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Effect of Film Thickness on the Coercivity of Electrodeposited Cobalt Film in Mesoporous and Macroporous Templates

A.A. AL-OWAIS[1] and I.S. EL-HALLAG[2,*]

[1]Chemistry Department, College of Science, King Saud University, Riyadh 12372, Saudi Arabia
[2]Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

*Corresponding author: E-mail: i.elhallag@yahoo.com

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In this work, the effect of film thickness on coercivity of electrodeposited nanostructured cobalt film has been investigated. The technique described here, provided highly ordered magnetic nano-structures of the length of 9 nm, with 3 D architecture, obtained *via* pluronic lyotropic liquid crystal template as mesoporous template. Polystyrene spheres with pore sizes in the range of 200-1000 nm were used as macroporous templates. Variation of the film thickness of the electrodeposited film allowed us to fabricate nanomaterials with predetermined magnetic properties, including the dependence of the coercive field on the film thickness.

Keywords: Magnetic properties, Coercive field, Film thickness, Polystyrene sphere.

INTRODUCTION

For a number of different electrode surfaces, the electrodepostion of cobalt has been investigated and reported [1-7]. It was reported that electrochemical deposition of magnetic metals *via* templates, using liquid crystalline and self-assembled polystyrene spheres, produced structures with 3-D architecture [8-10]. For the development of magnetic media with high recording density efficient techniques are required to prepare patterned magnetic structures. Combination of sub-micron lithography with thin film growth techniques is a standard for this task.

Ferromagnetic materials deposition has received considerable attention motivated by potential applications, which include biotechnology or as storage media of much higher density than 10^8 bit cm^{-2} or magnetic sensors for the automobile industry [11]. Cobalt ($4s^2$ $3d^7$) is such ferromagnetic material which provides excellent properties in electrode electrocatalysis, batteries and corrosion protection. It is also an important material for magnetic thin films. The mechanism of cobalt deposition has been found to be strongly dependent on the nature of cobalt complex in solution, which in turn depends on pH of the solution [12].

The demonstration of electrodeposition of cobalt in electrolyte solution of pH 4.6 was combined of three different parallel nucleation processes: 2D progressive nucleation, 2D instantaneous nucleation and 3D progressive nucleation [13].

One which used as versatile nanoscale molds for the formation of highly ordered mesoporous materials, such as inorganic oxides and metals is the lyotropic liquid crystalline phases of polyethylene surfactants [14,15]. It was found that the surfactant molecules aggregate into three-dimensional supramolecular assemblies in the presence of water, which at surfactant concentrations higher than 30 wt. %, spontaneously organize to form a lyotropic liquid-crystalline phases. The orientationally ordered disposition and the spatially periodic of the surfactant aggregates provides a mold in which the material is formed [15,16].

In this work, the effect of film thickness of the electrodeposited cobalt on the magnetic properties of mesoporous cobalt films was described and discussed. The dependence of coercivity and porosity of the cobalt films on the thickness of electrodeposited films was investigated. The effect of pore size of polystyrene sphere and film thickness of polystyrene sphere on coercive field was demonstrated.

EXPERIMENTAL

All chemicals used were extra purified and used as supplied. Cobalt acetate ($Co(OAc)_2 \cdot 4H_2O$) with percentage 99.5 % and potassium acetate (KAc) with percentage 99 % were obtained from Fluka. Pluronic 84 was purchased from Sigma-Aldrich Co. The polystyrene latex spheres monodisperse with diameters of 200, 500, 750 and 1000 nm were supplied from Alfa Asear as a 2.5 wt. % solution in water, *p*-xylene (99 %) and boric acid were obtained from Aldrich. Water reagent grade (18 MΩ cm) was used as solvent for preparation of solutions and lyotropic liquid crystalline template (LLC).

The plating mixtures were prepared according to the method established in literatures [9,16]. The H_1 phase of the mixture is stable at room temperature for more than a month. Electrodeposition process was carried out at room temperature. The surfactant was removed after deposition by rinsing the electrodes with triple distilled water. The working gold electrode was cleaned by sonication in propanol (BDH) for 1 h followed by rinsing with triple distilled water.

