ELECTROLESS DEPOSITED NANOSTRUCTURED NiCo FILMS

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1. Abstract

Nanostructured metal films and coatings with unique properties can be synthesized using solution chemistry. In this paper, the non-aqueous electroless polyol synthesis, characterization and properties of NiCo films are discussed.

2. Introduction

Nanostructured films and coatings with unique properties can be fabricated by many methods. Physical vapor techniques, such as thermal evaporation and sputtering, are generally line-of-sight processes suited for deposition on planar surfaces. The limitation in these processes is caused by the high sticking coefficients of atoms that cannot readily move around after impacting the surface. On the other hand, chemical vapor deposition and solution chemistry methods are generally free from such limitation, since the atoms have smaller sticking coefficients and higher mobility at the surface. Thus, these techniques are suitable for depositing films on not only planar but also hidden and complex surfaces. Further, high-cost vacuum technology is not needed in wet chemistry processing.

Using solution approach, nanostructured ceramic films can be prepared by sol-gel method, and metal films can be synthesized using electrodeposition and electroless deposition. Electrochemical technology finds many applications ranging from traditional surface finishing to high-tech fabrication of advanced materials for microelectronics and media storage [1].

2.1. AQUEOUS ELECTRODEPOSITION

In electrodeposition [2], metal precursors in the solution are reduced by the application of an electric current, resulting in deposition of the metal film on the conductive substrate. Aqueous electrolytes are extensively used because water is a

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good solvent for many salts and it is inexpensive. Experimental parameters, such as electrolyte composition, pH, temperature and agitation, applied potential and current, are controlled to optimize the thickness, grain size and composition of deposited films. Special care is required to deposit films on substrates with sharp corners and irregular surface, since the electric field distribution may not be uniform at these regions. For electroplating of non-conductors such as plastics and ceramics, they must be pre-plated with metal by another process such as electroless plating. Thick deposits can be formed on a mandrel by electroforming and subsequently removed and machined for applications.

Nanostructured materials, for example, compositionally modulated multilayers [3] and GMR films [4,5], have been synthesized using electrodeposition. Polycrystalline, nanostructured Ni was synthesized by pulsed electrodeposition in a bath containing saccharin [6]. The grain size was in the range of 10 to 40 nm and showed initial rapid decrease with increasing saccharin concentration. The deposits were smooth and bright. The growth texture was dependent on the concentration of saccharin in the plating bath. Industrial applications of electrodeposited nanocrystals include, for example, corrosion and wear resistance, magnetic materials, fuel cells and catalysis [7].

2.2. AQUEOUS ELECTROLESS DEPOSITION

In electroless deposition (often known as electroless plating) [8], electrons are produced by chemical reactions without the application of an external current. Unlike electrodeposition, electroless metallization can be applied to both conductor and insulator. This process may occur by one of the following: deposition by ion or charge exchange, deposition by contacting the metal to be plated, and autocatalytic deposition on catalytic surfaces in solutions containing appropriate reducing agents. For autocatalytic electroless deposition, the surface to be metallized is initially treated with catalysts such as nanosized Pd colloids. Reduction of metal ions or metal complexes by the reducing agent in the plating bath results in metal deposition on the substrate surface. Each freshly deposited metal layer then becomes the catalyst for subsequent metal deposition. Electroless plating allows for the deposition of uniform films on irregular-shaped objects with complex and hidden surfaces.

Electroless films and coatings find applications in wear resistance, corrosion resistance, solar absorber optics and electronics. Nanostructured Ni and Co films were electroless deposited [9]. Self-assembled biomolecular tubular microstructures were electroless coated with nanostructured metal films for application as high-current density cathode in vacuum field emission [10,11,12]. Generally, the crystallinity and the grain size (ranging from 2 – 100 nm) can be controlled by controlling the composition of the plating bath and performing suitable post-deposition heat treatment. The control of the size of adsorbed catalysts is also critical in controlling the particle size of nanostructured electroless Ni deposits. Smaller catalysts were bound to the chemically modified substrate surface and led to a reduction of particle size in the deposits by 3-4 times [13]. Electroless deposition was also used to deposit CoNiP films consisted of oriented hcp crystallites [14]. The crystallite size decreased

from about 37 nm to 25 nm with increasing ammonia concentration. The coercivity of the films decreased from about 2600 Oe to less than 1000 Oe with decreasing crystallite size.

