UNIVERSITAT DE BARCELONA
FACULTAT DE QUÍMICA
DEPARTAMENT DE QUÍMICA FÍSICA

Programa de Doctorat de Tecnologia de Materials

Bienni 2004-2006

Electrochemical preparation of Co-Ag nanostructured materials for GMR applications

Memòria que presenta JOSÉ MANUEL GARCÍA TORRES per optar al títol de Doctor per la Universitat de Barcelona

Directores de la tesi:

Dra. Elvira GÓMEZ VALENTÍN
Professora Titular de Química Física
Universitat de Barcelona

Dra. Elisa VALLÉS GIMÉNEZ
Professora Titular de Química Física
Universitat de Barcelona

CHAPTER 8

CONCLUSIONS

8

CONCLUSIONS

During the course of this thesis, the electrochemical and chemical preparation of Co-Ag nanostructured materials has been revealed successful to fabricate materials with good prospects regarding their properties. Moreover, the versatility of electrodeposition to prepare such different nanostructures is patently obvious. The main conclusions for each kind of nanostructured material are summarized as follows:

With regard to the granular films:

- The electrodeposition conditions for silver deposition at high negative potentials from a thiourea-based bath (containing thiourea, sodium gluconate and boric acid) have been optimized. Thiourea presence delayed silver reduction toward negative potentials. Sodium gluconate and boric acid improved film's quality and expanded the potential range in which non-dendritic silver films were obtained. From this complex formulation the viability of electrodeposition to grow Co-Ag films has been demonstrated.
- The electrochemical method has also been employed as analytical technique to quantify cobalt and silver content into the films. A new voltammetric method has been developed and successfully implemented to analyze silver concentrations down to a few milligrams per liter.
- Cobalt-silver heterogeneous films have been fabricated from the thiourea-based electrolytic bath with modulated properties depending on the electrodeposition conditions: applied potential, temperature or applied signal. These deposits were characterized by high roughness and sulphur presence which amounted up to 2 wt.%. fcc-Ag and hcp-Co and a metastable

phase were present in the films. Ferromagnetic deposits were obtained but only giant magnetoresistance was detected at 40 K. Low bath temperatures allowed improving film cohesion and compactness. No effect of temperature on the magnetotransport properties was observed.

- The thiourea-based bath has allowed obtaining both cobalt and cobalt-silver metastable phases not predicted by the equilibrium diagram. The characterization allowed indexing these phases as a primitive cubic structure for cobalt (e-Co) and a hexagonal close packed structure of formula $CoAg_3$ for Co-Ag. Hcp-$CoAg_3$ metastable phase has been detected from the very early deposition stages. Its proportion into the coating depended on electrodeposition conditions (temperature, bath composition or substrate) which in turn were reflected on the film's magnetic properties.

- Bath composition reformulation led to films with lower amounts of sulphur, which allowed improving GMR but only at cryogenic temperatures.

- The use of a thiosulphate-based electrolyte was demonstrated feasible to prepare heterogeneous Co-Ag films with very low roughness values although with higher amounts of sulphur than those detected in films prepared from the thiourea-based electrolyte. Sulphur was partly dissolved in the cobalt lattice and the rest was placed in the magnetic/non-magnetic interface. These films with high sulphur content did not show GMR even at 40 K, making in evidence that sulphur presence is detrimental to the magnetotransport properties.

- The chloride electrolyte bath used (a sulphur-free bath) allowed obtaining granular Co-Ag films in which a random distribution of nanometric cobalt particles in the silver matrix was detected. Compositional analysis discarded the incorporation of third species coming from the electrolyte. In all conditions GMR was detected at room temperature.

- Magnetotransport properties were dependent on the electrodeposition conditions (bath Co(II) concentration, applied potential, deposition time or electrochemical technique). The variation of the film microstructure/nanostructure (grain size and size distribution, density of particles or surface area to volume ratio) was the responsible for the observed differences in the magnetoresistance. Thermal treatment had a highly negative effect on the GMR.

- The numerical analysis of the MR(H) curves allowed quantifying the ferromagnetic (FM) and superparamagnetic (SPM) contributions in the films prepared. A high SPM contribution was observed in all the as-deposited films, contribution which was reduced drastically after the thermal treatment of the samples. The highest SPM contributions always led to the highest GMR values measured.

With regard to the multilayers:

- Co-Ag/Ag multilayers with GMR have been prepared from a perchlorate-based electrolyte. The electrodeposition conditions optimization of both cobalt and silver (Co(II) bath concentration, cobalt deposition current density and silver deposition potential) was crucial to achieve the highest magnetoresistance. GMR values were dependent on the individual layer thickness. The maximum GMR measured was for the samples with the layer structure Co-Ag(3 nm)/Ag(6 nm). The magnetotransport properties analyses and the structural characterization by XRD were in agreement with a granular-type multilayered structure formation.

With regard to the nanowires:

- Cobalt and cobalt-silver nanowires have been successfully prepared into the pores of a polycarbonate template by electrodeposition. Depending on the applied signal (continuous or pulses) either granular or multilayered nanowires were obtained. Both heterogeneous systems showed fcc-Ag and hcp-Co structure. The electrodeposition conditions variation allowed modifying the microstructure/nanostructure (cobalt content or particles size for granular nanowires and individual layer thickness for multilayered ones) which in turn affected the magnetotransport properties.

With regard to the nanoparticles:

- Co-Ag nanoparticles with a core-shell structure have been successfully prepared by the microemulsion method. Nearly monodisperse nanoparticles with sizes in the range 3-5 nm depending on the silver shell thickness were obtained. XPS analyses revealed the protective character of the silver shell against total oxidation of the cobalt nucleus. The prepared nanoparticles showed magnetoresistance. The strategy developed was successful for the GMR measurement.