

Structure Analysis of Vacuum-Deposited Mg Thin Films

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Thin films of Mg, in the thickness range of 23,000 ~ 93,000 Å, were prepared at 10^{-6} Torr pressure and 45°C temperature. The x-ray diffraction spectra (XDS) have been measured for several reflections with crystal monochromated and Ni-filtered $\text{CuK}\alpha_1$ radiation. A detailed Fourier analysis of the broadening of x-ray lines indicated very strong effects of the oxidation of the surface, thermal stress along 100 and 002 planes, and preferred orientation along 002 planes parallel to the surface of the substrate.

1. Introduction

In our continuing interest in the investigation of the structure and properties of hexagonal close packed (HCP) metals, we would like to report the results of x-ray diffraction spectra (XDS) of vacuum deposited thin films of Mg. This will constitute the fourth paper in our series of publications [1–3] on this subject.

The HCP metal Mg differs very much from the HCP metals Cd and Zn both from the chemical and physical standpoints. For instance, Mg is prone to oxidation very rapidly and it has rather unusual Fermi surface. The surface property studies of x-ray photoelectron spectra [4] (XPS) and Auger electron spectra [5] (AES) have also indicated that even in a vacuum of 10^{-8} ~ 10^{-10} Torr Mg thin films show both chemisorbed and stoichiometric oxidation. Furthermore, a Fourier analysis [2] of the XDS of Mg polycrystalline powder resulted in an average domain size $\bar{D} = 295$ Å, a root mean square strain $e_L \cong 0$, and a deformation (α) and growth (β) fault probability of about 10^{-4} . These results differ considerably from those of Zn and Cd polycrystalline powder. For Zn we² have obtained $\bar{D} = 675$ Å, $e_L \cong 0$ and $\alpha = \beta \cong 10^{-5}$, and for Cd, we found $\bar{D} = 650$ Å, $e_L \cong 10^{-3}$, $\alpha \cong 3 \times 10^{-3}$ and $\beta = 0$. It, therefore, appears that an XDS study of Mg thin films should be quite interesting and give results leading to an explanation of many chemical and physical effects.

Recently some studies have been reported by others [6–7] on the XDS of Cd and Zn thin films, but none on Mg thin films. As we [3] have pointed out earlier in our Cd thin film work, there are

several major difficulties associated with XDS studies of thin films such as treating of the effect of preferred orientation and geometrical function. Once again we reiterate that these two effects must be appropriately visualized and removed before interpreting the results of XDS.

Many workers [6–9] seem to believe that XDS of a metal thin film should be an extrapolation or interpolation of that of the corresponding metal polycrystalline powder. Unfortunately this is not so. For HCP metals [3, 10] the maximum intensity and broadening is observed for thin films along the direction of 002 planes parallel to the surface of the substrate. The corresponding plane for FCC metals [11–14] is in 111 direction. This is due to preferred orientation effect. There is no way, to the knowledge of the present authors, one could completely eliminate this effect. However, by making thin films at oblique [15] and normal incidence with respect to the direction of easiest film growth one can probably estimate the preferred orientation parameter and introduce appropriate correction factors to the observed results. These types of studies are, however, presently lacking. Alternatively, one could make [3] analytical models and propose working functions for the preferred orientation including the geometric function. Then by deconvoluting [16] the measured XDS, it is possible to derive the line broadening parameters free of large errors. We shall follow the latter approach in this work and illustrate by computer calculations of line broadening parameters for Mg thin films.

