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The Influence of Ammonia on the Electroless Deposition of CoB Alloys from Alkaline Citrate containing Baths

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ABSTRACT

When adjusting the pH of deposition baths, ammonia (NH_3) is often used instead of sodium hydroxide (NaOH), but its effects on the chemical and/or electrochemical processes are not usually considered. Here the influence of NH_3 on the deposition rate, composition and magnetic properties of amorphous cobalt-boron (CoB) alloys deposited from alkaline plating baths containing citrate is discussed. We have observed that when the pH of the solution was adjusted with NH_3, CoB films were deposited at higher rates and the B content decreased with increasing pH. Opposite trends were observed when NaOH was used to adjust the bath pH. These observations were discussed in terms of the complex species distribution in solution and of the buffering characteristics of NH_3. The reducing agent, dimethylaminoborane, has its electrooxidation also affected by the presence of NH_3 in solution. Amorphous, soft CoB magnetic films with coercivity values varying from 40 Oe to 80 Oe, inversely dependent on the B content of the film, were obtained.

1. Introduction

As it is well known, electroless deposition of metallic films has many applications as it shows advantages over electrodeposition such as low power consumption and the possibility of deposition on non-conducting surfaces. For example, electroless deposition has long since been the standard deposition method for anticorrosive nickel based alloy coatings [1]. In Electronics, this process has been used to deposit metallic contacts, anti-diffusive layers, as well as magnetic materials for recording media, like nonmagnetic NiP layers and high coercivity CoP and CoNiP magnetic alloys for data storage media [2]. For such applications, both electric and magnetic properties are dependent on the phosphorus content of the films [1–4].

Besides phosphorus, alloying magnetic metals with low quantities of other non-metallic elements is also an effective way of controlling microstructural and magnetic properties of the resulting alloys [2]. Generally, such impurities originate low coercivity alloys just after deposition because of the formation of nanocrystalline, amorphous material. Particularly, boron is known by its capacity to induce the growth of smaller grains (amorphization) of metallic alloys [5]. In fact, very low coercivity cobalt based alloys have been obtained from baths containing various additives along with the application of a strong magnetic field during deposition [6,7].

It is customary that electroless plating baths are commonly composed by a salt of the metal to be deposited, the reducing agent and a complexing agent (or a mixture of) to prevent uncontrolled reduction of the metal and to provide a buffer system. Many different additives such as acetate, lactate, citrate, succinate or glycolate were already tested for Co deposition [8], and ammonium salts are normally used as alkaline buffers [9]. Dimethylaminoborane (DMAB) is the most used reducing agent as it can be employed in both alkaline and acidic baths [8].

It is expected that some of these usual bath components induce modifications in both composition and microstructure of the deposits, depending on their nature and concentration. Particularly, it was already shown that the presence of ammonia can accelerate the deposition rate of Cu [10]. Also, ammonia in the solution has the property to modify the microstructure and therefore the magnetic properties of CoNiP alloys [11]. These observations were rationalized either in terms of modifications of the copper complexes distribution in the bath because of the addition of ammonia [10] or in terms of ammonia adsorption on the growing surface of the metallic film [11]. Considering the fact that ammonia was shown to modify microstructure and even accelerate metal deposition, a better understanding of its role in electroless deposition processes is desirable. Therefore, we have decided to study the influence of ammonia on the plating rate, composition and magnetic properties of amorphous CoB deposited

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from neutral and alkaline cobalt-citrate baths. We have observed that ammonia plays different roles in the process, not only by buffering the region next to the surface of the growing film, but by forming mixed complexes with Co^{2+} ions as well. An explanation about the accelerating effect of ammonia on the deposition of CoB and its capacity in determining the deposit composition is discussed.

2. Experimental

Electroless depositions of CoB thin films were carried out on copper foils (4 cm^2) which were activated with an electrochemically deposited Ni thin layer. The films were grown for 30 minutes at 65°C from alkaline baths containing 0.1 mol L^{-1} $CoSO_4$ and 0.15 mol L^{-1} of sodium citrate $Na_3C_3H_5O(COO)_3$ (Na_3Cit) as the complexing agent. The concentration of the reducing agent, dimethylaminoborane (DMAB), was 0.02 mol L^{-1}. To determine film growth rates, films were deposited for different periods of time. Bath pH was adjusted at different values ranging from 6.0 to 12.5 with either ammonia (NH_3) or sodium hydroxide (NaOH) solutions, depending on the experiment. To minimize the evaporation of NH_3, the experiments were performed in a home-made electrochemical cell with a proper Teflon cap, so a small amount of NH_3 would escape from the cell. In both cases, the pH was measured before and after plating on some samples and it was observed rather small changes. In the NH_3 baths, the pH typically decreased 0.2 to 0.3 units from the initial values, which means that the solutions were kept buffered over the deposition time.

The composition of the films was determined by dissolving the deposits in a 1% HNO_3 solution and subsequent analysis by inductively coupled plasma atomic emission spectroscopy (ICP). The thickness of the CoB deposits was estimated from the amount of deposited cobalt and assuming the density of pure cobalt and the magnetic properties were measured using a VSM EG&G PAR model 4500 with magnetic field sweeping between -15 and +15 kOe.

