Rare Metal Materials and Engineering
Volume 41, Suppl. 1, February. 2012
Cite this article as: Rare Metal Materials and Engineering, 2012, 41(S1): 0???-0???.

Co Filled Porous Anodic Alumina Film Fabricated on ECR-Al Film with Silicon Substrate

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Abstract: Magnetic Co nanodots embedded in the porous anodic alumina films (AAFs) on silicon substrate can be used as the magnetic recording material with high area recording density. For this purpose, pure aluminum films were deposited on Si substrate with the Electron Cyclotron Resonance (ECR) plasma sputtering technique, and AAFs with vertical nano holes were synthesized with the two-step anodization process in oxalic acid. Finally magnetic material Co was deposited into the nano holes with electrochemical method. The results showed that polycrystalline ECR-Al films are homogenous and fit for the synthesis of AAFs with uniform distributed nano holes when ion sheath formed in front of the substrate surface. The diameters of AAF nano holes were in the range from 30 to 70 nm, and the hole pitches were approximately 100 nm, the AAF on silicon substrate was about 100 nm thick after two-step anodization. Magnetic Co nanodots filled into the nano holes of AAF exhibited both fcc and hcp structures.
Key words: ECR-Al film; anodic alumina film (AAF); nano hole; Co nanodot

Porous anodic alumina film (AAF) has been studied because of the simple fabrication method, low cost, uniform distribution and the size controllable properties. These properties make AAF a desirable material for the fabrication of magnetic [1], semiconductor [2], sensor [3], and photonic crystal [4] materials. Especially, when the AAF with the hole pitch of 25 nm is used to deposit magnetic materials, high area recording density up to 1 Tbits/in^2 can be realized if each nanodot was taken as a single domain magnetic memory unit [5].

Porous anodic alumina film was fabricated with two step anodization of aluminum foil at first [6]. However, in order to use AAF as template to synthesize nanowires or nanodots on substrate, most of the time, a procedure of transferring the porous AAF onto a substrate was needed. Therefore, people studied the fabrication of AAF on substrate directly [7-8], and then all kinds of physical and chemical methods were used to fabricate composite materials with nano holes, or synthesize quantum dots directly on a substrate. O. Rabin et al. fabricated thick porous AAF on Si substrate and deposited nanowire arrays [9]. M. T. Rahman et al. introduced the method of depositing magnetic recording material (Co/Pt) on the side walls of anodic alumina pores on Si substrate [10]. Y. Lei and W. K. Chim studied the fabrication of highly ordered nanodots with controllable shapes and sizes on Si substrate by using the AAF as mask [11]. These studies mainly focused on the structures of AAF and properties of the final deposited material.

The uniformity and structure of aluminum film affect the anodization process of AAF. Most of the Al films used for the synthesis of AAF were deposited with the method of evaporation. D. Crouse et al. took the 2 μm thickness Al film prepared with thermal evaporation as the anodization substrate [7]; J. P. Zou et al. prepared a 450 nm thickness Al film with the method of electron beam evaporation, and used it as the anodization substrate [12]; M. T. Wu et al. also used the E-beam evaporation method to prepare multilayer Al films with thickness of 1.2 μm on Si substrate which were used for the further fabrication of AAFs [13]. However, it has been reported that the difference of the thermal expansion coefficients between Al film and silicon substrate gave rise to large thermal stress, which resulted in hillock or whisker formation when the stresses were compressive [14]. If large hillocks existed, the Al film cannot be anodized uniformly, therefore, it is necessary to examine the structure of Al film before anodization.

In this work, Al films are deposited with the Electron Cyclotron Resonance (ECR) plasma sputtering on Si substrate with different sputtering energies. Then, ECR-Al films are anodized in oxalic acid. Finally, magnetic material Co is filled into the AAF with electrochemical deposition. The surface morphologies of ECR-Al films, AAFs and Co filled AAF surfaces are observed by SEM, the nano structure of ECR-Al films are observed with HRTEM and the crystalline structure of Co filled AAF is investigated by XRD.

