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# TEXTURE AND RELATED MICROSTRUCTURE AND SURFACE TOPOGRAPHY OF VAPOR DEPOSITS

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## ABSTRACT

The texture of vapor deposits(PVD and CVD) changes from the orientation that places the lowest energy latttice plane 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 planes parallel to the substrate as the atom or ion concentration adjacent to the deposit increases. However, in the early stage of deposition, the deposit-substrate interface energy and the surface energy constitute the most important energies of the system. Therefore, if the lattice match is established between the substrate and the deposit without generating much strain energy, the epitaxial growth takes place to reduce the interfacial energy. When the epitaxial growth does not take place, the surface energy is dominant in the early stage of deposition and the lowest energy crystal plane tends to be placed parallel to the substrate up to a critial thickness. The thickness depends on the deposition condition. If the deposition condition does not favor placing the lowest energy crystal plane parallel to the substrate, the initial texture will change to that compatible with the deposition condition as the film thickness increases, and the texture turnover thickness will be short. The microstructure and surface topography of deposits are related to their texture.

## INTRODUCTION

Vapour-deposited films are well known to have texture or preferred orientations in them, the texture of the vapour deposits being, in general, dependent on deposition conditions. The present author [1] advanced a model in which a preferred orientation is developed by the selection for survival of grains which are favorably oriented. The model is a growth theory of the development of preferred orientation unlike Walton's nucleation theory [2]. It is generally accepted that a random polycrystalline structure is obtained up to a critical film thickness unless an epitaxial growth condition is satisfied.

The preferred growth model [1] suggests that the preferred orientation or texture of physical or chemical vapor deposits changes from the orientation that places the smaller surface energy crystal plane normal to the growth direction under the condition of low atom or ion concentration adjacent to the deposit to the orientation that places the higher energy crystal planes normal to the growth direction as the atom or ion concentration

adjacent to the deposit increases, unless the deposition temperature is high enough for recrystallization to take place. At such high temperatures, the minimum energy crystal plane tends to be placed normal to the growth direction to minimize the total energy of the system, because the surface energy may be a source of the largest energy in the growing system.

The present author has received many valuable criticisms and comments. In this paper themodel has been elaborated and the more experimental evidences, which are in favor of the model, have been reviewed.

## DEVELOPMENT OF PREFERRED ORIENTATION (THE PREFERRED GROWTH MODEL)

Fig. 1 shows a two-dimensional model of two adjacent crystals. The surface energy of a crystal plane 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 closely 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 crystal 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

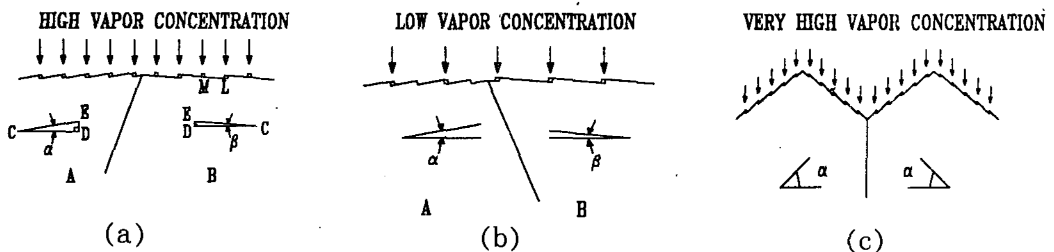



Fig. 1 Two-dimensional model explaining development of texture of vapor deposit.

atoms is larger for crystal A than for crystal B, because angle a is larger than angle $\beta$. 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 ease of high concentration, because atoms are not sufficiently supplied. This situation is 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.

This preferred growth model is based on the assumption that the crystal growth front is flat, the direction of impinging ions or atoms is normal to the deposit, the surface diffusion rate is high enough for reduced atoms or condensed species to adjust themselves to stable positions, and the relative lattice surface energies are not influenced by atmosphere covering the deposit.

If the ion or atom concentration is too high for the ledges on flat deposit surface to accept, the deposit surface roughens to increase the ledge density(Fig. 1c). This is compatible with the fact that rough surfaces are often observed in deposits with texture of higher surface energy crystal plane parallel to the substrate plane. If impurity elements like oxygen are codeposited, the crystal growth is hindered by the impurity and the deposit tends to have very fine grains with the random orientation.

