Development of superlattice during thermal annealing in Pt/AlN multilayer films

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Abstract. The structures of Pt/AlN multilayer films were characterised by a combination of X-ray reflectivity (XRR) and X-ray diffraction (XRD). As-deposited film has accurate periodicity and abrupt interfaces, which make possible specular reflections up to $2\theta = 15^\circ$. The reflectivities of 1st Bragg reflection of the specimens annealed at temperatures below 600°C are almost constant about 65%. By annealing, intensity modulations overlap on the 111 Pt reflection, indicating the formation of a kind of superlattice in the multilayer films. Annealing is considered to cause the release of sputtering gases, recovery and small orientation adjustment of Pt layers. On the other hand, AlN layers do not show changes during annealing at these temperatures. As a result, adjacent Pt layers with preferred orientation come to show a correlation in diffraction intensity although they are separated by AlN.

1. Introduction
We have reported the magnetic and structural properties of fcc-CoPt/AlN multilayer films prepared by the double facing targets D.C. magnetron sputtering system [1]; As-deposited films show in-plane magnetic anisotropy and those annealed at 400°C show perpendicular magnetic anisotropy. There are almost no structural changes between the films before and after annealing. Therefore, such structural stability of metal/AlN multilayers for heat treatment should be applied to X-ray mirrors.

Generally, the larger the difference in electron density between two materials in X-ray mirrors, the higher the reflectivity [2]. Therefore, we have fabricated Pt/AlN multilayer films and measured the X-ray reflectivity [3]; the reflectivity was found to be sufficiently high and the films were stable at annealing temperatures up to 600°C. In addition, we found that superlattices develop during thermal annealing. In this paper, we describe the characteristics of the X-ray reflectivity (XRR) and X-ray diffraction (XRD) experiments and discuss the origin of the superlattice formed by annealing.

2. Experimental procedure
Films were deposited at room temperature by two D.C. magnetron-sputtering sources with Pt and Al targets. The base pressure was better than $5 \times 10^{-5}$ Pa and working pressure was kept at 0.50 Pa. The sputtering gases consisted of a mixture of Ar and N$_2$, and the flow ratio was 2:1. Under these conditions, Pt was deposited on the substrate as Pt and Al was deposited as AlN. Deposition rates were approximately 3 nm/min for Pt and 2 nm/min for AlN. Films were deposited on Si(001) wafers or quartz glass substrates; surface roughness was 0.5 nm or 0.8 nm, respectively. For all substrates, AlN
was deposited first and then AlN/Pt was deposited five times. The final AlN layer also acts as a cap layer.

3. Results

Figure 1 shows X-ray diffraction profiles of AlN(8 nm)/[Pt(3 nm)/AlN(8 nm)]\textsubscript{5}/Si(001) before and after annealing at 200, 400, 600 and 800°C in a vacuum. The angular range of measurement was from 2\(\theta\) = 5 to 100°. Bragg reflections due to formation of multilayer structures were clearly observed in the low angle region. In the medium angle region, a sharp reflection peak assigned to 002 reflection of AlN and a broad peak due to 111 reflection of Pt were observed. Although reflection of 222 for Pt was observed, no other reflection was detected.

Figure 2 shows the X-ray reflectivity curves of the Pt/AlN multilayer films. At around 2\(\theta\) = 0.6°, a sudden drop in the intensity of reflectivity occurred. This was due to the end of total reflection. Then, Bragg peaks with intervals of 0.8° continued up to 2\(\theta\) = 15°. The order of the reflection observed at around 2\(\theta\) = 14.7° was 19\textsuperscript{th}. This indicates fabrication of well-defined multilayers and that the layer structure is very stable with annealing at 600°C. There are two important features on the intensity profile. One is a moderate intensity oscillation, with minima at about 3, 6 and 9°. This moderate intensity change is because the Pt layers in the multilayer are thin. The thickness estimated from the moderate intensity change is 3 nm and it is coincident with final simulated thickness of Pt. The other feature is the existence of subsidiary peaks between Bragg peaks. As the thickness of each Pt layer is fixed and the number of Pt layers is low, we can observe the subsidiary maximum of the Laue function. The number of subsidiary peaks is 3 and we can confirm the number of Pt layers in the multilayer is 5. Therefore, we concluded that Pt/AlN multilayer films with accurate periodicity and abrupt interfaces were fabricated in this study. The intensity profiles were simulated using Leptos-2 with the multilayer model of AlN/[Pt/AlN]\textsubscript{5}/Si in which each Pt or AlN layer has the same thickness and roughness. The results of the analyses are listed in Table 1.

In the case of the as-deposited film on Si substrates, the reflectivity of the first Bragg reflection for Cu \(\text{K}\alpha\) X-ray was 65% and there was almost no change in reflectivity after annealing at temperatures up to 600°C. This property is indispensable for X-ray mirrors for use at high temperatures. With increasing annealing temperature, the positions of the Bragg peaks due to the multilayer structure shifted slightly toward the low angle side. This observation indicated that the period of the multilayer increases slightly with increasing annealing temperature.

