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Effect of Annealing and Co contents on the Structural and Physical Properties in AlN Thin Films

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Abstract Aluminum nitride (AlN) thin films containing various amounts of Co content have been deposited by using a two-facing targets type sputtering (TFTS) system. The deposited films were also annealed successively and isothermally at different temperatures. Annealing treatment can control the physical properties as well as the microstructure of AlN films with Co particles. High magnetization and high resistivity are obtainable in AlN films containing dispersed Co particles. The coercivity of the films does not depend on annealing time, but it increases with increasing annealing temperature due to the increase of the grain size. A high saturation magnetization of 46 kG and resistivity of 2200 μΩ-cm was obtained for AlN films containing 25 at% Co.

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1. Introduction

Nanostructured composite films have attracted both scientific and technological interests in recent years because of their size dependent novel properties and the fact that the properties can be altered by adjusting the deposition parameters, which makes these kinds of films very promising in a wide variety of applications [1]. Generally, these films are fabricated by sputtering laser ablation of composite targets, and by reactive sputtering of pure metal targets. The configuration of the films covers the combinations of metal-insulators and metal semiconductors [2, 3].

Recently high technology developments of electronic devices have led to a demand for miniaturization of magnetic devices [4], operating at frequencies higher than 50 MHz. For such devices, it is required that the magnetic materials have a sufficiently large electrical resistivity ρ and are in the form of thin films, because of the suppression of eddy current losses. In the field of magnetic recording, ferrite heads, connected with oxide media have been in great use from a long period of time. On the other hand, metal heads [5, 6], for use with high Hc metal media [7, 8] utilizing metallic materials such as metal sendust and single-phase amorphous films have also been introduced in order to achieve high-density recording. There exists a great deal of core loss in high frequency range. However, ferrite heads have a related problem when applied to high-density technology, that is, the low Bs of soft magnetic ferrite makes them incompatible with metal media. In order to solve those two major problems, high resistive metal films possessing a very fine two-phase hetero-amorphous structure have been studied, and magnetic granular system, where the magnetic particles are embedded in an insulator matrix, has also been studied. But it is necessary to improve the overall performance of the high density recording materials. Moreover, no work has been reported till now on Co based soft magnetic materials, where Co as a magnetic element is embedded in a good insulating matrix. An ideal high-density recording magnetic material should have high permeability, high electrical resistivity, large saturation magnetization

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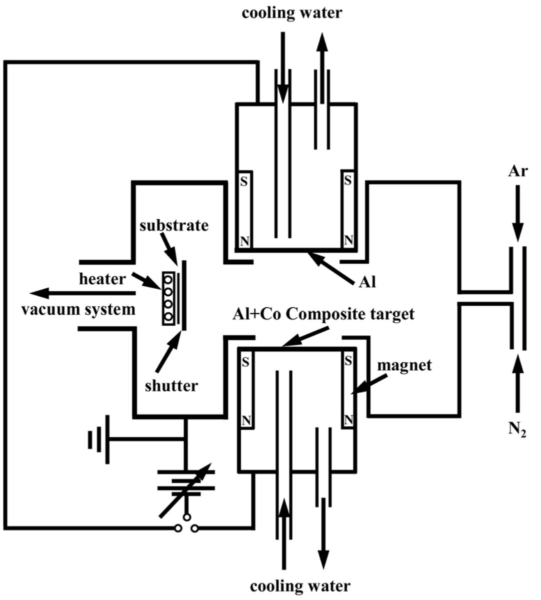

Fig. 1. Schematic diagram of a TFTS system.

coupled with low energy loss and also a high corrosion resistance. That is why we used AlN as a high resistive and high corrosion resistance insulator matrix and Co as a magnetic particle embedded or dispersed in that matrix. In this paper, we describe the processing of AlN films containing various amounts of Co content and also examine their magnetic properties and electrical resistivity in relation to the microstructure of the films.

