. Conf. El. Micro., Delft 1960, p. 270.

some light on this matter. Fig. 5 shows three silver nuclei before and after coalescence. A lattice defect is introduced at the merging line. Similar structures have also been found to develop in isolated growing crystallites. Occasionally these structures disappear again when the growth proceeds, and sometimes a smaller nucleus is absorbed by a larger one without leaving a trace of the merger.

Two more interesting elementary growth processes that were mentioned before are presented in the next micrograph (Fig. 6). First can be seen the loss of shape in the participating crystallites during coalescence and the regaining of it during later growth stages. In addition it will be noted that after each merger the original crystallites may still be distinguished. This phenomenon can be followed through many growth stages. The phenomenon of "recollection" of previous overgrowth forms is unusual because of the rather violent contrast fluctuations in the composite crystallite during merger which indicate a very high mobility of the silver overgrowth. Differences in image contrast after merger show, however, that the composite crystal is thicker at the former location of the original crystallites. Therefore the assumption is made that the area between the original crystallites can be filled in during coalescence without eliminating all differences in thickness of the composite crystal.

Moiré patterns produced by the superposition of substrate and overgrowth lattices are useful for investigating epitaxial phenomena on an almost atomic scale. Both BASSETT and MATTHEWS have used this technique successfully to detect very small orientational misalignments of silver nuclei on molybdenite and mica substrates. The spacing of the normal silver-molybdenite parallel moiré is 17 Å, and the moiré is of the $(220)_{Ag} - (1120)_{MoS_2}$ type (BASSETT [13]). In the diffraction pattern (Fig. 7) the six double reflexions surrounding the (1010) reflexions are of this (220) type. Their distance from the (1010) spot corresponds to the 17 Å spacing, and their directions determine the ⟨211⟩ directions of the moiré fringes.

In addition three other types of weak reflexions can be clearly distinguished in the diffraction pattern. The set of (422) type double reflexions can best be seen surrounding the central spot; the corresponding moiré spacing is 8.5 Å and cannot be resolved in the micrographs. The other two additional reflexions were tentatively identified as (311 + 220) type and (331 + 220) type triple reflexions. The corresponding moiré spacings are 24 Å for the (311 + 220) type and 28 Å for the (331 + 220) type, and the moiré directions should be ⟨211⟩ and ⟨110⟩, respectively. These new moirés have been found in a fraction of silver crystallites on MoS_2 (Fig. 8). The agreement of moiré directions and spacings with those deduced from the diffraction pattern is good except for sometimes small deviations of the (331 + 220) moiré directions. These deviations have not yet been explained.

If the above interpretations prove correct, then consideration can be given to the fact that both wider-spaced moiré types involve (311) and (331) reflexions and that these moirés can be found only in a fraction of the overgrowing crystallites. The (311) and (331) reflexions are not being excited in a pure {111} orientation of silver. The chance of these reflexions being excited is, however, much greater in a {111} twin orientation. The new moirés might therefore be an indication of double positioning in some silver crystallites.

The Growth of Metals on Single-Crystal Metal Substrates

Single-crystal metal films lend themselves as thin substrate materials for in-situ growth studies for the following reasons: (1) the structure of electron-transparent thin-metal layers has been studied extensively by transmission electron microscopy using both diffraction contrast and moiré techniques (e. g. THOMAS [26]); (2) many well-developed preparation methods are known to produce excellent thin-metal films for electron-microscopy purposes (electrolytic polishing, evaporation, vapor decomposition); (3) large-area, uniform, single-crystal metall films can be obtained easily in different orientations by evaporation onto various single-rcystal substrate materials (MAYER [15]; PASHLEY [27]); (4) the usually high sputtering yield of metals makes possible the preparation of continuous and highly electron-transparent metal substrates inside the microscope by low-energy ion bombardment of relatively thick films, thus providing cleaned, high-resolution substrates for epitaxial studies (POPPA [14]); and (5) some quantitative data

[26] G. THOMAS, Transm. El. Micro. Metals, Wiley 1962.

[27] D. W. PASHLEY, Phil. Mag. 4, 316 [1959].

exist for a number of metals on free surface energy values, which are of interest in various aspects of epitaxial theories.

The following sections present examples of the growth of metals on metals and deal only with combinations of noble metals. The use of such combinations minimized the chances of additional complications of epitaxial problems by chemical reactions of the metals with residual gas molecules.

Silver on {111}-Platinum

Earlier epitaxy theories often postulated that the first layers of condensing materials nucleate and grow in a two-dimensional manner. Today it is well known that this occurs only in specific cases and is by no means a generally valuable concept of epitaxial growth. BAUER [22b], investigated questions of this nature more thoroughly on a thermodynamic-phenomenological basis. According to the results, two-dimensional nucleation or two-dimensional layer growth in the very early growth stages is only possible if

$$\sigma_s \geqq \sigma + \sigma_I$$

(σ_s = specific free substrate surface energy, σ = specific free surface energy of the overgrowth material, and σ_I = specific free energy of the interface overgrowth-substrate).

Since the free surface energies of silver and platinum are 960 erg/cm² and 1800 erg/cm², respectively, a two-dimensional growth behavior can be expected for this combination of materials during the early stages of growth. (The free surface energy of layer structures like mica and molybdenite is much smaller than that of silver, which agrees with the observed three-dimensional growth processes examined.)

Motion pictures recording the growth of silver on single-crystal platinum films, which were obtained in a {111} orientation by evaporating platinum onto silver-on-mica (BASSETT et al [10]), show clearly the two-dimensional growth behavior. The silver condenses in patches of undefined shape, which at 10 000 X magnification convey the impression of a cloud-like structure. Two series micrographs of higher magnification confirm this (Fig. 9). The dark patches contain the expected 37 Å parallel silver-platinum moirés. Whether the lighter areas between patches are completely covered by a very thin silver layer cannot be decided. There are, however, strong indications that this may be so since the moirés often extend into the open spaces and the moiré contrast is dependent upon film thickness and local orientation of the specimen foil.