2. Thin Film Preparation and XDS Measurement

Mg samples of 99.999% purity obtained from Ventron Corp. were used with ultrasonically

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cleansed microscopic glass slides. The details of the film preparation and recording of the x-ray pattern are the same as discussed in our earlier publications [3, 5]. Several high quality films in the thickness range of 22,800 to 92,710 Å were prepared. These are described in Table I. These films were made purposely thick because the diffracted x-ray intensities from Mg films in the smaller thicknesses, especially below about 10,000 Å, were very low due to small atomic number of Mg ($Z=12$) compared to Zn ($Z=30$) and Cd ($Z=48$). Mg films were found to be extremely oxidation prone and rather porous. The thickness measurement was done using a Sloan DEKTAK measuring system. It should be pointed out that any gravimetric measurement for thickness, as sometimes done, is impractical for Mg thin film, due to its extremely low density ($=1.74$ g/cc). The usual correction factors due to satellite radiations, nonpolarization of the x-ray beam and absorption effect were applied. The angular-dependent-satellite-separating function δ_l yielded [17] much less modulation on the high angle side of $\text{CuK}\alpha_1$ diffraction peak than when constant satellite separating function δ_0 was used.

Films	Thickness (Å)
F1	$22,800 \pm 100$
F2	33,020
F3	33,528
F4	58,420
F5	91,440
F6	92,710

Table 1. Thickness of the Mg films prepared at a pressure of 10^{-6} Torr and temperature of 45°C .

The computer analysis of the measured XDS has already been described in the Cd thin film work [3]. As it has been shown there it was not necessary to measure the Fourier coefficients of the geometrical functions, since a Gaussian function with a geometrical parameter K could be used. Furthermore, this procedure does not require any absolute magnitude of K as long as one is concerned with the particle size, mean strain and fault parameters ($3\alpha + \beta$) and ($3\alpha + 3\beta$). On the other hand, one could estimate this parameter K and the preferred orientation parameter S from this type of deconvolution procedure. One of the major efforts in this work will be to determine K and S for Mg thin films.

3. Results and Discussions

3.1. Normalized Fourier Coefficients of the Observed Spectra

The real part H_r' and imaginary part H_i' of the Fourier coefficients are shown in Figure 1. For Mg thin films, reflections 002 and 100 without faulting and reflections 101, 102 and 103 with faulting could be recorded. The reflections 104 and 004 were very weak or missing in most instances. On the other hand the reflections 002 and 100 always showed considerable intensity and broadening. The peak heights in general showed gradual enhancement with increasing thickness. The peak shifts of the measured reflections did not represent any regular pattern.

The general features of the coefficients H_r' of the films F1–F4 are the same. However, from the magnitude point of view they do not indicate any systematic pattern. We shall see later the reason for this. Contrastingly, for the coefficients H_i' , we find in the region of small distance, $0 < L < 200$ Å, two sets of trends — one set has positive coefficients, but the other set has negative

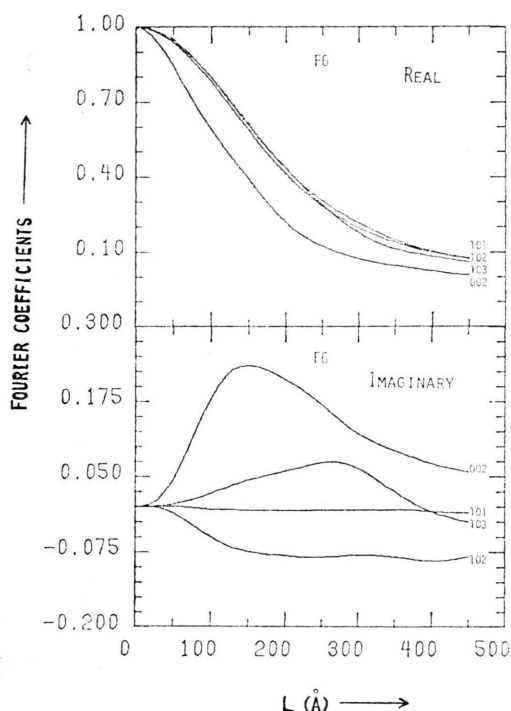


Fig. 1. The plots of the normalized real and imaginary parts of the Fourier coefficients for one of the films (F6).

coefficients. In other words, these modulations indicate that the two sets of H_1' do not begin with the same phase and amplitude.