Table 1. Deposition Conditions

Target	Al(99.95), Co(99.98)
Composite Target	Area ratio of Co (TAF) Co/(Al+Co)=0.021, 0.047, 0.087
Substrate	Corning glass
Substrate Temperature	Lower than 323 K
Target Voltage	DC -300 V to -500 V
Sputtering Current	400 mA
Composite Gas	N_2 partial gas pressure of 0.52
Initial Pressure	Lower than 2×10^{-4} Pa
Total Gas Pressure	0.4 Pa

Table 2. Saturation Magnetization and resistivity of AlN films containing Co

Co target area fraction (at% of Co(approx.))	Magnetization Gauss (kG)	Resistivity μ-Ω-cm
0.021 (10 at%)	41 ~ 51	49750
0.047 (20 at%)	41 ~ 51	2900
0.087 (25 at%)	69 ~ 84	990 ~ 1360

2. Experimental Procedure

Aluminum nitride (AlN) thin films were deposited on glass substrate by using a two facing targets type dc sputtering (TFTS) system at various nitrogen partial pressures (PN_2). Their deposition characteristics, crystallographic orientation and microstructure were examined to determine the best deposition condition. Thus predetermined conditions were applied to prepare AlN thin films containing Co particles by only replacing an aluminum target by an 'Al-Co' composite target in this system. The composite target was fabricated by inserting a Co plate with various diameters into a hole cut in the central part of Al target. In this system, a pair of permanent magnets are installed behind both targets, as shown in Fig. 1. The magnetic field from these magnets confines the plasma between the two targets. Consequently, the films can grow without disturbance from plasma because the substrate is located out of the plasma. The deposition conditions are listed in Table 1. As-deposited Al-N-Co thin films were annealed both successively and isothermally in a vacuum of 2.6×10^{-4} Pa at different temperatures. The microstructure of prepared films was examined by X-ray diffraction (XRD), transmission electron microscope (TEM) and film texture by field emission scanning electron microscope (FE-SEM). Atomic percentage of the contents of the films was checked by electron dispersive spectroscopy (EDS), as listed in Table 2. Magnetic and electrical properties were examined by a vibrational sample magnetometer (VSM) and the four point prove method respectively.

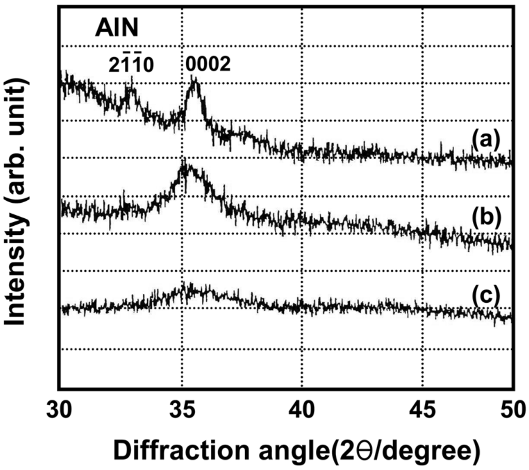

Fig. 2. XRD profiles of as-deposited films containing Co at% of (a) 10, (b) 20 and (c) 25.

3. Results and Discussion

3.1 As-deposited Al-N-Co thin films

3.3.1 Microstructure

The microstructure of Al-N-Co films strongly depends on Co content in the films. Fig. 2 shows XRD profiles deposited with different Co target area fractions (Co / (Co + Al) = TAF). For the film prepared with a TAF = 0.021, only two AlN peaks are observed. These AlN peaks are not sharp and are shifted to smaller angle side, which suggests that some of N atoms in the AlN structure are substituted by Co atoms to form a defected AlN crystal structure. For films prepared with higher TAFs, AlN 0002 peak becomes broad with increasing Co content, and finally disappears in diffuse scattering ascribed to amorphous state. The results of TEM micrographs (shown in Fig. 3) are consistent with the XRD results. As shown in the micrographs, the grain size decreases with increasing Co content, and corresponding electron diffraction pattern shows only the AlN rings for the film containing 10 at% Co. The films with higher Co contents show that the grain size decreases and the diffraction rings diffuse with increasing Co content.

