EPITAXIAL GROWTH OF THIN FILMS

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All the theories of epitaxial growth put forward so far[1–5] either assume that a small misfit is an essential condition for the occurrence of an oriented overgrowth or they are based on the concept of basal plane pseudomorphism. According to Pashley[6] the present experimental evidence does not completely support any of these assumptions. The degree of misfit, however, does appear to have some significance. In the light of this an attempt is made here to put forward a theory of oriented growth on oriented substrate. This theory is essentially an extension of the theory[7] put forward (Dixit, 1933) for oriented growth on amorphous surfaces.

Metal atoms evaporated on cleavage planes of crystals

Dixit prepared thin films by evaporating metal atoms on flat amorphous surfaces. The electron diffraction study of these films showed fibrous orientations, which in their turn showed a characteristic dependence on the temperature of the substrate. This was explained by assuming that the atoms in such a layer behave like a two-dimensional gas and obey an equation $\pi A = RT$,

where

π is the two-dimensional pressure (surface tension);

A is the area occupied by the atom on the substrate;

R is the gas constant

and

T is the absolute temperature.

The evaporation of metal atoms on the cleavage planes of crystals, however, introduces a significant difference in our considerations. An amorphous flat surface only serves as a reasonably flat support and there is no interaction between the atoms of the substrate and the deposited atoms. The cleavage surface not only serves as a flat support, but there will also be a force of attraction between the ions of the substrate and the deposited neutral metal atoms. (As before we shall consider the formation of the first atomic layer only.) The additional force of attraction, which now manifests itself between the ions of the substrate and the deposited neutral metal atoms, can be reasonably assumed to be of the polarisation or van der Waals' type. This force will introduce an additional term in the equation already given, which will depend on the van der Waals' energy and the area occupied by the atom. The equation thus becomes:

$$\pi A + ACr^{-6} = RT$$

where r is the distance between the two atoms, one of the substrate and the other of the deposit.

or

$$r^2 = r_1^2 + r_2^2 + l^2$$

where

r_1 is the atomic distance for the substrate;

r_2 is the atomic distance for the deposit

and

l is the distance between the two planes, namely, the substrate plane and the deposit plane.

In the above equation if the term ACr^{-6} is absent we get the same relation as before, showing orientation as a function of the temperature. The effect of this term is to effectively reduce the term RT on the right-hand side, *i.e.*, the temperature at which any particular orientation occurs in the presence of the attractive force of the substrate is less than the temperature at which the same orientation would occur in the absence of the attractive force, or the epitaxial temperature will be less than the amorphous orientation temperature. Further even here as before

$$A_{111} < A_{100} < A_{110}$$

and therefore

$$T_{111} < T_{100} < T_{110}.$$

Both these conclusions appear to agree with experimental observations.[7–9] The modifying term can be written as:

$$\begin{aligned} ACr^{-6} &= AC\,(r_1^2 + r_2^2 + l^2)^{-3} \\ &= ACr_1^{-6}\left\{\left(\frac{r_2 - r_1}{r_1}\right)\left(\frac{r_2 - r_1}{r_1} + 2\right) + 2 + \frac{l^2}{r_1^2}\right\}^{-3} \\ &= ACr_1^{-6}\left\{\text{misfit (misfit} + 2) + 2 + \frac{l^2}{r_1^2}\right\}^{-3} \end{aligned}$$

l^2/r_1^2 will be of the order of unity. Introducing A_1 and A_2 which are the areas occupied by the atoms in the substrate and deposit respectively, we get

$$\frac{A_2}{A_1} = \frac{r_2^2}{r_1^2} = \text{misfit}\,(\text{misfit} + 2) + 1.$$

Now writing

$$\text{misfit}\,(\text{misfit} + 2) = x,$$

we get

$$ACr^{-6} \sim A_2CA_1^{-3} \sim \frac{CA_1^{-2}}{27}\left(1 + \frac{x}{3}\right)^{-3}(1 + x)$$

or ACr^{-6} will depend on $A_1^{-2}(1 - 4/3\ \text{misfit}^2)$ if we neglect powers of x higher than the first.

This indicates that the effect of the additional force of attraction can be expressed in terms of the area occupied by an atom in the cleavage plane of the substrate or its lattice constant and orientation. In addition it depends on the misfit. In deriving these relations we have not made any arbitrary assumptions about the misfit or the extent of the misfit or about basal plane pseudomorphism. All the experimental observations appear to follow as a natural consequence of the two-dimensional behaviour of the deposited atoms, subjected to the polarisation forces in addition to the forces of a two-dimensional pressure. Most of the experimental observations on the epitaxial growth of evaporated metals on cleavage surfaces appear to agree reasonably well with this theory.