3.2. Particle Size and Microstrain

As explained in our previous publication [3], the particle size D and effective particle size D_{eff} are represented by the initial slopes of H_r' versus L plots. Similarly, the initial slope of H_1' versus L plots is a measure of the microstrain. We use the symbols \bar{e}_L for the mean strain, e_L for the root mean square strain, K for the geometrical constant and S for the preferred orientation parameter as defined previously [3]. One can plot these values versus thickness and give equal weighting effect to every point to study thickness dependence. One

would be tempted to take advantage of these values of D_{eff} and \bar{e}_L to find the numerical magnitude of $(K + S)$. However, the equation that was suggested in the Cd thin film work, for instance, Eq. (3.20) of reference (3), is no longer of any value in this case, since reflection 004 is not available. Despite our repeated and strenuous effort to measure the reflection 004, we were not successful. Alternatively, therefore, we will suggest another way to resolve this problem.

3.3. The Geometrical and Preferred Orientation Parameters

To gain an insight about the parameters K and S we suggest the following equations, which have not been published before,

$$\frac{\partial H_r'(L)}{\partial L} = \left[-\frac{4\pi^2 L}{d_{hkl}^2} (1 - L/D_{\text{eff}}) (e_L^2 + K + S) - \frac{1}{D_{\text{eff}}} \right] \exp \left[-\frac{2\pi^2}{d_{hkl}^2} (e_L^2 + K + S) L^2 \right] \quad (1)$$

$$\text{and } \frac{\partial^2 H_r'(L)}{\partial L^2} = \left\{ -\frac{4\pi^2}{d_{hkl}^2} (1 - L/D_{\text{eff}}) (e_L^2 + K + S) + \frac{4\pi^2 L}{d_{hkl}^2 D_{\text{eff}}} (e_L^2 + K + S) \right. \\ \left. + \left[\frac{1}{D_{\text{eff}}} + \frac{4\pi^2 L}{d_{hkl}^2} (1 - L/D_{\text{eff}}) (e_L^2 + K + S) \right] \frac{4\pi^2 L}{d_{hkl}^2} (e_L^2 + K + S) \right\} \\ \cdot \exp \left[-\frac{2\pi^2}{d_{hkl}^2} (e_L^2 + K + S) L^2 \right]. \quad (2)$$

These equations in the limit $L \rightarrow 0$ will reduce to

$$\left(\frac{\partial H_r'(L)}{\partial L} \right)_{L=0} = -1/D_{\text{eff}} \quad (3)$$

and

$$\left(\frac{\partial^2 H_r'(L)}{\partial L^2} \right)_{L=0} = -\frac{4\pi^2}{d_{hkl}^2} (e_L^2 + K + S). \quad (4)$$

If we repeat this differentiation procedure for the imaginary part of the Fourier coefficients we obtain

$$\frac{\partial H_1'(L)}{\partial L} = \left[-\frac{4\pi^2 L^2}{d_{hkl}^2} (K + S) (1 - L/D_{\text{eff}}) \left(\frac{2\pi \bar{e}_L}{d_{hkl}} \right) + \frac{2\pi \bar{e}_L}{d_{hkl}} (1 - L/D_{\text{eff}}) - \frac{2\pi e_L L}{d_{hkl} D_{\text{eff}}} \right] \\ \cdot \exp \left[-\frac{2\pi^2}{d_{hkl}^2} (K + S) L^2 \right] \quad (5)$$