2.3. NON-AQUEOUS, ELECTROLESS POLYOL DEPOSITION

When the substrate and deposited materials are susceptible to hydrolysis and oxidation, adverse material properties may result from using aqueous chemical processes. For deposition of nanostructured metallic materials with significant amount of surfaces and interfaces, these problems may become more acute. Therefore, a simple and non-aqueous approach has been sought as an alternative to aqueous processing. The polyol method, a non-aqueous electroless process, has been used to synthesize micron, submicron and nanostructured powders [15,16,17,18]. Recently, we have extended this polyol method to synthesize nanostructured metal films [17]. The process involves the reduction of metal salts in refluxing ethylene glycol to deposit metal films on the substrates. Film deposition can occur on planar or complex surfaces of both suitable conductor and insulator substrates, without any pre-deposition surface treatment such as the catalyzation of insulator surface as in traditional electroless plating. For example, Co was deposited on WC substrate [19] and Cu was deposited on AlN [20].

In this paper we describe our work on polyol deposition of nanostructured Ni_xCo_{100-x} films [21]. Nickel-cobalt find applications as decorative bright coatings, engineered hard coatings, and magnetic films and coatings.

3. Experimental

Nickel (II) acetate tetrahydrate and cobalt (II) acetate tetrahydrate were suspended in 200 ml ethylene glycol. The total precursor concentration was kept at 0.1M. The nominal compositions of Ni_xCo_{100-x} films were obtained from the starting precursor molar ratio. Coarse-grained, polycrystalline Cu substrates with a (200) texture were vertically suspended in the mixtures. The mixtures were heated and refluxed at 194° C for 1 h for film deposition. For Co_{100} film, the deposition was carried out for 7 h due to the greater difficulty to reduce Co under these conditions. The structure of deposited films on Cu substrates was studied using θ-2θ X-ray diffraction (XRD). The diffraction peaks were analyzed using a profile fit routine. Average crystallite size (x-ray coherence length) was estimated from the XRD line broadening. The film thickness was measured from cross-sectioned films with scanning electron microscopy (SEM). The hysteresis loops were measured with vibrating sample magnetometry (VSM) at room temperature using a maximum field of $\pm$50 kOe. Both in-plane (//) and perpendicular-to-plane ($\perp$) measurements were made. The Vickers microhardness (HV) of deposited films on substrates was measured using a load of 25 gf for 10 s.

Nickel and cobalt are miscible. The thickness of deposited Ni_xCo_{100-x} films was in the range of 0.6 to 1.6 μm. The XRD data showed that the films had a single fcc phase with a (111) texture. Figure 1 shows the XRD results of films with x = 30, 50 and 70. The (111) diffraction peaks were observed for $x \leq 30$. For $x \geq 50$, higher fcc

reflections were also observed. For Co_{100}, in addition to the predominant fcc phase, a weak signal that could be assigned to hcp phase was detected. The average crystallite size (estimated from (111) line broadening) increased with x from 15 to 64 nm (Fig. 2). Since Ni was more easily reduced than Co, a higher Ni precursor concentration favored the growth of larger Ni-rich crystallites in Ni-rich films. Because of the very close lattice parameters of fcc Ni (3.5238 Å) and fcc Co (3.5447 Å), the appearance of a single set of fcc peaks as shown in XRD results could not be used to ascertain if the films were solid solutions or composites.