However, in the early stage of deposition, the deposit-substrate interface energy, the grain boundary energy and the surface energy constitute the important energies of the system. Therefore, if the lattice match is established between the substrate and the deposit without generating high strain energy, the epitaxial growth takes place to reduce the interfacial energy. When the lattice match between the substrate and the deposit is impossible or deposition takes place on an amorphous substrate, the epitaxial growth cannot take place, because it may generate very high strain energy which exceeds the interfacial energy. If the epitaxial growth does not take place, the strain, grain boundary and surface energies will control the texture. When strain energy is dominant, the lattice plane whose biaxial elastic modulus(Appendix) is minimum will be placed parallel to the substrate, whereby the strain energy of the thin deposit becomes minimum. In case that the surface energy becomes dominant, the minimum energy lattice plane will be placed parallel to the substrate. Since vapor deposition proceeds by the interaction between vapor and deposit surface, the surface energy seems to be more important than the strain energy. In the initial stage the grain size of deposit is very small and so the grain boundary energy becomes very important. Therefore, grains try to be oriented so that their minimum surface energy lattice plane can be placed parallel to the substrate to minimize the surface layer energy.

As the deposit thickness increases, the columnar grain diameter increases, and the interface and grain boundary energy effects decrease. Therefore, the texture becomes controlled by the surface energy and the vapor concentration adjacent to the deposit as explained in Fig. 1. The total strain energy of thick deposit cannot be related to the texture formation, unless the temperature of deposit is high enough to cause recrystallization, in which temperature range the atomic mobility in the bulk becomes important.

## DISCUSSION

### Fcc metals

In fcc metals, the {111} planes have the smallest surface energy and the {110} planes have the highest surface energy among low index planes(Fig. 2) Therefore, the preferred growth model suggests that the orientation of fcc metals changes from <111> to <100> and finally to near <110> with increasing deposition temperature unless the temperature is high enough to cause recrystallization, because the increase in temperature tends to increase the concentration of vapor atoms or ions adjacent to the growing deposit(Fig. 3). At temperatures high enough for recrystallization to take place, the <111> orientation will be again obtained, because the surface energy controls the texture of thin films unless the surface energy is not very much modified by any surface adsorption.

Dutta and Wilman[4] studied the structure of silver films deposited at $7\times0^{-6}$ to $7\times10^{-3}$ torr on 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 <111>, <110>, <110>+<211> orientations as shown in Fig. 4.

The initial random and subsequent <111> orientations are expected from the preferred growth model. The turnover from <111> to <110> with increasing film thickness may be attributed to an increase in temperature of the deposit due to heat of condensation of atoms to form a lattice(condensation heat of silver : 633J/g at 298K) and radiant heat be attributed to an increase in temperature of the deposit due to heat of condensation of atoms to form a lattice(condensation heat of

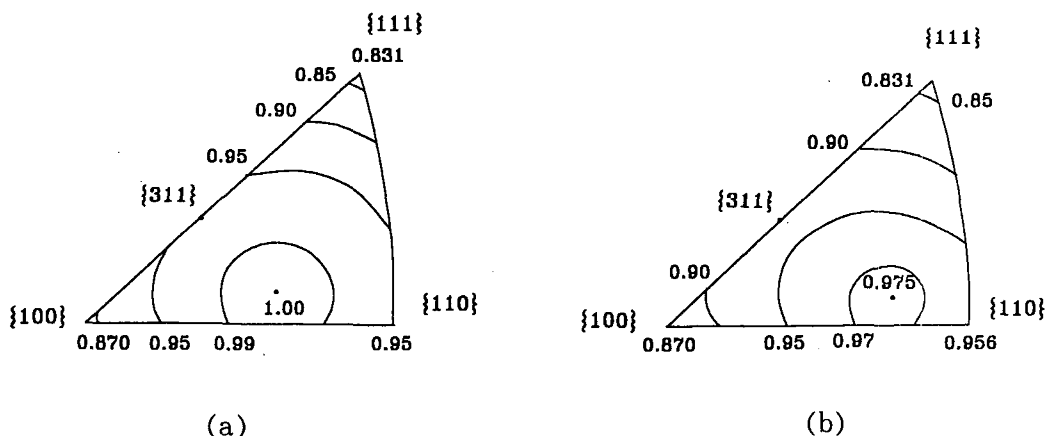



Fig. 2 Surface energy plots for fcc crystals, (a) theoretical and (b) experimental results(3).

