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A model for development of orientation of vapour deposits

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The texture of vapour deposits changes from the orientation that places the lowest energy crystal facets parallel to the substrate under the condition of low atom or ion concentration adjacent to the deposit, to the orientation that places the higher energy crystal facets parallel to the substrate as the atom or ion concentration adjacent to the deposit increases.

1. Introduction

Vapour-deposited films are well known to have preferred orientations in them, the texture of the vapour deposits being, in general, dependent on deposition conditions. Walton [1] proposed a theory of texture formation on the basis of the orientation of a critical nucleus which was assumed to control the orientation of the deposit. The critical nucleus was defined to contain one atom less than the smallest stable cluster and its configuration was such that addition of a single atom in the appropriate location would produce the smallest stable cluster. He assumed that the configuration of nucleus varied with deposition conditions. The theory predicted that face centred cubic (fcc) crystal orientation could change from the [1 1 1] orientation to [1 0 0] and finally to [1 1 0] with decreasing supersaturation. Dutta and Wilman [2] studied the structure of silver films deposited on to glass substrates at room temperature as a function of the film thickness. They observed a random polycrystalline structure up to a critical film thickness. Further deposition led to the successive development of [1 1 1], [1 1 0], [2 1 1] orientations. The results cannot be explained based by the nucleation model.

Recently Lee *et al.* [3–11] studied the orientation of copper, chromium and nickel electrodeposits. They advanced a model in which a preferred orientation is developed by the selection for survival of crystals which are favourably oriented. The favourable orientation changes with electrolysis conditions. The electrolysis condition of higher cathode overpotential favours the growth of crystals whose smaller surface energy lattice plane is oriented parallel to the substrate at the expense of other crystals and vice versa. The concept is a growth theory of the development of preferred orientation and it may be applied to vapour deposits, because of similarity between the process of electrodeposition and vapour deposition.

The purpose of this paper is to review experimental results on orientations of vapour deposits and to advance a qualitative explanation of the development of the orientations.

2. Development of preferred orientation

Fig. 1 shows a two-dimensional model of two adjacent crystals. The surface energy of a crystal facet parallel to plane CD of grain A is larger than that of grain B, that is, crystal A has a higher ledge density than crystal B ($\alpha > \beta$). Planes parallel to plane CE must be the most closley packed planes which have the minimum surface energy. Arrows indicate impinging atoms or ions. Squares attached to the surface of the crystal indicate newly condensed atoms. Atoms are not always condensed directly on to ledges. Atoms condensed on flat surfaces (M in Fig. 1a) are in a less stable state than atoms at ledges, because they are less bonded than atoms at ledges. Therefore, they are liable either to diffuse to ledges or to re-evaporate depending on vapour deposition conditions.

The atom concentration adjacent to the deposit will be high at high substrate temperatures and evaporation rates. This situation may be depicted schematically as shown in Fig. 1a. In this case crystal B is expected to have more atoms condensed between the ledges than crystal A, because the average diffusion distance on crystal A is shorter than on B. Therefore, the configuration on crystal A is more stable than that on crystal B, resulting in the growth of crystal A at the expense of crystal B. In this case the deposit will assume the orientation of crystal A which has a higher surface energy plane normal to the direction of deposit growth. This situation can be equivalent to that for low polarization in elecrodeposition.

The atom concentration adjacent to the deposit will be decreased with decreasing substrate temperature and evaporation rate. The situation is shown in Fig. 1b. In this case, the surface area to be covered by condensed atoms is larger for crystal A than for crystal B, because angle α is larger than angle β. Therefore, crystal B will grow at the expense of crystal A. Thus the deposit will assume the orientation of crystal B. It should be noted that the shorter diffusion distance to ledges on crystal A cannot make the crystal grow faster as in the case of high concentration, because atoms are not sufficiently supplied. This situation is