The deposition of the silver was carried out at a substrate temperature of $T = 450$ °C in the area of

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Fig. 1. Three successive stages of growth of silver on mica at a substrate temperature of $T = 300$ °C. Note filling of areas between original nuclei.

Fig. 2. a) One of a series of 12 transmission micrographs taken during the growth of silver on mica at lower supersaturation ($T = 450$ °C). b) Superimposed aequidensitometry copies of three growth stages of silver on mica. The specimen area is the same as in Fig. 2 a.

Fig. 3. Four series micrographs of the growth of silver on molybdenite at $T = 450$ °C. (The picture are taken from a series of 28 micrographs exposed at intervals of about 1 min.)

Fig. 4. Increase of evaporation rate during growth causes the formation of new nuclei (silver on molybdenite).

Fig. 5. Introduction of a lattice defect structure during coalescence of silver crystallites.

Fig. 6. The formation of composite silver crystallites during growth on molybdenite (for details see text).

Fig. 7. Transmission electron diffraction pattern of silver on molybdenite.

Fig. 8. 24 Å and 28 Å parallel moirés which are probably caused by double positioning of the silver crystallites.

Fig. 9. Successive stages of growth of silver on a thin {111} platinum substrate at $T = 450$ °C.

Fig. 10. Later growth stage of silver on {111} platinum. Three sets of parallel moirés of 37 Å, 32 Å and 24 Å can be distinguished.

Fig. 11. Early (a) and later stage of growth of silver on {111} gold.

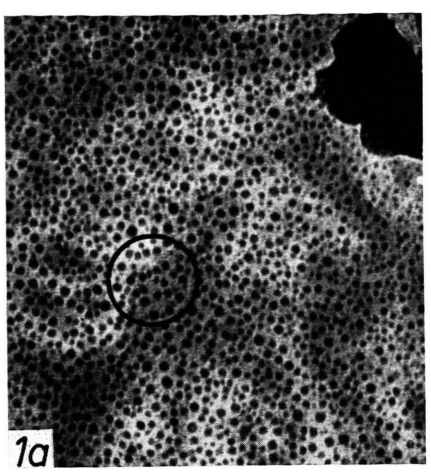
Fig. 12. Decoration of surface contamination by preferred growth of silver around holes in a {111} gold substrate.

Fig. 13. Representative transmission electron diffraction pattern of polycrystalline and single crystalline gold and a {111} palladium substrate. The polycrystalline gold is deposited on an unidentified "skin" spanning holes in the substrate. (Only the innermost two faint gold rings can be distinguished, the (220) and (311) rings were lost during print.)

Fig. 14. Three sets of (220) moirés and two sets of smaller spaced (311) moiré in a composite gold-palladium film. (The (311) moirés running perpendicular to the (220) moirés in the circle are not resolved by the print.)

Fig. 15. Three stages of annealing of a composite palladium-gold film obtained by epitaxial growth at 50 °C. The normal (220) parallel moiré of 30 Å spacing deteriorates progressively during the annealing process. (The 30 Å spacing in 15 a is not resolved in the print.)