Received date: May. 25, 2011
Foundation item: NSFC(90923027 and 51050110137); The Fundamental Research Funds for Central Universities
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1 Experiment

Pure aluminum films were prepared on p-type <100> oriented silicon substrate (20 mm × 20 mm) with ECR plasma sputtering technique, and the schematic diagram of which is shown elsewhere [15]. When the DC bias of -300 V was acted on the aluminum target, aluminum atoms were sputtered by the argon plasma, and then deposited on the substrate. ECR-Al films were prepared with the substrate bias voltage of +20 V and +40 V, and then the films are annealed at 400 degrees C to increase the mean size of nano grains and decrease the internal residual stress. Two-step anodization process was used to synthesize the AAF with nano holes by anodizing the ECR-Al film on Si substrate. A piece of copper was contacted at the back side of the sample forming an ohmic contact, which was served as the anode, and a platinum electrode was fixed facing to the aluminum film and served as the cathode. The ECR-Al films were anodized in the oxalic acid aqueous solution (5% in weight) at 5 degrees C with DC anodic voltage of +40 V. After the first anodization, the alumina film was removed using a solution of 6% w.t. H_3PO_4 and 1.8% w.t. CrO_3 acid at 60 degrees C for 15 minutes. Then, the remaining aluminum was reanodized under the same conditions as the first round anodization. 5 percentages w.t. H_3PO_4 solution was used to increase the hole diameter. Afterwards, alternating current (AC) electrochemical deposition method was used to deposit Co in AAF template. The electrolyte used in this work contained $CoSO_4 \cdot 7H_2O$ (1.2 mol/L), H_2PtCl_6 (0.012 mol/L), and H_3BO_3 (30 g/L). The pH value of solution was adjusted to 5.5 with H_2SO_4. The electrochemical deposition was performed at the potential of +5 V for 1 minute. The whole experimental procedure is shown in Fig. 1.

The surface morphologies of the ECR-Al film, AAF and Co filled AAF were observed by a 30 kV Scanning Electron Microscope (SEM) of JSM-6700F. The thicknesses and the nano structures of ECR-Al films were measured with High Resolution Transmission Electron Microscope (HRTEM) of JEM-3010 operated at 300 kV (the two-point resolution is 0.17 nm). The crystalline structure of Co nanodots in the AAF was tested with X-ray Diffraction (XRD).