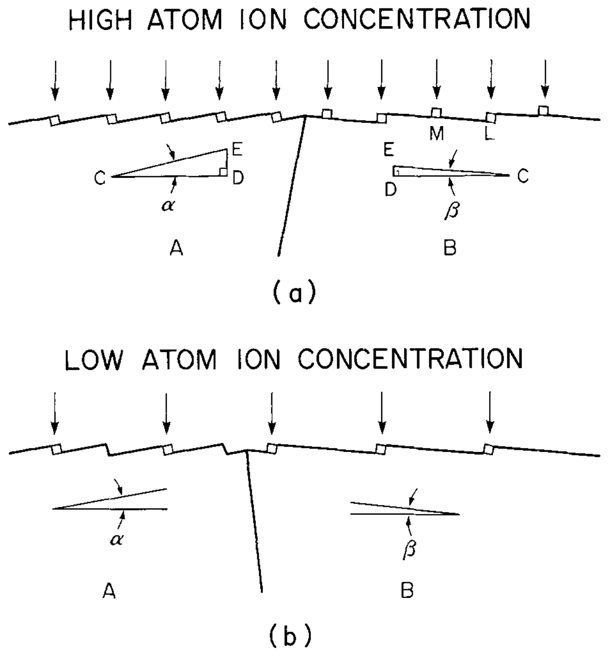

Figure 1 A two-dimensional model leading to a preferred orientation.

similar to the case of a high polarization in electrodeposition.

At sufficiently low temperatures, impinging atoms will be frozen but will not be able to rearrange themselves because of difficulty in surface diffusion and the crystallites cannot grow extensively and therefore a preferred orientation does not develop. The deposit will consist of very fine grains with nearly random orientation. When the substrate temperature is high enough to cause recrystallization, the deposit will assume recrystallization textures or nearly random orientation.

3. Discussion

3.1. Fcc crystals

Mah *et al.* [12] studied the preferred orientation of silver coatings which were deposited from a hollow cathode source with substrate bias voltage between 0 and −80 V. The preferred orientation changed from [1 1 1] to [1 0 0] and back to [1 1 1] with increasing bias voltage. They also found that the columnar grains formed at low-bias voltages were coarsened by higher bias voltages and the microhardness was lowered. They attributed the grain coarsening and lowered hardness to the fact that an increase in the kinetic energy of the vapour ions with increasing bias voltage raises the substrate temperature.

The model in the previous section suggests that the orientation of fcc metals changes from [1 1 1] to [1 0 0] and finally to [1 1 0] with increasing substrate temperature if recrystallization does not occur, because the surface energy of the {1 1 1} facet is the smallest and that of the {1 1 0} facet is the highest. The transition from [1 1 1] to [1 0 0] orientation with increasing bias voltage (absolute voltage) is in agreement with the model. However, the [1 1 1] orientation at −80 V may be caused by a recrystallization.

At low argon pressures and T/T_m, fcc copper and aluminium alloy coating sputter deposited on glass and stainless steel substrates in the post and hollow cathodes had the [1 1 1] preferred orientation. An increase in T/T_m at low argon pressures caused copper and aluminium alloy coatings deposited with both the post and hollow cathodes to assume the [1 1 0] orientation. Minor [3 1 1] orientations were consistently observed with the post cathode. Elevated argon pressures in the hollow cathodes caused copper to assume the [1 1 0] and aluminium alloy to assume the [1 0 0] orientation [13]. Similar observations have been reported by others [1, 14]. However, copper and aluminium alloy coatings deposited at high argon pressures with the post cathode had the [1 1 1] orientation at all temperatures from 20 to 800° C.

These results can be explained based on the model in the previous section. At low temperatures, the fcc metals assumed the [1 1 1] orientation, whereas at high temperatures, the fcc metals had the [1 1 0] orientation regardless of the type of cathode, because the atom concentration adjacent to the deposit would be low at the low temperatures and high at the higher temperatures. When other conditions were the same (elevated argon pressures), the hollow cathodes tended to give rise to the higher surface energy crystal facets oriented parallel to the deposit surface (causing copper to assume the [1 1 0] and aluminium alloy to assume the [1 0 0] orientation), whereas the post cathode tended to cause the lower surface energy facets oriented parallel to the deposit surface (copper and aluminium alloy coatings had the [1 1 1] orientation), because the hollow cathode would guide vapour into the more restricted area than the post cathode, and hence yield a higher atom concentration next to the coatings than would the post cathode.

Itoh *et al.* [15] studied chemical vapour deposition (CVD) of TiN film to the inner walls of long low-carbon steel tubes. The reactant gas mixture for deposition of TiN was composed of $TiCl_4$, N_2 and H_2. $TiCl_4$ vapour was saturated in the H_2 gas at a given temperature (30 to 70° C) and was carried to the steel tube in the deposition zone of the furnace. The temperature profile and film thickness distribution in the CVD furnace is shown in Fig. 2. The texture of films at various positions of the substrate are expressed in terms of the texture coefficients in Table I. The texture coefficient is define as follows

$$\mathrm{TC} = \frac{I(h\,k\,l)/I_0(h\,k\,l)}{(1/n)\sum\,[I(h\,k\,l)/I_0\,(h\,k\,l)]} \qquad (1)$$

where $I(h\,k\,l)$ and $I_0(h\,k\,l)$ are the integrated intensities of $(h\,k\,l)$ reflections measured for an experimental specimen and a standard powder sample, respectively, and n is the total number of reflection planes.

