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DEVELOPMENT OF ORIENTATION AND MICROSTRUCTURE OF VAPOR DEPOSITS

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ABSTRACT

The texture of vapor 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 condition 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 vapor pressures tend to assume the orientation which places the lowest surface energy crystal facets parallel to the substrate under most evaporating conditions. The microstructure, surface topography and preferred orientation are interrelated. For fcc deposits, the [110] texture is related to columnar structure and rough surface of grooved asperities, whereas the [111] texture gives rise to the smoother surface.

INTRODUCTION

Vapor deposited films are well known to have preferred orientations in them. The texture of vapor deposits is, in general, known to vary with deposition conditions. Walton[1)] proposed a theory of texture formation on the basis of the orientation of critical nucleus which was assumed to control the orientation of deposit. Dutta and William[2)] studied the structure of silver films deposited onto glass substrate 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 succesive developement of [111], [110], [211] orientations. The results can not be explained based on the nucleation model.

Recently Lee[3)] advanced a growth model on development of preferred orientation of vapor deposits, which is basically equivalent to his earlier model on development of orientation of electrodeposits. According to the model, the texture of vapor 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 deposits increases. Lee[4] also pointed out that the cross-sectional microstructure, surface morphology and texture of the deposits were interelated.

The purpose of this paper is to discuss experimental results of the texture, cross-sectional structure and surface topography of vapor deposits.

DISCUSSION ON PREPERRED ORIENTATION

FCC Crystals At low argon pressures and T/T_m, fcc copper and aluminum alloy coating sputter deposited on glass and stainless steel substrates in the post and hollow cathodes had the [111] preferred orintation. An increse in T/T_m at low argon pressures caused copper and aluminum alloy coatings deposited with both the post and hollow cathodes to assume the [110] orintation. Minor [311] orientations were consistently observed with the post cathode. Elevated argon pressures in the hollow cathodes caused copper to assume the [110] and aluminum alloy to assume the [100] orientation [5] However, copper and aluminum alloy coatings at high argon pressures with the post cathode had the [111] orientation at all temperatures from 20 to 800° C.

This results may be explained based on the growth model. The lower temperatures would tend to yield the [111] orientation, whereas the higher temperatures would tend to yield the [110] orientation because the atom concentration adjacent to the deposit would be low at the lower temperatures and high at the higher temperatures. When the other conditions were same (elevated argon pressures), the hollow cathodes tended to give rise to the higher surface energy crystal facets oriented parallel to the deposit surface whereas the post cathode tended to cause the lower surface energy facets oriented parallel to the deposit surface (copper and aluminum alloy coatings had the [111] orientation), because the hollow cathode would guide vapor into the more restricted area than post cathode and hence yield the higher atom concentration next to the coatings than the post cathode.

Itoh *et al.* [6] studied chemical vapor 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. $TiCl_4$ vapor was saturated in the H_2 gas at a given temperature (30 to 70 ^{o}C) and was carried to the steel tube in the deposition zone of furnace. The temperature profile and film thickness distribution in the CVD furnace is shown in Fig. 1. The texure of films at various positions of the substrate are expressed in terms of the texture coefficients in Table 1. The results can be explained by the growth model. At the inlet side (14.2 to 15.1 cm), the quantity of $TiCl_4$ vapor saturated in H_2 gas is largest but its temperature must be lowest because the

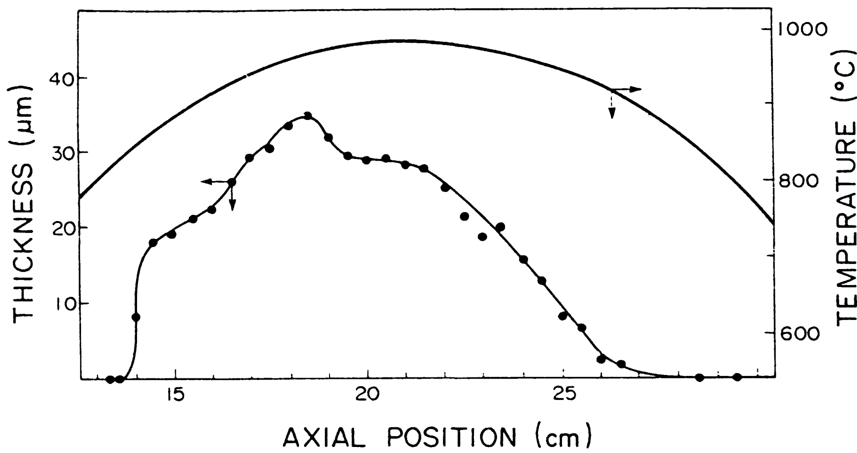

Fig. 1 CVD furnace temperature profile and film thickness distribution.

Table 1. Texture coefficents of reflection planes of CVD TiN films.

Substrate position (cm)	(111)	(100)	(110)	(311)
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

incoming gas has the lower temperature of 30 to 70°C. Therefore effective vapor concentration adjacent to the deposit surface must be low as can be seen from the depressed thickness. Consequently the deposit has the [111] texture. At the position from 16.5 to 17.3 cm, the vapor concentration adjacent to the deposit surface must be highest. Therfore the deposit has the [110] texture as expected from the model. As the position approaches the outlet, vapour is being consumed, and hence the vapor concentration adjacent to the deposit decreases as can be seen from decreasing thickness. It follows t hat the texture coefficent of (110) decreases while the texture coefficent of (111) increases.