Fig. 16. Combination of a normal and a deteriorated set of moiré fringes of a palladium-gold film at the beginning of the annealing process.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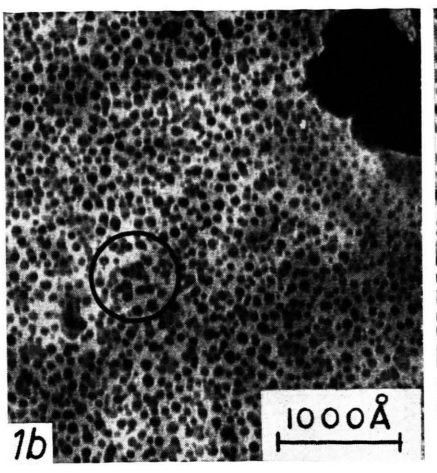
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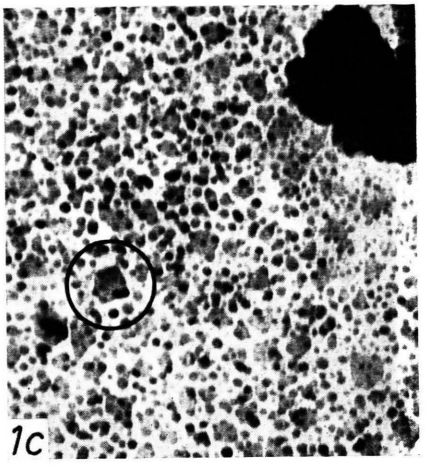
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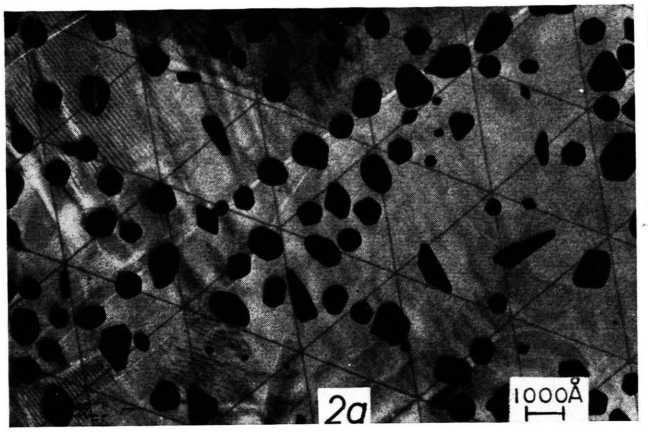
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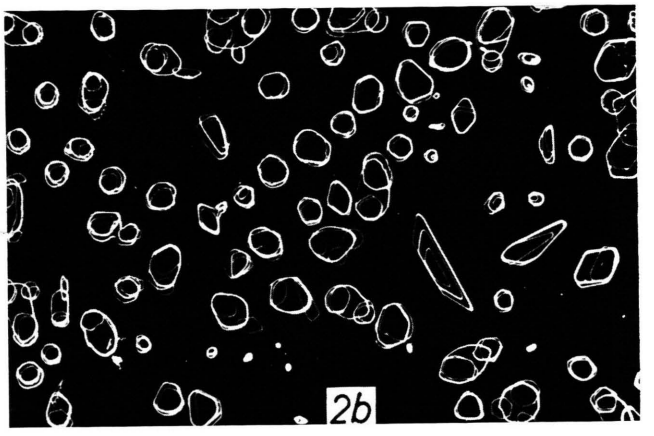
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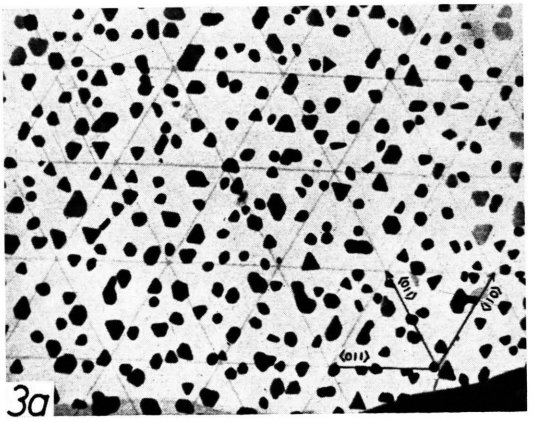
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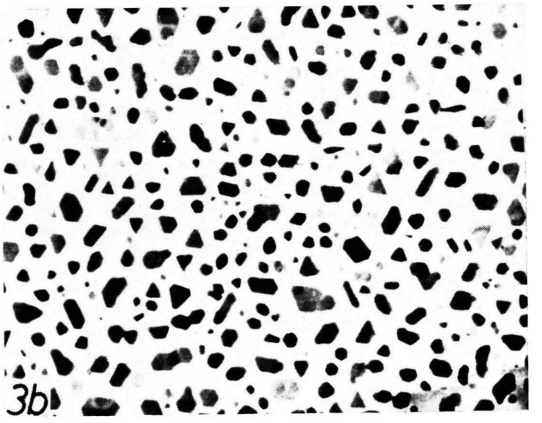
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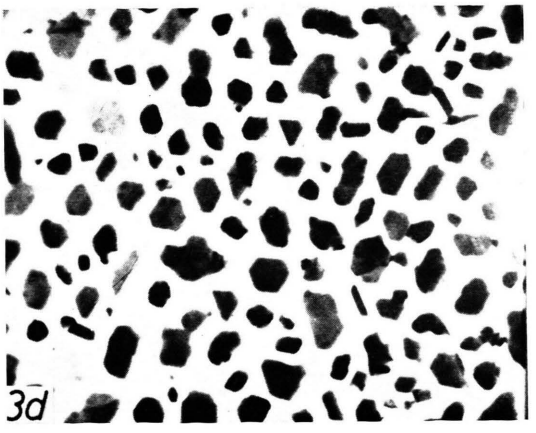
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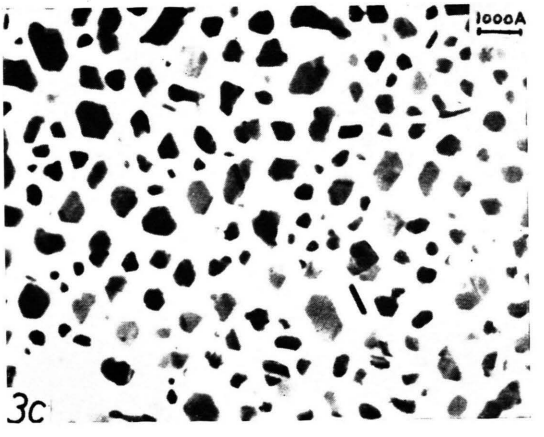
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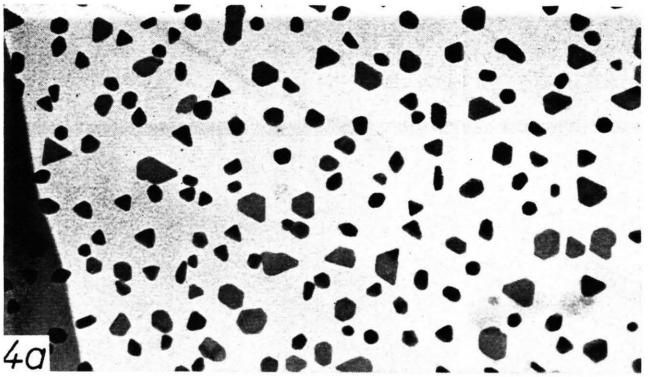

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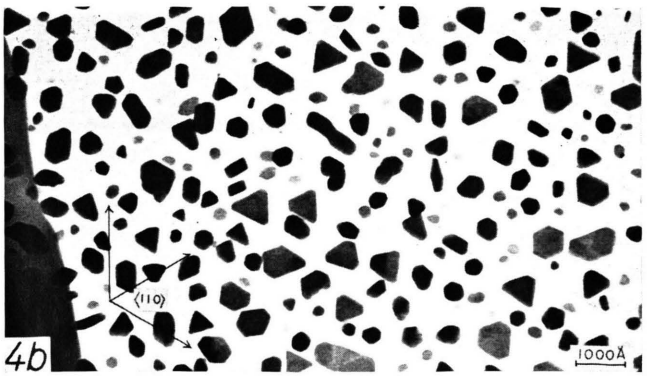

