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Letter

Structural and magnetic properties of sputter deposited cobalt–silica nanocomposite thin films

Rajan Walia [a], J.C. Pivin [b], A.K. Chawla [a], R. Jayaganthan [c], Ramesh Chandra [a,*]

[a] Nanoscience Laboratory, Institute Instrumentation Centre, Indian Institute of Technology Roorkee, Roorkee 247667, India
[b] Centre Spectrometrie Nucleaire et de Spectrometrie de Masse (CSNSM), IN2P3-CNRS, Batiment 108, 91405 Orsay Campus, France
[c] Department of Metallurgical and Materials Engineering, Indian Institute of Technology Roorkee, Roorkee 247667, India

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ABSTRACT

The present study was focused to investigate the effect of Co concentration on structural and, magnetic properties of Co–SiO_2 nanocomposite thin films. Co–SiO_2 nanocomposite films with different cobalt atomic concentration up to 49 at% were synthesized using direct current (DC) and radiofrequency (RF) magnetron co-sputtering. TEM and XRD analyses reveal the formation of both FCC (1 1 1) and HCP (1 0 1) phases in all the samples. The particle size and surface roughness of these films is found to increase with increase in cobalt concentration. Magnetic measurements reveal that the embedded cobalt nanoparticles behave as superparamagnets when their size is ≤16 nm. The coercivity at 3 K decreases while value of blocking temperature increases with increase in the size of embedded Co nanoparticles.

1. Introduction

Nanocomposite thin films made of transition metal particles embedded in insulating matrix such as Co–SiO_2, Ni–SiO_2, and Fe–SiO_2 exhibit superior magnetic and optical properties, which may be exploited for optoelectronic device applications [1]. The properties of magnetic nanoparticles are different from those of the bulk magnets because, in nanoparticles, an increasing fraction of the magnetic atoms lies at the surface, thus reducing the average number of neighbors and favoring the interaction with the surrounding atoms of the matrix. Below a critical diameter of 10–100 nm (values for typical materials) the magnetic particle supports only one domain. Single domain magnetic particles are attractive for technological applications, such as high coercive films for data storage and giant magnetoresistance for read heads. The interest in nanocomposites consisting of nanometric magnetic particles embedded in an insulating matrix such has silica has grown considerably in recent years due to new magnetic properties presented by these kind of materials. For metal volume fraction well below the percolation limit, the insulating host matrix prevents the interaction among nanoparticles, thus giving an ideal frame to investigate their intrinsic magnetic properties. The magnetic properties of such systems are closely related to the particle size and concentration [2–5]. For example, Sen et al. have recently studied the effect of concentration of Co nanoparticles in SiO_2 matrix [6]. Lu et al. have studied the effect of SiO_2 matrix on the growth of Co nanoparticles [7]. However, from the basic research point of view it would be much more interesting to synthesize such systems in which all the parameters affecting the average magnetic properties, such as particle size and size distribution, crystalline phase, spatial arrangement of nanoparticles, could be varied independently and their effects could be studied. Co nanoparticles below a critical size, show superparamagnetism due to their lower magnetic energy in the form of single domains [3]. Within single domain particle magnetic moments flip all together as a supermoment between easy magnetization axes when thermal energy is larger than the anisotropy energy barrier. Thus the magnetic behavior of an ensemble of this kind of single-domain particles is paramagnetic-like [8–10]. It is well known that paramagnetic nanoparticles are not suitable as memory storage since thermal fluctuations result in losing stored data. Several efforts have been made to stabilize the residual magnetization of nanoparticles under zero applied field, for instance by embedding them in an antiferromagnetic matrix [9]. A shell of CoO or SiO_2 around Co particles could play such a role [11–13]. The studies on magnetic properties of sputter deposited Co–SiO_2 thin films are limited in the literature [14,15]. However study of Co–SiO_2 system synthesized by other techniques like sol–gel and ion implantation has been done by several authors [6–8,16–22]. Therefore, the present

* Corresponding author. Tel.: +91 1332 285743; fax: +91 1332 286303.
E-mail address: ramesfic@iitr.ernet.in (R. Chandra).

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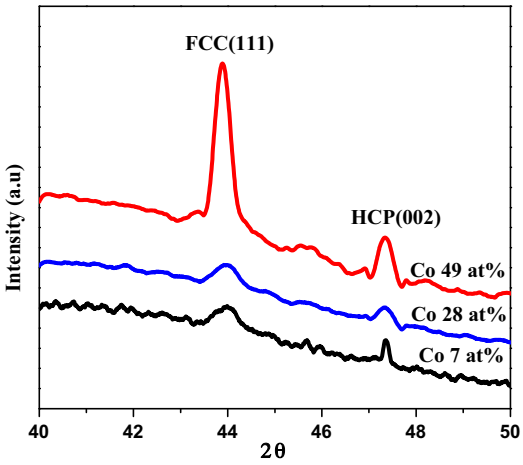

Fig. 1. XRD pattern showing the most intense peaks of FCC and HCP cobalt phases at low angles in samples having different cobalt concentrations.

work is focused on to fabricate Co–SiO_2 nanocomposite films by using DC/RF magnetron co-sputtering and investigate the effect of cobalt concentration on their magnetic behavior. The nanocomposite thin films were characterized by XRD, TEM, AFM, FE-SEM/EDS, and SQUID to substantiate the influence of size effect of Co nanoparticles on their magnetic properties.

