

Nanomagnetic domains of chromium deposited on vertically-aligned carbon nanotubes

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ARTICLE INFO

Article history:

Received 25 May 2012

Received in revised form

17 July 2012

Available online 28 July 2012

Keywords:

Nanomagnet

Carbon

Nanotube

Electrodeposition

Chromium

ABSTRACT

The drive to create ever smaller magnetic memory devices has led to the development of new nanomagnetic domains on surfaces. This paper reports the development of nano-chromium magnetic domains obtained using electrodeposition on vertically aligned carbon nanofibers arrays. Attempts to achieve this using conventional aqueous solutions were unsuccessful even after thin nickel underlayers were applied. The use of a novel electrolyte, a deep eutectic solvent, made from choline chloride: chromium (III) chloride enabled highly conformal overcoatings of chromium on individual bare carbon nanotubes to be obtained. Very high aspect ratio metal microstructures could be obtained by this novel technology. Magnetic imaging of the coated nanoarrays showed there to be clear magnetic character to the coating when the thin coatings were applied but this disappeared when the deposits were thicker and more contiguous.

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1. Introduction

Vertically aligned carbon nanotubes (VA-CNTs) have become a popular subject for study since Ren et al. first reported their preparation using plasma-assisted chemical vapor deposition (PACVD) [1]. Since then, many research groups have investigated both the underlying science and applications of these novel materials which include field emission displays [2], cold cathodes for vacuum electronics [3], thermal management materials [4], and sensors [5] amongst many others. A recent review of potential applications demonstrates the high level of interest in these materials [6].

The high surface area of thin films of carbon nanotubes offers considerable potential for applications in energy storage, composites, new magnetic materials, catalysis and sensors. In the area of energy storage, interest in these materials for hydrogen storage by direct surface adsorption has waned although commercial success has been realized in lithium-ion batteries where bulk CNT fibers are used as an essential reinforcing agent in the electrode [7]. Without this reinforcement, battery life would be restricted to only a few cycles of charge/discharge making this battery technology practically unviable. Metal coated carbon nanotubes promise a route to metal matrix composites by mechanical consolidation and

these materials have been shown to exhibit excellent wear resistance [8].

There has been increasing interest in the deposition of metals directly onto carbon nanotubes by chemical or electrochemical means, particularly for applications in composite materials [9–17]. Electrodeposition of nickel onto multi-walled nanotubes (MWNT), ultrasonically dispersed in standard Watt's bath has been described by An et al. [18]. Here the MWNTs were adsorbed onto a copper cathode where the nickel deposition takes place. Hence the characteristics of the cathode change with time as more MWNTs co-deposit with the nickel and are not the same as with a surface pre-coated with nanotubes. Xing et al. electroplated nickel from a simple chloride-only bath onto nanotube paper made from MWNTs and smooth deposits were obtained [19]. Overall, the aspect of metal coating of carbon nanotubes by electrodeposition has so far been largely focused on nickel coatings and metal coating on high surface area templates deserves further exploration as a general technology. Metallic nanostructures have been previously realized using electrodeposition using liquid crystal templates [20] or self-assembled polymer nanospheres as templates [21]. At a more fundamental level, the electrochemistry of carbon nanotubes has been recently discussed by Dumitrescu et al. [22].

This paper reports the electrodeposition of chromium onto vertically aligned arrays of carbon nanotubes formed as thin films using PACVD. The industry standard chromic acid plating bath was replaced by a novel ionic liquid [23,24]. Abbott et al. showed that eutectic mixtures of choline chloride and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ could be used for the deposition of chromium with much higher current

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efficiency, typically in excess of 90% [25]. The magnetic properties of chromium coated CNTs were examined using a magnetic force microscope and this showed that the nanoclustered deposits exhibited magnetic properties but these were lost when thick coatings were created.

2. Experimental

All CNT thin films were grown in a simple DC PACVD system based on a quartz bell jar very similar to that described elsewhere [26] operating at 8 mbar pressure using 50:200 sccm $C_2H_2:NH_3$ flows at a temperature of ca. 700 °C. Substrates for CNT growth included titanium nitride coated silicon chips or polished stainless steel. The CNT fibers had lengths of 5–7 μm . Chromium electroplating was initially conducted with chromic acid ($250 g dm^{-3} CrO_3$, 0.25 ml H_2SO_4 with lead–silver alloy (10% Ag) anodes) operated at 50 °C [27]. A TTI EX4210R bench power supply was used with currents of up to 10 A for chromium electroplating trials.

Chromium electrodeposition was carried out using a choline chloride and chromium chloride based ionic liquid (Cromline 200 from Scionix Ltd., UK) which was used as received. The deposition was conducted in an open beaker at 20 °C. Currents of not more than 0.15 A were used with a platinized titanium anode.