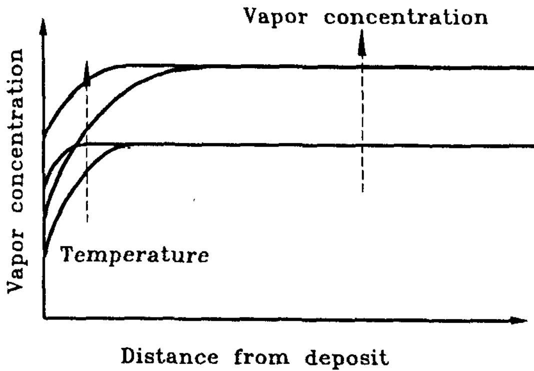



Fig. 3. Effects of deposition conditions on depositing material vapor concentration distribution Arrows indicate increasing directions.

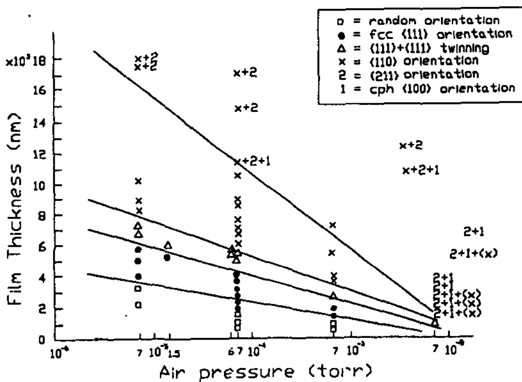



Fig. 4 Surface orientation of silver films condensed at 3.0~3.5 nm/s on glass substrate initially at room temperature depending on film thickness and residual air pressure(4).

silver : 633J/g at 298K) and radiant heat from the hotter source of vapor. The higher surface temperature can give rise to the higher vapor concentration adjacent to the deposit(Fig. 3), which in turn placed the higher surface energy lattice plane {110} parallel to the substrate. The texture turnover may be argued to be due to an increase in strain energy of the deposit with increasing thickness. If the strain energy controlled the texture, the <100> texture would have been obtained, because the mean biaxial elastic modulus, which is proportional to the strain energy of thin deposit, of silver is minimum in the {100} planes(Fig. 5). Appearance of the <211> texture at a much later stage of deposition may be due to a lattice plane whose surface energy is higher than that of the {110} planes placed parallel to the substrate(Fig. 2).

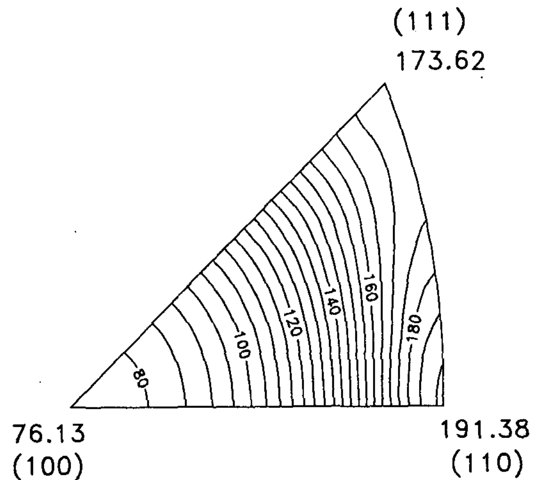



Fig. 5 Calculated mean biaxial elastic modulus of silver at room temperature.

**Bcc metals**

The refractory bcc metals, which have high melting points and low vapour pressures, tend to prefer orientations that place the lowest crystal surface energy plane 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 the atom or ion concentration becomes very low(low temperature curves in Fig. 3), which in turn gives rise to

the orientation that places the lowest surface energy plane parallel to the substrate(Fig. 6).