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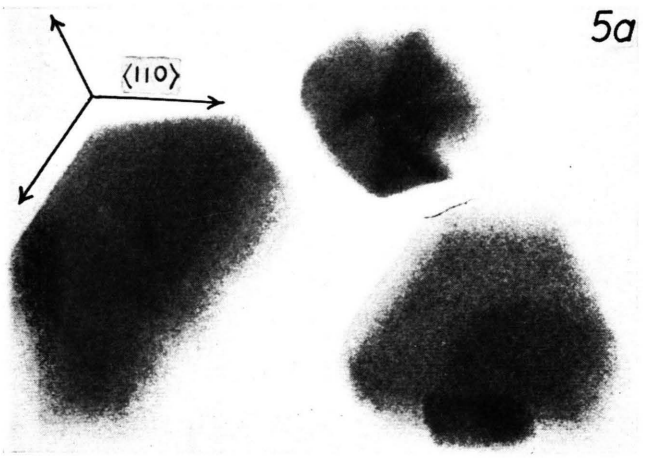
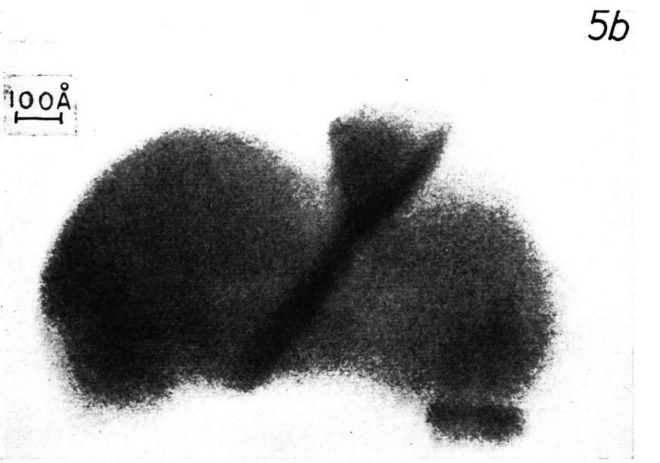


5a



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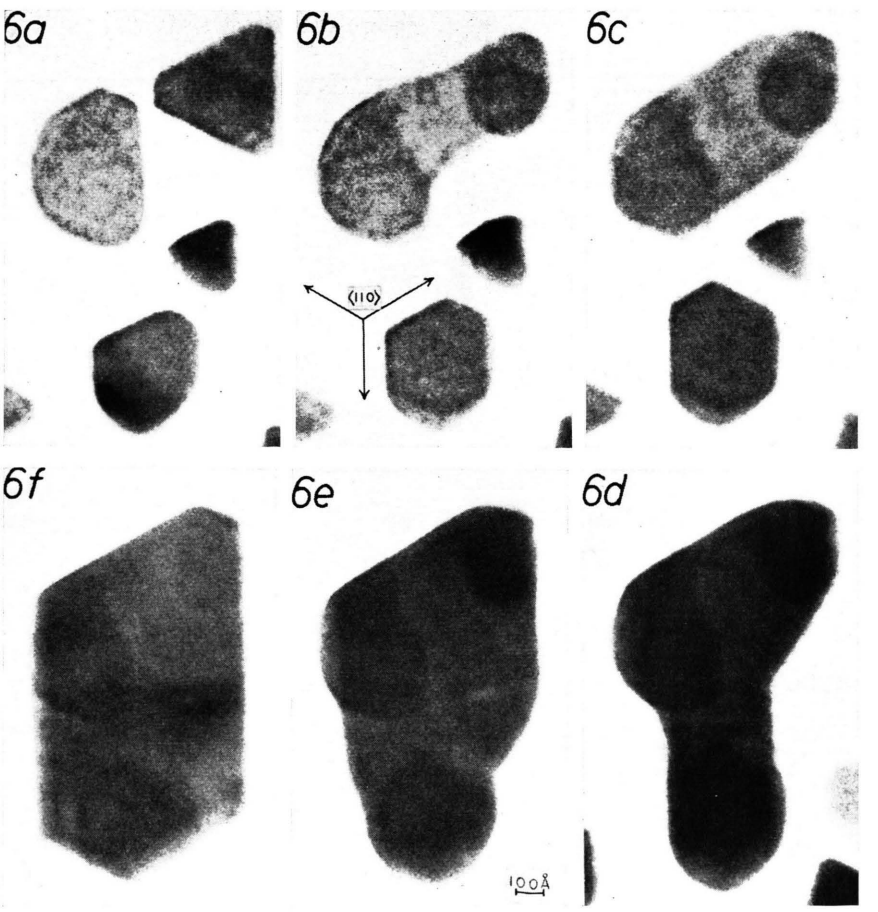
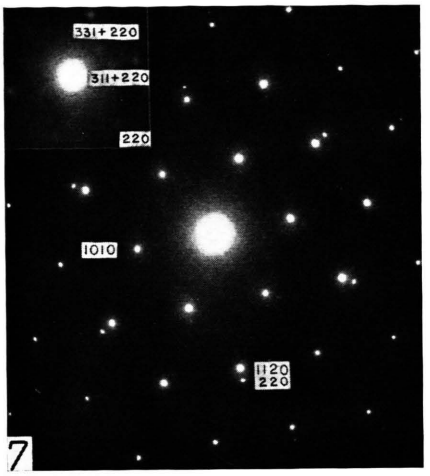
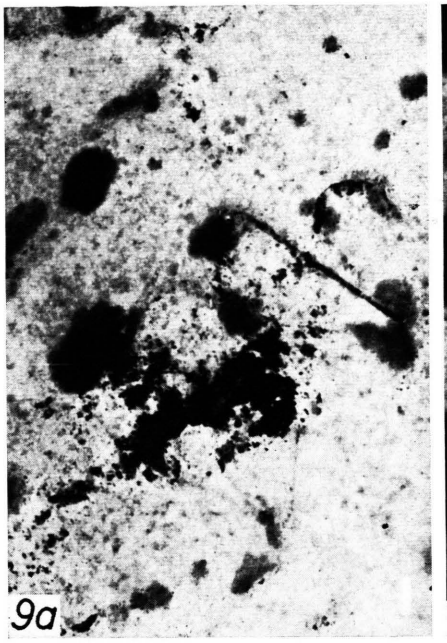