2. Experimental

Cobalt–silica nanocomposite films were prepared by co-sputtering of silica and cobalt on Si(1 0 0) substrate by DC/RF magnetron sputtering. Depositions were performed at substrate temperature of 600 °C in Ar atmosphere at a pressure of 20 mTorr. The RF-power to the 2 in. diameter silica target was fixed at 250 W during depositions, while the relative amount of cobalt was changed by varying the DC power (from 10 to 50 W) applied to the 2 in. diameter cobalt target (purity 99.95%). Before deposition, the Si substrates were etched in HF then ultrasonically cleaned in propanol-2. All depositions were carried out in three steps: a first single deposition of silica was made for 5 min (to avoid the diffusion of Co in Si Substrate) followed by the co-deposition of silica and cobalt (60 min duration for all samples). As a final step in the preparation, a single silica deposition was performed for 5 min (to avoid oxidation of cobalt). Nanocomposite films with different concentrations of Co were prepared following the same procedure. The thicknesses of final nanocomposite films were measured by cross sectional FE-SEM (FEI, QUANTA 200F) image. The cobalt concentrations present in the samples were measured by using the EDAX attachment in the FESEM.

X-ray diffraction (XRD) (Bruker AXS, D8 advance model) was used to study crystallinity, phase formation and particle size of the sputter deposited samples. X-ray diffraction patterns were recorded by using Ni-filtered Cu K_α radiation (30 mA, 40 kV) in air at room temperature with step size of 0.02° in a 2θ scattering angle with time taken per step as 0.5 s. Transmission electron microscopy (TEM) investigation was carried out using a TEM (FEI, TECNAI G^2) microscope operated at 200 kV. Selected area electron diffraction (SAED) revealed the nature of crystalline phases present in the samples. The surface morphology and roughness of the thin films were examined by AFM (NT-MDT, Ntegra), operated in semicontact (tapping) mode.

The magnetic properties of the films were studied using a SQUID (Quantum Design, MPMS XL) magnetometer. Field-cooled (FC) and zero-field-cooled (ZFC) measurements were performed on the films in the temperature range of 3–300 K, under a magnetic field of 500 Oe. Hysteresis loops were recorded at room temperature and 3 K, with a magnetic field up to 10 kOe.

3. Results and discussion

XRD diffraction (shown in Fig. 1) shows that two types of cobalt nanoparticles precipitate in all the studied films showing FCC (1 1 1) and HCP (0 0 2) structures. The films contain FCC particles with a mean size of 10, 16 and 29 nm for cobalt concentration of 7, 28 and 49 at%, respectively. Particle size increases with increase in cobalt concentration which may be due to the agglomeration of cobalt particles takes place at higher concentration. Particle sizes were

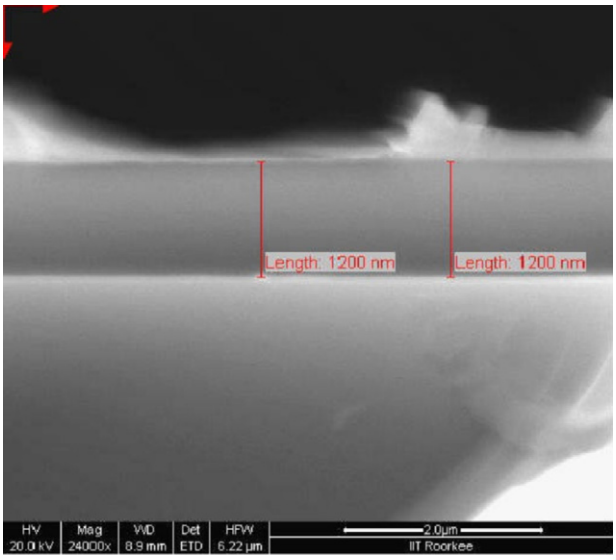

Fig. 2. Cross sectional image of 7 at% Co sample.

calculated by using Scherrer formula [23], given as

$$t = \frac{0.9\lambda}{B\cos\theta}$$

where B is the full-width at half maximum (FWHM) of a Bragg peak in radian, λ is the wavelength of X-ray (1.54 Å for the Cu target), and θ is the Bragg angle.

In our opinion the fact that deserves attention is the simultaneous presence of the FCC and HCP Co phases in the particles studied. In bulk polycrystalline alloys, the HCP Co phase is stable; the polymorphic transition to the FCC phase occurs above 420 °C. Numerous experimental studies, which were aimed at the production and analysis of nanocrystalline Co and Co nanoparticles, demonstrated that FCC Co is stable in these structural modifications at room temperature [24–29]. A study of free Co nanoparticles [25] showed that at room temperature in Co particles $\leq$20 nm in size there is only an FCC phase; in particles of 20–40 nm, a mixture of the FCC and HCP phases is observed; and in Co particles $\geq$40 nm in size, the HCP structure is revealed. Note that the contact of nanoparticles and the matrix material naturally can change the ranges of the particle sizes in which the FCC and HCP phases are stable [30–34]. For example, the HCP phase is stable, along with the FCC phase, in cobalt particles

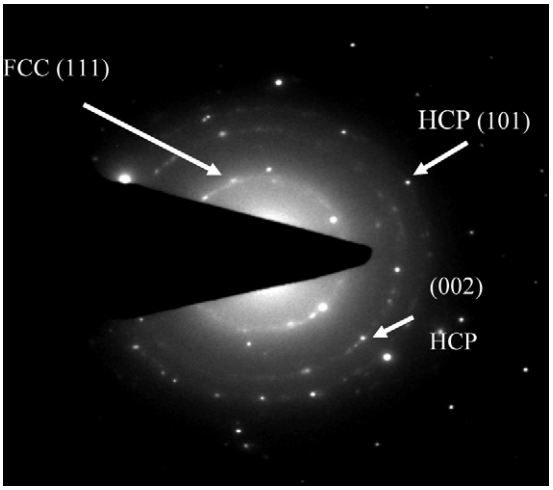

Fig. 3. SAED image of sample having 28 at% Co.