Drusedau et al[5]. studied the texture and surface topography of molybdenum thin films deposited on a silica substrate by magneton sputtering. A magneton source with a 90mm diameter, 99.95% molybdenum target, operating at 20W dc-power in argon (99.9999%) atmosphere was used. The substrate temperature was kept at 470K. Argon pressure was varied between 0.45 and 4.7 Pa and the deposition rate was less than 0.1nm/s. The density of the films decreased monotonically with increasing argon pressure from 96% to 48% of bulk Mo. The low density films were amorphous and nanocrystalline with <110> texture at thicknesses of 30 nm and 3$\mu$m, respectively. For the dense films(density around 96%) deposited at 0.45Pa, their X-ray diffraction spectra showed that the 23nm thick film had only the (110) peak, the (211) peak appeared too in the 290nm thick film, and the (211) peak became the dominant signal at a thickness of 990nm. For the 290nm specimen, a peak related to $Mo_5Si_3$ appeared, which is thought to be related to interfacial reactions with the silica substrate and the molybdenum film. Upon increasing film thickness to 2.6$\mu$m, the peak related to $Mo_5Si_3$ monotonically decreased and a peak related to $MoSi_2$ appeared. The surface roughness of the films increased with thickness from 0.8 nm to 7 nm.

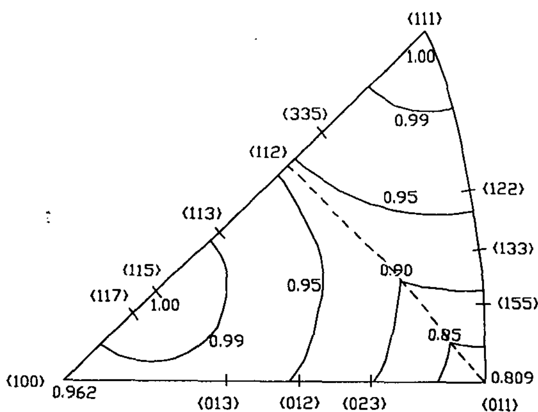



Fig. 6 Relative surface energy plot for bcc crystal based on the broken-bond model of Mackenzie et al. (3)

The above results indicate a turnover of the film texture with film thickness from the <110> texture to the <211> texture. The turnover of texture may be explained based on the preferred growth model. As already mentioned above, the most probable texture is the <110> texture. As the thickness increases, the temperature of film surface increases, because the heat of condensation of molybdenum vapor(6851 J/g at 500K) is increasingly difficult to be removed with increasing thickness of specimen at a given substrate temperature. The formation of the molybdenum silicides reflects the increase in film temperature. The increase in temperature will increase the concentration of metallic vapor adjacent to the surface of deposit, which in turn will place the higher surface energy lattice plane parallel to the substrate plane, according to the preferred growth model. This may be the case of development of the <211> texture at the higher thickness. The increase in surface roughness with thickness is expected from explanation of Fig. 1c.

It may be argued that the stress and so the strain energy of deposit increase with increasing thickness, which in turn gave rise to the texture turnover. Fig. 7 shows the biaxial elastic modulus(Appendix), which reflects the strain energy of deposit under plane stress, as a function of orientation. The dif-

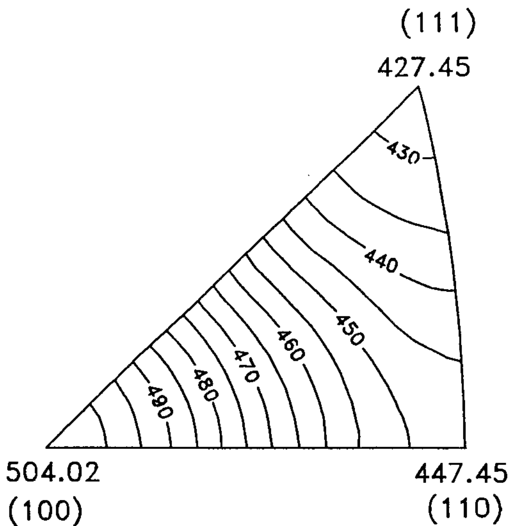



Fig. 7 Calculated mean biaxial elastic modulus distribution of Mo.

ference between the moduli for the <110> and <112> orientations is negligible (the biaxial moduli of <110> and <112> are calculated to be 447.45 and 444.6 GPa, respectively, at room temperature) and so the strain energy effect can be excluded.