Nickel coatings as a smooth underlayer prior to chromium deposition were obtained with a standard nickel sulfamate bath but with no additional additives [28]. The sulfamate bath composition was 30 g/L of boric acid, 315 g/L nickel sulfamate and 1 g/L nickel chloride (pH 4) and operated at 54 °C. The nickel chloride is added to the sulfamate bath to maintain anode activity but is kept to a minimum to avoid internal stress in the deposit. Pure nickel anodes were used. A constant current of 10 mA was used for nickel plating. This is about one tenth of the normal current density for nickel plating of flat surfaces [28] when the total area of the carbon fiber is factored in. The carbon fiber arrays give an increase in surface area of some sixty-fold over the flat surface when fiber density, diameter and length are measured by SEM. Lower than standard current densities were used to ensure that plating occurred down at the fiber base and that the upper levels were not ‘plated out’ first. After electroplating, all samples were washed in water and then in iso-propyl alcohol before drying. The resulting electroplated microstructures were examined in a field-emission SEM (FEI XL30) at 12–15 kV.

Atomic/Magnetic Force Microscope AFM/MFM images were acquired using a Digital Instruments (DI, Veeco) Nanoscope IV, Dimension 3100 instrument in resonant (tapping) mode (software version 6.12) and the designated quartz liquid-mode cantilever mount supplied directly by Veeco. The probe tip used to obtain these images was the MESP-RC model. The TM deflection images were acquired by passing the probe tip 40 nm above the sample to measure any magnetic response. All images were obtained at a scan rate of 0.600 Hz.

3. Results and discussion

The electrodeposition of electronegative metals from aqueous solutions is notoriously inefficient. Chromium electrodeposition on fibrous carbon nanotube materials proved very difficult to achieve using chromic acid baths because high currents were required to create deposits even onto the CNT-free areas of the chips. It is well known that electroplating using chromic acid is very inefficient, typically around 12%, [27] with most of the current being used for gas production. Negligible plating was observed on the CNT pads although some decoration around the pad was observed presumably due to insufficient current density

in the CNT coated region. To circumvent this, an insulating ceramic coating (AREMCO Ceramabond 509) was applied to the chip edge and a pointed lead rod anode was employed to focus current towards the center of the chip. Using this approach it was possible to successfully electroplate chromium using a constant current of 6 A for 30 s. Fig. 1a shows a typical SEM image of the deposit obtained under these conditions using chromic acid. The chromium deposits were formed as a dense crust rather than as a coating of each individual CNT. Using various current densities from 6 A down to 0.15 A did not improve the nanotube coating and lower current densities than this did not result in material deposition. To improve on this result the CNTs were first individually coated with nickel using a standard nickel sulfamate bath (120 s at 10 mA, 1.2 C) before chromium plating. Fig. 1b shows an SEM image of the nickel coated carbon nanotubes and it can clearly be seen that a conformal nickel coating is achieved. Repeating the chromic acid plating experiment with the Ni coated CNTs did not improve the deposition of chromium as can be seen from Fig. 1c where strong clustering of the chromium at the nanotube ends has occurred.

Under these conditions some columnar growth was observed but the growths appear quite nodular in appearance and certainly much rougher than the nickel under-layer plated on the CNT fibers. The effect of a nickel underlayer is however beneficial in that the chromium plating is now closer to conformal although still not ideal.

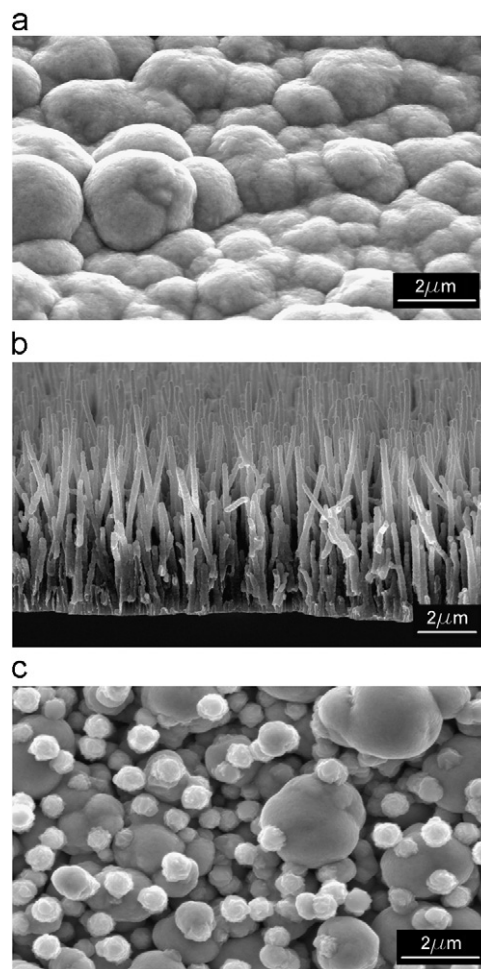


Fig. 1. Chromium and Nickel electrodeposits on carbon nanotubes. Chromium electrodeposit obtained on bare nanotube fibers (a) using chromic acid as the electrolyte after 60 s at 6 A. Nickel-coated nanotube fibers (b) are used as base template for chromium electrodeposition. Chromium coating deposited on nickel modified CNTs (c) using chromic acid as the electrolyte after 376 s at a current of 10 A.

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