Effect of Alloying on the Epitaxy*

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The mechanism of the epitaxy has not completely been elucidated up to the present. A theory based on pseudomorphism, proposed by Frank and van der Merwe, is an ingenious idea and seems to be most promising, but it cannot be said that experimental evidence for it has so far been obtained. The present work proposes that alloying between deposit and substrate is possible to be an origin of the epitaxy in some cases, based on experimental results concerned with the growth of gold on palladium, aluminium on palladium and copper on gold. It is shown that in the first and last couples the alloying reasonably results in the parallel growth of deposit and necessarily generates misfit dislocations, just as the pseudomorphism does. It is thus emphasized that the effect of alloying on the epitaxy should not be underestimated.

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I. Introduction

It is well known that the epitaxy occurs in the overgrowth of deposit on substrate crystals in solution and vapor phases, and especially, by vacuum condensation. It seems that a great many experimental results have been obtained in the last case in which the epitaxy can be observed by transmission electron diffraction⁽¹⁾. There are two kinds of crystal growth in such film formation, i.e., a three-dimensional nucleation and a two-dimensional monolayer overgrowth. What determines the epitaxy is the orientation of nuclei and the coalescence of them in the former, and the orientation of the overgrowth itself in the latter. It is a question in both cases by what mechanism the orientation of initial deposits is determined. Various ideas have so far been proposed as to this mechanism. However, the following seems most promising. It is a mechanism of pseudomorphism, proposed by Frank and van der Merwe⁽²⁾, in which the first layer of deposit is forced to follow the substrate in the atomic arrangement, irrespective of any difference in

the proper lattice parameter, giving rise to much stress in the layer itself.

In order that the epitaxy may actually occur, elevation of the substrate temperature is necessary in almost all cases. If the substrate temperature is raised, the alloying between deposit and substrate will necessarily result, provided the solubility exists between both. The substitutional alloying may act as an intermediary in succession of the orientation by deposit and cause the epitaxy to take place. That is to say, even if an ingenious mechanism, pseudomorphism, is not realized, there is a possibility that the epitaxy can be explained by the alloying. The present work has been undertaken in order to prove such a possibility, dealing with three cases of gold on palladium, aluminium on palladium and copper on gold, in each case of which the alloying certainly takes place. These four metals have the same crystal structure. The first and last couples make solid solutions in all proportions. On the other hand, in the second couple palladium dissolves a little aluminium and the latter does not dissolve the former.

II. Experimental

Specimens were prepared by vacuum evaporation. In any cases substrate single crystal films and deposit ones were successively formed on potassium chloride crystals, the former films being almost always 500 Å thick and the latter 30–200 Å thick. Composite films

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were isolated in water and examined by electron diffraction and electron microscopy.

1. Gold on palladium

Successive evaporation of palladium and gold was made at 300°C. Complete parallel growth took place at the thickness of gold ranging from 300 to 500 Å. In an electron diffraction pattern in Photo. 1, where the thickness of gold was 200 Å, diffraction spots from the deposit and the substrate are seen. The misfit parameter $f = (b - a)/a \times 100\%$, in which a is the lattice parameter of the substrate and b that of the deposit, was determined by electron diffraction. Figure 1 shows the behavior of f with changing deposit thickness. The horizontal full line represents a misfit parameter corresponding to the proper lattice parameters of gold and palladium, and the broken line indicates a theoretical relation by van der Merwe⁽³⁾. The observation deviates considerably from the theoretical relation. Figure 2 depicts

Photo. 1 Electron diffraction pattern of a composite film of gold and palladium.

Fig. 1 Change in the misfit parameter with the thickness of gold deposited on palladium.

Fig. 2 Relation between the misfit parameter and the thickness of gold deposited on palladium at various temperatures.

the relation between f and the thickness with changing temperature. This relation means that at the same deposit thickness, the lower the substrate temperature, the faster f approaches the value corresponding to the proper lattice parameter. Figure 3 shows that f at the fixed deposit thickness, 100 Å, decreases gradually with increasing substrate temperature. That is, the higher the substrate temperature, the later f approaches the value corresponding to the proper lattice constant.