TABLE I Texture coefficients of reflection planes of CVD TiN films

Substrate position (cm)	(1 1 1)	(1 0 0)	(1 1 0)	(3 1 1)
14.2–15.1	1.419	0.408	0.826	1.350
16.4–17.3	0.979	0.270	1.948	0.803
18.3–19.5	0.549	0.372	2.685	0.394
22.0–22.9	0.879	0.485	1.834	0.802
24.3–25.2	0.940	0.606	1.683	0.770

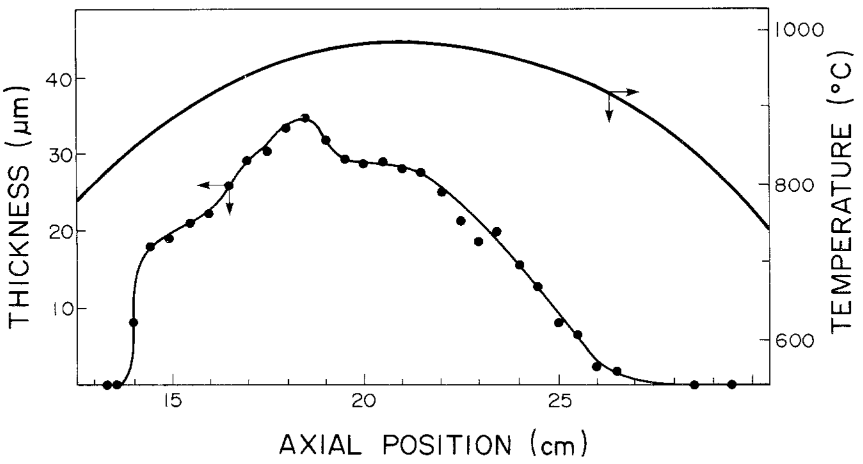

Figure 2 CVD furnace temperature profile thickness distribution [15].

When the TC of all reflection planes is unity, the distribution of crystal orientation is random. When the TC of any (*h k l*) plane is larger than unity, a preferred orientation exists in which grains are oriented with their (*h k l*) planes parallel to the surface.

The texture coefficients of TiN films in Table I were calculated using peak intensities in Itoh's paper instead of integrated intensities which are not available. Therefore, the TC may be slightly erroneous. However, they are good enough for the purpose of the present discussion.

Table I indicates that the film deposited at the position from 14.2 to 15.1 cm has the major [1 1 1] + minor [3 1 1] texture, while the film from 16.4 to 25.2 cm has the [1 1 0] texture. The strongest [1 1 0] texture is located at the position from 16.5 to 17.3 cm where the film thickness reaches its maximum and the furnace temperature approaches the maximum. As the position approaches the outlet from the peak thickness position, the texture coefficient of (1 1 0) decreases while the texture coefficient of (1 1 1) increases.

The above result can be explained by the present model. At the inlet side (14.2 to 15.1 cm), the quantity of $TiCl_4$ vapour saturated in the H_2 gas is largest, but its temperature must be the lowest because the incoming gas has a lower temperature of 30 to 70° C. Therefore, effective vapour concentration adjacent to the deposit surface must be low as can be seen from the depressed thickness. Consequently, the deposit has the [1 1 1] texture. At the position from 16.5 to 17.3 cm, the vapour concentration adjacent to the deposit surface must be highest. Therefore, the deposit has the [1 1 0] texture as expected from the model. As the position approaches the outlet, vapour is being consumed, and hence the vapour concentration adjacent to the deposit decreases as can be seen from decreasing thickness. It follows that the texture coefficient of (1 1 0) decreases while the texture coefficient of (1 1 1) increases.

A recent study [16] on the orientation of plasma vapour deposit of TiN showed that the [1 1 1] orientation was obtained in most deposition conditions, whereas [1 0 0] texture was obtained in the case of larger plasma concentration and higher bias voltage of the substrate, which are expected to give rise to the higher vapour concentration adjacent to the deposit. Therefore, the results are also compatible with the model.

