The Nucleus ***53****, No. 4 (2016) 260-263*

www.thenucleuspak.org.pk

The Nucleus

ISSN 0029-5698 (Print)

ISSN 2306-6539 (Online)

Effect of Deposition Temperature and Electrolytic Cell Concentration on Phase Transformation at Nanoscale

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ARTICLE INFO

Article history:

Received :28 October, 2016

Revised : 16 December, 2016

Accepted :22 December, 2016

Keywords:

Nanostructure;
Electrodeposition;
Hcp and Fcc cobalt;
Crystal growth

ABSTRACT

The coexistence of both hcp and fcc phases for Co nanowires was studied in this work. Both hcp and fcc Co nanowires with diameter of ~ 50nm were successfully prepared by adjusting the deposition parameters. The systematic results show the effect of electrolytic cell with different cobalt sulfate concentration and different deposition temperatures with same pH and potential for the formation of (fcc and hcp) Co nanowires. The fabricated nanowires were characterized by X-ray diffraction, and the morphology of the electrodeposited nanowires was explored by scanning electron microscope.

1. Introduction

Indeed, the growth mechanism and the structure of Co nanowires need to be dignified. Several groups [1-3] had found the co-existence of changeable extents of the two hcp (hexagonal close packing) and fcc (face-centered cubic) cobalt (Co) phases. The metallic cobalt has hcp phase at temperatures below 420°C and an fcc phase at temperatures above 420°C. On the other hand, fcc Co, the high temperature phase, can be shaped in electrochemical deposition at ambient temperature [4-6]. The full understanding of the growth mechanism sponsoring in the materialization of Co films by electrochemical deposition is still not there. During electrochemical deposition process, by regulating deposition parameters such as the pH value of bath solution[7], pulse electro deposition [8-10], applied potential [11], current density[12], and deposition temperatures [13], the structure of electrodeposited Co nanowire was adjusted in view of that. But only a few reports are found on the dependence of crystal orientation of cobalt nanowires with bath temperature [14], and electrolyte concentration [1].

In this paper, we first provide the systematic results about the electrolyte concentrations and different deposition temperatures and then made an effort to explain that why the phase of Co nanowires shift from fcc to hcp phase by using different electrolyte concentrations and providing different deposition temperatures.

2. Experimental Detail

The porous Anodic Alumina Oxide (AAO) templates were made by a two-step anodization procedure [15-19]. The steps involve are as follows;

a. Pretreatment of Al foil
b. First anodization
c. Etching of the aluminum layer mixture of phosphoric and chromic acid
d. Second anodization
e. Removing aluminum from back side
f. Dissolve into acidic solution
g. Sputtering of gold (Au) on back side of template

The templates obtained by above procedure were hexagonal and well arranged. Direct current electrode position was escorted by using two-electrode cell having different concentration of cobalt sulfate solutions and by providing different deposition temperatures. Electrolytes used in this study were mixture of $CoSO_4 \cdot 7H_2O$ having three different concentrations (0.71M, 0.53M, and 0.35M) and H_3BO_3(0.68M) in aqueous solutions. The pH of the electrolyte bath was set to 2.5 by using 1M H_2SO_4solution. The depositions for Co nanowires were carried out at deposition potential of -3V under different temperatures (5^oC-60^oC). The area of the electrode containing AAO template was $0.608cm^2$ ($=0.25\pi(0.88cm)^2$) and the area of the counter electrode was $14.7cm^2$ ($=4.2cm \times 3.5cm$).

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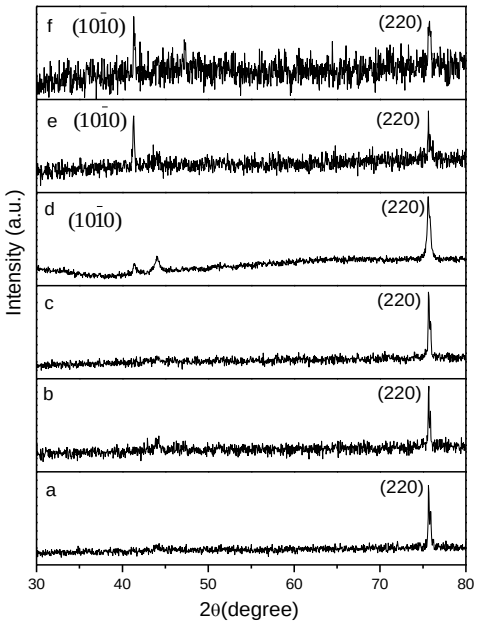

Fig. 1: XRD pattern for electrochemically deposited Co nanowires in the pores of AAO template at different temperatures having concentration of 0.71M, a) 5°C b) 15°C, c) 25°C d) 45°C, and e) 60°C

The metal nanowires were characterized by XRD named as (XRD, Y-2000) with CuKα radiations (λ 0.154178 nm). The images of deposited metal nanowires were obtained by SEM named as (SEM, JEOL JSM-6700F). For XRD measurements the film of Au was mechanically polished away. For SEM interpretations, the AAO templates were partly dissolved in NaOH solution (5 wt%) , and then sensibly washed with deionized water for more than a few times.

