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Coaxial metal and magnetic alloy nanotubes in polycarbonate templates by electroless deposition.

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Abstract.

We present a novel technique for the preparation of coaxial metal and magnetic alloy nanotubes, which is demonstrated for the coaxial nanotubes of Ni/Co and Ni/CoNiFe alloys deposited in activated polycarbonate templates using electroless plating. For each metal or alloy the tube wall thickness was controlled to be less than 100 nm. The process involved two consecutive deposition steps from hypophosphite and/or borane reducing agent based electroless plating solutions. We further characterise the magnetic properties of the ternary magnetic alloy films and coaxial nanotubes. The coaxial tubes show homogenous wall thickness and composition, which is delineated from the magnetic measurements.

Keywords.

Coaxial, Electroless, Nanotube, Template, Alloy

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1. Introduction

Metal nanotubes are of interest as active materials in sensor, catalyst, filtration, magnetic and electronic devices [1,2]. A number of researchers have demonstrated templated metal nanotube formation using chemical vapour deposition, [3] electroplating [4,5] electroless plating [6-9] and supercritical fluids [10]. Of these techniques, the simplest in terms of equipment and processing is electroless deposition. This requires the pretreatment of the insulating template support, typically using Sn based sensitising solutions. The sensitisation is followed by immersion in Pd or Ag based solutions, wherein the more noble metal ion is reduced and the Sn^{2+} ions are oxidised to Sn^{4+}. The deposited catalyst facilitates localised electron transfer at the substrate from the reducing agent to the metal ion of the electroless plating solution. An autocatalytic metal deposition process develops where the metal deposited catalytically oxidises the reducing agent to continue the deposition. The electrochemical reactions proceed at the sidewall of the template which then grows radially into the host tube. The process is simpler than electrolytic deposition which requires either the predeposition of 'molecular anchors' on the internal tube walls [4] or the selection of deposition conditions to encourage gas evolution and tube formation by forcing the reaction to occur at the walls [5]. Solid nanowire deposition is observed in the absence of gas evolution [11]. Electroless deposition, by the nature of the reducing agent reaction, evolves hydrogen gas during deposition which ensures tube formation when combined with the required growth from the catalytically activated sidewalls. In this work we demonstrate the deposition of coaxial metal and alloy nanotubes by a process which may be extended beyond the magnetic materials shown here to other applications such as catalysis where the combined use of high

surface area nanotubes and the bilayer structure of metals or alloys may exhibit enhanced catalytic activity. Examples of the substrate influence on the outer active materials layer has been demonstrated recently by a number of researchers. [12-16]

2. Experimental.

Commercial Cyclopore track etched polycarbonate membranes (25mm diameter with 400 nm diameter pores) were used to prepare the coaxial nanoscale metallic tubes. The substrates were activated by soaking for 10 min. in the sensitising 0.013 M $SnCl_2$ in 0.24 M HCl at 40 ^oC, followed by immersion for 10 min. in the catalyst 1.4 x 10^{-3} M $PdCl_2$ solution at 65 ^oC, to deposit active Pd nuclei on the internal walls of the membrane. The substrates were then dried at 85 ^oC for 15 min. Ni nanotubes were formed by immersion in Ni-hypophosphite (Nimax from McDermid Inc.) or Ni-borane (Niposit 468 from Shipley) based commercial electroless plating solutions which operate at 85 ^oC and 65 ^oC, respectively. The Pd nuclei catalyse the hypophosphite or borane oxidation thereby facilitating localised Ni ion reduction by the reducing agent provided electrons. This is followed by an autocatalytic Ni on Ni metal deposition process where the metal deposited catalytically oxidises the reducing agent to continue the deposition. Similarly Co nanotubes were deposited from a bath described previously [17]. CoNiFe tubes were deposited from a bath containing, nickel sulphate (0.019 M), cobalt sulphate (0.016 M), iron sulphate (0.013 M) diammonium citrate (0.052 M) lactic acid (0.143 M) and dimethylamine borane (0.07 M) at a pH of 9 and 65 ^oC.

