



Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 5(1), 2009 [16-20]

Electrochemical and magnetic properties of electrodeposited nanostructured macroporous cobalt films using polystyrene sphere templates

I.S.El-Hallag

Chemistry Department, Faculty of Science, Tanta University, Tanta, (EGYPT)

E-mail : ielhallag@yahoo.co.uk

Received: 19th November, 2008 ; Accepted: 24th November, 2008

ABSTRACT

The electrodeposition synthesis of highly ordered macroporous films of cobalt with regular arrays of spherical pores with diameter 0.2, 0.5, 0.75 and 1 μm was carried out into the interstitial spaces of a template formed by polystyrene latex spheres self-assembled on gold electrodes to produce a highly periodic, hexagonal close packed, interconnected network of mono-disperse spherical pores within the metal film, the size of which is determined by the diameter of the polystyrene latex particles used to prepare the template. Nanostructure of the films is studied by scanning electron microscopy, also the magnetic studies of the films are carried out by Aeronomic 3001 vibrating sample magnetometer. © 2009 Trade Science Inc. - INDIA

KEYWORDS

Electrochemical deposition;
Macroporous;
Polystyrene latex;
Chronoamperometry;
Magnetic properties.

INTRODUCTION

Metal electrodeposition is of great importance, both for the basic science involved in this process and for its major technological applications in electroplating, metal electrofining and electrowinning^[1].

Porous metals are important for many engineering applications, such as filters, catalyst, supports, heat exchangers, fuel cells, electrolytic cells, thermal screens, and vibration dampers^[2]. In many applications, a high specific surface area is required. The production of materials with micron and submicron scale structure in two and three dimensions is of importance in a range of applications, such as photonic materials, high density magnetic data storage devices, microchip reactors and biosensors^[3-7].

The electrochemical deposition of nanoscale Ni and Au meshes through templates made from close-packed silica sphere array have been described by Xu et al^[8]. It

was found that there are several important differences between the method described in this work over that of Xu et al which summarized as : (i) the polystyrene latex particles used are commercially available in a range of sizes; (ii) the close-packed templates can be prepared by evaporation in 2 d rather than by sedimentation over a period of several months; (iii) there is no need to sinter the template; (iv) the metal deposition is achieved in a few minutes rather than over 36 h; (v) the template can be removed by dissolving the polystyrene in toluene rather than requiring the use of HF.

In this article we report the preparation of highly ordered macroporous metal films. The preparation of the structured macroporous films was carried out via the electrochemical reduction of CoSO_4 in aqueous solution within the interstitial spaces of a close packed polystyrene latex sphere template, self assembled on a gold surface. The influence of the pore diameter of polystyrene latex spheres on the magnetic properties of the

electrodeposited Co films is reported. The nucleation and the growth mode of Co onto gold substrates, were investigated via current – time transient curves during potentiostatic deposition. The morphology of the Co films have been investigated with Scanning electron microscopy (SEM). Magnetic hysteresis curves have been recorded with an Oxford Instruments Aerosonic 3001 vibrating sample magnetometer at room temperature.

EXPERIMENTAL

Materials and substrates

All solvents and chemicals were of reagent quality and were used without further purification. The mono-disperse polystyrene latex spheres, with diameters of 200, 500, 750 and 1000 nm, were obtained from Alfa Aesar as a 2.5 wt% solution in water. Propanol and toluene were obtained from Aldrich. The gold electrodes used as substrates were prepared by evaporating 10 nm of a chromium adhesion layer, followed by 200 nm of gold, onto 1 mm thick glass microscope slides. The gold electrodes were cleaned by sonication in propanol for 1 hr followed by rinsing with deionized water. All solutions were freshly prepared using reagent grade water (18M Ω cm) from a Whatman RO 80 system coupled to a Whatman ‘Still Plus’ system.

Instrumentation

An analytical scanning electron microscope (JEOL 6400) was used to study the morphology and thickness of the electrodeposited cobalt films. Magnetic hysteresis loops were measured using An Oxford Instruments Aerosonic 3001 vibrating sample magnetometer. Electrochemical deposition was carried out in a conventional three electrode configuration using an EG and G 273. A large area platinum gauze was used as the counter electrode, saturated calomel (SCE) reference electrode and the template coated gold substrate as the working electrode.

