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Structural and phase transformation of cobalt films grown on amorphous carbon

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ABSTRACT

Structural evolution of the ultra-thin cobalt layers grown on amorphous carbon by DC magnetron sputtering were studied in detail by transmission electron microscopy and low-angle X-ray diffraction for a range of the cobalt thickness from 1.5 nm to 4.6 nm. It was shown that atomic structure of cobalt layers was amorphous at the layer thicknesses below 2 nm, an amorphous matrix with embedded nuclei of the crystalline phase with in-plane size of 1–2 nm in the thickness range from 3 nm to 3.2 nm, and polycrystalline with the randomly oriented HCP cobalt grains at thicknesses over 4 nm. Increase of the cobalt thickness from 3.2 nm to 4.6 nm led to growth of the cobalt grains with in-plane average size up to ~70 nm by the normal grain coarsening process. Transition of the atomic structure of cobalt from the isotropic amorphous state to the anisotropic crystalline state in the thickness range of ~2–4 nm was accompanied by deterioration of the magnetization vector direction within the ferromagnetic domains due to high magnetic anisotropy of HCP lattice of cobalt.

1. Introduction

Recent advances in the technology of deposition of ultrathin layers of different chemical elements and their compounds allowed development of variety of the functional multilayer coatings with new physical properties. The soft X-ray optics [1–3] is one of the areas where the multilayer coatings were effectively applied. Multilayer X-ray mirrors made from the layered structures of several materials provided development of the optic instruments for a soft X-ray irradiation in the wavelength range of 1–60 nm, where there are no suitable natural crystals with a lattice period matching the radiation wavelength.

Deposition of multilayer compositions from the most combination of materials is accompanied by significant interlayer interaction resulting in formation of the intermixed zones at boundaries of the individual layers. Atomic structure and thickness of an intermixed zone depend on combination of the layer materials and the conditions of their growth. For example, in such metal/silicon combinations as Mo/Si [4–6], Ti/Si [7], and Sc/Si [8] the amorphous intermixed zones were observed. With decreasing of the multilayer period and the thickness of individual layers, both the fraction of intermixed zones in total multilayer composition and the contribution of intermixed zones to the net multilayer properties increase. Thus, it is important to have the detailed information about structural and phase transformations in the thinnest layers near interfaces of two materials for development of new multilayer materials with novel properties [9].

Recently the Co/C multilayers attracted a lot of attention due to their perspectives on various applications. First of all, they were used for development of high reflective X-ray mirrors for the wavelength range called "carbon window" (4.4–5.0 nm). This range is very important for an absorption microscopy of the carbon-based materials, including medical and biological objects. In contrast to optical and electron microscopy, absorption microscopy in the range of "carbon window" allows investigate relatively thick (up to 30 μm) samples [10]. Also the Co/C multilayer coatings could be used effectively in the areas where extremely high wear resistance and low friction coefficient required [11].

Most of the physical properties of the multilayer coatings are structure-sensitive and dependent strongly on distribution of the chemical elements in a multilayer volume. It was found that structure of ultra-thin layers of cobalt have significant effect on their magnetic properties. The coercive force of cobalt layers with an amorphous structure was negligible (~0.3 mT) while after crystallization with formation of the textured HCP structure at higher thickness the coercive force of cobalt raised up to 4 mT [12].

In this work, we studied the effect of thickness of the cobalt layer on its atomic structure and the ferromagnetic domain structure in three-layer C/Co/C and the Co/C periodical multilayer coatings.

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2. Experimental details

The Co/C periodical multilayer, three-layer C/Co/C and the single-layer coatings of carbon and cobalt were prepared by a dual DC magnetron sputtering process in an argon atmosphere at DC power of 420 W and 115 W for C and Co, correspondingly. The multilayer coatings were deposited onto polished (111) Si and glass substrates at the substrate-target distance of 6.5 cm. The roughness of the glass substrates was below 0.4 nm (RMS). The three-layer coatings were deposited onto (111) Si and the monocrystalline KCl substrates.

Graphite (99.99%) and cobalt (99.95%) targets with a diameter of 100 mm were used. The base pressure in a vacuum chamber before deposition was about 10^{-3} Pa. The argon pressure during deposition was maintained at 0.2 Pa. The volume fraction of argon in the working atmosphere was 99.993%, and the volume fractions of oxygen and nitrogen did not exceed 0.0007% and 0.005%, respectively. The mass water vapor concentration was not higher than 0.007 g/m^3.

The thickness of the individual layers was controlled by adjusting the exposure time with a resolution of 1 ms. A substrate temperature was maintained below 50 °C during the sputtering process. The deposition rates for carbon and cobalt were about 0.15 and 0.3 nm/s, respectively. Annealing of the multilayer coatings was not applied.

The Co/C periodical multilayer coatings were used for precise calculation of the deposition rates. The thicknesses of cobalt and carbon layers were found by using low-angle X-ray diffraction (LAXRD) with a computer simulation. Experimental LAXRD spectra were measured by DRON-3 M diffractometer with $CuK_{\alpha 1}$ radiation ($\lambda = 0.154051$ nm). The computer simulation of LAXRD was performed with commercial software based on the recursive method [13] for evaluation of the thicknesses and a density of individual layers and roughness of the interlayer boundaries. These parameters were varied to achieve exact matching between experimental and simulated LAXRD patterns (Fig. 1). Deposition rates of cobalt and carbon were calculated for given conditions based on the deposition times and corresponding thicknesses of the individual layers obtained from the simulation. Structure of the Co/C periodical multilayer coatings was also evaluated by transmission electron microscopy (TEM) of the multilayer cross-sections using JEOL JEM-ARM200F.