When the coherent inhomogeneities of nanostructured materials are below a critical size, conventional XRD should not be used alone to determine the structure of a composite or solid solution [22]. For example, other complementary techniques such as extended x-ray absorption fine structure (EXAFS) and nuclear magnetic resonance (NMR) have been used for structure determination of nanostructured Co-Cu powder [18]. Recently, the structure of these polyol-deposited Ni_xCo_{100-x} films has been studied using anomalous x-ray scattering (AXS) [23]. The association of an element in-question with a specific Bragg peak was investigated. It was shown that nanostructured NiCo films did not necessarily form solid solution as expected from their phase diagram or suggested by the results of conventional XRD. Further work to elucidate the nanostructures of these films is currently pursued using AXS, EXAFS and high-resolution transmission electron microscopy.

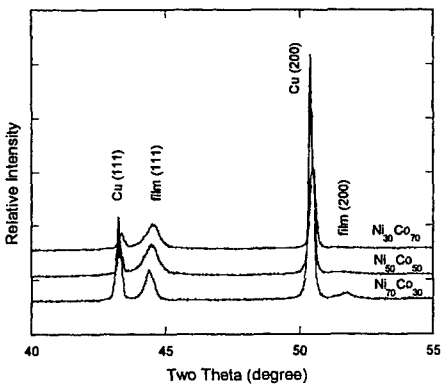

Figure 1. XRD of Ni-Co films, x = 30, 50 and 70

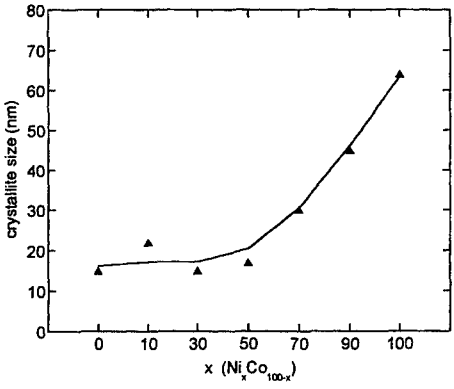

Figure 2. Dependence of crystallite size on composition

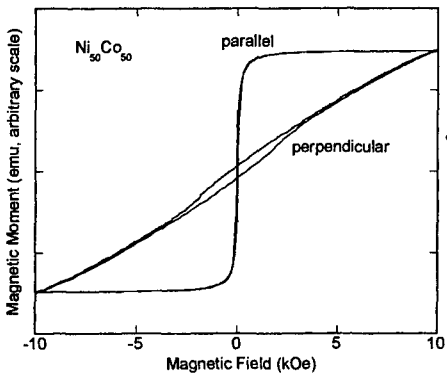

Figure 3. Hysteresis loops of $Ni_{50}Co_{50}$ in parallel and perpendicular directions

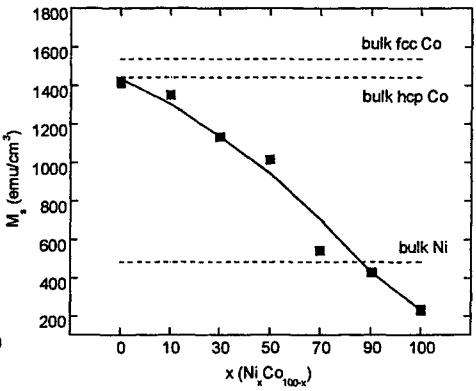

Figure 4. Dependence of $M_{s//}$ on composition

Saturation magnetization (M_s) of bulk fcc Ni, fcc Co and hcp Co are 484, 1538 and 1442 emu/cm^3, respectively. The hysteresis loops of Ni_xCo_{100-x} films showed in-plane magnetization anisotropy. Figure 3 shows the hysteresis loops of $Ni_{50}Co_{50}$ in the parallel and perpendicular directions. Figure 4 shows the dependence of in-plane saturation magnetization ($M_{s//}$) on composition. The M_s of the Ni_{100} sample was 236 emu/cm^3, but it could approach the value of bulk Ni by increasing the deposition time [24]. The M_s increased with increasing Co content and reached as high as 1421 emu/cm^3 for Co_{100}. For example, $M_{s//}$ and remanent magnetization (M_r) of $Ni_{50}Co_{50}$ were 1016 and 636 emu/cm^3, respectively, thus giving a remanence squareness (M_r/M_s) of 0.63. The M_s of $Ni_{50}Co_{50}$ film compared well with that reported for bulk $Ni_{50}Co_{50}$ (997 emu/cm^3) [25]. The remanence squareness of the $Ni_{50}Co_{50}$ film suggested that some texturing existed in the film.