Assembly of the colloidal templates

The polystyrene sphere templates were assembled by sticking a 1.0 cm internal diameter Teflon ring on to the gold substrate using double-sided tape. Approximately 0.3 cm³ of an aqueous suspension of the mono-disperse polystyrene spheres of 200, 500, 750 and 1000

nm diameter diluted with water to 0.5 wt% was spread over the area of the gold electrode surrounded by the Teflon ring (0.785 cm²)-this corresponds to forming a template layer about 20 μ m thick. The sample was then kept in a controlled humidity chamber and allowed to dry slowly over a period of 3 to 4 days. After all of the water had evaporated the Teflon was removed to leave a circular area covered by the template. The templates are robust and adhere well to the gold substrate. There is no evidence for the re-suspension of the latex particles when they are placed in contact with the deposition solutions.

Synthesis of highly ordered macroporous cobalt films

The electrochemical deposition was performed at a fixed potential of -0.95 V vs. SCE. The Cobalt films were grown with constant and gradient thickness. The gradient was ranging from 0.0 to 1.5 μ m across the 1 cm diameter sample. This was done in order to allow a systematic study by SEM measurements of the properties of the films as a function of the film thickness. After the electrochemical deposition was complete (25 -30 min), the cobalt films were soaked in toluene for 24 h to dissolve away the polystyrene template. All experiments were performed at room temperature (20 -23°C).

RESULTS AND DISCUSSION

Chronoamperometry characterization

Chronoamperometry is a most widely used tech-

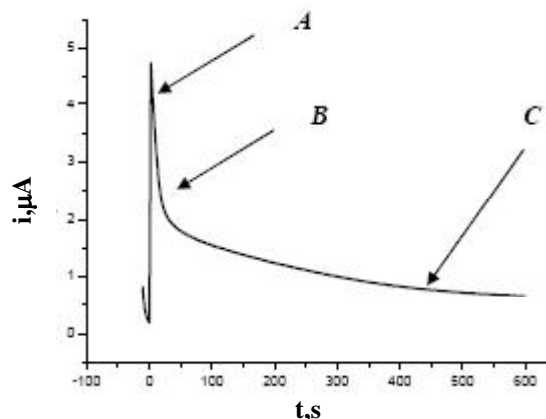


Figure 1: Current – time curve during deposition of cobalt

Full Paper

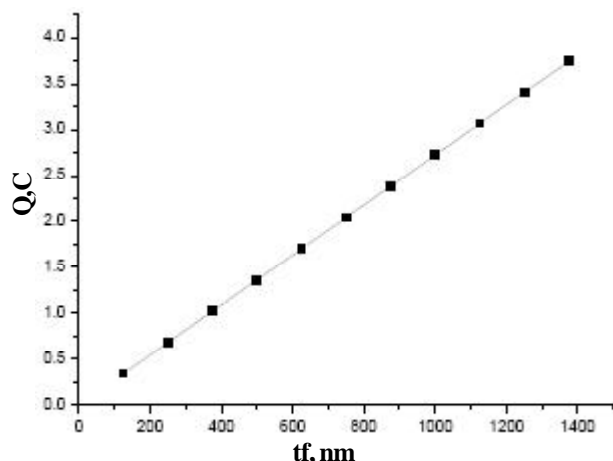


Figure 2: Plot of film thickness versus deposition time of cobalt films

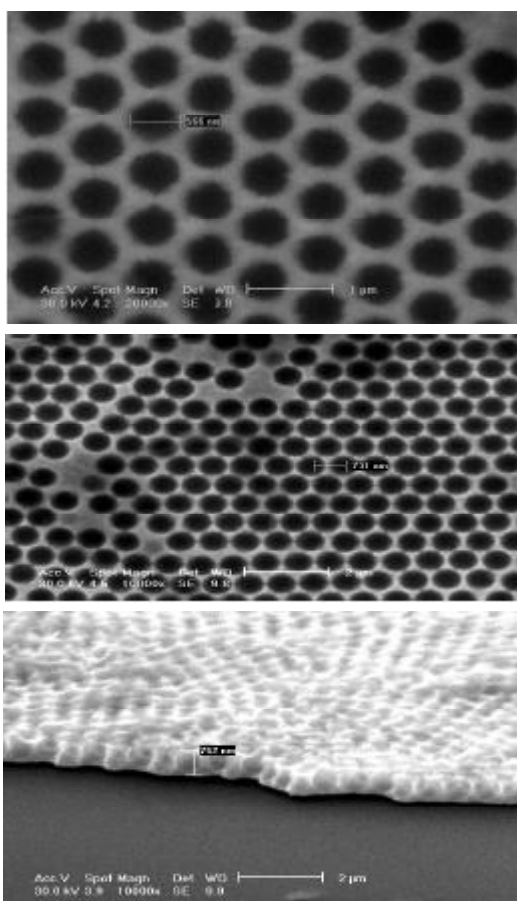


Figure 3 : (a): SEM image of nanostructured cobalt film with template diameter 500 ± 20 nm; (b): SEM image of nanostructured cobalt film with template diameter 750 ± 20 nm; (c) : Cross-section image of deposited cobalt film using template 500 nm

