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ORIENTATION SELECTION AND MICROSTRUCTURAL EVOLUTION OF EPITAXIAL Pt FILMS ON (001) MgO

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ABSTRACT

Thin platinum films were deposited at several different deposition rates and with varying thickness on (001)-cut MgO single crystal substrates by electron beam evaporation. A mixture of two epitaxial Pt orientations were detected in the films by X-ray diffraction and planar ion channeling experiments: (001) [100] Pt // (001) [100] MgO (the "cube-on-cube" orientation) and (111) [110] Pt // (001) [110] MgO. The effect of deposition rate on film orientation indicated the (111) Pt orientation was preferred under conditions of high driving force for nucleation. The volume fraction of the films occupied by the (111) orientation increased with nominal film thickness, at a constant substrate temperature and deposition rate. This result indicates crystallites having the (111) Pt orientation grew more quickly following nucleation than the (001). The mosaic spread of the Pt orientations decreased markedly as the nominal film thickness increased from ~ 1.5 nm (isolated islands) to 20 nm (continuous film).

INTRODUCTION

Epitaxial metal films evaporated on to ionic substrates have been studied for many years.[1-3] Initially, epitaxial deposition was seen as a simple means of preparing thin, high quality metal crystals for fundamental structural studies. More recently, possible technological applications in information storage and processing have caused renewed interest in thin metal films and multilayers.[3, 4] Epitaxial platinum films deposited on to (001) MgO substrates have been investigated as initial epilayers in Pt/Fe multilayers intended for magneto-optic media.[5, 6] Lu et al.[7] have also used platinum thin films on (001) MgO as an epitaxial electrode material for growth of highly-oriented $BaTiO_3$ films. The present work is intended to develop a more detailed understanding of the nature and mechanisms of orientation selection in Pt films deposited on to the (001) MgO surface.

Noble metal films deposited on to (001) MgO through a variety of deposition techniques[4, 5, 8, 9] frequently have a mixed orientation with both (001) and (111) Pt planes parallel to the substrate surface. The (111) orientation tends to dominate in polycrystalline Pt films deposited on to non-lattice-matched substrates because the (111) plane has the lowest surface energy and fastest in-plane growth rate in fcc metals. Lairson et al.[5] prepared Pt films on (001) MgO by magnetron sputtering with substrate heating that were essentially completely (111)-oriented at 400°C and almost completely (001)-oriented at 680°C. The (001)-oriented Pt films prepared at high substrate temperatures had a "cube-on-cube" epitaxial relationship with the substrate. They also found that deposition of an initial thin "seed" layer of iron on to (001) MgO, prior to Pt deposition, resulted in nucleation and growth of platinum films that contained only the "cube-on-cube" orientation, the (111) Pt orientation was completely suppressed.[5] The importance of "seeding" the MgO surface with iron prior to deposition of the desired epitaxial film had previously been demonstrated by Etienne and coworkers in MBE growth of metallic multilayers on (001) MgO.[4] Narayan et al.[8] investigated pulsed laser deposition of Pt films on to (001) MgO without pre-deposition of a seed layer. These workers identified the temperature range of (111) to (001) orientation switching as 200-500°C and observed excellent crystalline quality in epitaxial

Pt films deposited at 700°C. Narayan et al. hypothesized that differences in kinetic energy of the incident vapor flux present in different deposition techniques affects the temperature range for orientation switching. The effective deposition temperature increases with bombardment by low energy ions present in the vapor during sputtering and (low pressure) pulsed laser deposition.[8]