**Hcp metals**

The texture of beryllium changed from the [0002] orientation at low deposition temperatures to the [11$\bar{2}$0] orientation at high deposition temperatures[6]. For zinc, the [0002] texture was observed for coatings evaporated at 423 to 523K[7, 8]. At a substrate temperature of 323K, this texture was pronounced. At higher evaporation rates, the [10$\bar{1}$2] texture was observed[8]. Titanium coatings deposited on 293K glass substrates were in hcp a phase with a high degree of basal plane orientation[9]. Titanium coatings deposited on 473K glass substrates assumed the [0002] texture, whereas coatings deposited on 673K steel substrate assumed the [01$\bar{1}$1] texture[10].

The above results are in agreement with the prediction of the preferred growth model in that the [0002] texture would be obtained at low deposition temperatures, whereas as the metallic vapor concentration increases (high deposition temperatures, and high evaporation rates) the deposits assume the orientation that places the higher surface energy planes, for example, {11$\bar{2}$0} or {10$\bar{1}$2} planes, parallel to the substrate.

Jang[11], in his RF sputtered Co-Cr deposits, found unusual phenomenon that deposits formed on water cooled polyimide substrates had the larger grain size than the deposits formed on 473K polyimide substrates. Fig. 8 shows TEM images and SAD patterns of 50nm thick Co-17%Cr films formed on water cooled and 473K polyimide substrates. The SAD pattern of the film deposited on the water cooled substrate shows very strong (20$\bar{2}$0), (11$\bar{2}$0) and (10$\bar{1}$0) rings suggesting a good c-axis alignment to the growth direction, whereas (0002), (10$\bar{1}$1), (10$\bar{1}$2) and (10$\bar{1}$3) rings which should be excluded for a good c-axis alignment appear with relatively strong intensity in the film formed on the 473K substrate. The results are in agreement with the prediction of the the preferred growth model in which a good c-axis alignment to the growth direction is favored at the lower deposition temperature.

Fig. 8 also shows that the film deposited on the water cooled substrate has the larger grain size than the film formed on the 473K substrate. This is opposite to the usual observation that the lower temperature gives rise to the finer grains. The grain size of the deposit whose grains are oriented so that their minimum surface energy plane (0002) may be parallel to the substrate tends to be larger