nique for the deposition and to observe the growth process during the film formation. Chronoamperometric

curve in figure 1 shows three different regions, in which A region corresponds to rapid increase in current with applied potential of -0.95 V vs SCE, further slow current decay is observed in B region which is followed by a constant current in C region. The rapid surge and exponential decay of the current observed in region A is due to double layer charging. A continuous decay current observed in region B, corresponds to the formation of cobalt films^[9] and after that the current in region C is the characteristic of diffusion controlled growth^[10]. Thus, (i) a cobalt deposition after double layer charging, (ii) critical nuclei formation, and (iii) further diffusive controlled growth of the cobalt films, are the responsible steps for the nucleation formation and subsequently growth of cobalt thin films. Cobalt thin films were deposited from optimized both composition by applying -0.95 V vs SCE deposition potential for various time periods. Figure 2 shows the plot of films thickness against the amount of charge required for the deposition of films. It was observed that the film thickness increase with increasing the charge quantities.

It was found that by selecting the data points from the experimental data selected in figure 1 at short time, a Cottrell plot is obtained as current versus the reciprocal square root of time. The slope of cottrell plot yields a diffusion coefficient $D = 5.2 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$.

SEM characterisation

Figure 3a shows an example response of SEM images of the surface of macroporous cobalt films onto gold substrate covered with templates made of 500 ± 20 nm diameter polystyrene spheres. The electrochemical deposition was carried out at potentials of -0.95 V vs. SCE (total charge passed 2 C cm^{-2}). The SEM images show that the spherical voids left in the gold films after the removal of the polystyrene sphere are arranged in a well ordered single domain, close packed structure. Measurements of the centre to centre distances for the pores in Figure 3a and for similar images of other films confirms that the spherical voids within the cobalt films have the same diameter as the polystyrene spheres used to prepare the template. Figure 3b shows an image for a macroporous cobalt film prepared through a template of 750 nm diameter spheres. Figure 3c indicate cross-sectional images of cobalt film prepared using templates formed from $0.75 \mu\text{m}$ polystyrene latex

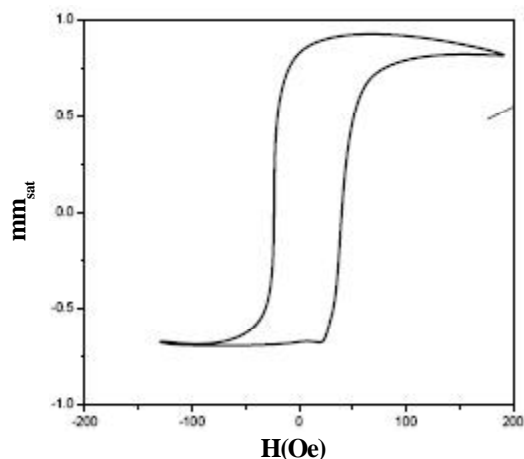


Figure 4: Normalized in-plane magnetic hysteresis loop using 500 nm

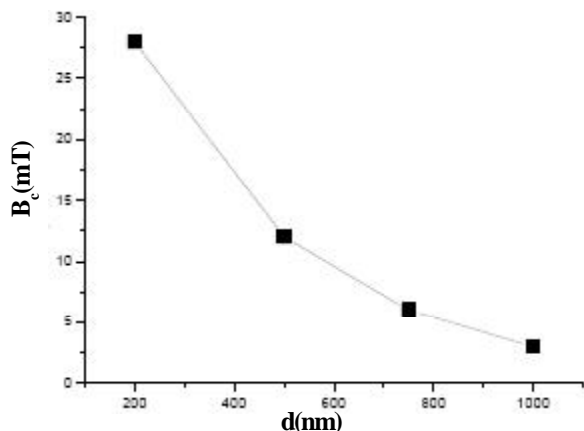


Figure 5: Presentation of the measured coercivity versus the diameter of polystyrene sphere

spheres. These micrographs also demonstrate the formation of three dimensional macroporous films. The spherical voids have a diameter determined by the diameter of the polystyrene latex spheres used for the template and are arranged as part of an hexagonal lattice, again indicating that the polystyrene latex particles were arranged in three-dimensional hexagonal close packed structure. This was also confirmed by scanning electron micrographs of the template themselves before the deposition of the metal.