In previous work,[9] we investigated the temperature range of orientation switching in Pt films deposited on to (001) MgO substrates by e-beam evaporation, without the non-thermal energy contributions present in sputtering or pulsed laser deposition. These films were completely (111)-oriented at substrate temperatures (T_s) below 500°C. A mixture of (111) and (001) Pt was observed at $T_s = 700$°C. These results indicate the orientation switching temperature range is higher in Pt deposition from a thermal vapor than in sputtering or pulsed laser deposition, in keeping with Narayan's hypothesis. Planar ion channeling and X-ray diffraction studies of the evaporated films indicated the (001)-oriented Pt had the "cube-on-cube" epitaxial relationship with the (001)-cut MgO single crystal substrates. A strong in-plane alignment was also detected in the (111)-oriented Pt: (111) [110] Pt // (001) [110] MgO.[9] This orientation relationship was not reported by Lairson et al[5] or Narayan et al[8] It has, however, been observed in Au films evaporated on to cleaved (001) NaCl,[2] and appears to be a general feature of epitaxy between fcc metal films and ionic single crystal substrates having the rocksalt structure. Iron "seed" layer suppression of (111)-oriented Pt was also observed in the e-beam evaporated films at substrate temperatures as low as 25°C.[10]

In the work reported here, X-ray diffraction and Rutherford backscattering spectrometry (RBS) were used to characterize the effects of deposition rate and film thickness on selection of these two epitaxial Pt orientations. The results are rationalized based on the different in-plane growth rates and interfacial energies of Pt crystallites having the (001) and (111) orientations.

EXPERIMENTAL PROCEDURE

A detailed description of the platinum film deposition process is given elsewhere.[9] In brief, films were evaporated in a cryo-pumped chamber with a base pressure of approximately 1 x 10^{-8} torr. The polished (001) MgO substrates were used as-received from the vendor, with only brief ultrasonic solvent cleaning. Substrates were fixed to a nickel heater block with silver paste and the block was installed in the chamber in intimate contact with a planar resistive heating element. Temperature measurements were made using a Type K thermocouple buried in the nickel block, between the heating element and the substrate. Specimens were heated to 700°C and held at that temperature for 30 min prior to deposition. All films were deposited at a nominal substrate temperature of 700°C. Deposition rate was measured by an oscillating quartz crystal rate monitor.

Film orientation was characterized by X-ray diffraction and planar ion channeling during RBS. The crystalline quality of the Pt films was estimated from the ratio of the backscattering yield behind the Pt surface peak during axial channeling to that measured in a random sample orientation (χ_{min}). X-ray diffraction was performed with Cu Kα radiation and a four-circle goniometer. Rutherford backscattering spectrometry measurements were performed with 1.6 MeV $^4He^+$ ions and a scattering angle of 108°. Transmission electron microscopy (TEM) studies of the film microstructure were also performed. The TEM results will be discussed very briefly here and at greater length in a future publication.

RESULTS AND DISCUSSION

Figure 1 contains θ-2θ X-ray diffraction scans obtained from Pt films of 20 nm nominal thickness that were deposited at ~ 0.05, and 0.8 nm/s. The 2θ positions of the Pt (111), MgO (002), and Pt (002) reflections are labelled in the figure. No other film reflections were detected outside of the range of 2θ shown in the figure. The maximum diffracted intensity of the Pt (111) peak is over an order of magnitude greater in the high deposition rate film than it is in the low rate film. However, the Pt (002) reflection of the high rate films is significantly less intense than that of the lower rate sample. The ratio of peak intensities for the Pt (111) and (002), $I_{(111)}/I_{(002)}$, is 95.6 for the film deposited at 0.8 nm/s and 1.7 for the film deposited at ~0.05 nm/s. The intensity ratio measured for the lower rate specimen is similar to that previously reported for Pt films deposited at a rate of 0.2 nm/s at the same substrate temperature.[9] The in-plane alignments of the two film orientations are also identical to those reported in reference 9.

