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Ternary CoPtP electrodeposition process: Structural and magnetic properties of the deposits

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ABSTRACT

Ternary CoPtP electrodeposition process in an acid bath has been studied and CoPtP films have been electrodeposited over silicon/seed-layer. The influence of bath composition, temperature and pH on ternary electrodeposition process, deposits composition, structure and magnetic properties has been studied. Homogeneous and bright ternary deposits have been obtained with magnetic properties from soft magnetic to hard magnetic. A clear enlargement of films coercivity was obtained when platinum percentage in the deposits was around 30–40 wt%. Susceptibility of the CoPtP films has increased after annealing of the samples. Deposits show hexagonal structure with gradual Pt incorporation in the Co crystalline lattice.

1. Introduction

There has recently been a growing interest in the miniaturization of hard magnetic materials and in their integration in micromechanical systems (MEMS) because this fact would enable the efficiency of these devices. The integration of soft magnetic materials with microfabrication processes has indeed been successfully achieved.

Nowadays, the electrodeposition of cobalt alloys films is of particular interest because these films show magnetic properties that are useful in different applications. Some of these films can be incorporated in magnetic recording media and in micro-electromechanical systems (MEMS) such as actuators and sensors where films of permanent magnets are required. Most of the magnetic microactuators developed include electrodeposited films of binary and ternary cobalt alloys as CoNiB, CoNiP, CoNiZnP, CoNiReP, CoNiFe, CoNiMo, CoMo, CoB, CoFeB, and CoFeCr [1–7].

Recently, the possibility of preparing hard magnetic films by electrodeposition is being analysed in order to prepare permanent magnets in the microscale to be used in micro-devices. Hard magnetic properties in fact required anisotropic, often ordered, crystal structures and closely controlled microstructures, down to the deep sub-micron scale. Electroplating is an attractive technique because of the simple experimental setup. It is easy scalable for high mass-production and it allows a fast deposition rate as well as preparing directly patterned samples over silicon-based substrates. Different Co alloys have been prepared by electrodeposition for this purpose [8] and even electrodeposition through lithographically defined masks is sometimes used [9]. Some CoPt and CoPtP alloys seem to be promising candidates due to their good hard magnetic properties [10–16]. Although some authors describe how CoPt films with optimum hard magnetic properties can be prepared by electrodeposition, few studies deal with the electrochemical behaviour of the binary or ternary electrodeposition process [17].

The aim of the present work is to study the electrodeposition process of the CoPtP system in order to control the preparation of ternary films over silicon/seed-layer substrates with modulate magnetic properties. The influence of the deposition bath and the deposition conditions (bath composition, temperature, pH) on the composition, structure and coercivity of the magnetic films were analysed. Some CoPtP deposits with different magnetic properties from soft to hard were obtained. A dependency of the coercivity with the composition of deposits was observed. The annealing effect was also studied.

2. Experimental

Electrochemical study and deposits preparation have been performed in a conventional three-electrode cell with control of the temperature. Solutions contained $CoCl_2$, Na_2PtCl_6 and sodium hypophosphite in boric acid and NH_4Cl, all of analytical grade. Solutions were freshly prepared with water which was first doubly distilled and then treated with a Millipore Milli Q system. The solution pH was adjusted with HCl or NaOH solutions. Solutions were de-aerated by argon bubbling before each experiment and maintained under argon atmosphere during it.

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Electrodeposition has been carried out using a microcomputer-controlled potentiostat/galvanostat Autolab with PGSTAT30 equipment and GPES software. Vitreous carbon rods (Metrohm) and silicon/Ti(1000 Å)/Ni(500 Å) substrates supplied by IMB-CNM.CSIC (Centro Nacional de Microelectrónica) have been used for electrochemical study. Deposits were prepared over the silicon/seed-layer substrates. Vitreous carbon electrode was polished to a mirror finish using alumina of different grades (3.75 and 1.87 μm) and cleaned ultrasonically for 2 min in water. The silicon-based substrates were cleaned with acetone, ethanol and rinsed in water before deposition. The reference electrode was an Ag/AgCl/1 mol dm^{-3} NaCl electrode. All potentials were referred to this electrode. The counter electrode was a platinum spiral.

Voltammetric experiments were carried out at 50 mV s^{-1}, scanning initially from 500 mV towards negative potentials. A single cycle was run in cyclic voltammetric experiments.

Leica Stereoscan S-360 scanning electron microscope was used to analyse deposits composition. Quanta 200 FEI, XTE 325/D8395 scanning electron microscope and AFM Nanoscope Extended Multimode were used for morphology observation.

Structure of deposits were studied by means of a Philips MRD diffractometer with parallel optical geometry using Cu Kα radiation (λ = 1.5418 Å) and a texture goniometer that allows control of the sample rotation about the three axes.

Magnetic properties were characterized by means of a SQUID magnetometer at room temperature.

Roughness (rms) and thickness of the coatings were measured using a white-light interferometer from Zygo Corporation.