To study the effect of NH_3 on the DMBA oxidation, linear potential sweep experiments were run at a sweep rate of 50 mV s^{-1}. These experiments were intended to be carried out in conditions as close as possible to those of the electroless plating experiments. However, to avoid additional DMAB oxidation by eventual Co nanoparticles in the bulk solution, rather than in the anode, we have used Na_2SO_4 was instead of $CoSO_4$, keeping the ionic strength constant. The electrolyte was then 0.15 mol L^{-1} Na_3Cit + 0.2 mol L^{-1} DMAB + 0.1 mol L^{-1} Na_2SO_4, at different pH. The pH was adjusted with $NH_{3(aq)}$ or $NaOH_{(aq)}$. The working electrode was a CoB film grown on a copper foil (geometric area 1.1 cm^2). The counter electrode was a Pt wire and a Ag|AgCl electrode was used as reference. The potentials are referred to this electrode. The electrochemical experiments were performed using an EG&G PAR model 273 A potentiostat/galvanostat. The temperature was kept at 25°C.

Interfacial pH was measured using a flat-bottomed pH electrode (Thermo Ross, Model Orion 8135BNUWP) positioned close to a Co electrode, according to a setup described elsewhere [12]. The Co electrode was prepared by electrodepositing a Co layer on a Pt mesh, so that the conditions met during the CoB electroless deposition would be better simulated. Although electroless deposition was carried out at 65°C, to avoid damage of the glass membrane because of the high ionic strength and relatively high working temperature, the interfacial pH measurements were run at 25°C. In these experimental conditions, the variation of the interfacial pH was recorded at 1 minute intervals for 15 minutes.

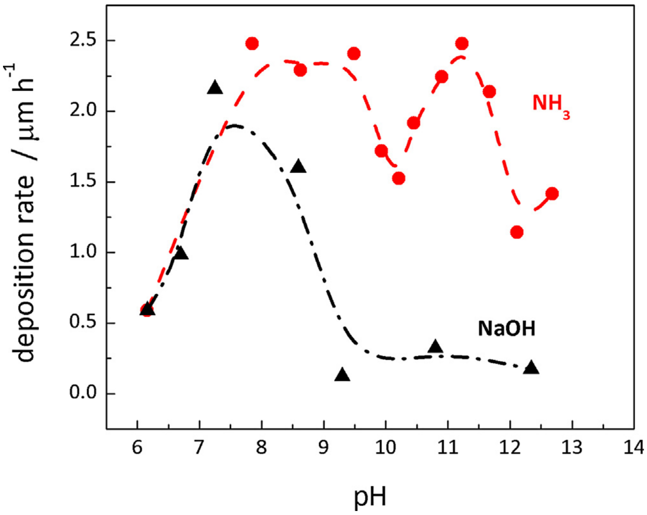

Fig. 1. Effect of the pH of the plating bath on the deposition rate of CoB films when the pH is adjusted with NaOH or NH_3. Bath composition: $[CoSO_4]$ = 0.1 mol L^{-1}; $[Na_3Cit]$ = 0.15 mol L^{-1}; [DMAB] = 0.02 mol L–^{1}; T = 65°C.

3. Results and discussion

CoB films were obtained by electroless deposition using solutions containing Co^{2+} and citrate (Cit^{3-}) with a metal:additive molar ratio of 1:1.5, at different pH (from 6 to 12.5). To investigate the effect of ammonia (NH_3) on the properties of the films, two different sets of baths were studied: in one, the pH was adjusted with NaOH; in the other, with NH_3.

Fig. 1 shows the effect of the pH of the plating bath on the deposition rate of CoB films, for both sets of solutions. When the pH is adjusted using NaOH, the deposition rate is low at pH 6 (0.5 µm h^{-1}), reaches a maximum at pH around 7.5 (2.2 µm h^{-1}), and then decreases to around 0.2 µm h^{-1} for pH > 9. When NH_3 is used to adjust the pH of the solutions, at pH around 6 the deposition rate is also low (0.5 µm h^{-1}), then it reaches a maximum of 2.4 µm h^{-1} at pH just below 8, approximately the same maximum value as when NaOH is employed. Therefore, when using quasi neutral baths, the deposition rate is not affected by the presence of NH_3. However, differently from when NaOH is used, the deposition rate stays high for a wide range of pH (from 8 to 11), with a decrease at pH around 10, though. For pH > 11, deposition is inhibited and its rate decreases, although it is still higher than when NaOH is used at these pH. From these experiments we see that, in the absence or the presence of NH_3, deposition rate tends to increase with increasing pH up to pH 9.

It has been accepted that electroless depositions using dialkylamine borates as reducing agent occur faster at higher pH [13,14]. Ohno [14] in his studies varied the baths pH from 7 to 9.5; and our results confirm his findings in the sense that within that range of pH indeed deposition rate increases with increasing pH. Nevertheless, we have also shown that for pH > 9 in fact there is a decrease in the deposition rate when using a common-used complexing agent, the citrate ion. However, the presence of NH_3 in the bath prevents this decrease for higher pH.

The accelerating effect of Co electroless deposition was formerly observed by Alberts et al. [9]. Interestingly, after their conclusions, they made a final remark by saying that “New or modified techniques will have to be used to study the rate and magnetic variations caused by NH_3 and to improve the understanding of the deposition processes”. To explain the effect that NH_3 has on rate of the electroless deposition process, the complex species present in solution must be taken into consideration. The distribution of complex species in solution depends on the pH and