The planar ion channeling plot in Figure 2 displays the in-plane alignments for the high rate film of both the Pt (111) and (001) orientations (solid trace), with the planar channeling pattern of the (001) MgO substrate provided for comparison (dashed trace). The ordinate in the figure is the backscattering yield and the abscissa represents the 320 tilt increments of 0.2° used in tilting the sample from +8° to -8° and back about two mutually orthogonal axes that are themselves perpendicular to the ion beam. A dip in the spectrum corresponds to channeling along a set of planes that have been brought parallel to the ion beam by tilting the specimen. Channeling along the {100} and {110} planes was responsible for the deepest minima detecred from the MgO substrate and the (001)-oriented Pt. Coincidence of {100} and {110} planar channeling minima in Figure 2 confirms that the (001)-oriented Pt had the "cube-on-cube" epitaxial relationship with the substrate. Additional minima present in the Pt and not in the MgO trace are indicated by asterisks in the figure. These eight strong minima were produced by channeling along the {110} planes in the (111)-oriented Pt. The {110} planes have the deepest channeling minima of any planes normal to the (111) face of an fcc crystal.[11] The resulting orientation relationship for the (111)-oriented Pt is then (111) [110] Pt // (001) [110] MgO, as previously[7] reported.

These results indicate a significant increase in (111) orientation occurs in Pt films deposited at rates above 0.2 nm/s. Combined with earlier observations of the substrate temperature effect on Pt film orientation,[9] the data in Figure 1 indicate (111) Pt crystallites tend to dominate in films deposited under conditions of high driving force for nucleation (low temperature, high rate).

X-ray diffraction was used to characterize orientation changes with thickness in Pt films deposited at ~0.2 nm/s for varying lengths of time. Figure 3 contains overlaid θ-2θ scans from films of 1.5, 3.0, and 20 nm nominal thickness. In the thinnest film, a Pt (111) peak cannot be discerned above the background. A very weak, broad Pt (002) reflection may be present in the shoulder of the (002) MgO peak at 2θ≈46°. Both (111) and (002) reflections are discernable in the scan of the intermediate-thickness film. The intensity ratio, $I_{(111)}/I_{(002)}$, is 0.18, indicating a strong preference for the "cube-on-cube" orientation in this thin island film. Plan view TEM studies indicated the 1.5 and 3.0 nm nominal thickness films characterized in Figure 3 were discontinuous with average island diameters of 10 nm and 50 nm, respectively. Island coalescence had not occurred in the 1.5 nm thick films but had evidently begun in the intermediate thickness film, based on the presence of high angle grain boundaries separating the (111) and (001) Pt orientations within individual islands. The Pt film of 20 nm nominal thickness was continuous with small pinholes along the boundaries between some of the islands. The θ-2θ scan for this specimen in Figure 3 shows a definite preference for the (111) Pt orientation. The intensity ratio is 4.6 in this case. The 2θ positions of the (111) and (002) reflections are consistent with the bulk d-spacings of these planes. The film and substrate were elastically relaxed, in keeping with the

Moire fringe spacings observed in the TEM images.

The change in Pt film orientation with increasing thickness indicates nucleation of (001) islands is preferred. Those (111)-oriented islands that do form appear to grow more rapidly following nucleation than the "cube-on-cube" islands. They, therefore, occupy an increasing fraction of the total film volume as the deposition time and nominal film thickness increase. Fecht and Gleiter[13] used rotating particle experiments to demonstrate that both the (001) and (111) orientations observed here result in low energy interfaces between fcc metal films and ionic rocksalt-structure substrates. In the Au/(001) MgO system, the "cube-on-cube" orientation resulted in the lowest energy interface. The (111) [110] Au // (001) [110] MgO interface had somewhat higher energy. The preference for "cube-on-cube" Pt islands during nucleation probably results from their lower film/substrate interfacial energy.