3. Results and discussion

3.1. Voltammetric study of the electrodeposition process

The influence of the different parameters in the electrodeposition process was analysed by recording voltammetric curves. Voltammetric study was performed mainly in vitreous carbon electrode because this electrode allows to detect the oxidation processes of the studied systems in a wide potential range without oxidation of the own electrode. Fig. 1 shows the voltammograms of a blank solution B ($NH_4Cl + H_3BO_3 + NaH_2PO_2$) (curve a), B + $CoCl_2$ (curve b) and B + $PtCl_6^{2-}$ (curve c) over vitreous carbon electrode. When Co(II) was present in the solution a cobalt reduction current around −1.0 V was detected during the negative going sweep (curve b) and a ratio between oxidation respect to reduction charge (Q_{ox}/Q_{red}) around 22% was obtained. Some oxidation current was detected due to the oxidation of both molecular hydrogen retained over the electrode and electrodeposited cobalt. In the case of $PtCl_6^{2-}$, platinum reduction current and proton reduction over the platinum was observed [18] from around 0.0 V, previous to the massive hydrogen evolution (curve c). Very low Q_{ox}/Q_{red} value (around 8%) was obtained, as it was expected for platinum deposition.

In the solutions containing both $CoCl_2$ and Na_2PtCl_6, the current related to platinum reduction was slightly decreased whereas the onset of simultaneous cobalt reduction was advanced, due to an easier nucleation of cobalt over previous deposited platinum (Fig. 2). Three oxidation peaks were detected in the anodic scan: One detected around −0.35 V that disappeared when the anodic scan was recorded in stirring conditions, which revealed that this peak corresponded to the oxidation of molecular hydrogen retained over the electrode [18–20]. The second oxidation peak, around −100 mV, was assigned to some cobalt or alloy oxidation whereas oxidation current around 0.8 V was due to platinum oxides formation [21,22]. Intermediate Q_{ox}/Q_{red} values between those corresponding to Co–P and Pt–P systems in voltammetric experiments with similar cathodic limits were obtained. No difference in the voltammetric responses was observed between pH 4.5 and pH 5.5. Similar voltammetric curves were recorded at different bath temperatures, although by increasing the temperature the deposition process was advanced and the reduction current increased. Q_{ox}/Q_{red} values decreased slightly with an increase in the temperature or a decrease of the solution pH.

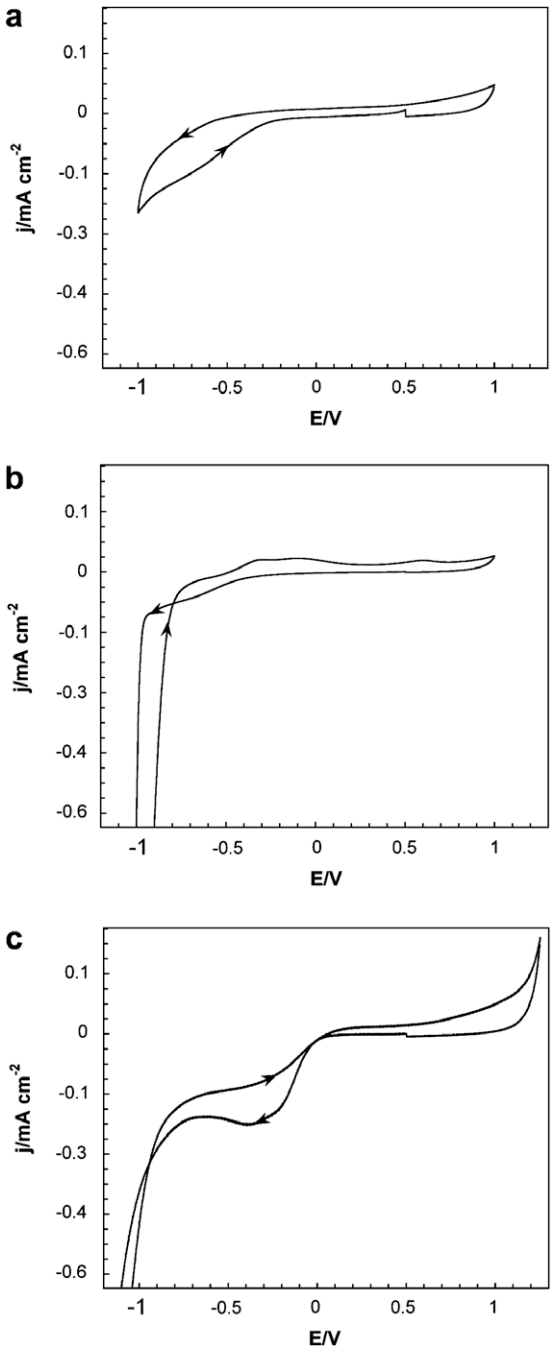

Fig. 1. Cyclic voltammograms of (a) blank solution B (1 M NH_4Cl + 30 g/l H_3BO_3 + 5 × 10^{-2} M NaH_2PO_2), (b) B + 2.5 × 10^{-3} M $CoCl_2$ solution, and (c) B + 1.01 × 10^{-3} M $PtCl_6^{2-}$ solution. T = 25 °C, pH 4.5. Quiescent conditions. Vitreous carbon electrode.

When Si/seed-layer substrate was used, a significant reduction current was detected from −0.7 V due to simultaneous alloy deposition and hydrogen evolution (Fig. 3). Oxidation scan showed the two first peaks previously detected. Anodic limit was shortened in the voltammetric experiments performed with Silicon/Ti/Ni substrates due to the seed-layer oxidation.