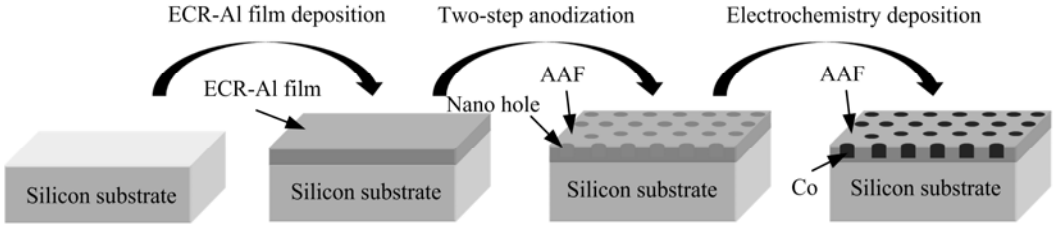

Fig.1 Schematic of the experimental procedures

2 Results and Discussion

2.1 Characterization of the prepared ECR-Al film

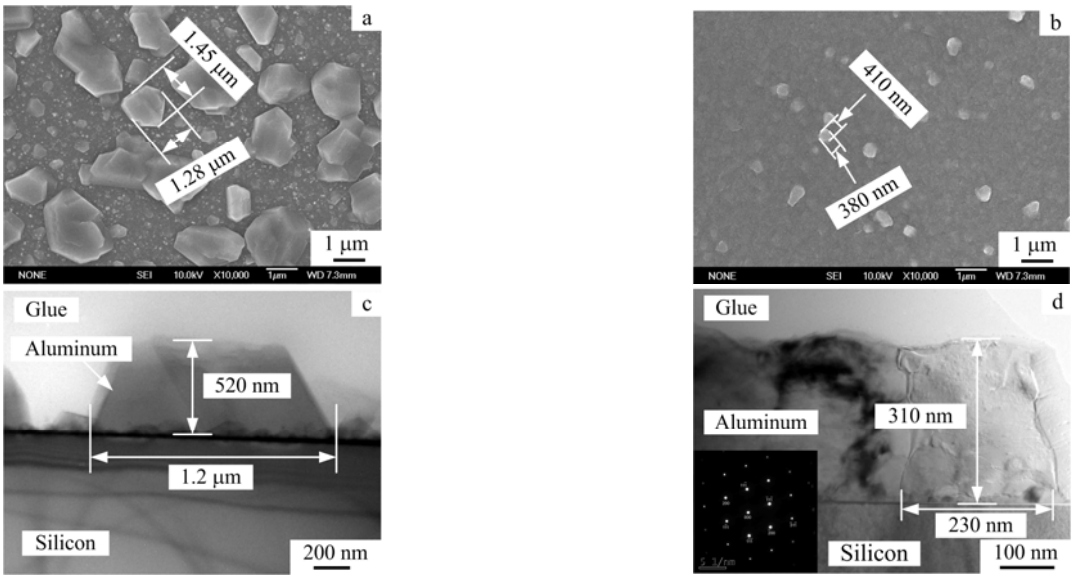

Fig.2 Surface morphologies of ECR-Al films with different substrate biases: (a) +40 V, (b) +20 V; and cross-sectional HRTEM pictures: (c) +40 V, (d) +20 V.

Figure 2 shows the surface morphologies and cross sectional HRTEM pictures of ECR-Al film deposited with substrate bias voltage of +40 V and +20 V. Considering the deposition mechanism of film in ECR plasma sputtering system [15]. During the process of Al film deposition, electron sheath was formed in front of the substrate when the substrate bias is +40 V, depositing particles adsorbed on the surface, hillocks were generated as shown in Fig. 2 (a). On the contrary, ion sheath was formed when the substrate bias is +20 V, argon ions were accelerated to sputter the weak bond off, and the surface morphology shown in Fig. 2 (b) is homogeneous with small prominences. From the view of cross section, hillocks were obvious in Fig. 2 (c) and the thickness changed from tens to hundreds of nanometers. However, the thickness of Al film in Fig. 2 (d) is relatively uniform with the value of 310 nm, and the grains grown vertically to the film surface with nearly the same size. Diffraction pattern in Fig. 2 (d) shows that the film has polycrystalline structure in a single grain.

2.2 Observation of the AAF with nano holes

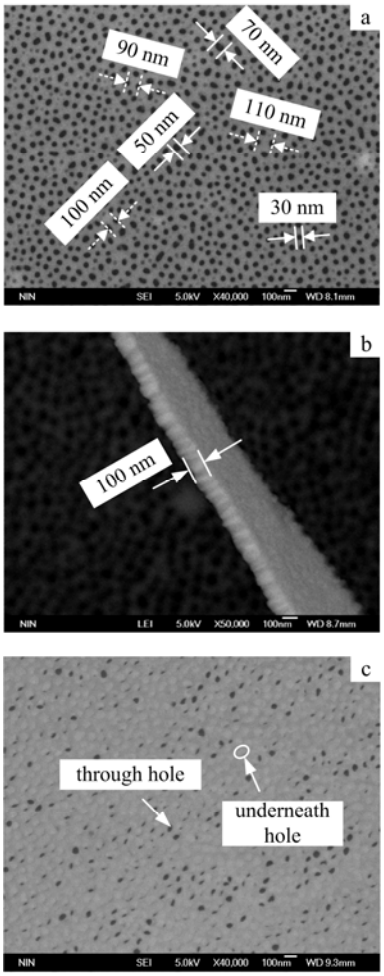

Fig.3 AAF with nano holes. (a) top view, (b) cross-sectional view, (c) backside view

ECR-Al films prepared with substrate bias of +20 V and +40 V were anodized in the oxalic acid aqueous solution. Because the thickness distribution of ECR-Al film with substrate bias of +40 V was not uniform at all, in the step of anodization, the thinnest place was consumed first and then the leftover film dissolved gradually. Thus, the structure of vertical nano holes cannot be formed. Uniform distributed nano holes were fabricated by anodizing the ECR-Al film with substrate bias of +20 V. Figure 3 shows the top, cross-sectional and backside views of AAF with nano holes. The diameters of nano holes are in the range of 30-70 nm, and the hole pitches are approximately 100 nm (90-110 nm), as shown in Fig. 3 (a). The thickness of the alumina film is about 100 nm from the cross-sectional SEM image in Fig. 3 (b). Figure 3 (c) shows the backside of the alumina film, not all of the holes got through the entire ECR-Al film and reached the silicon substrate, and the underneath of hole shows small prominences.

2.3 Characterization of the Co filled AAF on silicon substrate

Figure 4 shows the surface morphology of Co filled AAF on silicon substrate. By using H_3PO_4 solution to enlarge the nano hole, the hole diameter increased to about 80 nm with much more uniform distribution before magnetic Co was filled. After electrochemical deposition, Co nanodots were filled into the nano holes of AAF, as shown in Fig.4, and the crystalline structure of Co nanodots embedded in AAF was examined with XRD.