The Ni nanotube was imaged using a JEOL 2000FX transmission electron microscope (TEM) operating at an accelerating voltage of 80 kV. The scanning electron microscopy (SEM) analysis was performed using a Hitachi S-400 field emission scanning electron microscope with a PGT IMIX energy-dispersive X-ray (EDX) system with intensity correction for elemental analysis of deposit composition.

Room temperature static magnetic properties of deposits were characterized using a BH loop tracer made by SHB instruments. Magnetic measurements were carried out on CoNiFe thin films on 1 cm^2 Si wafer substrates (p-type, 4 inch in diameter) with sputter coated Ti adhesion layer (20 nm) and Cu seed layers (200 nm) and membrane pieces incorporating coaxial nanotubes of Ni/CoNiFe 0.5 cm^2 in size. Saturation magnetisation values were determined at an applied field of 100 Oe for the films and 1000 Oe for the coaxial metallic nanotubes.

3. Results and discussion.

A TEM image of a Ni nanotube formed following immersion in an electroless Ni plating solution is shown in Fig. 1a. The dark particles, approximately 50 nm in size, are Sn^{4+} activator remaining after immersion in the Pd solution determined by EDX. It has previously been shown [18] that the Pd particles represent a very small fraction of the surface coverage while the Sn coverage can be up to 25%. This remains as Sn^{4+} following immersion in the Pd solution when all of the divalent Sn is oxidised. The polycarbonate template was partially removed by etching for 15 min. at 300 W in oxygen plasma following electroless metallisation. The partially etched membrane facilitated the microscopic examination of the deposits while ensuring the membrane

remained intact for handling purposes. Samples were then imaged by FE-SEM to illustrate the tubular nature of the deposit with tubes of up to 10 μm in length, as shown in Fig. 1b. The SEM analysis of the Ni nanotube growth indicated that it deposited at a decreasing rate. After 40 s the tube wall was approximately 60 nm, or it had deposited at approximately 1.5 nm/s in the 400 nm pore template. The rate decreased to 1 nm/s after two minutes immersion. This may be rationalised by noting that the initial deposition reaction was catalysed by dispersed highly active Pd nuclei. As the layer growth progressed the catalyst material became the deposited Ni which grew to form a continuous tube. Ni has been shown to exhibit a lower borane oxidation rate capability than Pd at the potentials of electroless plating baths [19]. It is expected, therefore, that the deposition rate would decrease during nanotube growth.

The goal of this work was to achieve coaxial deposition of nanotubes using a simple chemical solution based approach. To investigate this, the template was plated with a Ni nanotube approximately 70 nm in thickness followed by a subsequent immersion in a second electroless plating solution of a different metal, which led to the formation of coaxial metal nanotubes. Both metal tubes had a wall thickness of less than 100 nm as shown in Fig. 2. The second bath utilised in this case, Fig. 2a, was an electroless Co solution with ammonia borane as the reducing agent [17, 20] operated at 45 ^{o}C. The versatility of this approach was further demonstrated by the deposition of a ternary magnetic alloy, CoNiFe, Fig. 2b inside a Ni nanotube. To the best of our knowledge, this is the first report of such coaxial electroless alloy nanotube deposition. EDX analysis, Fig. 2c, of the Ni/CoNiFe coaxial nanotubes (ignoring the minor elements Sn, arising from the sensitising $SnCl_2$, and P, from the hypophosphite) gave the following overall composition $Co_{25}Ni_{65}Fe_{10}$. On planar substrates, the alloy

plating bath composition typically results in the deposit composition $Co_{55}Ni_{20}Fe_{25}$ [21]. It is consistent, therefore, that the outer Ni nanotube would lead to Ni enrichment observed in the combined elemental analysis of the coaxial Ni and CoNiFe nanotubes.

The magnetic characteristics of the electroless deposited CoNiFe alloy thin films were determined. The magnetisation curve shown in Fig. 3a is for a planar 1.9 μm $Co_{55}Ni_{20}Fe_{25}$ deposited thin film. During sample preparation no external magnetic field was applied to the samples, however magnetic measurements reveal a degree of in plane anisotropy with clear easy and hard axis preferential directions for films. The significant features of this material are the relatively high saturation magnetisation ($\mu_0 M_s$) value of 2.15 Tesla with a low coercivity (H_c) of 1.22 Oersteds (97.6 A/m). The films show in-plane anisotropy with an anisotropy field (H_k) of about 20 Oe (1.6 kA/m). Such high saturation magnetisation can lead to more compact device design in applications incorporating the magnetic material, while low coercivity implies lower energy losses.

