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ScienceDirect
Surface & Coatings Technology 201 (2007) 4832–4836
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

Effects of incidence angles on the microstructure of Co–Nb thin films prepared by ion beam assisted deposition

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Available online 14 August 2006

Abstract

Ion incidence angle plays an important role during the ion beam assisted deposition process. In this study, incidence angle effects on the microstructure, morphology and thermal stability of $Co_{30}Nb_{70}$ thin films deposited by ion beam assisted deposition have been investigated. The films were deposited at a fixed ion energy of 4 keV and ion current density of 12 μA/cm^2. The experimental results show that $Co_{30}Nb_{70}$ amorphous alloy is formed, when incidence angles are from 0° to 75°. To investigate stability versus incidence angle, all the samples were annealed at 300 °C and 450 °C, respectively. It was found that most of the $Co_{30}Nb_{70}$ films remained amorphous after being annealed at 300 °C for 30 min, while a bcc metastable phase appeared in the film deposited with incidence angle of 45°. After being annealed at 450 °C for 30 min, the new bcc phase dissolved into amorphous phase again and some films became partially crystallized. The possible mechanism of microstructure evolution is discussed in terms of the mixing, thermal spike, internal stress, and the variations of the process of film growth induced by incidence angles.

PACS: 61.80; 68.55
Keywords: Amorphous phase; Ion beam assisted deposition; Incidence angle; Co–Nb film

1. Introduction

Ion beam assisted deposition (IBAD) is a technique having many special effects, such as enhanced nucleation [1,2], enhanced surface diffraction [3,4] and texture establishment [5,6]. In recent years, it has extensively been used for the preparation of amorphous films [7], metal nitrides films [8], metal oxides films [9,10], and some diamond-related films [11]. As we know, the IBAD process depends on the deposition conditions, i.e., ion energy, ion current density, deposition rate, temperature, and ion incidence angle. Among these deposition conditions, ion incidence angle plays an important role during the IBAD process. For instance, Dong et al. successfully controlled the growth of {110} out-of-plane texture in Nb thin films [6]. Furthermore, a metastable fcc structure was observed at various incidence angles in Co–Cu alloy films [12]. Recently, some metallic amorphous films were observed at various incidence angles in Co–Mo and Fe–Nb systems [7,13]. Some theories were developed to explain the phenomenon such as ion-channeling theory [14] and sputtering yield theory [15].

Owing to the superior soft magnetic properties of amorphous Co–TM (transition metals) alloys [16,17], the Co–Nb system was selected to investigate the effect of incidence angle on the microstructure, morphology and thermal stability. In a previous study, it was found that the Cu–Nb binary alloy system had a wide composition range of amorphous phase because of its negative mixing heat of −37 kJ mol^{-1} [18]. For example, Zeng and Pan [19] have found that the amorphization range of the Co–Nb system using the IBAD method is from Co 28 at.% to Co 68 at.%, while that is determined to be from Co 23 at.% to Co 80 at.% by ion beam mixing of multilayer films [20]. Therefore, the compositions of the Co–Nb films are selected as $Co_{30}Nb_{70}$, in the edge of amorphization and crystalline. The thermal stability of the $Co_{30}Nb_{70}$ films at 300 °C and 450 °C was also investigated.

2. Experimental details

$Co_{30}Nb_{70}$ thin films were prepared by alternative deposition of pure cobalt (99.99%) and niobium (99.99%) onto NaCl single-crystal chips with a freshly cleaved surface and Si

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doi:10.1016/j.surfcoat.2006.07.030

substrates in an IBAD system. The Ar (99.999%) ion beam bombardment during the vaporization process was provided by the Kaufman ion source with 8 cm diameter beam. The ion bombardment energy was selected at 4 keV and the ion beam current density was selected at 12 μA/cm^2. The background vacuum was 5×10^{-5} Pa. When the films were deposited, the partial pressure of Ar was approximately 4×10^{-3} Pa, and the deposition rates of Co and Nb are approximately 0.8 Å/s and 0.4 Å/s, respectively. The thickness of Co–Nb thin films was monitored by a quartz crystal oscillator. The total thickness of thin films was kept at about 50 nm to ease the sample preparation for transmission electron microscopy (TEM), and the modulation wavelength was kept at 6 nm. The composition of $Co_{30}Nb_{70}$ films was controlled by adjusting the relative layer thickness of constituent metals and was later confirmed by sequential X-ray fluorescence spectrometer (XRF) with an experimental error of 5%. After deposition, the substrates were dissolved by deionized water and the films were collected onto Cu grids for microstructure analysis. In this study, the substrates were rotated to attain different incidence angles, when the ion beam source and e-gun were fixed as shown in Fig. 1. Angle α is the ion incidence angle, and angle β shows the angle between the ion beam source and e-gun (or deposits), which was maintained at 20°. Six different incidence angles, α=0°, 15°, 30°, 45°, 60° and 75°, were selected. Annealing was performed in a vacuum furnace with a background of 4×10^{-4} Pa for half an hour at 300 °C and 450 °C, respectively. The structure and morphology characteristics of all samples were analyzed by selected area electron diffraction (SAD) and bright field examination of transmission electron microscopy (TEM).