The porosity (P) of the electrodeposited film was determined from the following equation:

$$\text{Porosity (P)} = 100\ (2\pi/\sqrt{3})(r_p/D_{int})^2 \qquad (1)$$

where r_p is the pore radius and D_{int} is the inter-pore distance [17].

Morphological surface parameters for the different samples, pore radius and interpore distance, as well as film thickness (t_f) were determined from SEM and TEM micrographs analysis.

A conventional three-electrode cell (15 mL volume capacity) and EG & G 283 potentiostat were used to carry out the electrochemical experiments. The working electrode was gold disk electrode with diameter 1mm, while the structure of nanomaterials cobalt films were characterized using flat sheet gold electrode with surface area 1 cm^2. 1 cm^2 platinum gauze and saturated calomel electrode (SCE) were used as a counter electrode and as a reference electrode respecively. Disk electrode with 1 mm diameter was polished with a polishing paper (grade 1200 grit/sheet) followed by alumina (Buehler) of two grades: 0.3 and 1.0 μm, then rinsed with very pure water.

The morphology and the measurements of film thickness were done using scanning electron microscope, SEM, (JEOL 6400). The nanostructure was characterized using JEOL 2000 FX transmission electron microscope, TEM, operating at an accelerating voltage of 200 kV. Cryogenic S600 SQUID susceptometer was used for measurement of magnetic hysteresis loops.

RESULTS AND DISCUSSION

Fig. 1a shows a scanning electron microscope (SEM) image of the nanostructured cobalt film revealing a hexagonal order of macroporous film on a gold substrate covered with templates made of 630 ± 10 nm diameter polystyrene spheres. The potential of electrochemical deposition was performed at -0.95 V *vs*. SCE. The SEM image shows that the spherical voids left in the gold films are arranged in a well ordered single domain, close packed structure. Fig. 1b shows a transmission electron microscope (TEM) image of the mesostructured cobalt film, which indicates the hexagonal arrangement of uniform pores running through the metal layer. From the TEM structure, the pore to pore center was determined and found to be 9 nm [18,19].

It was established that the template electrodeposition method has a significant advantage in comparison with standard lithographic techniques which allows us to create patterns in the direction transverse to the film plane. Cross-sectional SEM of electrodeposited cobalt film, which was used in determining the thickness of the electrodeposited cobalt film is shown in Fig. 1c.