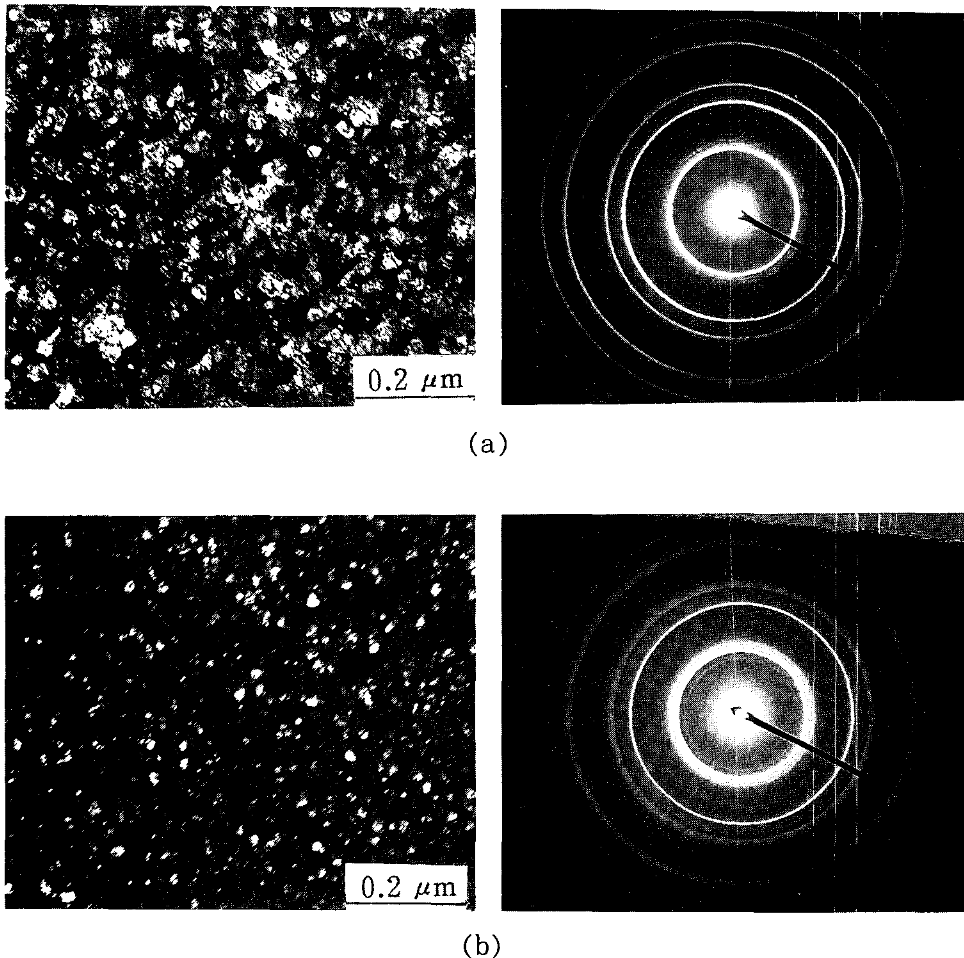


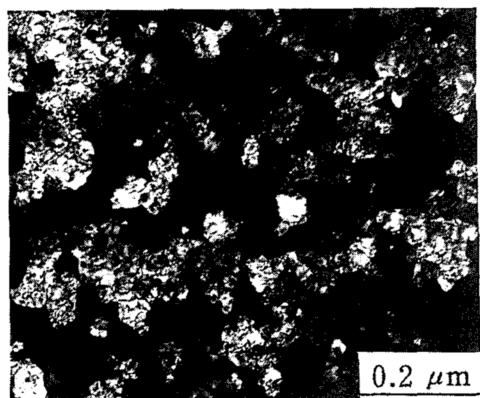

Fig. 8 TEM dark field images and SAD patterns of 50nm thick Co-17%Cr-17%Cr films RF sputtered on (a) water cooled and (b) 473K polyimide substrates(11).

than that of deposits having other orientations to reduce energy of the system. The degree of grain coarseness will depend on the surface and grain boundary energies. Thus, the coarser grains in the deposit formed on water cooled substrate is thought to be due to the well developed [0002] texture. The similar result was observed in fcc copper electrodeposits[12, 13], in which the <111> deposit showed the lower strength than the <110> deposit when they were obtained at the similar deposition conditions, due to coarser grains even though they were obtained at lower temperatures[14]. The Co-22%Cr films show the similar phenomenon(Fig. 9). The more results are given in papers by Jang et al[15, 16] If the texture is the same, the grain size decreases with decreasing deposition temperature.

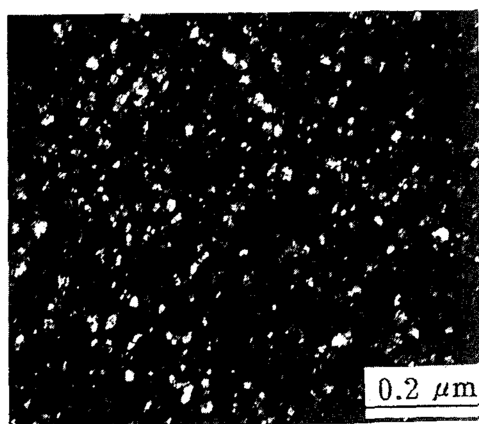
**Ceramics**

TiN

TiN film is widely used as a coating mate rial due to its high melting point and hard




(a)




(b)

Fig. 9 TEM dark field images of 50nm thick Co-22 %Cr film on (a) water cooled and (b) 473K polyimide substrates(11).

ness, good erosion and corrosion resistance, and good conductivity. The film is prepared by physical vapor deposition(PVD) or chemical vapor deposition(CVD). The texture of TiN films is known to vary with fabrication conditions.

Je et al[17]. studied the texture of TiN films grown on Si(001) substrates by radio frequency(RF) magneton sputtering in an X-ray sputtering chamber in which a TiN target was placed 10 cm away from the substrate. The sputter gun was operated with RF power between 6 and 12 W/㎠. Either $5 \times 10^{-3}$ torr Ar or a mixture of $5 \times 10^{-3}$ torr Ar and $1.5 \times 10^{-3}$ torr $N_2$ was used as carrier gases. The substrate temperature was fixed at 373K.

They found that during the very early stage of the film growth(<23nm) the random orientation distribution was obtained, indicating the nucleation and early stage growth took place in the random orientation. Following the random orientation growth, the (002) peak intensity increased rapidly until the film thickness reached about 100nm. After this stage, the intensity of the (111) peak began to increase rapidly.