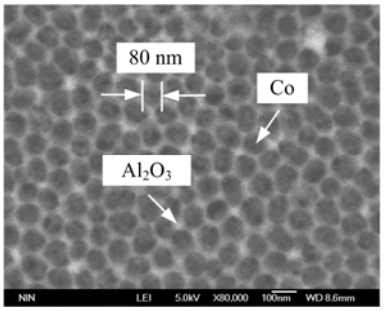

Fig.4 Surface morphology of Co filled AAF

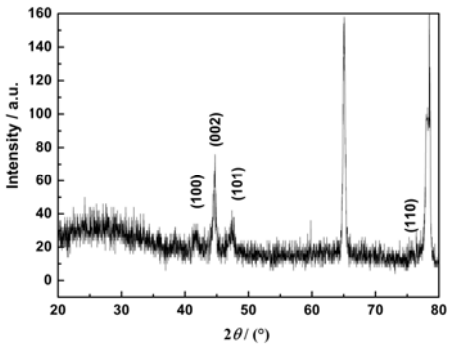

Fig.5 XRD patterns of Co nanodots embedded in AAF

Figure 5 shows the XRD pattern of the Co filled AAF, the peaks in the diffraction pattern include Co (100), Co (002), Co (101), Co (110), and another two peaks representing the left Al

peak. In the directions of Co (100), (111), and (110), the Co nanodots are crystallized in fcc structure, while in the direction of Co (002), hcp structure exhibits. The Co nanodots deposited with AC electrochemical method has both fcc and hcp structures. This is because that in the process of electrochemical deposition, the deposition rate is too fast to obtain Co nanodot with single crystalline structure.

2.4 Discussion

Thin anodic alumina films with nano holes were fabricated on silicon substrate through anodizing the 310 nm ECR-Al film with homogeneous polycrystalline structure in oxalic acid. Then magnetic Co nanodots with fcc and hcp structures were successfully deposited into the nano holes of AAF on silicon substrate, which makes it a potential magnetic recording material with high area recording density. The effect of structure uniformity of Al film on the anodization process of AAF was studied by preparing ECR-Al films with electron and ion sheathes formed in front of substrate.

It should be noted that when anodizing pure aluminum film on silicon substrate, the oxide barrier layer had a void beneath each pore separated by an alumina layer, as shown in Fig. 3 (c), we considered that the small concaves represent the voids and the convex parts were the remained alumina barrier layer. H. S. Seo explained the principle of void formation that is the stresses accumulated by volume expansion could be released owing to the formation of voids [16]. The voids under barrier layer weaken the bonding strength, and the barrier layer inhibits the deposition of Co nanodots on the silicon substrate, therefore, the step of increasing hole diameter together with the removing of barrier layer is important for further deposition of Co.

During the process of deposition Co nanodots in the nano holes of AAF, silicon substrate is semiconductor, and it is hard for growing Co with DC electrochemical deposition method. A conducting layer of Pt was deposited on silicon surface with thermal evaporation method. Although it turns to be easier to fill Co nanodots into the nano holes of AAF, the Co filled AAF is more likely to peel off from the substrate because of the weak adhesion between Pt and Si. Authors are going to find a better material acting as conducting layer with much stronger adhesive force.

3 Conclusions

Thin anodic alumina films with vertical nano holes were fabricated on silicon substrate through anodizing the 310 nm ECR-Al film in oxalic acid. Then Co nanodots was successfully deposited into the nanoholes. The main conclusions are summarized by the following:

(1) Polycrystalline ECR-Al film deposited with ion sheath at the substrate surface were homogenous and fit for the synthesis of AAF with uniform distributed nano holes, while the Al film deposited with electron sheath shows hillocks with non-uniform thickness distribution, which cause the dissolution of film during anodization without forming AAF with nano holes.

(2) The diameters of AAF nano holes obtained from the ECR-Al film on silicon substrate are in the range from 30 to 70 nm, and the hole pitches are approximately 100 nm, the AAF on silicon substrate is about 100 nm thick after two-step anodization.

(3) Magnetic Co nanodots filled into the nano holes of AAF have both fcc and hcp structures. The Co filled AAF on silicon substrate provides a potential magnetic recording material with high area recording density.

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