Figure 3 shows the XRD of the Pt/AlN multilayers before and after annealing. For the as-deposited film, there was a peak at about 36° and a broad peak at around 39°. The former was assigned to 002 reflection of AlN and the latter to 111 reflection of Pt. The broadening of the 111\textsubscript{Pt} can be explained by the thickness of Pt.
and it was estimated to be 3 nm. Although the peak position of AlN almost coincided with that of the bulk AlN, the top of the peak of Pt did not coincide with the bulk value of 39.8°. The position of the 111\textsubscript{Pt} peak top of as-deposited specimen was shifted considerably toward the low angle side, which suggested expansion of the Pt lattice. This was explained by the existence of interstitial atoms of sputtering gases. With the progress of annealing, three distinct changes occurred. The first was an increase in intensity for both AlN and Pt. The second was the intensity modulation overlapping on the intensity curve of 111\textsubscript{Pt}. The third was that the peak position of 111\textsubscript{Pt} shifted toward the higher angle side and finally coincided with the position of bulk Pt. By annealing, the sputtering gases incorporated in Pt are released from the Pt matrix and the lattice parameter of Pt approaches that of bulk. In addition, recovery and/or rearrangement of Pt occur inside each Pt layer and (111) preferred orientation of Pt develops. Generally, appearance of the intensity modulation of fundamental reflection indicates formation of a kind of superlattice. It is worth mention that a kind of superlattice has been shown to develop by thermal annealing in the Pt/AlN multilayer films.

To clarify the structure and the formation mechanism of the superlattice, a series of reciprocal space maps around the 111 reciprocal lattice point of Pt were measured for as-deposited and annealed films. The results are summarised in Fig. 4, where the intensity is normalised in each map. In the as-deposited film, the intensity distribution was relatively wide indicating both a smallness of lateral size and a low degree of preferred orientation. With the progress of annealing, the intensity distribution became concentrated. This is well explained by the orientation adjustment of Pt grains. It is important that the concentration of intensity distribution and the appearance of the intensity modulation on 111\textsubscript{Pt} reflection occurred at the same time. Therefore, development of preferred orientation of Pt nanocrystals is directly related to the superlattice formation.

Similar results were obtained from quartz glass substrate samples, but the degrees of layer structure were lower than those observed with Si wafer substrate samples.

### 4. Discussion
In the as-deposited Pt/AlN multilayer films, both AlN and Pt show remarkable preferred orientation structures. For the development of such texture, alternative deposition of AlN and Pt with a thickness on the nanometre scale was found to be important. We prepare a single layer of AlN or Pt, but no texture was detected. However, the Pt layer on AlN with random orientation showed remarkable preferred orientation. Pt layers show (111) preferred orientation when Pt is deposited on polycrystalline AlN. The second AlN layer on Pt is enhanced in the preferred orientation of (001). In
this way, highly oriented multilayer films consisting of nano-scale Pt and AlN are formed. A detailed discussion based on the experimental data will be presented elsewhere.

Although we use common Si wafers, we can detect Bragg peaks at about \( 2\theta = 15^\circ \). On simulation by Leptos-2, we only take account of Nevot-Croce type roughness. As TEM observation of the CoPt/AlN multilayer film revealed the columnar structure penetrating to several AlN layers, the interfacial roughness listed in Table 1 should be separated into random and correlated roughness [4]. However, there is no doubt that the period of the multilayer film is rigid.

Previously, heat resistant X-ray mirrors were fabricated using Pt/Al\(_2\)O\(_3\) multilayer [5,6]. Also, the Pt/AlN multilayer films are found to show heat resistance. The heat resistance of the multilayer films is good. In metal/ceramic multilayer films, metals are well annealed but ceramics show essentially no change at temperatures below 600°C. It is concluded that combination of stable nitride and non-active metal leads to fabrication of heat-resistant X-ray mirrors. In addition, crystalline AlN shows good thermal conductivity in comparison with amorphous Al\(_2\)O\(_3\). Therefore, the combination of metal/AlN is a promising candidate for multilayer type X-ray mirrors for high-temperature use.

The as-deposited films already show preferred orientations on both Pt and AlN. With increasing annealing temperature, the intensity of 111\(_P\) increases considerably, and the intensity of the centre in the reciprocal space map of 111\(_P\) increases accordingly. This indicates that the degree of preferred orientation to the direction perpendicular to the surface increases with increasing annealing temperature. As a result, adjacent Pt layers become correlated and this causes modulation on 111\(_P\) reflection. This is the formation of a kind of superlattice. The origin of the superlattice in Pt/AlN multilayer films is interference between two neighbouring Pt thin layers with preferred orientation. The key points for post-annealing superlattice formation are as follows. Mutually immiscible [1,7], large difference in melting point and development of preferred orientation in the as-deposited state. If the three conditions are satisfied, interference between two neighbouring metal layers will occur locally during annealing and superlattices will develop in the multilayer films.

References
[1] Y. Hodumi, J. Shi, and Y. Nakamura, Appl. Phys. Lett. 90, 212506 (2007)
[2] M. Yamamoto and T. Namioka. Appl. Opt. 31, 1622 (1992)
[3] T. Harumoto, J. Shi, and Y. Nakamura, Materials Science Forum, PRICM-6 Proceedings, (submitted)
[4] D. E. Savage, J. Kleiner, N. Schimke, Y. H. Phang, T. Jankowski, J. Jacobs, R. Karioti, and M. G. Lagally, J. Appl. Phys. 69, 1411 (1991)
[5] Ch. Morawe and H. Zabel, J. Appl. Phys. 80, 3639 (1996)
[6] Ch. Morawe and H. Zabel, Appl. Phys. Lett. 67, 2612 (1995)
[7] S.A. Barnett, A. Madan, Scr. Mater. 50, 739 (2004)