and

$$\frac{\partial^2 H_1'(L)}{\partial L^2} = \left\{ \left[\frac{4\pi^2 L^2}{d_{hkl}^2 D_{\text{eff}}} (K + S) \left(\frac{2\pi \bar{e}_L}{d_{hkl}} \right) - \frac{8\pi^2 L}{d_{hkl}^2} (1 - L/D_{\text{eff}}) (K + S) \left(\frac{2\pi \bar{e}_L}{d_{hkl}} \right) - \frac{4\pi \bar{e}_L}{d_{hkl} D_{\text{eff}}} \right] \right. \\ \left. + \left[\frac{4\pi^2 L^2}{d_{hkl}^2} (K + S) (1 - L/D_{\text{eff}}) \left(\frac{2\pi \bar{e}_L}{d_{hkl}} \right) - \frac{2\pi \bar{e}_L}{d_{hkl}} (1 - 2L/D_{\text{eff}}) \right] \frac{4\pi^2 L (K + S)}{d_{hkl}^2} \right\} \\ \cdot \exp \left[-\frac{2\pi^2}{d_{hkl}^2} (K + S) L^2 \right]. \quad (6)$$

In the limiting case we see

$$\left(\frac{\partial H_1'(L)}{\partial L} \right)_{L=0} = \frac{2\pi \bar{e}_L}{d_{hkl}} \quad (7)$$

and

$$\left(\frac{\partial^2 H_1'(L)}{\partial L^2} \right)_{L=0} = -\frac{4\pi \bar{e}_L}{d_{hkl} D_{\text{eff}}} \quad (8)$$

Another equation of some general interest may be derived from a linear combination of above equations,

$$e_L = \frac{d_{hkl}}{\pi L \sqrt{2}} \left[\ln \frac{H_1'(L)}{H_r'(L)} + \ln \frac{d_{hkl}}{2\pi \bar{e}_L L} \right]^{1/2} \quad (9)$$

Thus with the help of the above theory we can determine the exact value of $(K+S)$. It is, of course, not possible to isolate K from S and vice versa. A simpler way, which is a little less rigorous, would be to replace the root mean square strain term e_L of Eq. (4) by mean strain term \bar{e}_L of (7). In that case one can completely circumvent Eq. (9) and save considerable amount of computation time. We show in Table II some of the values of $(K+S)$ obtained in this way from Figure 2.

3.4. Fault Size and Fault Probabilities

For the fault size D_F and the two fault probabilities α and β we require the particle size D in that direction. As it has been demonstrated earlier [1–3] one could approximately choose the values of D of the 002 direction since no other data is available for this purpose. We adopted a similar approach and, for a set of $a = 3.2092 \text{ \AA}$ and $c = 5.2103 \text{ \AA}$, calculated the values of $(3\alpha + \beta)$ and $(3\alpha + 3\beta)$. From these values a clear cut thickness dependence was not observed. We then found it convenient to use the average values of D and D_{eff} over the entire thickness range. These values are shown in Table III. It seems quite clear that

Table 2. Preferred Orientation Parameters for Mg Thin Films along 002 planes. The slope means $(\partial^2 H_r(L)/\partial L^2)_{L=0}$.

Parameters	F1	F4	F6
slope (\AA^{-2})	0.428×10^{-5}	0.960×10^{-5}	1.189×10^{-5}
$d_{hkl}^2/4\pi^2$ (\AA^{-2})	0.1712	0.1712	0.1712
$e^2 + K + S$	0.732×10^{-6}	1.643×10^{-6}	2.034×10^{-6}
average e_L^2	0.357×10^{-6}	0.357×10^{-6}	0.357×10^{-6}
$K + S$	0.375×10^{-6}	1.286×10^{-6}	1.677×10^{-6}

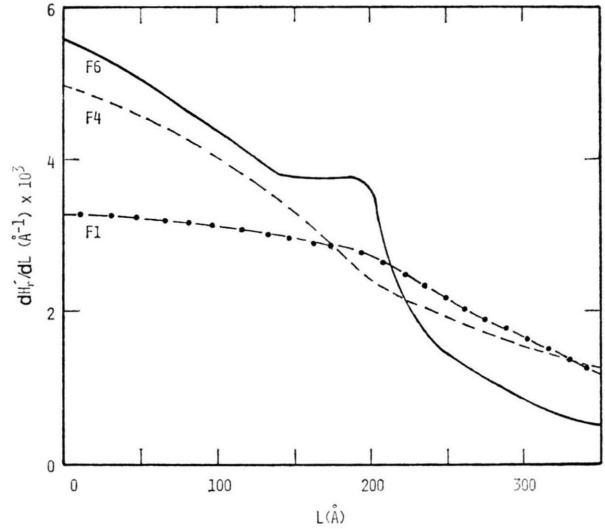


Fig. 2. The plots of $\partial H_r/\partial L$ for films F1, F4, and F6. The values of $(K+S)$ were determined from the initial slopes of these curves.