The random orientation in the initial stage of the film growth is due to the fact that the substrate temperature(373K) is too low (m.p. of TiN is 3203K) for atoms to be adjusted into more stable positions. As the film grow, the temperature of the deposit increases due to heat of condensation, which in turn increases atomic mobility, so that the <100> texture was developed, followed by the <111> texture. Here the {100} planes are thought to have the minimum surface energy. In ref. 1, the (111) plane was assumed to have the minimum surface energy for lack of experimental data. The turnover from the <100> texture to the <111> texture is compatible with the preferred growth model which places the higher surface energy lattice plane parallel to the substrate at the higher temperature. In fact, the deposits with the <111> texture were less strained than those with the <100> texture[17], which reflects the higher temperature in the <111> deposits, resulting in the higher atomic mobility and the less defects.

Je et al[17, 18]. attributed the texture turn-

over to the competition between the surface and strain energies of film. Their explanation is based on Pelleg et al.s suggestion that the texture of TiN thin film was caused to lower the overall energy of the film which is the sum of the surface and strain energies, and the film would grow toward the {100} planes with the lowest surface energy when the surface energy is dominant, whereas it grow toward the (111) plane with the lowest strain energy when the strain energy is dominant[19]. Oh and Je[18] attributed the texture turnover from the <100> to <111> to accumulated strain energy with increasing film thickness. They also claimed that the decrease in the texture turnover thickness with increasing RF sputtering power was due to the increased kinetic energy of sputtered particles, which was supposed to increase the film strain energy.

However the film growing process at low temperatures is basically the interaction between vapor and deposit surface. Therefore, the total energy of film cannot be a determining factor of the texture formation. If the total energy controls texture, the texture turnover from the <111> to <100> texture will not take place. However, it can happen as will be seen later. The increase in RF power is expected to increase the film temperature rising rate due to the increased kinetic energy of sputtered particles, which in turn shorten the turnover thickness. Thus the RF effect on the texture turnover thickness is expected from the preferred growth model.

They also found that the TiN films sputtered at 12W/㎠ with $5\times10^{-3}$ torr Ar underwent the turnover from the <100> to <111> texture with increasing thickness, whereas

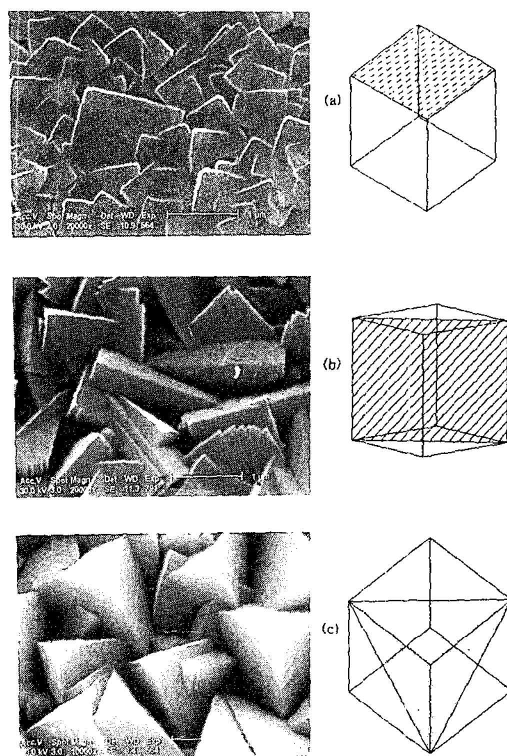



Fig. 10 Surface topographies and models of TiN films with (a) <100>, (b) <110>, (c) <111> textures(20).

the films sputtered at 12W/㎠ with a mixture of $5\times10^{-3}$ torr Ar and $1.5\times10^{-3}$ torr $N_2$ kept the initial texture <100>. The film growth rate also decreased from 1.2 to 0.6nm/min with the addition of $N_2$ gas[17]. The result can be explained by the preferred growth model as follows: The decreased growth rate reflects the lower vapor concentration adjacent to the deposit which in turn places the lower surface energy lattice planes {100} parallel to the substrate.