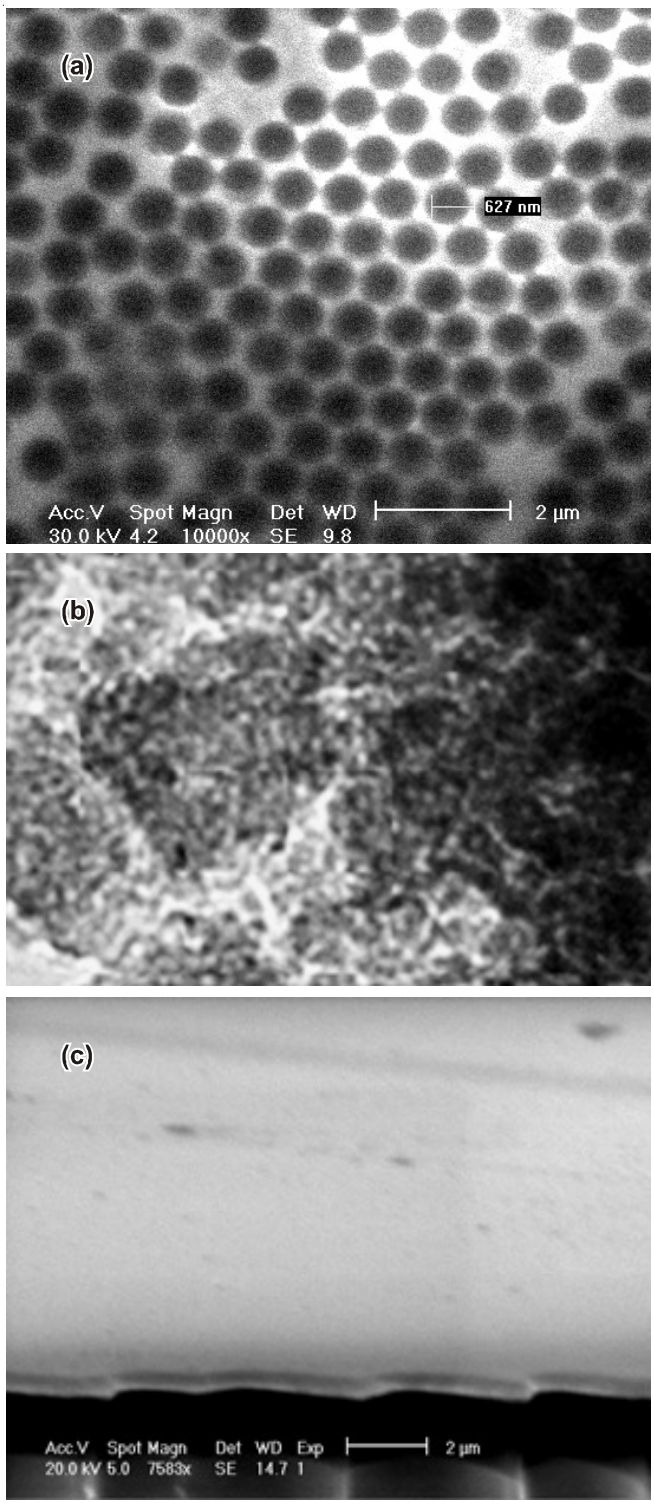

Fig. 1. SEM image of macroporous H_1-e, cobalt film electrodeposited from aqueous solution (a), TEM image of the H1-e, cobalt of mesoporous films deposited from pluronic lyotropic liquid crystal (b) and SEM cross-section image of H_1-e coblat (c)

Magnetic properties of cobalt films obtained using mesoporous template: The magnetic characteristics of 91 and 152 nm cobalt films on gold substrate are shown in Fig. 2. The coercivity of 91 nm cobalt film was found to be 223 Oe whereas the coercivity of 152 nm cobalt film is increased to 415 Oe. The hystresis loop shown in Fig. 2 indicates that as the film thickness increases the squareness is increases. This

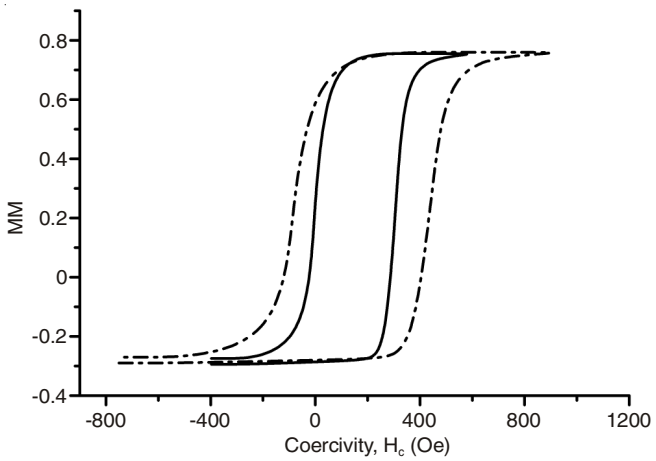

Fig. 2. Magnetization characteristics of electrodeposited cobalt film on Au electrodes, with the thicknesses of 152 nm (dashed line) and 91 nm (solid line)