The quality of the epitaxial relationship between the Pt islands and the substrate also improved as the film thickness increased. This was evident in the mosaic spread of reflections in electron diffraction patterns obtained during TEM, and also in the Pt χ_{min} measured in the films of 1.5, 3.0 and 20 nm nominal thickness. Figure 4 is a plot of χ_{min} versus nominal film thickness, with two data points for ~20 nm thick specimens. The high dechanneling yield of the thinner films was caused by slight misalignment of the [001] and [111] axes of the Pt islands relative to the substrate normal. The Pt χ_{min} decreased somewhat from 72.1% to 65.2% as the nominal film thickness increased from 1.5 to 3.0 nm. The χ_{min} of the continuous, 20 nm thick films was in the range 2.3-6.8%. In comparison, Barrett[12] measured a χ_{min} of 2.0% for a Pt single crystal during channeling with 2.2 MeV helium ions. A χ_{min} of ~3.0% was routinely measured for the MgO single crystal substrates used in this work. Smearing of electron diffraction spots acquired from

TEM specimens of the thinner films also indicated the existence of small rotations of the islands about the substrate normal. These misorientations were not observed in electron diffraction patterns taken from the 20 nm thick films.

CONCLUSIONS

Two epitaxial orientations were observed in thin Pt films evaporated on to (001) MgO substrates: (001) [100] Pt // (001) [100] MgO and (111) [110] Pt // (001) [110] MgO. Islands with these orientations nucleated and grew to coalesence through the Volmer-Weber mode of epitaxy. The (111)-oriented Pt islands dominated in films deposited at rates greater than 0.2 nm/s at a substrate temperature of 700°C. Together with previous results on the substrate temperature dependence of film orientation, these new results indicate the (111) epitaxial Pt orientation is preferred in films deposited under conditions of high driving force for nucleation. Rotating particle experiments reported in the literature suggest the "cube-on-cube" Pt orientation has a lower energy interface with the substrate than the (111) orientation. Our present studies indicate the "cube-on-cube" islands dominate in very thin (precoalesence) films. The (111) orienatation occupied a much larger fraction of continuous films (~ 20 nm thick) that were deposited under identical conditions. These results indicate the (001)-oriented Pt islands nucleated preferentially. Those (111)-oriented islands that formed, however, evidently grew more rapidly following nucleation than the (001) and made up an increasing fraction of the film volume as the film thickness increased.

REFERENCES

1. D.W. Pashley, Adv. Phys. 5, 173 (1956)

2. J.W. Matthews and E. Grunbaum, Appl. Phys. Lett. 5, 106 (1964), Phil. Mag. 11, 1233 (1965).

3. M.N. Baibich, J.M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. **61**, 2472 (1988).

4. P. Etienne, J. Massies, S. Lequien, R. Cabanel, and F. Petroff, J. Crystal Growth **111**, 1003 (1991).

5. B.M. Lairson, M.R. Visokay, R. Sinclair, S. Hagstrom, and B.M. Clemens, Appl. Phys. Lett. **61**, 1390 (1992).

6. B.M. Lairson, M.R. Visokay, R. Sinclair, and B.M. Clemens, Appl. Phys. Lett. **62**, 639 (1993).

7. H.A. Lu, L.A. Willis, and B.W. Wessels, Appl. Phys. Lett. **64**, 2973 (1994).

8. J. Narayan, P. Tiwari, K. Jagannadham, and O.W. Holland, Appl. Phys. Lett. **64**, 2093 (1994).

9. P.C. McIntyre, C.J. Maggiore, and M. Nastasi, Appl. Phys. Lett.; to be published.

10. P.C. McIntyre, M.E. Hawley, C.J. Maggiore, and M. Nastasi; unpublished work.

11. W-K. Chu, J.W. Mayer, and M-A. Nicolet, *Backscattering Spectrometry* (Academic Press, Orlando, FL, 1978), p. 229.

12. J.H. Barret, Phys. Rev. B **3**, 1527 (1971).

13. H.J. Fecht and H. Gleiter, Acta Metall. **33**, 1113 (1985).

Figure 1. X-ray diffraction θ-2θ scans of Pt films deposited on to (001) MgO at 0.05 and 0.8 nm/s.

