Co-sputtered carbon-nickel nanocomposite thin films

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Abstract. Carbon-nickel nanocomposite thin films were prepared by co-sputtering a graphite target with a small Ni chip attached on its surface. The Ni concentration in the films was controlled by the size of the Ni chip and measured by in-situ X-ray photoelectron spectroscopy. Transmission electron microscopy images showed that the films have a granular structure with nanosized Ni particles embedded in an amorphous carbon matrix. The Ni particles have an average diameter of ~4 nm, with a rather narrow size distribution. Magnetization measurements revealed that films are superparamagnetic and present blocking temperatures $T_B < 15$ K.

Introduction

Nanosized particles (NP’s) of ferromagnetic metals as Fe, Co, and Ni have been extensively studied because of both the richness of their physical properties and a wide range of potential applications, including catalysts, high density magnetic recording media, ferrofluids, and medical diagnostics [1]. Although metallic NP’s can be easily prepared by a number of methods, including evaporation, sputtering, high-energy ball milling, ion exchange, and sol-gel [2,3,4,5], the particle size distribution and average size strongly depend on the preparation parameters and methods. In addition, these NP’s are highly reactive due to the large surface area to volume ratio and can be easily environmentally degraded. Within this context, oxide surface layers are formed leading to a shell-core morphology where an antiferromagnetic (AFM) oxide layer surrounds the ferromagnetic (FM) metallic NP. Such a morphology influences the magnetic properties due to the exchange interaction between the FM and AFM phases. As a result, two main challenges remain for the viable application of such NP’s: effective control of particle size and protection from oxidation and chemical degradation.

A favored approach to assemble and maintain metallic NP’s is to form nanocomposites whereby the NP’s are embedded in a non-magnetic matrix that provides mechanical and chemical stability [6]. Oxides such as silica and alumina have been extensively used as matrix to provide good magnetic and electric insulation. However, these oxides lack the mechanical and tribological properties required in magnetic storage devices applications such as hard disks. On the other hand, carbon based materials such as diamond-like carbon and amorphous carbon nitride alloys have been extensively applied as protective coatings in magnetic storage devices, due to their excellent mechanical and tribological characteristics [7]. Therefore, carbon-based thin films are excellent candidates for metallic NP hosting, since they can be directly incorporated in magnetic storage devices structures. In this work, a co-sputtering method was used to produce carbon-nickel nanocomposites thin films that present superparamagnetic behavior.
Experimental

Carbon-nickel (C-Ni) thin film nanocomposites were prepared by co-sputtering a high-purity graphite target containing a Ni chip glued on its surface, by using a 1500 eV argon ion beam. The glue used was a graphite colloidal suspension (Leit-C™ CCC Conductive Carbon Cement). The Ni concentration of the films was controlled by the area of the Ni chip. Polished silicon wafers were used as substrates and held at 350°C during deposition. Such temperature was chosen in order to provide enough thermal energy for the diffusion of Ni atoms (to form coalesced NP), but preventing the carbide formation. Pure carbon films produced under the same conditions showed a disordered graphitic structure, with atoms forming mainly sp² hybridized bonding [8]. While this material is not particularly hard, its mechanical properties can be easily optimized by the incorporation of nitrogen [8].

The chemical composition of the films was determined by in-situ x-ray photoelectron spectroscopy (XPS). The XPS spectra were collected by using an Al Kα line and a CMA type analyzer (VG), with an overall energy resolution of 0.85 eV. The Ni concentration in the films is determined from the XPS spectra of the individual C 1s and Ni 2p peaks, by weighting the peak integrated areas with the respective photoionization cross-sections. The structure and morphology of the nanocomposites were examined by high-resolution transmission electron microscopy (HRTEM), using a JEM 3010 URP with 1.7 Å point-resolution. The ~ 500 nm-thick films were thinned by standard polishing and ion milling procedures for HRTEM observations. Magnetization measurements M(T,H) were performed in the as-grown samples by using a SQUID magnetometer with applied magnetic fields between 0 and 7 T and temperatures ranging from 5 to 350 K. In this work we will focus on the results of the sample containing 22 wt% of Ni.

Results and discussion

Fig. 1 depicts a typical XPS spectrum of a C-Ni composite film. The Ni concentration for the film of Fig. 1 is 22 wt.%. Moreover, the observed contributions to this spectrum are from C and Ni atoms. In particular, no contribution from oxygen O 1s electrons (520-530 eV) can be distinguished from the inelastic background (see inset), indicating an oxygen contamination below ~ 0.5 at.%.