EPITAXIAL GROWTH FROM SOLUTION

Here we have to consider two separate cases; one when the new layer grows from solution on a cleavage face of a crystal like rocksalt by natural sedimentation of neutral atoms and the other when the new layer grows from solution by the process of electrolytic deposition of ions.

In the first case neutral atoms are deposited on the cleavage face of an ionic crystal. Here, all the forces we considered in the evaporation of neutral atoms on the cleavage faces of ionic crystals, will be there. But in addition there will be the van der Waals attraction between the deposited neutral atom and the dipoles present in the solution. This external attraction will reduce the attraction exerted by the particles in the substrate. Our modified equation will be

$$\pi A + ACr_{\text{solid}}^{-6} - Br_{\text{liquid}}^{-6} = RT,$$

where,

r_{solid} is the same as the term r in the vapour state;

r_{liquid} is the average distance between the deposited atoms and the dipoles present in the solution

and

B is a constant which depends on the polarisability of the deposited neutral atom and also on the dipole moment of the dipoles present in the solution;

Now if we express r_{liquid} in terms of r_{solid} (or r of vapour deposition equations) we can write

$$r_{\text{liquid}}^{-6} = \lambda r_{\text{solid}}^{-6}$$

where λ is a parameter.

With this modification our energy equation becomes

$$\pi A + ACr^{-6}\left(1 - \frac{B\lambda}{AC}\right) = RT.$$

This equation, except for the multiplying factor $(1 - B\lambda/AC)$, is similar to the equation we have solved in the vapour state. The term B (including the polarisability of the deposited atom and the dipole moment of the dipole in the solution) is now effective in addition to the term A (the area occupied by the atom in the plane of the deposit). Further if we compare the equations for the deposition in the vapour state with the deposition from solution, and if we also assume that the other terms in the equation remain almost unaltered, we get to the same approximation

$$\left\{1 - \frac{4}{3}\,(\text{misfit})^2 \text{ vapour deposition}\right\} \text{ is comparable with}$$

$$\left(1 - \frac{B\lambda}{AC}\right)\left\{1 - \frac{4}{3}\,(\text{misfit})^2 \text{ solution deposition}\right\}.$$

This indicates that other conditions being comparable, the misfit values of the growth, for vapour deposition can be greater than the misfit values of growth for solution deposition. This simple theory gives us the following results:

(1) The epitaxial growth from the solution phase is essentially similar to that from the vapour phase,

(2) The epitaxial growth from the vapour phase is possible with larger misfit values than from the solution phase.

(3) The polarisability of the deposited atom and the dipole moment of the dipoles in the solution can exert an appreciable influence on the epitaxial growth from the solution phase.

These conclusions appear to agree reasonably well with all experimental observations. They are specially supported by the work of Schulz[10] (1951) (Conclusion 1); of Royer[1] (1928), Schulz[10] (1952) and Sloat[11] and Menzies (Conclusion 2); and of Sloat[11] and Menzies (Conclusion 3) respectively.

In the other type of epitaxial growth we come across in the solution phase, the thin film is prepared by the process of electrolytic deposition. The substance on which the deposition takes place is a metal crystal. The charged ion moves towards it, under the applied electric field and is deposited on it. The force of attraction between the neutral surface atoms and the deposited ion will now vary inversely as the fifth power of the distance and the corresponding potential energy will vary inversely as the fourth power. Similar considerations will apply to the attractive forces between the ion and the dipoles in the solution. The energy equation in the present case will be

$$\pi A + K_1 r_{\text{solid}}^{-4} - K_2 r_{\text{liquid}}^{-4} = RT$$

or

$$\pi A + K_1 r_{\text{solid}}^{-4} - K_2 \mu r_{\text{solid}}^{-4} = RT$$

or

$$\pi A + K_1 r^{-4}\left(1 - \frac{K_2 \mu}{K_1}\right) = RT$$

where μ is a parameter.

By comparison with the vapour phase equations it will be seen that the term r^{-4} will vary as $(1 + x/3)^{-2}$ or as (1 — 4/3 misfit) to the same approximation. This will also lead to the same rule that under similar conditions the vapour phase epitaxial growth can tolerate a larger misfit than the electrolytic deposition epitaxial growth, the general mode of epitaxial growth continuing to be similar to that in the vapour phase. Lastly, in this case, the epitaxial growth is governed by the terms K_1 and K_2, *i.e.*, by the polarisability of the atoms in the substrate and the dipole moment of the molecules in the solution.

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