It was noted that self-assembled layers of polystyrene latex particle is formed on gold surfaces by slow evaporation of water from the latex suspension can be used as templates through electrochemical deposition of metal films. In the resulting metal/polystyrene composite the polystyrene spheres are in contact and can

be dissolved out of the metal to leave a regular array of interconnected spherical voids. The size of these voids is determined by the size of the polystyrene latex particles used. Since polystyrene latex particles of tightly controlled size distribution are readily commercially available controlled. Control over the quantity of charge passed in the electrochemical deposition of the films allows control over the final film thickness. Thus this method represents a simple route to the production of ordered macroporous films of metals with potential interesting and useful photonic, catalytic, magnetic, or other properties.

Magnetic properties of cobalt films

The films thickness were controlled by changing the diameter, d , of the polystyrene latex spheres, used to form the template, and the amount of charge passed during the electro-deposition process respectively^[11]. Consequently, the grain structure and morphology of the electroplated cobalt films obtained from water and from the template mixture may be significantly different. Figure 4 shows the normalized in-plane magnetic hysteresis loops measured at room temperature for cobalt film electrochemically deposited on gold substrate using 500 nm polystyrene sphere diameter. It was found that the hysteresis decrease with increasing the diameter of polystyrene sphere. Figure 5 indicate the presentation of the measured coercivity against the diameter of polystyrene sphere. It is clear that the coercivity is proportional to the inverse of the diameter of polystyrene sphere. The nano-structuring significantly affects the shape of magnetization loops and drastically changes the coercive field B_c which found to show a maximum with variation of sphere diameter^[12]. Measurements of the dependence of B_c on the thickness of the magnetic film, t_f , revealed a remarkable behaviour. It was found that the coercive force changes periodically with film thickness.

CONCLUSION

Using a simple method we have successfully produced nanostructured films of cobalt via electrochemical deposition using templates prepared by assembling close packed arrays on monodisperse polystyrene spheres which have different diameter (200 nm, 500 nm, 750 nm, and 1000 nm). The resulting electrochemi-

Full Paper

cal deposition is highly ordered three-dimensional macroporous thin films of cobalt are robust and stable when the template is removed. The diameter of the spherical voids is determined by the diameter of the polystyrene latex spheres employed to form the template. Scanning electron microscopy confirms the presence of a highly regular macroporous structure. The thickness of the films is controlled by varying the charge passed in their deposition.

It was noted that, the synthesising process obeys Cottrellian behaviour at short time. That mean that the diffusion controlled limiting current is proportional to $t^{1/2}$.

Magnetic measurements shows that the magnetic properties of cobalt films were strongly influenced by the diameter of polystyrene sphere and the films thickness. It was found that the hysteresis loops and coercivity decrease with increasing the diameter of polystyrene sphere.

ACKNOWLEDGMENTS

The auther are grateful to Prof. P.N.Bartlett, School of Chemistry, University of Southampton, U.K., for providing the materials for this work.

REFERENCES

- [1] Y.Jyoko, S.Kashiwabara, Y.Hayashi, W. Schwarzacher; *Electrochem.Solid State Lett.*, **2**, 67 (1999).
- [2] C.R.Martin; *Chem.Mater.*, **8**, 1739 (1996).
- [3] J.C.Hulteen, C.R.Martin; *J.Mater.Chem.*, **7**, 1075 (1997).
- [4] C.R.Martin, R.V.Pathasarathy; *Adv.Mater.*, **7**, 787 (1995).
- [5] J.P.Chan, K.M.Lee, C.M.Sorensen; *J.Appl.Phys.*, **75**, 5876 (1994).
- [6] J.L.Weston, A.Butera, J.A.Barnard; *J.Magn.Magn. Mater.*, **193**, 515 (1999).
- [7] G.S.Attard, P.N.Bartlett, N.B.R.Coleman, J.M. Elliott, J.R.Owen, J.A.W.Wang; *Science*, **278**, 838 (1997).
- [8] L.Xu, W.L.Zhou, C.Frommen, R.H.Baughman, A.A.Zahkidov, L.Malkinski, J.Q.Wang, J.B.Wiley; *Chem.Commun.*, 997 (2000).
- [9] G.Okam, P.M.Vereecken, P.C.Searson; *J.Electrochem.Soc.*, **146**, 1436 (1999).
- [10] T.J.Kemp; 'Southampton Electrochemistry Group', *Instrumental Methods in Electrochemistry*, Hills Horwood, Chichester, UK, (1985).
- [11] P.N.Bartlett, P.R.Birkin, M.A.Ghanem; *Chem.Comm.*, 1671 (2000).
- [12] P.A.J.de Groot, A.A.Zhukov, R.Boardman, G. Bordignon, H.Fangohr, P.N.Bartlett; *J.Mag.Magn. Mater.*, **310**, e846 (2007).