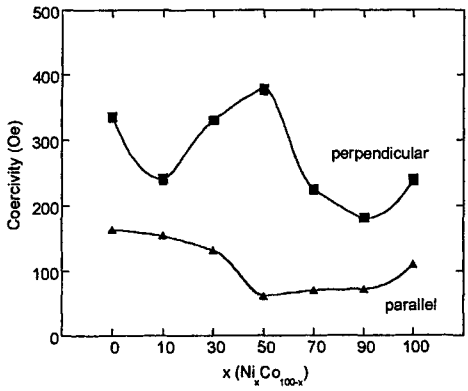

Figure 5. Dependence of coercivity on composition

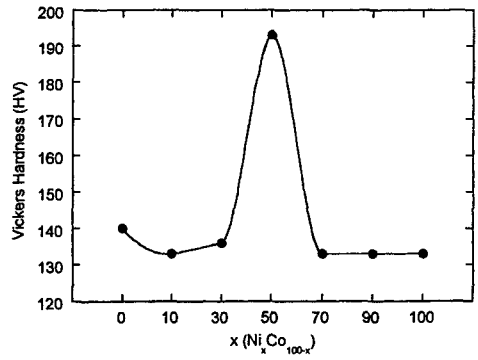

Figure 6. Dependence of microhardness on composition

The coercivity showed an interesting dependence on composition (Fig. 5). $H_{c\perp}$ was higher than $H_{c//}$ in these films. For example, $H_{c\perp}$ of $Ni_{50}Co_{50}$ film was 379 Oe, which was about six times that of $H_{c//}$. The value of H_c of electrodeposited NiCo alloy films, depending on the composition, was in the range of 200 to 500 Oe [26]. A possible explanation of the perpendicular coercivity anisotropy in our films is that these films consisted of two components: a continuous film and a small fraction of magnetically isolated particles with some form of anisotropy (such as shape) in the perpendicular direction [27].

Good film adhesion was observed, and the critical load for film delamination increased with increasing Ni concentration as determined from the microscratch tests [27]. Figure 6 shows the dependence of Vickers microhardness on film composition. The HV of the Cu substrate, bulk Ni and bulk Co samples were found to be 75, 144 and 288, respectively. The films provided enhanced surface hardness for the underlying soft Cu substrate. Interestingly, the $Ni_{50}Co_{50}$ film had very good saturation magnetization, the highest hardness and largest magnetic anisotropy compared to other samples. These good properties can be further optimized for magnetic applications.

In vapor deposition, a constant flux of atoms to the substrate can be maintained by controlling deposition parameters. In solution deposition, film formation is a more complicated process as it depends on the chemistry of reactions. Recently we have investigated how the solution chemistry and film deposition chemistry changed with reaction (deposition) time in the polyol process. It was found that the composition and properties of $Ni_{50}Co_{50}$ films varied with deposition time due to the change in solution chemistry with increasing time [28]. The solvent was found to have the corrosive activity on deposited Ni films when deposition time was increased [24]. Further work is needed to understand the solution chemistry and film deposition chemistry in the polyol process in order to optimize the film properties.

4. Summary

The non-aqueous, electroless polyol approach has been used to deposit nanostructured metal films for various applications. Film deposition can take place on exposed or hidden, and planar or complex surfaces. In this paper the work on polyol-synthesized Ni_xCo_{100-x} films was described. The magnetic films showed in-plane magnetization anisotropy with higher perpendicular coercivity. The $Ni_{50}Co_{50}$ film showed good magnetic properties with high hardness. Current focus is placed on understanding the solution chemistry and the effects of applied electric field in polyol deposition of nanostructured films for longitudinal and perpendicular magnetic recording.

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