3. Results and discussion

The TEM SAD results indicated that all $Co_{30}Nb_{70}$ thin films deposited by IBAD with various incidence angles from 0° to 75° are amorphous, when the ion energy and ion current density are 4 keV and 12 μA/cm^2, respectively. To obtain the detailed microstructure of $Co_{30}Nb_{70}$ thin films, Fig. 2 gives some typical SAD patterns and morphologies of $Co_{30}Nb_{70}$ films deposited with incidence angle 0°, 30° and 60°. From TEM SAD patterns in Fig. 2(a)–(c), it can be concluded that the microstructure of

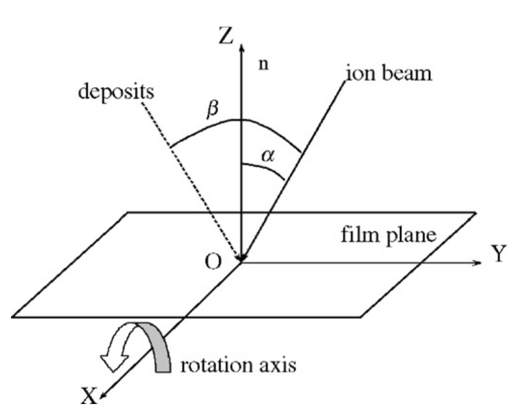

Fig. 1. Illustration about the incidence angle, normal direction, deposition direction and rotation axis of the substrate.

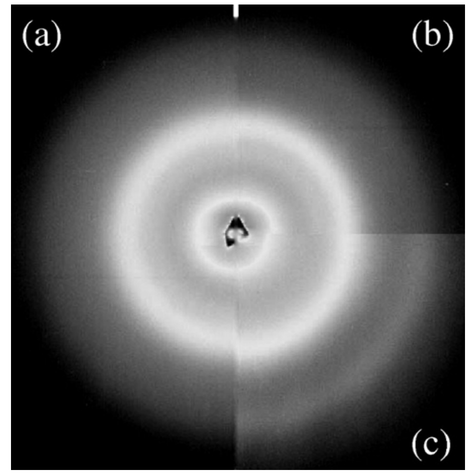

Fig. 2. TEM SAD patterns of as deposited films deposited with (a) incidence angle 0°, (b) incidence angle 30°, and (c) incidence angle 60°.

the amorphous phases was slightly different and influenced by incidence angle, though all the first diffraction rings have the same radius. For example, we cannot see the second diffraction ring in the SAD pattern of the sample deposited with incidence angle 0° in Fig. 2(a). When the incidence angle increased to 30°, the second diffraction ring appeared gradually as shown in Fig. 2(b). In Fig. 2(c), we can see the second diffraction ring more obviously than in Fig. 2(a) when the incidence angle was inclined to 60°. This result illustrates that when the ion beam bombardment was normal to the surface of the substrate, the mixture of Co and Nb atoms was much more thorough than that of films deposited with other incidence angles.

Furthermore, the morphologies of all the samples were investigated by TEM bright field examination. We found that all the samples deposited with glancing incidence angles had a pattern of relief with preferred direction as shown in Fig. 3 denoted by the arrows. In recent years a similar morphology was represented in the study of Zeng et al. [12] in Co–Cu films deposited by IBAD at an oblique ion incidence angle. From the morphologies of the samples in Fig. 4(a), we can see a porous microstructure, which shows that the films were covered by a lot of low-density regions called holes (or voids [21,22]).

In order to investigate the stability of the amorphous phase and the influence of the ion beam incidence direction we annealed all $Co_{30}Nb_{70}$ samples deposited with different ion incidence angles at the same time for half an hour at the temperature of 300 °C and 450 °C, respectively. The vacuum was 4×10^{-4} Pa.

After being annealed at 300 °C for half an hour, all $Co_{30}Nb_{70}$ samples remained in amorphous phase except the one deposited with incidence angle 45° as shown in the second row in Table 1. Fig. 4(d) shows that a bcc TEM diffraction pattern with lattice constant of a=4.12 Å, and the crystalline indices of the zone axis perpendicular to the substrate were determined as <001> (the possibility of the effect of crystalline sodium chloride substrate can be eliminated, because lattice of constant of sodium chloride is 5.45 Å). Meanwhile, the morphology of the sample did not change a lot when comparing Fig. 4(a) and (b).