means that the process of magnetization of thin films of cobalt on gold substrate is greatly affected by variation of the thickness film. Fig. 3a shows the dependence of coercivity on the thickness of cobalt films on gold substrate. As indicated, the coercivity increases with increasing the film thickness up to 207 nm. With further increase of the film thickness up to 311 nm, the coercivity decreases then increases up to 524 nm thickness. Coercivity reaches its higher value of 820 Oe, which is about approximately 4 times larger than its lower value (about 223 Oe). The lower value of H_c might result from the smaller amount of ordered phases in thin-film samples due to shortage of nucleation sites [20]. It might also be concluded that the enhanced coercivity of cobalt film is due to the surface roughness of the film. Although these films have a homogeneous composition of magnetic materials we have found that for all investigated deposited films the coercive force does not change periodically with thickness. This is a clear manifestation of the structuring in the direction transverse to the film and the 3D architecture of these structures. Fig 3b represents the variation of H_c *versus* the amount of charge passed during electrodeposition process. It can be noted that the plot of coercivity in Fig. 3b exhibits similar behaviour to that in Fig. 3a. The dependence of film thickness on the quantity of charge passed is depicted in Fig. 3c. It is observed that there is an increase in the film thickness with increasing the amount of charge consumed in electrodepostion.

Fig. 4a shows the effect of film thickness on the porosity and the dependence of coercivity on the porosity of cobalt films using pluronic lyotropic liquid crystal template shown in Fig. 4b. The porosity of cobalt films is found to decrease with increasing the film thickness. This result indicates that there is a strong dependence of porosity on film thickness and the coercivity on the porosity of films. Usually, magnetic properties of thin films with such thicknesses depend greatly on the porosity of films, because the domain walls in thin magnetic films interact with the top and bottom surfaces of the film.

For a relatively thick film the relationship between coercivity and porosity is more complicated than a simple monotonic relationship [18]. In modulating the magnetic properties the porosity appearing in the film plays a significant role. It was established that a high carrier density in gold