331+220
311+220
220
1010
1120
220
7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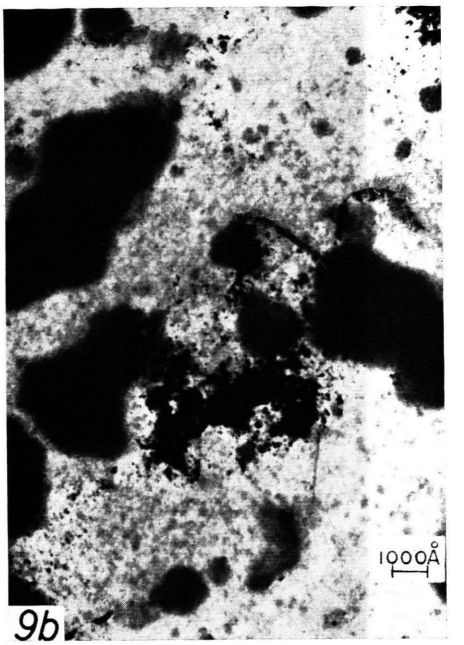
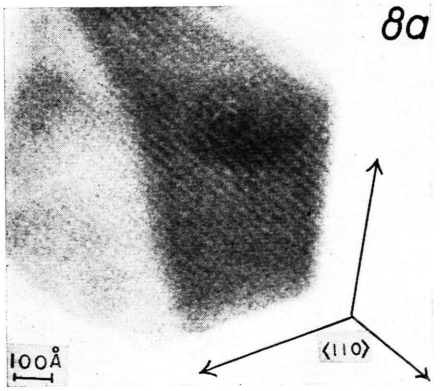
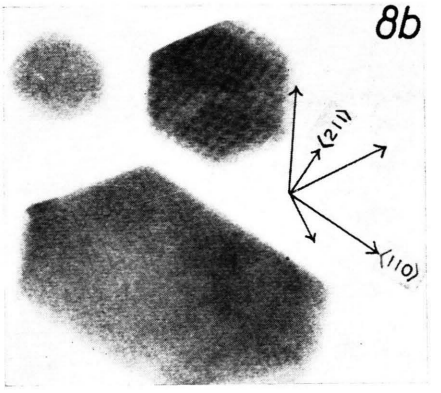
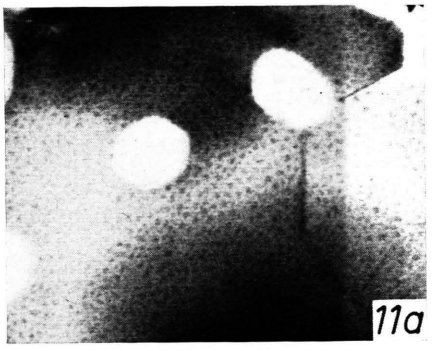
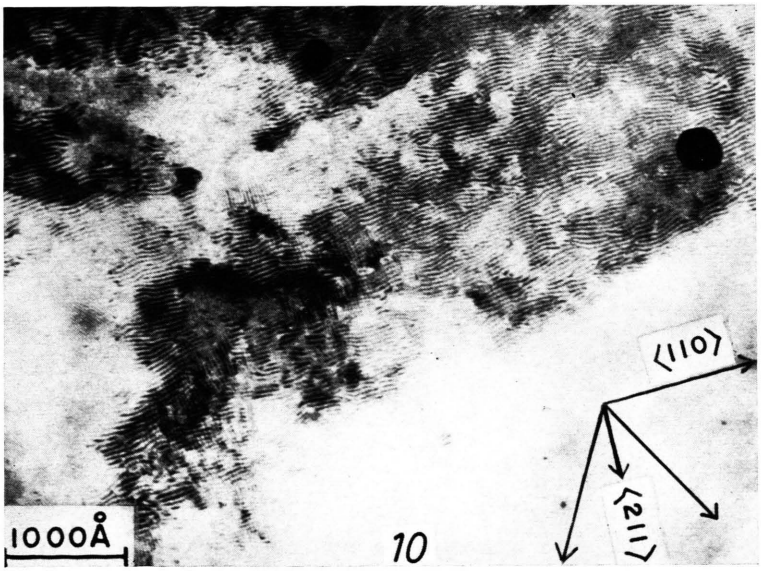
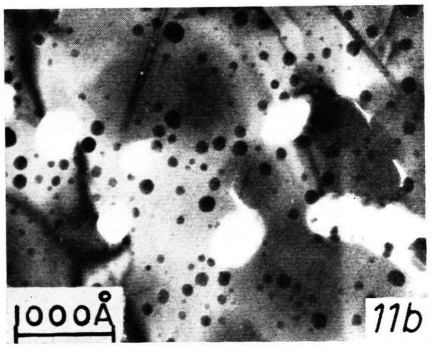