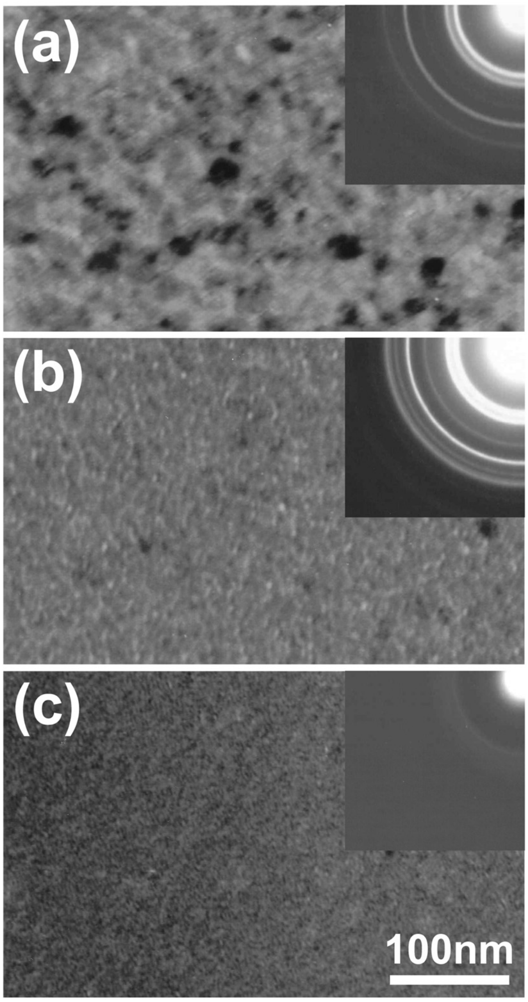

Fig. 3. TEM bright field images and SAED patterns of AlN-Co films containing Co at% : (a) 10, (b) 20 and (c) 25.

From the cross sectional view of the FE-SEM observations, as shown in Fig. 4, it is seen that film containing 10 at% Co shows columnar structure as like as pure AlN films [9], and for the films containing 25 at% Co the columnar structure disappears. This phenomenon can be explained from XRD and TEM observations: the films with small Co content show peaks for AlN (XRD) and rings for AlN (SED), so resulting in columnar structure as in the case of pure AlN films. Moreover, when the Co content increased, the AlN peak became broad and the rings became diffused, resulting in amorphous state. The decay of columnar structure is related to the degradation of crystallinity.

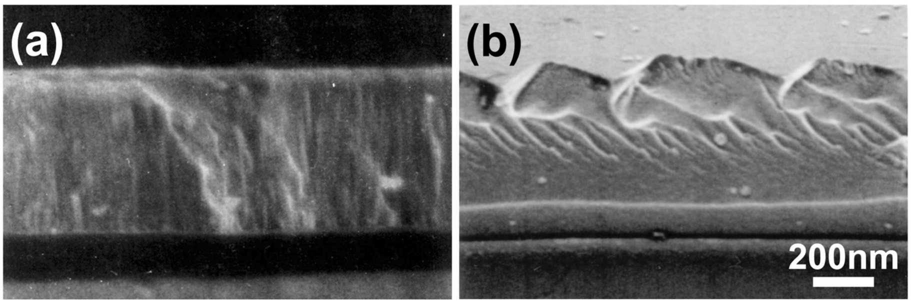

Fig. 4. FE-SEM photographs of cross-section of AlN-Co films deposited with area fractions of containing Co at% : (a) 10 (TAF=0.021) and (b) 25 (TAF=0.087).

3.1.2 Magnetic properties and electrical resistivity

For as-deposited films, the saturation magnetization is very small irrespective of Co content. This may be due to that the as-deposited films are amorphous i.e., Co is not in crystalline state, and/or its Curie temperature decreases below room temperature. The resistivity increases with decreasing Co content due to the decrease of conducting element (Co) in the matrix. The numerical results for magnetization and resistivity with respect to Co content in the films are listed in the Table 2.

