

Effect of Alkali Reagents on the Crystal Structure of Chemically Deposited CoP Films

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Abstract—The effect alkali reagents have on the crystal structure of CoP films prepared via chemical deposition is investigated. It is shown that the use of sodium hydrogen carbonate and ammonium hydroxide in low concentrations leads to growth of the hexagonal phase in the films. As the concentration of alkali reagents is increased, the formation of a cubic or amorphous phase is observed.

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INTRODUCTION

Fabricating thin magnetic films with specified properties is one of the key problems of engineering physics, since they find wide application in electronic devices, including high-sensitivity sensors, memory cells, and magnetic recording and readout heads. Thin magnetic films have a high potential for application in spintronic elements, based on the possibility of varying film resistivity over a wide range by changing the magnetic state.

In terms of manufacturability, special attention has been given to the chemical deposition of films without electric current, based on chemical reduction of metals from solutions. The chemical fabrication of CoP alloy-based magnetic films, first performed by Brenner in [1], is now widely used [2]. This technique is relatively simple and economical. In addition, it allows films to be deposited onto both metal and dielectric substrates. Another attractive feature of chemical deposition is that it allows sandwich structures with nanometer layers to be formed [3].

The aim of this work was to experimentally investigate the effect alkali reagents have on the crystal structure of CoP films prepared in different technological regimes, i.e., without reagents in solution and with both ammonia and sodium hydrogen carbonate in different concentrations.

EXPERIMENTAL

The samples for our investigation were fabricated via chemical reduction, using standard substrate pretreatment procedures. The CoP magnetic layers were deposited from working solutions of two types that included $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (10 g L^{-1}), $\text{Na}(\text{H}_2\text{PO}_2)$ (7.5 g L^{-1}), and

$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ (17.5 g L^{-1}) with different alkali reagents, 25% $\text{NH}_3 \cdot \text{H}_2\text{O}$ or NaHCO_3 . In the solution of the first type, the sodium hydrogen carbonate (NaHCO_3) concentration was varied from 1 to 10 g L^{-1} ; in the solution of the second type, it was constant and totaled 5 g L^{-1} . The concentration of 25% ammonium hydroxide changed from 0.5 to 3.3 mL L^{-1} .

Coercivity H_c was determined through the meridional Kerr effect. X-ray diffraction (XRD) analysis was performed on a DRON-3 X-ray diffractometer using Cu radiation ($\lambda = 1.5418 \text{ \AA}$).

The coercivity of the investigated films depended nonmonotonically on the ammonium hydroxide (Fig. 1a) and sodium hydrogen carbonate concentrations (Fig. 1b). It can be seen that the dependence first rises and then drops sharply.

The variation in coercivity is explained by the change in the crystal structure of the films. According to the XRD data, when fabricating films from the solution of the first type, we observe the growth of crystals with an imperfect structure similar to hexagonal at low (up to $1\text{--}1.5 \text{ g L}^{-1}$) sodium hydrogen carbonate concentrations (Fig. 2a). As the NaHCO_3 concentration is increased, the quality of the crystal structure improves, as is indicated by the emergence of pure hexagonal Co peaks in the diffraction pattern (Fig. 2b). When the NaHCO_3 concentration in the working solution is raised to more than 10 g L^{-1} , the crystal lattice transforms and peaks corresponding to the cobalt cubic phase emerge (Fig. 2c).

The initial composition of the second type of solutions yielded samples with a purely hexagonal structure that remained invariable upon adding ammonia to a concentration of 1.5 mL L^{-1} . When the ammonia

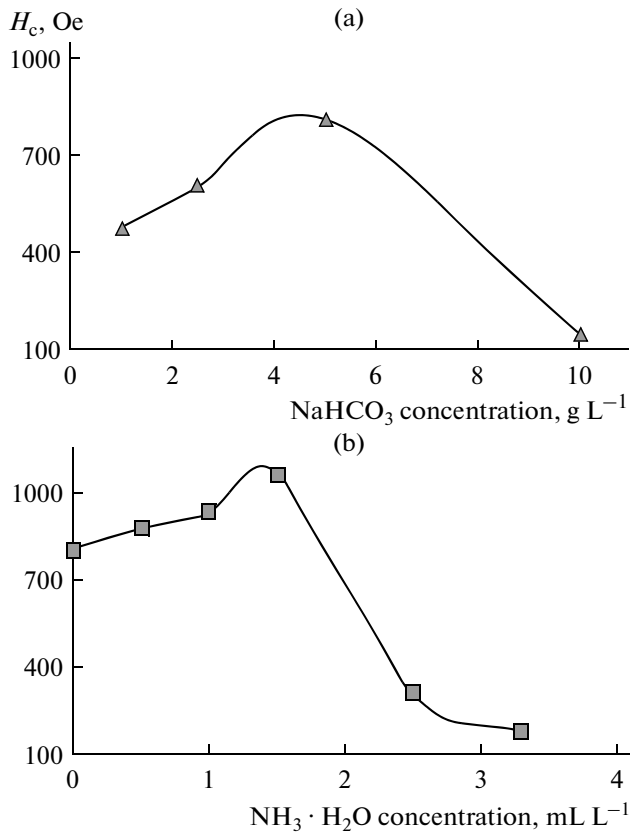


Fig. 1. Coercivity of the CoP films vs. the alkali reagent concentration for (a) sodium hydrogen carbonate and (b) ammonium hydroxide.

concentration was raised to 3.3 mL L^{-1} , the structure amorphized and the amount of the crystal phase was reduced.