1000Å
9b

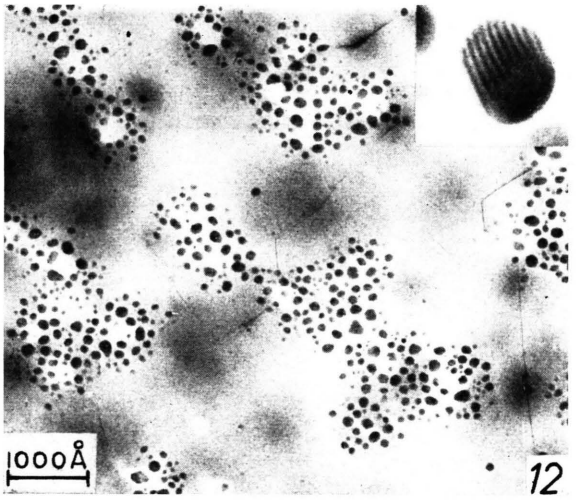

8a
100Å
⟨110⟩


8b
⟨211⟩
⟨110⟩


11a


⟨110⟩
⟨211⟩
1000Å
10


1000Å
11b



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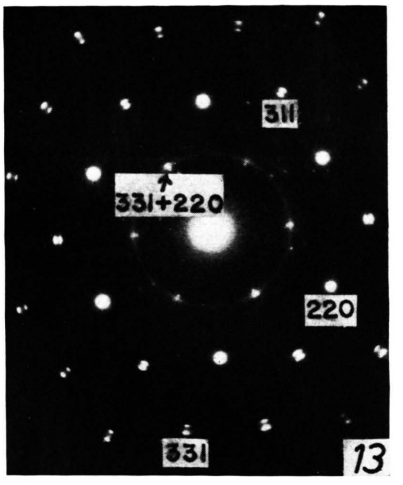

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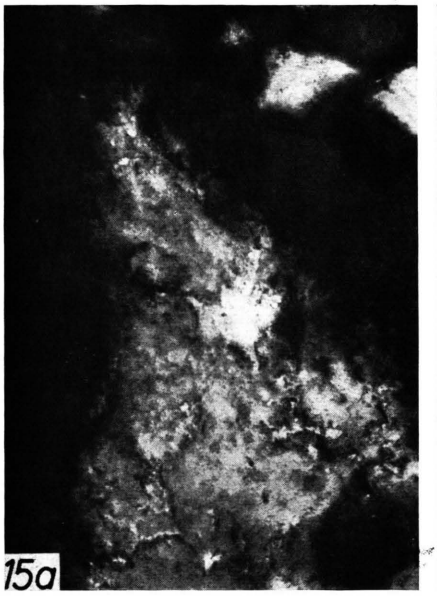

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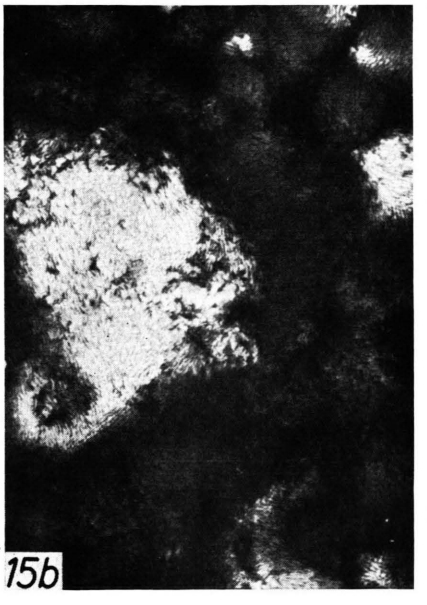

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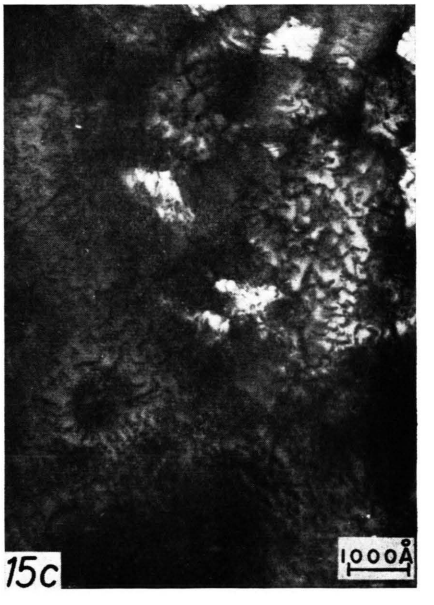
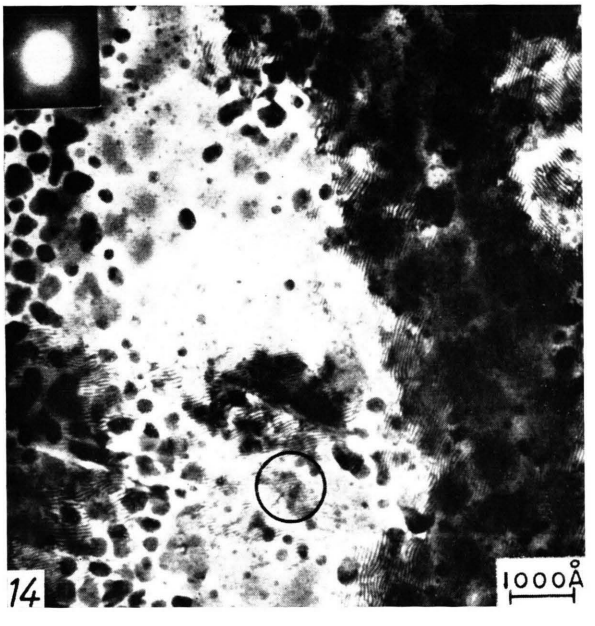