The structure and morphology of the prepared samples were analyzed by HRTEM. Fig. 2

![X-ray photoelectron spectroscopy spectra of C-Ni thin films with and 22 wt.% Ni concentration. The inset reveals that the oxygen concentration is below the detection limit of the equipment (< 0.5 at.%).](image-url)
presents bright-field images with different magnifications of a sample with 22 wt.% of Ni. It is observed that the films have a granular structure, whereby the Ni NP’s are clearly discerned as the darker regions surrounded by the lighter disordered carbon matrix. The NPs are homogeneously dispersed over the matrix and well separated from each other. They have a nearly spherical morphology with average diameter of ~ 4 nm. Selective area electron diffraction images (not shown) reveal a typical pattern of well defined rings associated with small size crystalline particles randomly aligned. The crystalline character of the Ni NP’s is also evidenced in Fig. 2(b), whereby the lattice planes can be clearly discerned inside the NP’s. HRTEM images of films with different Ni concentrations indicate that the nanocomposite morphology does not change significantly within the range of Ni concentration studied.

In order to determine the NP size distribution, TEM images such as the one in Fig. 1(a) were processed by using segmentation algorithms, wherein the NP contours were identified and the particles “isolated” from the amorphous matrix [9]. As a result, the dimensions of each isolated particle were estimated. Fig. 3 presents the results of a statistical analysis of ~ 400 particles for the film with 22 wt.% of Ni. The columns represent the frequency histogram as a function of the measured NP radius (assuming that the NP’s are spherical). The size distribution was found to be well described by a log-normal distribution (solid line) in agreement with other metallic nanoparticles systems [10,11]. In fact, the particle size distributions is rather narrow having maximum at r_{TEM} = 2.3 ± 0.2 nm and width σ = 0.39 ± 0.07 nm. The inset in Fig. 3 shows the elongation distribution of the Ni particles, defined as the ratio of the major and minor axis of assumed ellipsoidal particles. The elongation distribution shows a maximum at ~ 1.2, further confirming the observed nearly spherical morphology of Ni nanoparticles (Fig. 2 (a)).

The magnetic properties of the studied nanocomposites were also investigated. The temperature dependence of the magnetization measured under applied magnetic field H = 50 and 100 Oe is shown in Fig. 4. The magnetization curves were taken in the zero field cooled (ZFC) and field cooled (FC) conditions. Initially, the sample is cooled down to 5 K under zero applied field, the magnetic field is set and the magnetization data is collected upon warming up to 350 K (ZFC), then the data is collected upon cooling the sample down to 5 K (FC). The curves displayed in Fig. 4 exhibit clear features of superparamagnetic (SPM) systems: (1) the ZFC curves are rounded at T_B ~ 15 K, defined as the temperature of their maximum, indicating a blocking process of the small particles; and (2) a paramagnetic-like behavior above T_B. The T_B of a system of randomly oriented

![Fig. 2: High-resolution transmission electron microscopy images of the C-Ni nanocomposite thin film with 22 wt.% Ni. (a) lower magnification and (b) higher magnification.](image)
and noninteracting particles can be estimated by $T_B = K\langle V \rangle / 25k_B$, where $K$ is the anisotropy constant of bulk Ni, $\langle V \rangle$ is the average volume and $k_B$ is the Boltzmann constant [12]. Assuming spherical particles and $T_B = 13$ K, the radius $r_{TB}$ can be calculated resulting in $r_{TB} = 2.4$ nm, in perfect agreement with HRTEM analysis.

![Fig. 3: Histogram of the particle size distribution and log-normal fit (solid line) for the C-Ni nanocomposite film with 22 wt.% Ni determined from HRTEM analysis. The inset shows the particle elongation distribution (see text for details).](image)

![Fig. 4: Temperature dependence of the magnetization for the C-Ni nanocomposite thin film with 22 wt.% of Ni. Curves were taken in ZFC and FC processes at H = 50 and 100 Oe. The inset shows the low temperature region in detail and the arrows point to $T_B \sim 13$ K.](image)
Summary

In summary, carbon-nickel thin film nanocomposites with controlled Ni composition were produced by a co-sputtering method. The Ni nanoparticles are homogenously distributed within the disordered carbon matrix and have an average radius of ~ 2 nm with a rather narrow size distribution and elongation factor of ~ 1.2, confirming the nearly spherical shape of the particles. No evidence of oxygen was found through x-ray photoemission spectroscopy data, suggesting that the amorphous carbon film is a suitable matrix to preserve the NP’s from surface oxidation. The films present a superparamagnetic behavior with blocking temperature $T_B \sim 15$ K, which corresponds to a system comprised of spherical nanoparticles with radius of ~ 2.4 nm, in excellent agreement with high-resolution transmission electron microscopy analysis.

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