A work by Kobayashi and Doi [7] also showed that the orientation of TiN deposit by the biased activated reactive evaporation changed from [111] to [220] with increasing absolute value of negative bias voltage of substrate. The higher plasma concentration, temperature and bias voltage would give rise to the higher vapor concentration adjacent to the deposit. Ion - plated TiN coatings grown at about 500K were strongly [111] textured at low deposition rates, however, the preferred orientation changed towards [200] as deposition rate was increased.[8] The increased deposition rate may be an indirect evidence of increased concentration of ions or atoms adjacent to the substrate, which in turn might give rise to the less closely packed plane parallel to the substrate in accordance with the model.

BCC Crystals The crystallographic texture of physically vapor deposited chromium changed from the [110]-[112] texture at low deposition temperatures to the [100] textures at high temperatures within the measured temperature range from 600 to 1300 K. As temperature increased, the degree of [100] texturing increased markedly. At low deposition temperatures, a strong preferred orientation of [211] is generally observed in bcc iron [9]. 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 [110] orientation [5]. Titanium coatings sputter - deposited on liquid nitrogen cooled glass substrates were in bcc β phase with the [110] orientation [5].

The above observation are compatible with the growth model in a preference for orientations that place the most densely populated atomic planes or the lowest surface energy crystal facets ({110}, {112} planes) parallel to the substrate at low temperatures and that place the less densely populated atomic planes or the higher surface energy lattice planes ({100} 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 vapor 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 vapor pressure of the refratory metals imply the strong atomic bonding which in turn makes the substrate consume neighboring vapor atoms so rapidly that it takes the orientation that places the lowest surface energy facet parallel to the substrate.

HCP Crystal The texture of beryllium changed from the [0002] orientation at low deposition temperatures to the $[11\bar{2}0]$ orientation at high deposition temperatures [10]. For zinc, the [0002] texture was observed for coatings evaporated at 150 to 250°C [11),12]. At substrate temperature of 50°C, this texture was pronounced. At higher evaporation rates, the $[10\bar{1}2]$ texture was observed [12]. Titanium coatings deposited on 20 °C glass substrates were in hcp α - phase with high degree of basal plane orientation [5]. 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 [13].

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 condition 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 deposit assume 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.

CROSS SECTIONAL STRUCTURE AND SURFACE TOPOGRAPHY

Lee [4] pointed out that the microstructure, surface topography and preferred orientation were interrelated. For fcc deposits, the [110] texture may

be related to a fine field oriented texture type structure, whereas the [111] texture is related to a lamellar structure in field oriented columns whose boundaries are not very clear when twinning takes place, since the lamellar structure originates from traces of {111} twin planes. In the absence of twinning, the lamellar structure can not be observed.

The fcc copper electrodeposits with more or less the [111] texture had the smoother surface than those with the [110] texture. Surface asperities of deposits with the [111] texture were round and smooth, whereas those of deposits with the [110] texture had recessed grooves. For the fcc deposits with [111] texture, the asperities are not expected to grow high, because the higher aseprities would give rise to the higher surface energy than those of deposits with any other texture. For fcc deposits with the [110] texture, asperities can grow high, since the {111} planes can be parallel to the field direction. The grooves in the asperity originate from the {111} planes parallel to the field direction.

The cross sectional microstructure and surface topography of vapor deposits are also related to their texture. Figs.2 (a) and (b) show scanning electron micrographs of a chemical vapor deposit of TiN with the [110] texture and of an ion plated TiN film with the [111] texture, respectively [14]. The deposit with the [110] texture shows the well defined columnar structure and the rough surface having grooved asperities, whereas the deposit of the [111] texture shows a relatively smooth surface.

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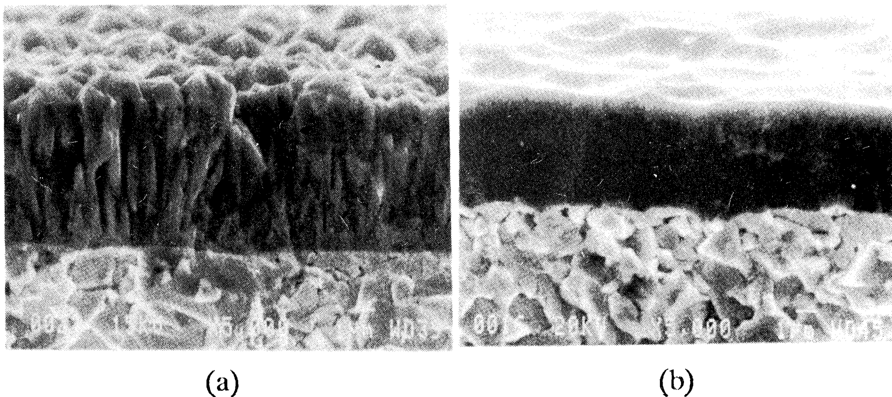

(a) (b)

Fig.2 Microstructure of cross section and surface topography of (a) CVD TiN of [110]texture and (b) PVD TiN of [111] texture.[14]

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