Table 3. Average Fault Size and Fault Probabilities.

Parameters	Reflections		
	101	102	103
\bar{D}	266 (\AA)	266 (\AA)	266 (\AA)
D_{eff}	243	256	233
D_F	2810	6810	1878
$(3\alpha + \beta)$	3.96×10^{-3}	1.05×10^{-3}	3.28×10^{-3}

for both 101 and 103 directions the two fault probabilities α and β have about the same magnitude and $(3\alpha + \beta) \cong 4 \times 10^{-3}$. But for 102 direction $(3\alpha + 3\beta) \cong 1 \times 10^{-3}$ indicating approximately about 4 times less total probability.

4. Major Contributions of this Study

4.1. Proposed Models for Mg Thin Films

The variation of the particle size over the entire thickness range studied here is observed to be much less than that of the mean strain. One could perhaps then interpret this fact as that, on the average, the particle size does not change and consider an overall average particle size of $\bar{D} \cong 266 \text{ \AA}$. In the same range the mean strain \bar{e}_L is changing by more than 50%. Not only that, the sign of the mean strain, which remains negative in most parts, changes to a positive value at least for the reflec-

tion 102. This is shown in the plots of Fourier coefficients plotted in Figure 1. In this sense, we find a very interesting result for Mg thin films. We might, in all probability, postulate that the source of the strain in Mg thin films has two possibilities:

- i) the usual thermal strain induced by mismatch of the linear thermal expansion coefficient between Mg ($\alpha_t = 25 \times 10^{-6}/^\circ\text{C}$) and glass ($\alpha_g = 9 \times 10^{-6}/^\circ\text{C}$),
- ii) the presence of two kinds of grain boundaries due to the formation of two types of oxides which must always be in satisfactory agreement with the conservation of energy of thermodynamic equilibrium.

A summary of these results shows a number of new features. If we just concentrate on the particle size D and mean strain $\bar{\epsilon}_L$ of the reflections 100 and 002 we find that vacuum deposited Mg thin films have two markedly defined phases: the first one is P1 in the region of $23,000 \sim 40,000 \text{ \AA}$ and the second one is P2 in the region of $40,000 \sim 93,000 \text{ \AA}$. In phase P1 we find, while the effect of D increases that of $\bar{\epsilon}_L$ decreases. However, in phase P2 the effect of particle size decreases but that of the mean strain increases. Vacuum deposited Cd thin films had mostly thermal strain, which we have already reported. In pursuing this point, since then we [18] have made additional investigations of Cd thin films by probing them with XPS and AES techniques, but detected no such oxidation phases as we predicted for Mg thin films.

The fault size D_F for Mg thin films is not seemingly altered by the film growth. The order of magnitudes of both the deformation and growth fault probabilities are about $\sim 10^{-3}$. It turns out that for directions $h-k=3N \pm 1$ with $l=\text{even}$ integer, we have one set of α and β , but another set for directions $h-k=3N \pm 1$ with $l=\text{odd}$ integer. This is quite conceivably due to the requirement of the stacking fault energies, which should again be linked to the adjustment of the potential energies of the atoms due to the formation of two oxides mentioned above.

4.2. Comparison with Other Thin Film Studies

From the present investigation including our previous investigations on other thin films [3–5], we consistently find that the structure and prop-

erties of polycrystalline thin films are very much different from their corresponding polycrystalline powder. For example, at room temperature in Mg powder, the strain value was zero, the particle size was 295 \AA , but the fault probabilities ($3\alpha + \beta$) and ($3\alpha + 3\beta$) were about the same order of magnitude as observed in Mg thin films.