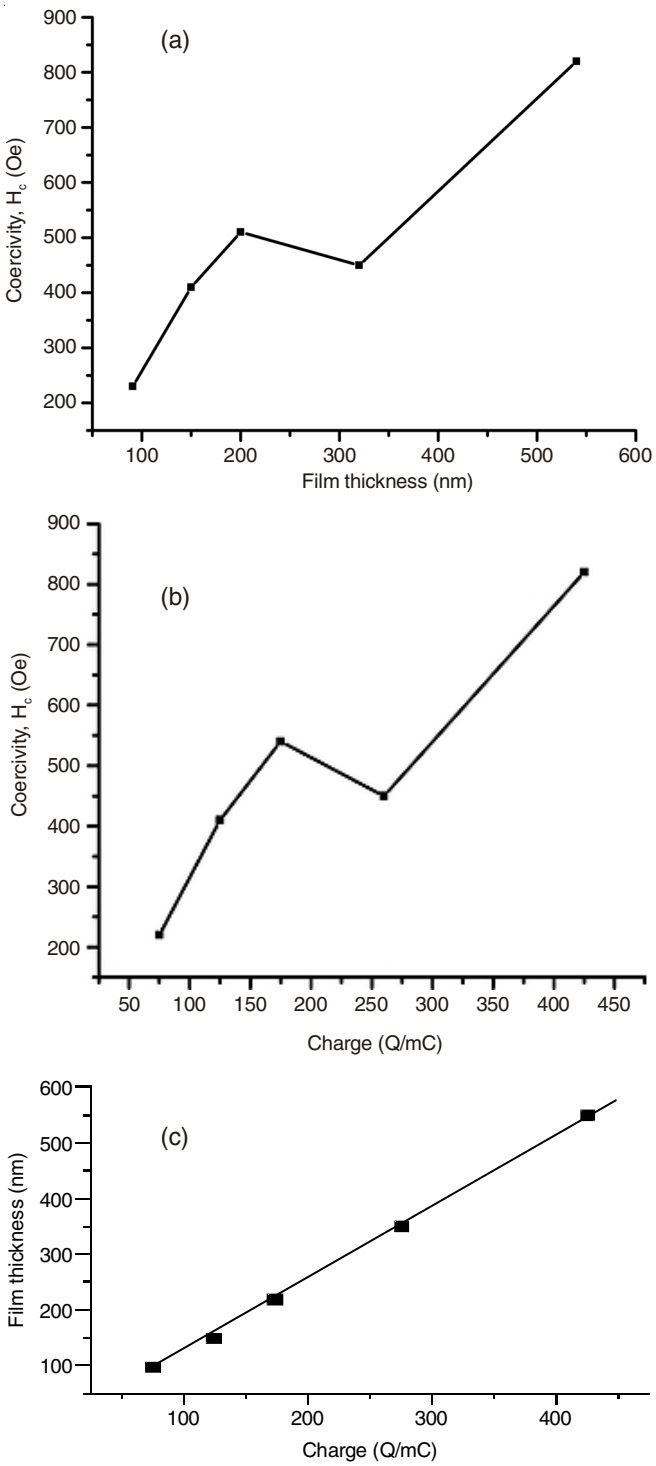

Fig. 3. Plot of coercivity *vs*. film thickness (a), coercivity *vs*. charge (b), film thickness *vs.* charge (c)

substrate may change the coercivity of the films and the magnetic properties of cobalt films and hence the magnetic anisotropy. Therefore, it would be reasonable to infer that the enhancement of coercivity of Co/Au thin films is due to gold substrate and a special interaction between cobalt film.

Magnetic properties obtained using macroporous template: It was found that in case of self-assembly template method using the pore diameter (d) in the range of 200-1000 nm, the loops of magnetization exhibited noticeable changes resulting from the nanoporous structure. As indicated in Fig. 5,

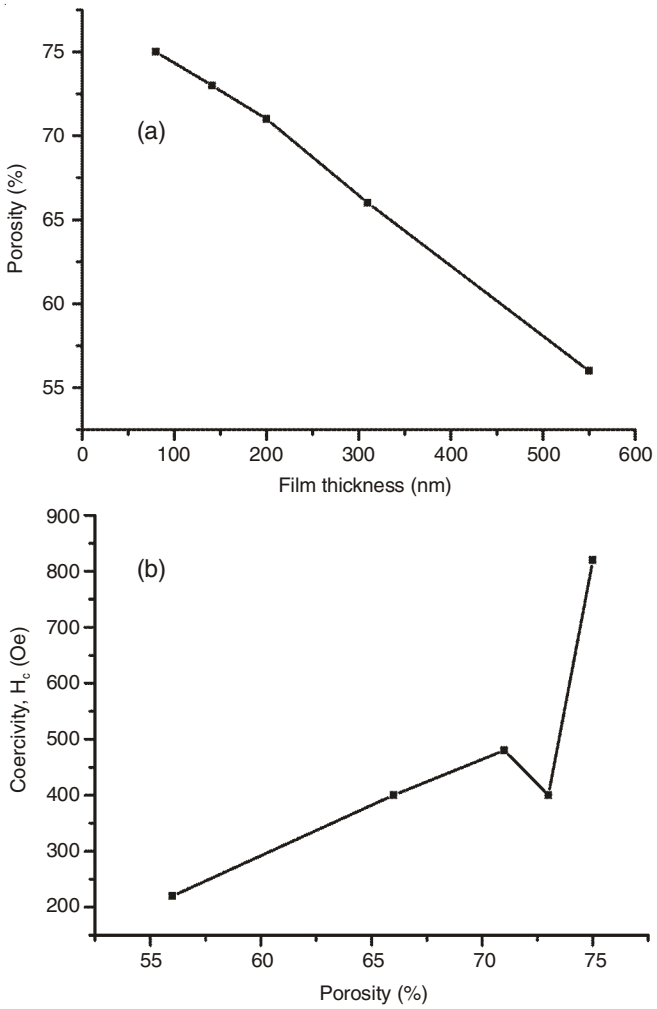

Fig. 4. Plot of porosity *vs*. film thickness (a) and coercivity *vs.* porosity (b)