Three-layer C/Co/C coatings were used for investigation of the structure of cobalt layers depending on their nominal thickness. The nominal thickness of a layer is the thickness that the layer should have without intermixing at the interfaces. The nominal thickness of the carbon layers was fixed at ~4 nm for all specimens. The nominal thickness of cobalt layers was varied in the range of 1.5–4.6 nm. Three-layer C/Co/C coatings were deposited onto the fresh cleaved KCl facets and detached from the substrates by immersion in distilled water at room temperature. After detaching, the specimens were caught on the supporting copper grids. TEM investigation of the three-layer coatings was performed using PEM-U microscope (SELMI, Sumy, Ukraine) having resolution measured by lines (atomic planes) ~0.2 nm. The accelerating voltage of 100 kV was used.

The magnetic domain structure of cobalt in the three-layer C/Co/C coatings was revealed by Lorentz microscopy realized by switching off objective lenses to avoid the effect of magnetic field on a structure of cobalt films.

3. Results

Fig. 2 shows TEM cross-sectional images of the Co/C periodical multilayer coatings with nominal thickness of the cobalt layers (t_{Co}^{nom}) in range from 2 nm to 3.8 nm and with nominal thickness of carbon layers (t_{C}^{nom}) about 4 nm. The carbon layers are bright and the cobalt layers are dark. The strips with intermediate gray contrast on the interlayer boundaries could be observed, especially for the specimen with $t_{Co}^{nom} =$ 2 nm (Fig. 2a). A nature of these strips is not clear because their formation could be attributed not only to intermixing between carbon and

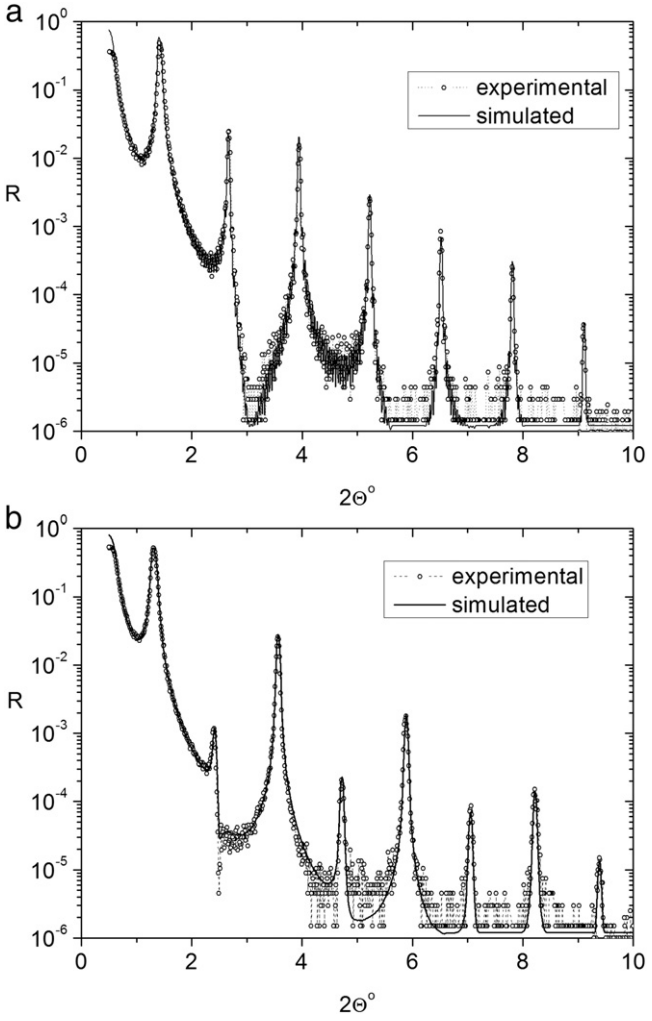

Fig. 1. Experimental (circles) and simulated (solid line) LAXRD spectra for the Co/C multilayers with 29 bilayers of Co(3.03 nm)/C(3.79 nm) (a) and 25 bilayers of Co(3.74 nm)/C(3.81 nm) (b).

cobalt but also to the tilt of a specimen in microscope. An alignment of cobalt atoms with formation of the atomic planes in tiny areas-nanoclusters is getting noticeable at $t_{Co}^{nom} \approx 3$ nm (Fig. 2b). This stage of the Co growth can be defined as an origin of crystallization of the amorphous cobalt. The size of the ordered areas expanded with increase of the Co thickness (Fig. 2c).

Assessment of the three-layer coatings C/Co/C by the TEM in the dark-field mode is the most informative method for investigation of the initial stages of the crystallization of thin amorphous films as it was shown on example of the three-layer Si/Mo/Si compositions in [9]. To perform this investigation, the 30 μm objective diaphragm was located on the position of first halo from amorphous cobalt around

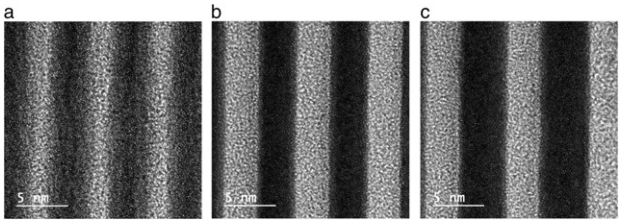

Fig. 2. TEM cross-sectional images of the Co/C periodical multilayer coatings with a nominal thickness of the cobalt layers $t_{Co}^{nom} = 2.0$ nm (a), $t_{Co}^{nom} = 3.0$ nm (b), and $t_{Co}^{nom} = 3.8$ nm (c). Substrate is located on the left of the images.