As mentioned in the introduction recently some studies on the Fourier analysis of line broadening have been reported for thin films of HCP Cd [6] and Zn [7] and FCC Cu [8, 14], Ag [9, 13], Au [11] and Al [13, 19]. There are some conflicting results, especially published by Sen Gupta and his co-workers [6–9]. These workers [6–9] studied HCP Cd and Zn thin films prepared by vacuum deposition at pressure about 10^{-5} Torr and at room temperature. Apparently, they used wider slits without any soller slits. Wider slits give very large geometrical broadening and can mask easily the important physical broadening due to the small structural defect present in the sample. Secondly, without soller slits the nonpolarization of the x-ray would be rather quite high and require very severe correction factors even beyond the limits of the Lorentz-polarization correction factors. Thirdly, without crystal monochromator in the path of the diffracted beam there will be spurious broadening due to fluorescent and satellite radiations including the Compton wavelength. If the deconvolution part is carried out inappropriately the Fourier coefficients, especially the real part $H_r'(L)$, will show some effects of error function modulations. These error functions are usually some sine functions whose periods critically depend on the errors, as evidenced in the published [6, 7] plots of Fourier coefficients, which are some sinusoidal waves developed in the range of L as small as 50 \AA . These plots should be smooth and oscillation free [20] at least in the range of $0 < L < 400 \text{ \AA}$. The effect of the large magnitude of these errors cannot be explained by the presence of insufficient tails of the background of the diffraction peaks. Nor can it be accounted for by the use of constant angular separating function δ_0 in the separation of α_1 peak from α_2 peak. Sen Gupta et al. [6, 7] have reported some negative numbers for α which are the results of manifestation of a variety of errors or mistakes in the deconvolution procedure. *The fault probabilities α and β can never be negative.* They should range from 0 to 1.

On the other hand, Cu thin films studies by Gangulee [14], and Ag thin films studies by Light and Wagner [12] point out correctly most of the difficulties mentioned above. The effect of the particle size and strain is of the right order of magnitude and the fault probabilities are either positive or zero, but never negative. The thickness and pressure dependence of the line broadening for Cu and Ag films have been also consistent with our theoretical understanding of the problem. The theoretical and computational studies of HCP metal thin films (Be, Cd, Co, Mg, Ti, Zn and Zr) by Witt and Vook [10] predicted thermally induced strain as a principal cause of line broadening. Naturally, to a large extent, this amount will depend on the selection of the substrate surface and temperature of deposition. The thermally induced strain from the theory of Witt and Vook [10] for our Mg thin films should be $\epsilon_T \cong 10^{-3}$. This value is indeed of the same order of magnitude that we have found from the present line broadening analysis.

4.3. Summary of the Results in the Present Study

In conclusion we may emphasize that an x-ray line broadening analysis of vacuum deposited Mg

thin films reveals a number of new results, which are very different from Cd thin films. There are three factors which contribute to the line broadening of Mg thin films—oxidation, preferred orientation and thermal stress.

The oxidation part further complicates the situation by presenting itself in two different states. We have identified them as Phase 1 (P1) and Phase 2 (P2) respectively. The particle size decreases and mean strain increases in P1. In P2 the particle size increases and the mean strain decreases.

The geometrical and preferred orientation parameters ($K + S$) do not influence the particle size and mean strain so far as their identities are concerned. They simply come out as additional members of the family of line broadening parameters, which can only be extracted through the second derivative of the Fourier coefficients. Finally, the effect of the thermally induced strain is always produced between the glass substrates and Mg thin films, but it could be minimized or made to disappear by lowering the substrate temperature during deposition or selecting substrates of equivalent linear thermal coefficient. These sorts of studies should be more interesting and could be pursued.

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