15c



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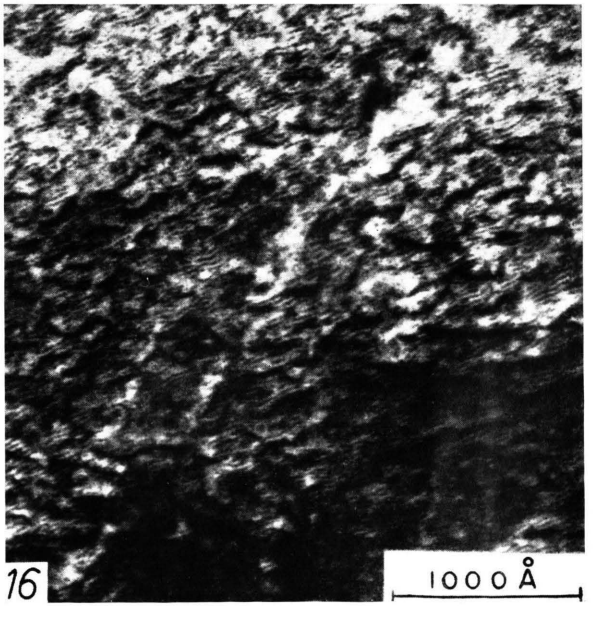

16

the illuminating electron beam. Outside this area the temperature can be as much as 100 °C lower (POPPA [14]). The supersaturation is therefore higher here and the silver film grows more continuously. In these regions of the substrate the moiré patterns are better developed, and later stages of growth can be examined. Fig. 10 gives an example of this and demonstrates particularly high dislocation densities. Besides various sets of moiré fringes of different spacings, two small and thick silver crystallites that are indicative of later stages of growth will be noticed. The directions and spacings of 37 Å, 32 Å and 24 Å identify the three sets of moirés as being of the (220), (311), and (422) type. A (311) moiré is unusual in a film of {111} orientation, but the corresponding diffraction pattern clearly shows (311) and (331) reflexes, which indicates double positioning (refer to the similar diffraction pattern of Fig. 13).

From the diffraction pattern the ratio p of the silver and platinum lattice constants can also be deduced,

$$p = a_{Ag}/a_{Pt} = 1.029$$

whereas the normal value of p is $p = 1.038$. It is assumed that this change in p is due to an alloying process by which silver and platinum form a solid solution. This would result in a mutual approximation of the lattice constants which, in turn, would lead to wider-spaced moiré patterns. Moirés in the hotter growth regions actually measured up to 50 Å in spacings, and this agrees well with a p of 1.029. In a small but extremely thin area of the specimen moiré patterns of even wider spacings were observed. Overheating and stronger alloying in these areas (caused by poor heat conductance properties) have been considered as possible explanations.

Silver on {111}-gold

The combination silver-on-gold can be arranged in the same category with silver-on-platinum as far as the related surface energies of these materials are concerned. Since gold is the harder metal, and the free surface energies are often in correspondence with hardness, a two-dimensional growth behavior was to be expected.

Layer growth was not, however, as easily detected as with silver-on-platinum because silver and gold form no parallel moiré. The lattice constants of the two metals are too similar. The two-dimensional growth during very early stages could only be determined indirectly from a definite darkening of the microscope image and from diffraction patterns. In contrast to the combination silver on platinum, intermediate growth stages were characterized by very fine-grained, three-dimensional silver crystallites (Fig. 11 a) and later stages by rounded, thicker crystallites (Fig. 11 b).

These experiments provided a demonstration of the surface cleaning effect of the ion bombardment treatment prior to growth. Quite thin gold substrates of {111} orientation can be grown by evaporation onto silver-on-mica. They still contain many holes. During preparation procedures the underlying silver layer is dissolved in nitric acid, which provides an opportunity for contamination of the upper gold surface through holes in the film. When silver is later evaporated onto this surface during an in-situ growth experiment without preceding ion bombardment cleaning, the contaminated areas around holes offer sites for preferred nucleation (Fig. 12). Only in these areas it happens occasionally that silver crystallites are so much misoriented with reference to the substrate that rotation moirés appear (see insert in Fig. 12). An adjacent area of the same gold substrate that was stricken by the bombarding ion beam shows no signs of preferred nucleation.

Gold on {111}-Palladium

The rather unusual results observed with this combination of metals do not concern so much the various modes of growth, which were similar in character to the two foregoing examples, but the strong alloying reactions between substrate and overgrowth.

The first growth runs were conducted at the usual high substrate temperature of $T = 450 - 500$ °C, but instead of the expected 30 Å (220) type parallel moirés only very weak patterns, with fringe spacings ranging from 50 – 150 Å, were observed. The corresponding selected area diffraction pattern explained this result.

In Fig. 13 the diffraction pattern shown is typical for most of the described {111} oriented metal-metal combinations. The photograph is deliberately overexposed to emphasize the otherwise weak DEBYE SCHERRER gold rings, which are caused by polycrystalline gold deposits condensed onto a very thin "skin" spanning holes in the substrate film. These holes are produced during ion bombardment. The

nature of the extremely thin "skin", which covers the entire rear side of the substrate foil, could not be determined. It is obvious, however, that the sputtering yield of the skin material is much lower than that of the noble metals. The origin of the skin is probably connected with reactions at the silver gold interface during preparation procedures. Some primary and double reflexion spots are indexed in Fig. 13. The unusual (311), (331), and nonintegral reflexions in the pattern can be explained by considering double positioning and double diffraction in accordance with BURBANK [28], GÖTTSCHE [8], THIRSK [29], and others. (Dark field pictures taken with these reflexes all showed a high number of bright twinned regions.)

The gold rings can be used as standards in order to calculate the lattice constant of the substrate material. In the case of gold growing on palladium at high substrate temperatures, this method leads to

$$p = a_{\mathrm{Au}}/a_{\mathrm{Pd}} = 1.025$$

(instead of $p_{\mathrm{normal}} = 1.048$) and with this

$$a_{\mathrm{Pd}} = 3.98 \text{ Å} \quad \text{(instead of } 3.89 \text{ Å)}.$$

Assuming no lattice constant change in the major part of the single-crystal gold overgrowth, this higher value of a_{Pd} would already lead to a parallel moiré spacing M of about $M(220) = 60$ Å. It is therefore probable that the experimentally observed wide moiré spacings can be explained by solid-solution alloying processes during epitaxial growth.