Photograph 2 is a bright field electron micrograph of a composite film consisting of a palladium film 500 Å thick and a gold film 50 Å thick formed at 300°C. Two sets of parallel

Fig. 3 Change in the misfit parameter of gold on palladium at various temperatures at the fixed deposit thickness.

Photo. 2 Bright field electron micrograph of a composite film of gold and palladium.

striations are seen along $[110]$ and $[\bar{1}10]$ directions. They are "misfit dislocations" as first observed by Matthews⁽⁴⁾, and according to the theory of pseudomorphism, they are considered as direct evidence of the relaxation of excess misfits.

2. Aluminium on palladium

Composite films were prepared in the same way as in the case of gold on palladium. Electron diffraction patterns produced by them were in general much complicated. Photograph 3 shows such a pattern produced from a composite film of an aluminium film 500 Å thick and a palladium film 500 Å formed at 300°C. Even after diffraction spots produced by double diffraction are removed, the pattern except the spots from palladium cannot be explained by

Photo. 3 Electron diffraction pattern of a composite film of aluminium and palladium.

Photo. 4 Bright field electron micrograph of a composite film of aluminium and palladium.

any kinds of aluminium oxide. The possibility of existence of intermetallic compounds of aluminium and palladium, such as βAlPd and Al_3Pd_2 , are considered. Photograph 4 is a bright field electron micrograph of a composite film consisting of a palladium film 300 Å thick and an aluminium film 200 Å thick. Two sets of misfit dislocations as observed in the case of gold on palladium do not appear here, but there are seen only wavy striations that are nothing but moiré fringes. When the thickness of the aluminium deposit was increased and the temperature of the substrate was raised above 300°C, diffraction patterns became more complicated. They showed the existence of palladium, Al_3Pd_2 , βAlPd , Al_3Pd and aluminium. It is conspicuous that these intermetallic compounds were produced even at 150°C. When aluminium was deposited on a palladium single crystal film at room temperature, no intermetallic compound but only polycrystalline aluminium was produced.

3. Copper on gold

Gold single crystal films 500 Å thick were first prepared on potassium chloride crystals heated at 420°C, and copper was evaporated at various temperatures. An electron diffraction pattern of a composite film consisting of a gold film 500 Å thick and a copper film 80 Å thick is shown in Photo. 5. Evaporation of copper was made at the substrate temperature of 300°C. This pattern indicates the formation of the superlattice CuAu I , though the heating of

Photo. 5 Electron diffraction pattern of CuAu I resulting from deposition of copper on gold.

Photo. 6 Bright field electron micrograph of the film giving rise to the pattern shown in Photo. 5.

the substrate was stopped as soon as the evaporation was finished. Photograph 6 is a bright field electron micrograph of such a CuAu I film, revealing an array of misfit dislocations.

III. Explanation of the Results of Observation

The lattice parameter of the deposit increases with its thickness in the case of gold on palladium, just as this follows from the theory of pseudomorphism, but a distinct discrepancy exists between the observation and the theory; that is, it is clear from Figs. 1 and 2 that the observed f values are much lower than the theoretical ones in the range of small thickness. An equilibrium elastic strain, $\epsilon_m^{(3)}$, resulting from the pseudomorphism, can be obtained from the difference between an actual f value

and a value corresponding to the proper lattice constant of the deposit. The f values observed result in very large ϵ_m values, that is, they are ten times as large as those predicted by the theory of pseudomorphism in the case of gold 100 Å thick. A similar conclusion was obtained by Matthews⁽⁵⁾ in the case of cuprous oxide on copper, gold on palladium, gold on silver and nickel on copper, and he attributed this discrepancy to the following three reasons; 1) a partial alloying between deposit and substrate, 2) straining of substrate and 3) difficulty in the generation of misfit dislocations. The second reason seems to be unimportant, because the straining of substrate may be very small unless it is too thin, and in the case of gold on palladium in the present work the substrate is much thicker than the deposit. The validity of the third reason may be denied by the following consideration. The third reason means that, if the generation of misfit dislocations is not easy in an overgrowth film, relaxation of the elastic strain in this film may be less than that theoretically predicted. Some reasons for the difficulty in the generation of misfit dislocation will be considered. According to Matthews, however, a uniform generation of misfit dislocations was observed at a deposit thickness of 250–300 Å in the case of gold on silver, while it would have occurred at 460 Å according to the theory. That is to say, the generation of misfit dislocations was not so difficult, and the above fact is entirely contrary to the sense due to the third reason.