Fig. 3b shows a typical magnetic hysteresis loop measured perpendicular to the nanotube long axis. The measurement was carried out on samples prior to the removal of the polycarbonate template with a magnetic field applied in the plane of the polycarbonate membrane. These measurements show a magnetic isotropic behaviour as expected due to radial symmetry of the tubes. The coercivity is one hundred times larger for the CoNiFe nanotubes than the planar thin films. This is expected as the magnetic coercivity is known to depend on a variety of parameters such as tube shape, thickness, crystalline structure, composition and the surface/interface of the deposit

[22]. The nanotubes are magnetically isotropic in the radial direction indicating homogenous tube wall thickness and composition. The coercivity of the nanotubes is due to shape anisotropy, which is in accordance with similar observations in Co (H_c = 250 Oe, 20 kA/m) and CoNiFe (H_c = 100 Oe, 8 kA/m) nanowires [23, 24]. The magnetisation could not be obtained for these samples as the polycarbonate membranes are irregular porous materials which would introduce a large error in any estimation of volume of magnetic material and hence magnetisation. The planned deposition in aligned smaller pore alumina templates may permit a more accurate estimate of the volume of the magnetic material deposited.

4. Conclusion.

A low-cost, electrochemical solution based method for sub-100 nm coaxial metal and alloy tube deposition has been demonstrated. The ability to control the deposition of the second material has been demonstrated for both single metal and ternary alloys. The examples demonstrated in this work are magnetic materials but the technique could be extended to a large variety of technologically significant materials such as catalytically active alloy combinations on support materials for specific reactions or core shell type combinations of functional materials. The tubular nature of the nanoscale deposits ensures a high active surface area. Future work involving the deposition in aligned alumina templates with smaller pore openings will facilitate their further characterisation.