The CVD can also yield different textures depending on preparation conditions. Min[20] studied the texture of TiN films prepared on Si(100), Si(111), glass and silica by low temperature CVD in which $TiCl_4$ and $NH_3$ as re

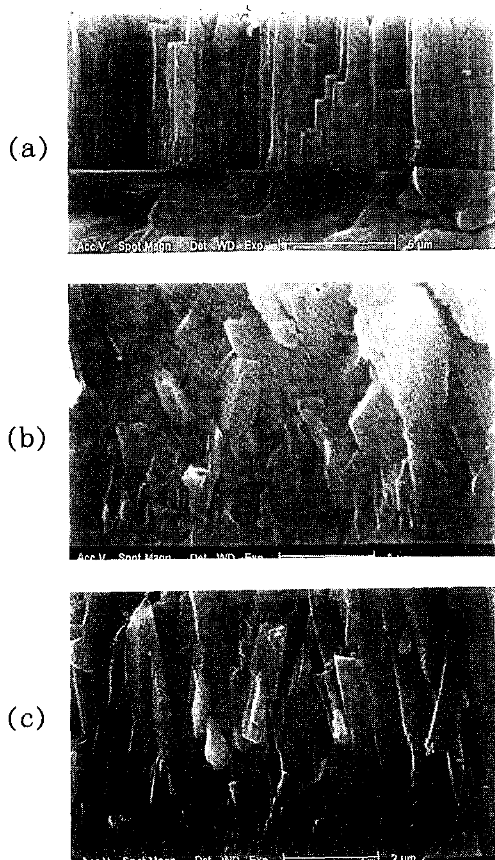
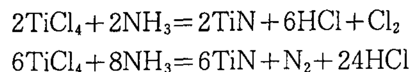



Fig. 11 Cross-sectional structures of TiN films with (a) <100>, (b) <110> and (c) <111> orientations(20).

active gases and Ar as carrier gas were used at a deposition temperature of 973K. The growth rate of TiN films increased from 0.2 to 30㎛/hr with increasing gas flow rate. The growth rate was very much influenced by the $NH_3$ flow rate. The texture of TiN films changed from the <100> to <110> or <111> orientation with increasing growth rate. However, the films obtained at the initial stage of growth yielded the <100> orientation, regardless of deposition conditions within the experimental range.

The results are in agreement with the prediction of the preferred growth model assuming that the (200) plane has the minimum surface energy as in PVD. The increase in growth rate was achieved by increasing gas flow rate which increased the vapor concentration adjacent the deposit, and placed the higher surface energy lattice plane parallel to the substrate. Under the deposition conditions which yield the <100>, <110> and <111> orientations at 973K, the decrease in the deposition temperature below 973K gave rise to the <100> orientation in agreement with the preferred growth model. As the film thickness increases, grains with the <100> orientation continued to grow stably under the condition in which the gas concentration adjacent to the growing deposit was low. The <200> orientation of the film changed to the <110> or <111> orientation when the condition favoring the <110> or <111> prevailed, and vice versa. If the total strain energy controlled the texture, the inversion from the <110> or <111> to the <100> texture would not have taken place. The proposed following reactions for the formation of TiN are endothermic.



$$2TiCl_4 + 2NH_3 = 2TiN + 6HCl + Cl_2$$
$$6TiCl_4 + 8NH_3 = 6TiN + N_2 + 24HCl$$

Therefore the texture turnover from the <100> to <110> or <111> texture did not take place during film growth unless the deposition condition changed, unlike in PVD.

Jiang et al [21]. obtained the similar texture trend in their TiN films prepared by CVD using $TiCl_4$, $NH_3$ and $H_2$ as reaction gases. They obtained the <100>, <110> and <111> textures at graphite substrate temperatures of 1373, 1673 and 1773K, respectively.

The surface topographies and the cross sec-

tional structures of TiN films are closely related to their textures as shown in Figs.10 and 11, respectively. The surface topographies are easily understood based on the fact that the surfaces are covered with the minimum surface energy lattice planes {100}. The cross sectional structures indicate that crystals tend to grow along the <100> directions and normal to the substrate.

## CONCLUSION

The texture of vapour deposits changes from the orientation that places the lowest surface energy crystal planes({111} for fcc metals, {110} for bcc metals, basal planes for hcp metals, and {100} for TiN) 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 planes 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.

The surface topography and the cross-sectional microstructure of vapor deposits are closely related to the their textures.

## ACKNOWLEDGMENT

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