After all, the first reason remains to be considered. Figure 1 in the case of gold on palladium indicates that the lower the substrate temperature, the faster changes the lattice parameter of the deposit to its proper value. Figure 3 shows that the higher the substrate temperature, the smaller the f values become. These facts can be well understood, if the alloying takes place between the deposit and the substrate. Figure 4 is a result of an experiment made to prove the alloying effect, and depicts the change in f with the time duration, during which the substrate temperature was kept constant after a gold film 100 Å thick was deposited on a (001) palladium film of 500 Å thickness heated at 300°C and then the tem-

Fig. 4 Change in the misfit parameter of gold deposited on palladium with the time duration at 400°C.

perature of the composite film was raised to 400°C. It is seen from this relation that the longer the time duration, the smaller f becomes, that is, the lattice parameter of the deposit gradually approaches that of the substrate. This fact cannot be explained without considering the effect of alloying. Misfit dislocations were also observed in this case, as shown in Photo. 7(a) and (b). The former corresponds to the initial stage in Fig. 4 and the latter to the time duration of 20 min. Misfit dislocations have no regular distribution in the latter.

Misfit dislocations may be generated to release the stress, according to the theory of pseudomorphism, but it is quite easy to show that they can necessarily be generated as a result of alloying. Figure 5 is a model in which a deposit represented by the large circles grows on a substrate represented by the small circles and the substitutional alloying occurs at the interface. An elevated temperature of the substrate facilitates the alloying. The mean lattice parameter should be changed from the substrate toward the deposit owing to the change in the concentration along the direction normal to the interface. In order to compensate the difference in the mean lattice parameter, edge dislocations are necessarily generated as misfit dislocations.

Observations of the growth of aluminium on palladium and copper on gold can reasonably be explained from the standpoint of alloying. The former case might be more favorable to the occurrence of pseudomorphism than the case of gold on palladium, because the difference

Photo. 7 Bright field electron micrographs of a composite film of gold and palladium heated at 400°C.

- (a) the initial stage of the heating.
- (b) 20 min time duration of the heating.

Fig. 5 Model of the interface between deposit and substrate where the substitutional alloying occurs.

in the lattice parameter is smaller in the former while elastic constants such as the shear modulus and the Poisson's ratio are not very different between aluminium and gold. However, the change in the lattice parameter of aluminium was never observed, and only the

formation of intermetallic compounds took place. This fact is understood only by the occurrence of alloying. The epitaxy and misfit dislocations cannot take place in this case, because intermetallic compounds have crystal structures entirely different from that of the substrate. In the case of copper on gold the superlattice formation took place, and misfit dislocations were clearly observed. This fact is a good example in which misfit dislocations can be explained by the substitutional alloying, even if the pseudomorphism which has been considered to be an ingenious mechanism for the occurrence of the epitaxy is not realized.

IV. Conclusion

Several investigators have so far observed misfit dislocations and monolayer overgrowth in various couples of deposit and substrate, which may support the mechanism of pseudomorphism⁽⁶⁾. It is noticed, however, that much solubility exists in most of these couples and the epitaxy does not occur without elevation of the substrate temperature, say, up to $\sim 300^{\circ}\text{C}$. These circumstances cause necessarily the alloying between deposit and substrate to occur.

The present work proved such alloying to actually take place in the couples of gold on palladium, aluminium on palladium and copper on gold, and showed the epitaxy and misfit dislocations observed in the first and last couples to result from the substitutional alloying. The present authors do not intend to say that only the alloying is an origin of the epitaxy, but they want to point out that there are cases in which the alloying should be considered to cause the epitaxy and misfit dislocations to occur which have so far been thought of as results of the occurrence of pseudomorphism, especially when the deposit and the substrate have the same crystal structure, there is much solubility between them and elevation of the substrate temperature is necessary for the epitaxy to occur.

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