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Captions

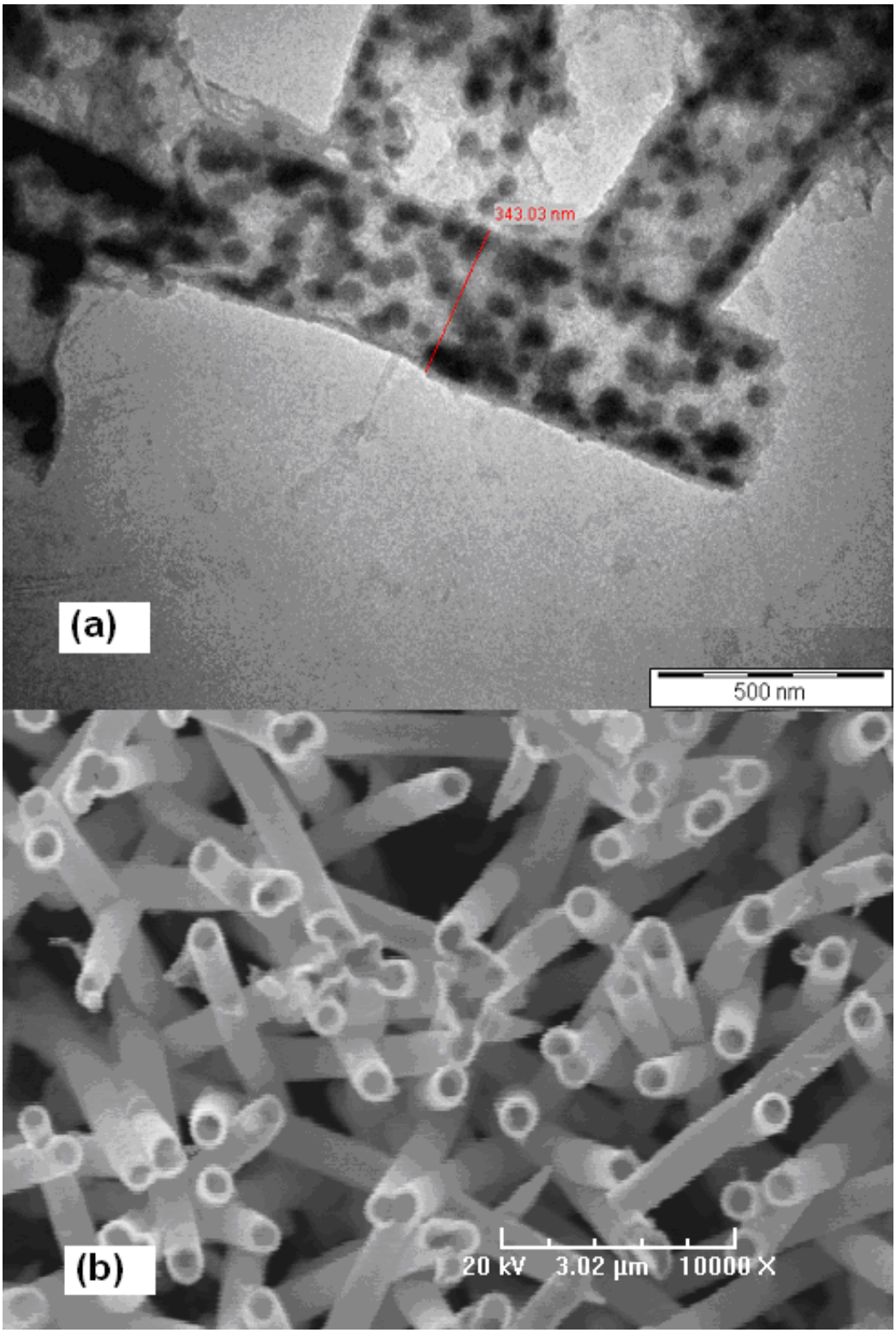

Fig.1 (a) TEM image of Ni nanotube showing remaining Sn particles from the sensitisation step and (b) SEM of Ni nanotubes after template removal.

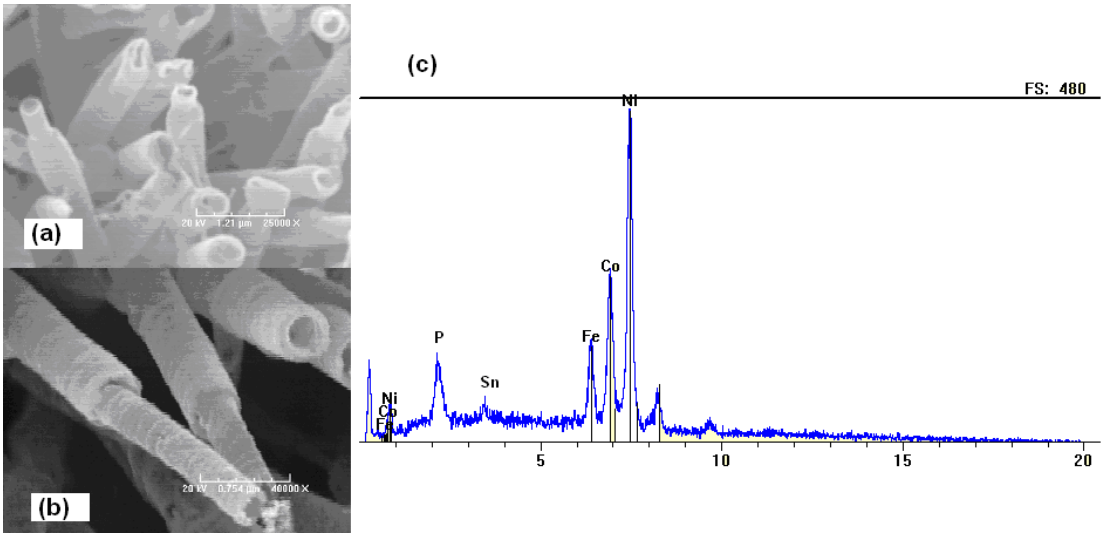

Fig. 2 SEM image of coaxial nanotubes formed in polycarbonate templates (a) Co inside Ni (b) CoNiFe alloy inside Ni (c) EDX spectrum of the CoNiFe in Ni coaxial nanotubes shown in Fig. 2(b)