3. Results and Discussion

Fig. 1 shows the XRD patterns of Co nanowires deposited in the solution with concentration of 0.71M at pH of 2.5 and at six different temperatures (5°C, 15°C, 25°C, 35°C, 45°C, and 60°C) under deposition potential of -3V. The XRD patterns were collected from the top side of nanowires. The coexistence of both hcp and fcc cobalt phases were seen. It is bring into being that the structure of prepared Co nanowires depends on the deposition conditions. When electrodepostion is implemented in a same electrolytic cell but at different temperatures, the phase changed from fcc (at low temperature) to hcp (at high temperature).Fig. 1 (a, b and c) represent that at low temperatures 5°C, 15°C, and 25°C, the well-known fcc structure of Co has been deposited, respectively, which is stable at temperatures above 422°C [7], while increasing the temperature to35°C-60°C both hcp and fcc structures exist there(see Fig. 1 (d and e)). From the figure one can also observe at 25°C the phase for deposited Co nanowires is fcc and result agreed with the result of Huang et al and Wang et al[11, 20].

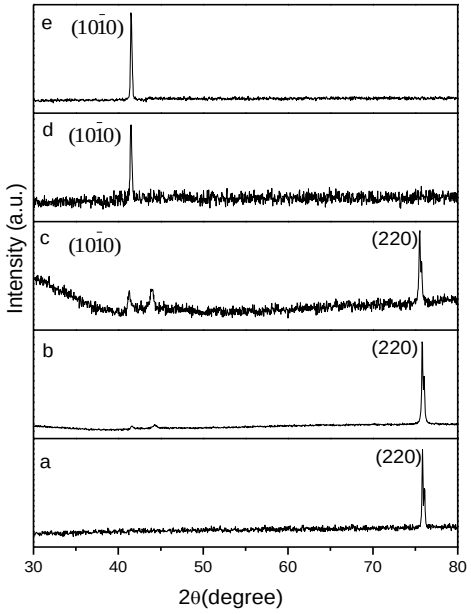

Fig. 2: XRD pattern for electrochemically deposited Co nanowires in the pores of AAO template at different temperatures having concentration of 0.53M, a) 15°C b) 25°C, c) 35°C d) 45°C, and e) 60°C

Fig. 2 illustrates the XRD patterns of Co nanowires which were deposited in electrolytic cell with solution with concentration of 0.53M (cobalt sulfate)and pH of 2.5.The deposition is performed at five different temperatures (15°C, 25°C, 35°C, 45°C, and 60°C) at deposition potential of -3V. From the Fig. 2 (a-e), the fcc structure is seen at low temperature of 15°C and 25°C, while the universal hcp $(10\bar{1}0)$ structure for the electrodeposited Co is obtained at temperatures of 45°C, and 60°C, respectively. At temperature of 35°C the coexistence of hcp $(10\bar{1}0)$ and fcc(220) diffraction peaks present that phase is being changed (see Fig. 2 (b)).

To find out the concentration effect with change in temperature Co nanowires were also deposited in a cell containing 0.35M concentration of cobalt sulfate at pH of 2.5. XRD results for this cell at four different temperatures (25°C, 35°C, 45°C, and 60°C) are shown in Fig. 3. From the Fig. 3 (a) the diffraction peaks at $2\theta =$ 41.5, and 75.6 degrees confirm the existence of hcp and fcc structure at temperature 25°C. At temperature 35°C there is a little increase in the intensity of $(10\bar{1}0)$ showing that a number of nanowires grow along $[10\bar{1}0]$ direction and rest of them along [220]direction. It can be seen from the Fig. 3 (c, and d) that further increases in temperature give the pure hcp phase. There is only a single peak along $(10\bar{1}0)$ plane, which indicates hcp structure and well-preferred growth of Co nanowires along $[10\bar{1}0]$direction at temperatures of 45°C, and 60°C.