Figure 2. Planar ion beam channeling plot of a specimen deposited at 0.8 nm/s (see text).

Figure 3. X-ray θ-2θ scans of Pt films of ~ 1.5, 3.0, and 20 nm nominal thickness on (001) MgO.

Figure 4. Plot of Pt χ_{min} versus film thickness for Pt films deposited at 700°C and 0.2 nm/s.

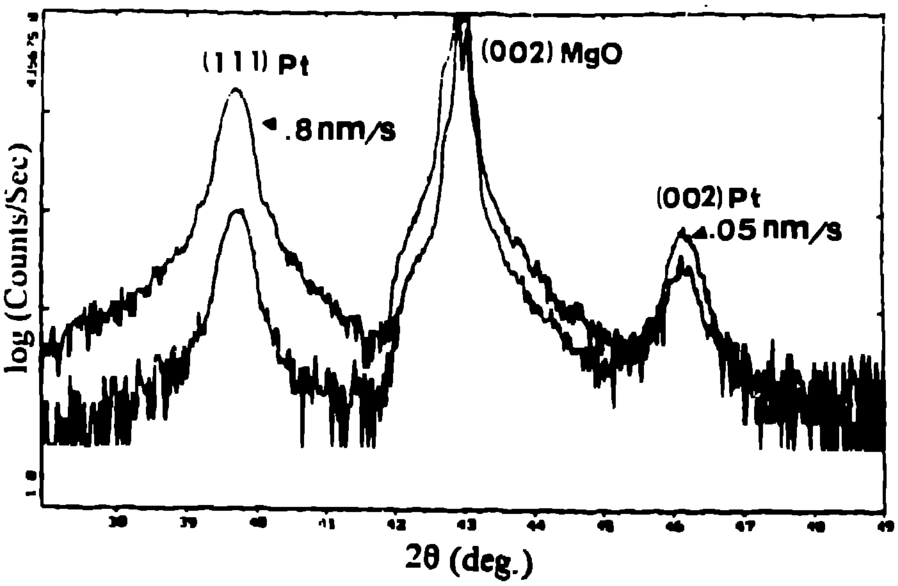
(111) Pt
.8 nm/s
(002) MgO
(002) Pt
.05 nm/s
log (Counts/Sec)
1.0
38
39
40
41
42
43
44
45
46
47
48
49
2θ (deg.)

Fig. 1

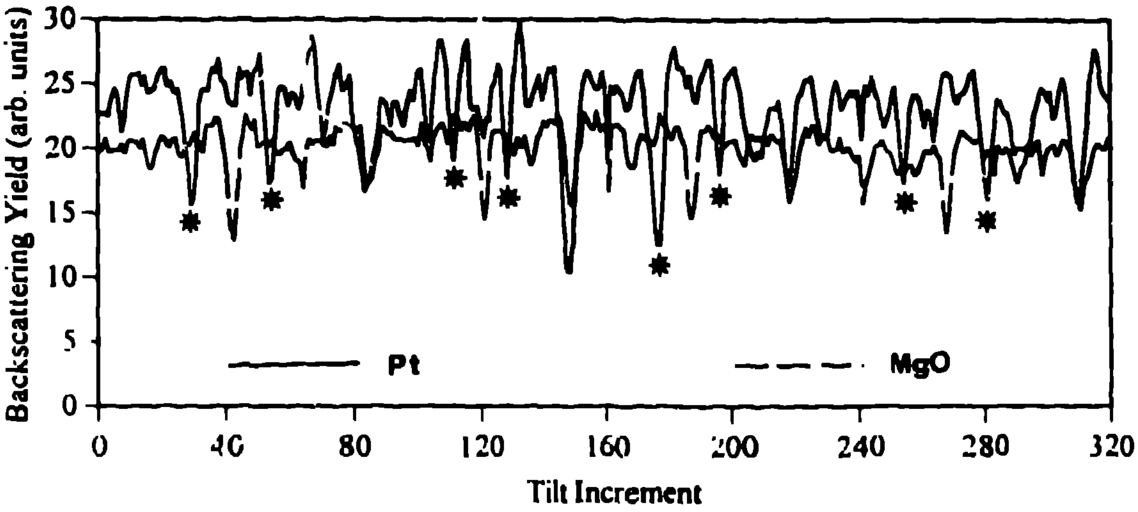
Backscattering Yield (arb. units)
30
25
20
15
10
5
0
*
Pt
MgO
0
40
80
120
160
200
240
280
320
Tilt Increment