3.2 Annealed Al-N-Co films

3.2.1 Change of magnetic and electrical properties caused by successive annealing

Fig. 5 shows the effect of successive annealing on the saturation magnetization and resistivity for the films prepared with a TAF of 0.087. The saturation magnetization is almost constant up to 573 K, and begins to increase abruptly from 673 K. The highest saturation magnetization of about 360 emu/cm^3 was obtained for films successively annealed at 973 K. The effect of successive annealing on resistivity is plotted in the same figure for the films deposited with a TAF 0.087 annealed for 10.8 ks. The resistivity slightly decreases with increasing annealing temperature up to 673 K and then begins to increase sharply with annealing temperature. The highest resistivity of about 11500 μΩ-cm was obtained for the annealing temperature of 973 K. Fig. 6 shows typical hysteresis loops after being successively annealed up to 973 K for 10.8 ks period.

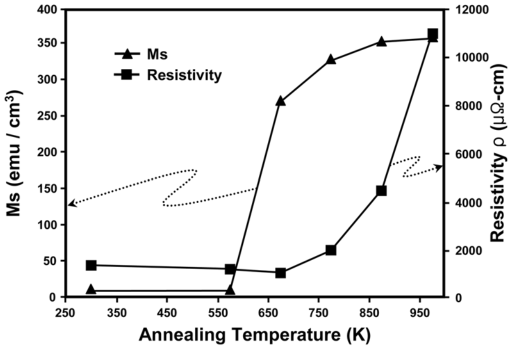

Fig. 5. Effect of successive annealing on saturation magnetization and resistivity of Al-N-Co thin films containing 25 at% Co.

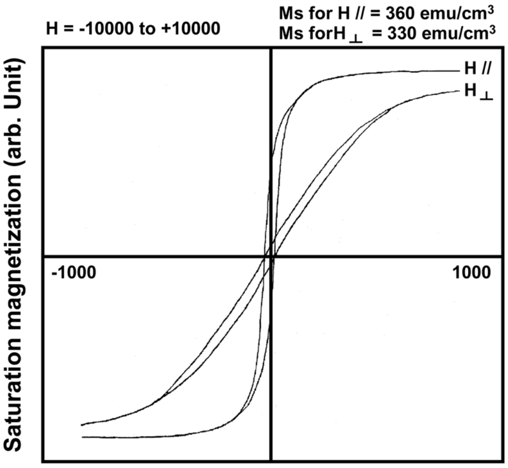

Fig. 6. Typical magnetic hysteresis loops measured for Al-N-Co thin films containing 25 at% Co annealed at 973 K for 10.8 ks.

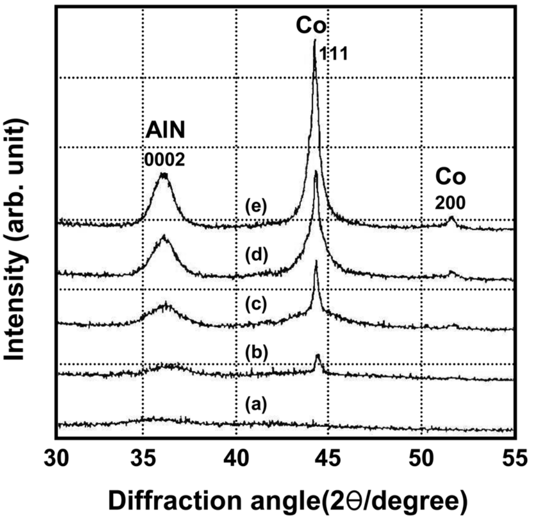

Fig. 7. XRD profiles of AlN-Co films (TAF=0.087); (a) as-deposited and (b), (c), (d), (e) annealed at 673 K, 773 K, 873 K, 973 K for 10.8 ks.