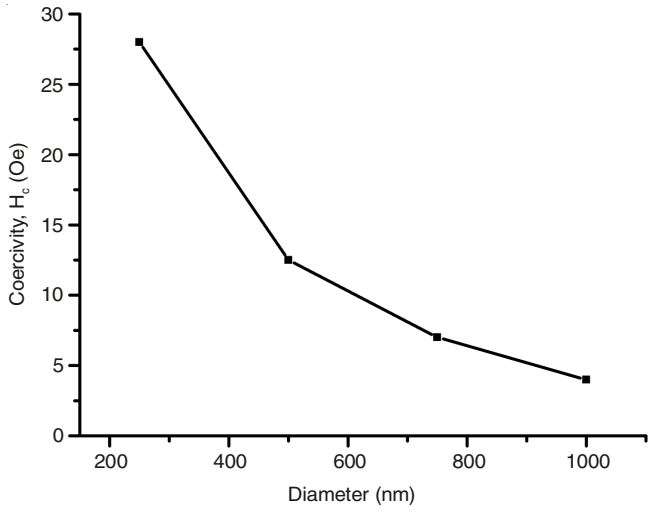

Fig. 5. Coercivity *vs*. pore diameter of polystyrene sphere

the coercivity (Hc) decreases with increasing the pore diameter (d) for large void diameter. This behaviour indicates that the magnetic properties are affected by the interaction of the voids with domain wall [21]. This interaction is sensitive to the relation between pore diameter and magnetic length-scales. Nucleation-controlled barrier is another explanation leading to an increase of Hc. This means that high nucleation fields hinder the development of formation process of a reversed domain.

Fig. 6 shows the dependence of coercivity on film thickness (t_f), of the electrodeposited cobalt film. As shown, the coercivity value (H_c), passes through a maximum when the film thickness (t_f), equals the pore radius (p_r) and passes through a minimum when the film thickness equals the pore diameter. From a similar consideration a minimum in H_c is expected for integer t_f/d values and a maximum for half integer values of t_f/d, where t_f is the film thickness and d is the pore diameter of the polystyrene sphere. This new effect on the magnetic properties opens up the possibility of designing new nanostructured magnetic materials where the magnetic properties can be tailored for a particular application.

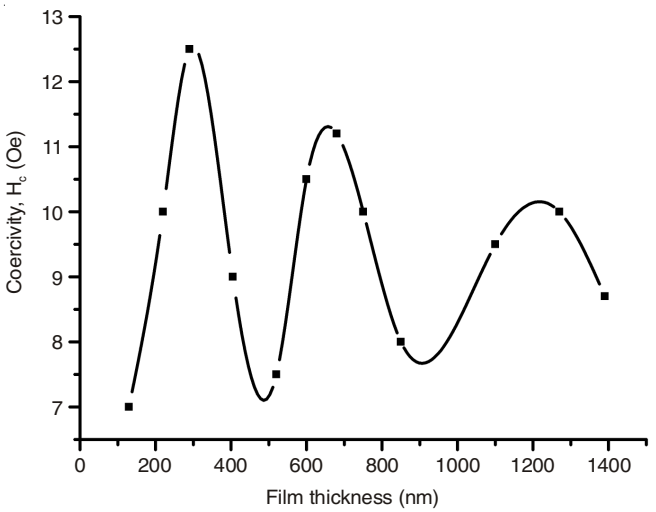

Fig. 6. Dependence of coercivity on film thickness of cobalt, t_f, obtained using 500 nm spheres

Conclusion

In this work, we have studied the magnetic properties of electrodeposited cobalt films in the interstitial spaces of pluronic lyotropic liquid crystal templates and self-assembled templates. It was observed that the coercivity of electrodeposited cobalt films using liquid crystalline template, varies with the films thickness. Also, the magnitude of coercivity increased from 223 to 820 Oe, as the thickness of cobalt films increased from 91 to 524 nm. In case of polystyrene sphere the coercivity decreased with increasing the pore size of the sphere. Also in the case of polystyrene sphere it was observed that the coercivity changes periodically with film thickness.

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