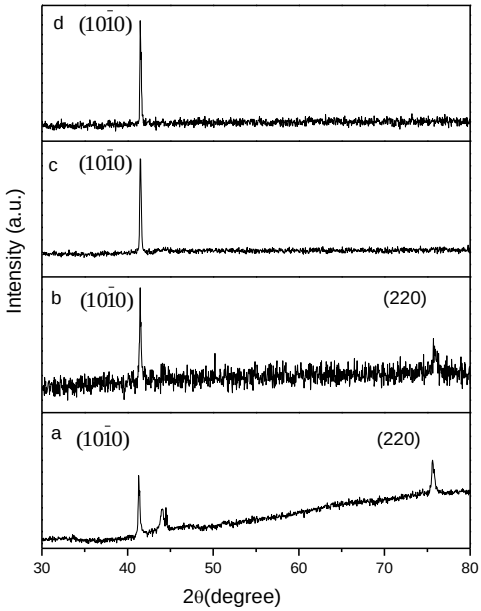

Fig. 3: XRD pattern for electrochemically deposited Co nanowires in the pores of AAO template at different temperatures having concentration of 0.35M, a) 25°C, b) 35°C, c) 45°C, and d) 60°C

In order to recognize the influence of solution concentration and the deposition temperature, the X-ray diffraction results are gathered in Table 1. From the table we can see three points. Firstly, the structure of the deposited Co nanowires is fcc at low temperature (<25°C) for all concentrations. Secondly, for all concentrations high temperatures (> 25°C) favor the growth in hcp phase. Moreover, higher temperature favors hcp phase while higher concentration favors fcc phase.

Table 1: XRD results for all concentrations and temperatures presenting the phase formation

Concentrations	Temperatures					
	5°C	15°C	25°C	35°C	45°C	60°C
0.71M	fcc	fcc	fcc	hcp and fcc	hcp and fcc	hcp and fcc
0.53M	-	fcc	fcc	hcp and fcc	hcp	hcp
0.35M	-	-	hcp and fcc	hcp and fcc	hcp	hcp

After the deposition of nanowires in pores, AAO templates were somewhat dissolved in 5 wt.% NaOH solution, and then cautiously cleaned with deionized water for more than a few times. Fig. 4 shows SEM images of Co nanowires detached from the AAO templates. Fig. 4 (a, b, and b) contain the SEM pictures for the Co nanowires deposited at 45°C in a electrolytic cell having concentration of 0.71M, at 25°C in a cell with concentration of 0.53M, and at 35°C with 0.35M concentration of the cell, respectively. The diameter of the Co nanowires (~50nm) is similar as that of the nanopores

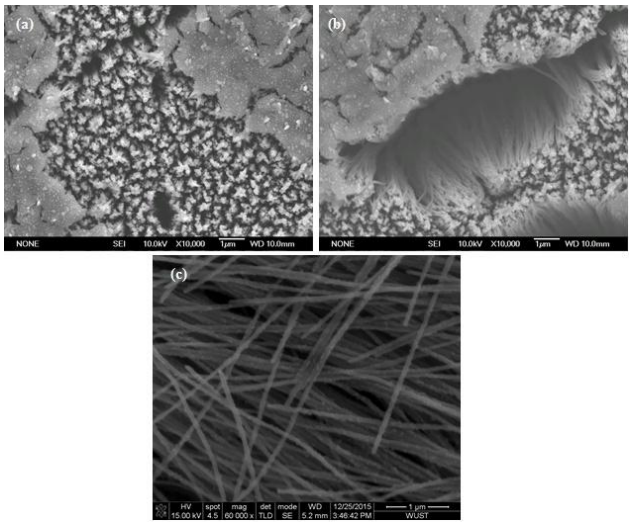

Fig. 4: SEM images of cobalt nanowires deposited at 45°C with concentration 0.71M(a), at 25°Cwith concentration 0.53M(b), and at 35°Cwith concentration 0.35M (c)

of homemade AAO template (~50nm), signifying that the tubular pores of the template were entirely packed with Co atoms in the course of electrodeposition.

4. Conclusion

The pure fcc phase is observed at low temperatures for all the concentrations. For 0.53M concentration at 25°C there exist both hcp and fcc phase, whereas for the other two concentrations 0.71M and 0.35M it took place at 45°C and 35°C, respectively. At lower concentrations (0.53M and 0.35M) pure hcp structure was found at >25°C. However, the co-occurrence of hcp and fcc phases were observed for high concentration at higher temperatures. All observed results are summarized in Table 1.

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