3.2.2 Microstructure

Fig. 7 shows some XRD profiles of Al-N-Co films deposited on glass substrate with TAF = 0.087, successively annealed at various temperatures for 10.8 ks at every step. It is clear from the profiles that the amorphous phase of as-deposited film separates into two distinct phases of AlN and fcc Co, and the peak intensity and sharpness increase with increasing annealing temperature. Fig. 8 shows two typical TEM micrographs of films containing 25 at% Co. The films were successively annealed at various temperatures for 7.2 ks. It is obviously seen that the grain size increases with increasing annealing temperature and the diffuse electron diffraction rings become sharper with increasing annealing temperature. When the film was annealed at 973 K, sharp rings for both AlN and fcc Co were clearly observed. It was also found that the Co grain size was much larger than the AlN grain size at elevated temperatures, especially for the films with higher Co contents. The average Co grain size is about 15 nm in diameter and AlN grain size is about 5 nm in diameter for the films containing 25 at% Co annealed at 973 K. The same results were also obtained for isothermal annealing. The results are summarized as follows; heat treatment can change the microstructure, and as-deposited films can crystallize to have two distinct phases of AlN and FCC Co.

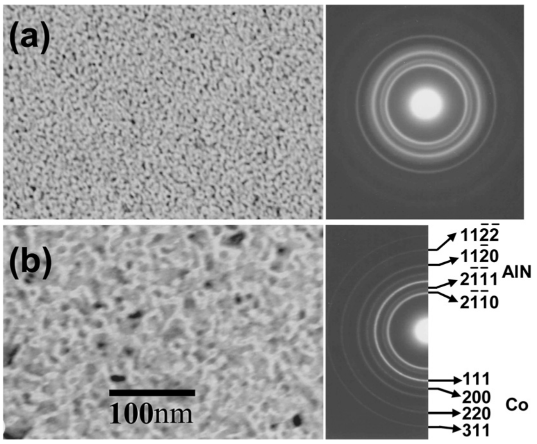

Fig. 8. TEM images and SAED patterns of AlN-Co films with TAF=0.087; annealed at (a) 773 K and (b) 973 K for 7.2 ks.

3.2.3 Magnetic properties

The magnetic properties of annealed films change in accordance with the changes in microstructure. Saturation magnetization as a function of annealing time at different annealing temperatures is shown in Fig. 9 for the films containing 25 at% Co. The graphs show almost the same behavior at 673 K and 773 K, except for the plots at 573 K; where the increasing tendency of saturation magnetization with increasing annealing time was seen up to 129.6 ks and the highest saturation magnetization of 3.7 kG was observed for a film annealed at 773 K for 32.4 ks. This phenomenon can be explained in terms of the changes in microstructure caused by annealing. As annealing time and temperature increase the separation of Co phase from AlNCo amorphous phase become more dominant and also the crystallinity of Co become more and more perfect. The Co phase dispersed in the AlN matrix leads to the increase of magnetization in the film.

The coercivity of annealed films was also measured as a function of both annealing time and annealing

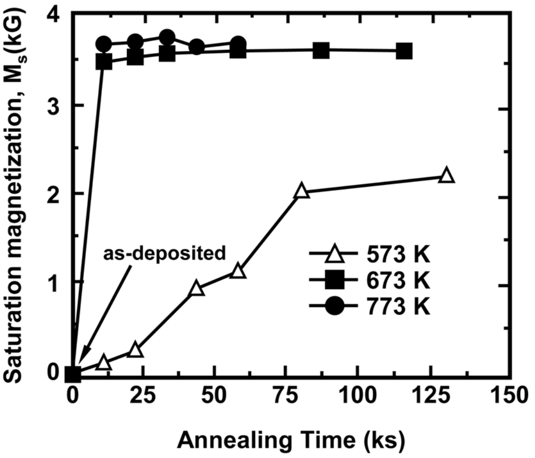

Fig. 9. Saturation magnetization as a function of the annealing time for the films prepared with 25 at% Co (TAF=0.087).

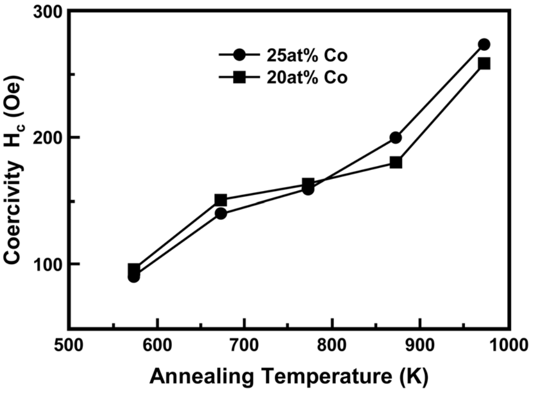

Fig. 10. Effect of annealing temperature on coercivity for AlN-Co films.

temperature. However, no effect of annealing time was found on the coercivity, but it was observed that the coercivity increases almost linearly with annealing temperature as shown in Fig. 10. The lowest coercivity of about 90 Oe and the highest coercivity of 275 Oe were obtained for the films annealed at 573 K and 973 K respectively, for the films prepared with a Co TAF of 0.087.