Fig. 2

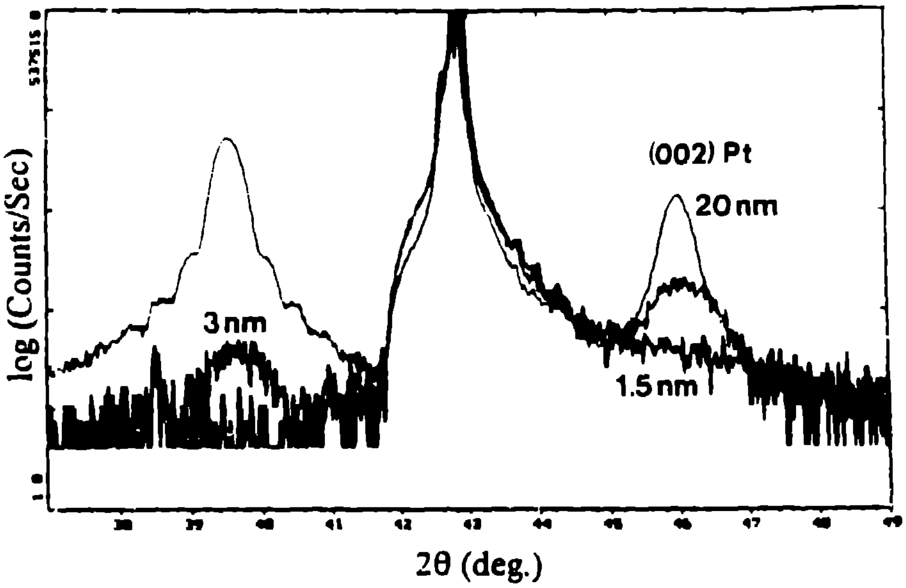
537515.0
1.0
log (Counts/Sec)
(002) Pt
20nm
3nm
1.5nm
38
39
40
41
42
43
44
45
46
47
48
49
2θ (deg.)

Fig. 3

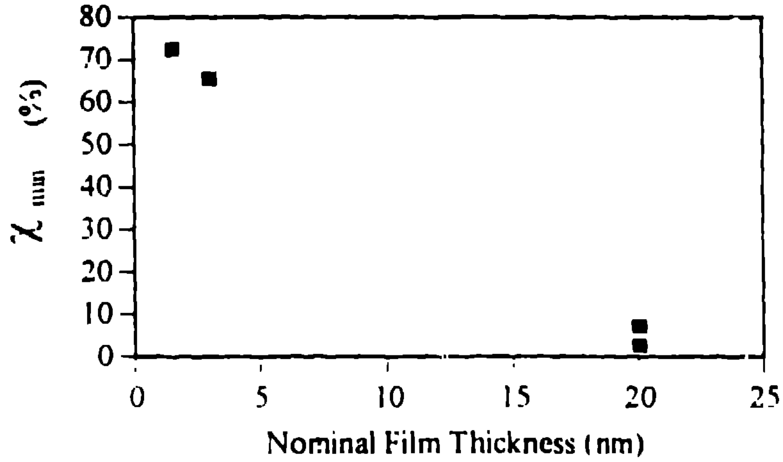
80
70
60
50
40
30
20
10
0
χ min (%)
0
5
10
15
20
25
Nominal Film Thickness (nm)

Fig. 4