RESULTS AND DISCUSSION

The variation in the cobalt crystal structure in the samples of the first series is easily explained: At a low (1 g L^{-1}) concentration of NaHCO_3 , the pH value of the deposition solution differed slightly from the neutral value of $\text{pH} \approx 7.3$.

We assume that under these conditions, the solution contains a considerable number of free electrons with excess energy that can reduce divalent cobalt ions Co^{2+} to metal cobalt [4] with the formation of an imperfect crystal lattice with somewhat increased parameters. When the NaHCO_3 concentration is increased, the pH value grows, the number and energy of free electrons fall, the film growth rate drops, and the classical hexagonal cobalt lattice with the regular structure forms ($\text{pH} \approx 8$). As we approach the critical NaHCO_3 concentration corresponding to $\text{pH} \approx 8.4$, however, the contribution from the hexagonal phase is reduced and cubic cobalt emerges, leading to a sharp drop in coercivity. It is assumed that depending on the

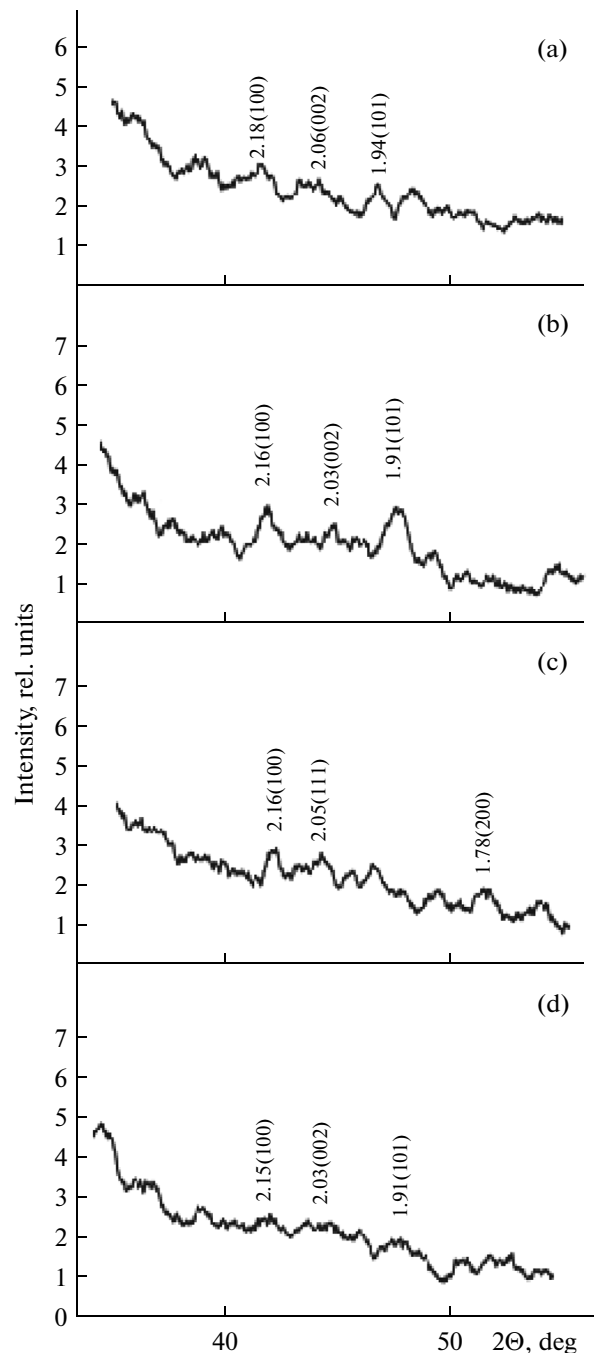


Fig. 2. X-ray diffraction patterns of the samples with (a) imperfect and (b) perfect hexagonal structure; (c) a blend of hexagonal and cubic phase; and (d) amorphous structure.

pH value, the crystal lattice whose bonding energy best corresponds to the maximum energy of the free electrons contained in the solution forms.

Another mechanism probably goes to work when the ammonium hydroxide concentration is varied. Depending on the concentration, NH_3 molecules form complexes $[\text{Co}(\text{NH}_3)_{1-6}]^{2+}$ with divalent cobalt atoms and, depending on the number of ligands (NH_3

molecules forming complexes with cobalt atoms), these complexes have different strengths that are expressed through instability constant pK_H . The lowest instability constant ($pK_H = 1.99$) (i.e., the highest strength for divalent cobalt) corresponds to $[\text{Co}(\text{NH}_3)]^{2+}$; the highest ($pK_H = 5.13$), to $[\text{Co}(\text{NH}_3)_5]^{2+}$. With an increase in the concentration of ammonia in the deposition solution, the pH value rises and ammonia complexes with high numbers of ligands (and thus lower stability) form. This is the most likely cause for the occurrence of the amorphous phase.

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