The coercivity is not affected by annealing time but increases with increasing annealing temperature. The grain size of the films increases with annealing temperature. This indicates that the coercivity is strongly related with particle size of the films. This also predicts that there may have some relationships between the grain size and the orientation of magnetic domain structure, which are considered to affect the coercivity.

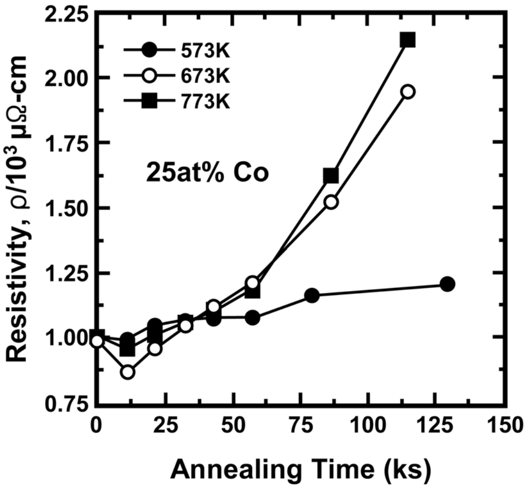

Fig. 11. Variations of resistivity ρ as a function of annealing time at different annealing temperatures for the films containing 25 at% Co (TAF=0.087).

3.2.4 Electrical resistivity

The resistivity increases with increasing annealing time and temperature. Fig. 11 also shows the variations of resistivity as a function of annealing time at different annealing temperatures for the films deposited with a TAF of 0.087. It is seen from the figure that the resistivity decreases with annealing time up to 10.8 ks and then increases with increasing annealing time for all the annealing temperatures. The resistivity of about 2200 μΩ-cm was obtained for a film annealed at 773 K for 115.2 ks.

For the films prepared with lower TAF's of 0.021 and 0.047, the resistivity increases with increasing annealing temperature and annealing time. On the other hand, for the films prepared with higher TAF's of 0.087 the resistivity first decreases up to 12 ks for all the annealing temperature and then increases with increasing annealing time and temperature. The origin may be explained as follows: in case of lower TAF's, the films are partially crystalline, the nitrogen content in these films is almost in the form of AlN compound. But for a higher TAF of 0.087, the films become amorphous. In as-deposited amorphous film, all the nitrogen contents are not in the form of AlN compound, thought some molecular nitrogen also exist in the film. A large amount of Co atoms are also constrained to be doped in the AlN lattice. Therefore, the decrement in resistivity during the initial stage of annealing is probably due to the escape or desorption of a few atomic N atoms before the formation of AlN. And when annealing time and temperature increase, as-deposited amorphous films crystallize into two different phases, AlN and Co, and as a result, compositionally separated into Co enriched region and AlN enriched region. In consequence of this, the resistivity increases caused by compositional separation with increasing annealing time and temperature.

4. Conclusions

Amorphous Al-N-Co films deposited by the TFTS system were annealed and their microstructure, magnetic properties and resistivity were investigated. The main results are summarized as follows,

1. This TFTS method is suitable for preparing AlN thin films containing various amounts of Co content. Annealing can control the physical properties as well as the microstructure of Al-N-Co thin films.

2. The coercivity of the films does not depend on annealing time, but it increases with increasing annealing temperature due to the increase of the grain size. A high saturation magnetization of 46 kG and resistivity of 2200 μΩ-cm was obtained for AlN films containing 25 at% Co.

3. High magnetization and high resistivity are obtainable in AlN films containing dispersed Co particles. Such films would be used on high density recording materials.

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