In order to reduce alloying, the substrate temperature was decreased to $T = 200$ °C in the next experiment. This resulted in $p = 1.037$, a_{Pd} (calc) $= 3.93$ Å and $M(220)_{\mathrm{calc}} = 38$ Å, which fringe spacing was actually observed. Now the temperature T was slowly increased to 400 °C and accordingly p changed to $p = 1.032$, which leads to

$$a_{\mathrm{Pd}} \text{ (calc)} = 3.95 \text{ Å}, \quad M(220)_{\mathrm{calc}} = 45 \text{ Å}$$

and

$$M(311)_{\mathrm{calc}} = 38 \text{ Å}.$$

Fig. 14 represents the corresponding micrograph showing all three sets of (220) moirés with $M = 45$ Å and two sets of (311) moirés with $M = 38$ Å. (The insert shows the fine structure of the central beam of the diffraction patern of Fig. 13.) If the annealing process is prolonged, the moiré patterns finally deteriorate so much that they can hardly be recognized as such.

Palladium on {111}-Gold

So far only such combinations of substrate overgrowth metals were investigated which, on the basis of their relative free surface energies, should exhibit twodimensional growth behavior according to BAUER's theory. It remained to be proven whether a hard metal growing on a softer metal substrate would develop three-dimensional nucleation and growth. It must be kept in mind, however, that the theoretical predictions are valuable only if no strong substrate-overgrowth-interactions exist. In view of the previously observed alloying processes, particularly with the combination gold on palladium, the applicability of these theoretical concepts is questionable.

Platinum, with the highest free surface engery of the noble metals, could not be evaporated successfully inside the electron microscope. Palladium was the highest melting noble metal that could be handled, and it was evaporated onto gold substrates at high ($T = 450$ °C), medium ($T = 200$ °C), and low ($T = 50$ °C) temperatures with use of both high and low evaporation rates. In no case was pictorial evidence for three-dimensional nucleation obtained although small palladium crystallites (50 Å – 100 Å diameter) always developed during later growth stages.

It has to be emphasized that the negative results regarding the detection of three-dimensional nucleation during very early growth stages may be due to the limited spatial resolution of thre transmission electron-microscopy technique. Nuclei of a diameter smaller than about 15 Å may have been formed but escaped detection. Also to be noted is the fact that growth experiments conducted at substrate temperatures lower than about 300 °C were not authentic in-situ studies. In view of the strong contaminating influence of the imaging electron beam at these temperatures, the small illuminated area of the specimen was used only for monitoring purposes. Micrographs and diffraction patterns were obtained from different and uncontaminated specimen areas.

Micrographs of palladium-gold films prepared at medium substrate temperatures frequently showed a striking similarity to pictures published recently by

[28] R. D. BURBANK and R. D. HEIDENREICH, Phil. Mag. **5**, 373 [1960].

[29] H. R. THIRSK and E. J. WHITMORE, Trans. Faraday Soc. **36**, 565 [1940].

MATTHEWS [11], with structures reminiscent of moiré patterns. Since the directions and spacings of these patterns could not be explained as regular moirés, MATTHEWS assumed that they resembled sets of interfacial dislocations. The changes in fringe spacing were also attributed by MATTHEWS to alloying processes.

Whatever may be the nature of such fringe patterns – interfacial dislocations or deteriorated moirés – alloying is most probably the cause for their appearance. Fig. 15 is considered proof of the deterioration hypothesis by demonstrating, in three successive micrographs, the annealing behavior of a composite palladium-gold film. The single-crystal palladium film was grown on a {111} gold substrate at $T = 50$ °C and showed the regular (220) type parallel moiré spacing of 30 Å (Fig. 15 a). When the specimen was then heated to $T = 450$ °C, these moirés deteriorated in the manner demonstrated in Fig. 15 b and 15 c. The original and the deteriorated sets of fringes (Fig. 16) were occasionally found simultaneously in thinner regions of the specimen during early stages of the annealing process. This probably indicates the existence of three layers, the original substrate and overgrowth layers, and an alloyed region at the gold-palladium interface.

Summary

The method of in-situ studies of thin-film growth was successfully applied to a number ob substrate-overgrowth combinations. Despite the basic shortcomings of this method, which include the rather high background pressure of 10^{-5} Torr and its associated restriction of growth parameter variability, the results elucidated such probably elementary epitaxial processes as (1) preferred growth of individual nuclei in certain directions; (2) coarse rotational misalignments of nuclei with reference to the substrate; (3) loss and regaining of crystallographic shapes during coalescence of overgrowth crystallites; (4) development of internal nucleus structures; and (5) the "recollection" phenomenon of previous overgrowth forms after merger.

The influence of various degrees of supersaturation and the effect of free surface energies of substrate and overgrowth materials were also observed. The results agree with theory when the growth conditions are suitable and reasonably well defined, which is true for the growth of noble metals on mica and molybdenite substrates. However, when metals are grown on metal substrates, alloying occurs and nucleation processes become more complex. This is probably the reason why three-dimensional nucleation of a higher free surface energy metal on a lower free-surface-energy metal substrate was not observed. All examined metal-metal combinations exhibited two-dimensional growth behavior during initial growth stages. It was only during intermediate or later stages of growth that three-dimensional forms of overgrowth developed.

Continuous observation of composite noble metal substrate and overgrowth films during annealing showed significant changes of moiré structures. The parallel moiré spacings are usually higher than normal shortly after deposition at low substrate temperatures and increase in width continuously while the film is annealed. This is attributed to alloying processes and interpreted as deterioration of moiré patterns; it is not considered evidence of interfacial dislocation reactions. Approximation of lattice constants by progressive formation of solid solutions probably causes the increase in frings spacings.