3.2. Bcc crystals

The crystallographic texture of physically vapour deposited chromium changed from the [1 1 0]–[1 1 2] texture at low deposition temperatures to the [1 0 0] textures at high temperatures within the measured temperature range from 600 to 1300 K. As temperature increased, the degree of [1 0 0] texturing increased markedly. At low deposition temperatures, a strong preferred orientation of [2 1 1] is generally observed in bcc iron [17].

At low argon pressures and T/T_m, bcc chromium and molybdenum coating sputter deposited on glass and stainless steel substrates in the post and hollow cathodes had the [1 1 0] orientation [13]. Titanium coatings sputter deposited on liquid nitrogen-cooled glass substrates were in bcc β phase with the [1 1 0] orientation [13].

The above observations are compatible with the model in a preference for orientations that place the most densely populated atomic planes or the lowest surface energy crystal facets ({1 1 0}, {1 1 2} planes) parallel to the substrate at low temperatures and that place the less densely populated atomic planes or the higher surface energy lattice planes ({1 0 0} planes) parallel to the substrate at the higher temperatures. It is also noted that the refractory bcc metals, which have high melting points and low vapour pressures, tend to prefer orientations that place the lowest surface energy facet parallel to the substrate in most evaporating conditions. The high melting point and low vapour pressure of the refractory metals imply the strong atomic bonding which, in turn, makes the substrate consume neighbouring vapour atoms so rapidly that it assumes the orientation that places the lowest surface energy facet parallel to the substrate.

3.3. Hcp crystals

The texture of beryllium changed from the [0 0 0 2] orientation at low deposition temperatures to the [1 1 $\bar{2}$ 0] orientation at high deposition temperatures [18]. For zinc, the [0 0 0 2] texture was observed for coatings evaporated at 150 to 250° C [19, 20]. At a substrate temperature of 50° C, this texture was pronounced. At higher evaporation rates, the [1 0 $\bar{1}$ 2] texture was observed [20]. Titanium coatings deposited on 20° C glass substrates were in hcp α phase with a high degree of basal plane orientation [13]. Titanium coatings deposited on 200° C glass substrates assumed the $[0002]$ texture, whereas coatings deposited on 400° C steel substrate assumed the $[01\bar{1}1]$ texture [21].

The above results also imply that the deposits assume the orientation that places the lowest surface energy crystal facet, basal plane, parallel to the substrate under the conditions of low atom concentration adjacent to the substrate (low deposition temperatures) and as the atom concentration increases (high deposition temperatures, and high evaporation rates) the deposits assume the orientation that places the higher surface energy facets, for example, $\{11\bar{2}0\}$ or $\{10\bar{1}2\}$ planes, parallel to the substrate, in agreement with the present model.

3.4. ZnO

The preferred orientation of ZnO films prepared by r.f. sputtering was studied by Murti and Bluhm [22]. ZnO films were deposited at deposition rates from 0.03 to 0.3 nm sec^{-1} on to Corning 7059 and NESA glass substrate with and without the application of bias voltage to the substrate. It was found that at relatively low deposition rates (0.03 nm sec^{-1}) the film had a preferred $[0002]$ orientation which changed to $[11\bar{2}0]$ with increasing deposition rate. At higher deposition rates (0.3 nm sec^{-1}) the film had the $[10\bar{1}0]$ orientation. They also found that neither the crystallinity of the glass substrate nor the bias voltage applied to the substrate significantly affected the orientation of ZnO films, but the deposition rate significantly affected the orientation of the films.

The results imply that the deposition rate was mainly controlled by sputtering power. The lower deposition rate corresponds to lower sputtering power, which in turn gave rise to lower atom or ion concentrations adjacent to the deposited film. Therefore, the closest packed atomic plane (0002) was formed parallel to the substrate in agreement with the present model. The higher deposition rate or the higher sputtering power yielded higher atom or ion concentration adjacent to the film, which in turn gave rise to preferred orientations of less densely packed atomic planes such as $(11\bar{2}0)$ and $(10\bar{1}0)$ planes.

4. Conclusion

The texture of vapour deposits changes from the orientation that places the lowest surface energy crystal facets ($\{111\}$ for fcc, $\{110\}$ or $\{112\}$ for bcc, and basal planes for hcp) parallel to the substrate under the conditions of low atom or ion concentration adjacent to the substrate, to the orientation that places the higher energy crystal facets or the less densely populated atomic planes parallel to the substrate with increasing atom or ion concentration adjacent to the substrate.

The bcc metals which have high melting temperatures and low vapour pressure tend to assume the orientation which place the lowest surface energy crystal facets parallel to the substrate under most evaporating conditions.

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