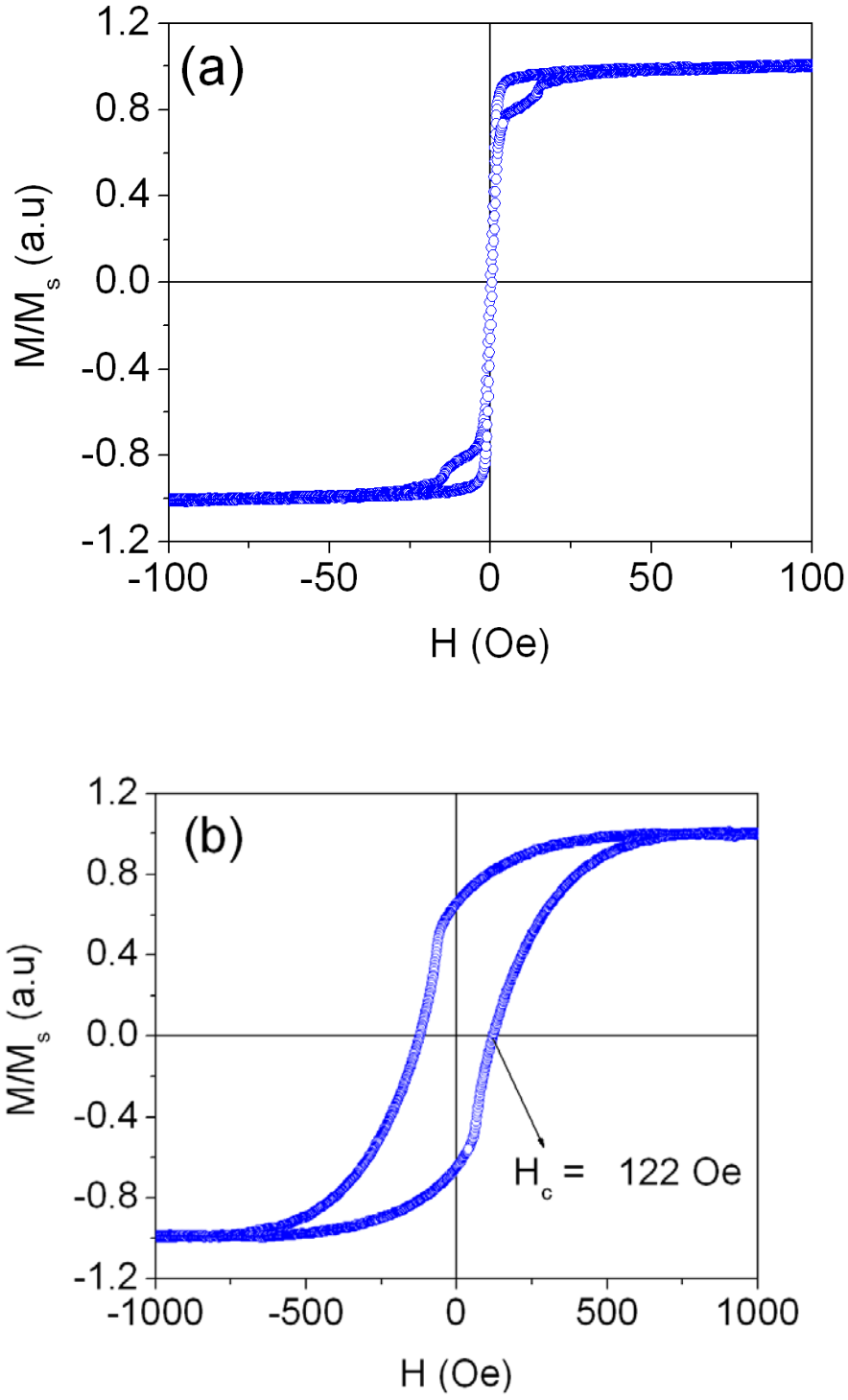

Fig. 3. Room temperature magnetisation measured (a) in the plane of the thin film CoNiFe and (b) perpendicular to the long axis of the coaxial nanotube Ni/CoNiFe electroless deposits.