Diamond & Related Materials 19 (2010) 553–556

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

High coercivity magnetic multi-wall carbon nanotubes for low-dimensional high-density magnetic recording media

S.C. Ray [a,*], S. Bhattacharyya [a], S.L. Wu [b], D.C. Ling [b], W.F. Pong [b], M. Giorcelli [c], S. Bianco [c], A. Tagliaferro [c]

[a] School of Physics, University of the Witwatersrand, Private Bag 3, WITS 2050, Johannesburg, South Africa
[b] Department of Physics, Tamkang University, Tamsui 251, Taiwan
[c] Department of Material Science and Chemical Engineering, Politecnico di Torino, Torino 10129, Italy

ARTICLE INFO

Available online 4 February 2010

Keywords:
MWCNTs
Coercivity
Magnetic recording media

ABSTRACT

Fe-embedded multi-wall carbon nanotubes (MWCNTs) were fabricated using Fe-catalyst by the chemical deposition method. Microscopic characterizations showed that the well-aligned MWCNTs were ~80 mm in length, with outer diameter of 20–50 nm and inner diameter of 10–20 nm. Magnetic properties were characterized in temperatures of 5 K and 305 K, which revealed that the MWCNTs exhibited high coercivity of 2600 Oe at 5 K and 732 Oe at 305 K. These values are much higher than that of bulk iron (~0.9 Oe) and Fe/Co/Ni nanoparticles or nano-wire arrays (~200–500 Oe) at the room temperature. This high coercivity and the structure of single-domain Fe nanoparticles isolated by anti-ferromagnetic MWCNTs make it a promising candidate for low-dimensional high-density magnetic recording media.

1. Introduction

Ferromagnetic materials such as 'Fe' catalyst based carbon nanotubes (CNTs) have potential application in various areas such as "magnetic storage media" that include the traditional tapes and videocassettes, hard disks for mainframe computers, floppy disks for personal computers (PC), portable ZIP and MO disks (magneto-optic) with high storage capacity [1,2]. These Fe, Co and Ni based carbon materials are also used in magnetic toners in xerography and magnetic inks or ferrofluids, as well as in bio-engineering applications such as drug delivery and magnetic resonance imaging [2]. Their development has covered a wide historical period, ranging from the industrial era to the mainframe and PC eras and up to the post-PC era. For storage capacity, a minimum signal spot of <100 nm is required for a terabyte capacity and of <20 nm for greater than terabyte capacity. These magnetic storage media can be broadly divided into two categories, i.e. the horizontally oriented and vertically oriented types. These results indicate that the horizontally oriented magnetic storage media may reach the limit in physics for storage capacity of >40 Gbit/in.^{2} [3,4]. In the present commercial hard-disk market, the horizontally oriented type is generally adopted for all magnetic storage media, except MO media. A few hard-disk manufacturers and research institutes have successfully designed such prototype media to demonstrate their feasibility [3,5,6].

However, many problems must be solved before commercialization that include (i) design and fabrication techniques for a high-precision recording head and servo driving system; (ii) fabrication parameters for storage media, such as size uniformity (dispersion <10%), morphology control, higher magnetic properties (higher coercive field strength H_c, higher squareness ratio S, higher anisotropic magnetic crystal, lower noise, etc.); lower cost, etc. Focusing on these behaviors for the fabrication of magnetic storage media using MWCNTs, we report in the present work about the magnetic properties of iron particles embedded aligned MWCNTs (as-grown and high-temperature ~2100 °C annealed) were characterized and their possible potential applications of the magnetic particles for data storage media were discussed. The magnetic properties of Fe-embedded MWCNTS show that the high-temperature annealed (2100 °C) MWCNTs may have the effect on high-temperature anisotropy of the magnetic materials inside the MWCNTs and/or the combine effects of MWCNTs. In addition we have also examined the structural phases by the SEM, TEM and XRD to correlate the magnetic properties of these MWCNTs.

2. Experimental details

These materials can be synthesized by different techniques/processes like electrical arc-discharge technique, pyrolysis of non-graphitising carbon materials and catalytically assisted chemical vapour deposition (CCVD) etc. [2]. The MWCNT with Fe-catalyst samples used in this work are synthesized using an approach described elsewhere [7]. *As-grown* (at 850 °C) and annealed (at 2100 °C for 30 min in Ar atmosphere) MWCNT samples were used. The tube morphology and microscopic details of the structure were determined by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The X-ray diffraction (XRD) was used to determine the lattice structure. The

* Corresponding author. Tel.: +27 117176806; fax: +27 117176879.
E-mail addresses: raysekhar@rediffmail.com, Sekhar.Ray@wits.ac.za (S.C. Ray).

0925-9635/$ – see front matter
doi:10.1016/j.diamond.2010.01.031

magnetization (M) was measured versus applied magnetic field strength (H), using a commercial physics properties measurement system (PPMS) at a temperature range between 5 K and 305 K.

3. Results and discussion

Fig. 1(a) and (b) presents typical field emission scanning electron and transmission electron micrographs of *as-grown* MWCNTs, respectively. Most of the nanotubes are not completely vertically aligned and some of them are entangled. The inset in Fig. 1 reveals Fe nanoparticles embedded in the end of the MWCNTs, offering excellent oxidation protection, which can be effectively exploited in magnetic nanoprobes and spintronics. The core diameter of MWCNTs determined from HRTEM in Fig. 1(c) ranged from 20 to 25 nm; the thickness of the carbon shells was about 30 and 40 nm, and the surface morphology of the tubes includes kinks and curliness. However, HRTEM also reveals the effects of thermal annealing as the small fringes become aligned along the tubes because of straightening up, as shown in Fig. 1(d), which is indicative of graphitization (or crystallization) by post-annealing at 2100 °C for 30 min.

Fig. 2 presents a typical XRD pattern of the *as-grown* and annealed samples. The most significant graphite-like Bragg peaks are marked by Miller indices and the Fe-catalyst related peaks are indicated by (*); they are primarily associated with Fe-carbides with a couple from Fe-oxides, reflections are based on the powder diffraction file that is available from the International Center for Diffraction Data; ICDD file 35-0772 [8]. The diffraction peaks at $2\theta \sim 26^{\circ}$ (002) and $\sim 53^{\circ}$ (004) are associated with the interlayer spacing between the graphene planes. The peaks at $2\theta \sim 43^{\circ}$ (100) and $\sim 77.3^{\circ}$ (110) are characteristic of two-dimensional in-plane symmetry along the graphene layers. The position and width of the (002) peak are related to the structural ordering of the material. As we observed in the Raman spectra of our previous report [7] the narrowing of this peak ($3.2^{\circ} \rightarrow 0.9^{\circ}$) reflects the enhancement of structural ordering upon the annealing of the samples.

However, the expanded region in the range $2\theta = 40–46^{\circ}$ has the asymmetry of the (100) peak after the contribution of the sample holder is subtracted out, indicating the lack of complete stacking order (Fig. 2) of graphene layers/planes. Nevertheless, thermal annealing also promotes the transformation of metastable Fe-carbide phases into stable Fe-carbides phase, as qualitatively revealed by Fig. 2. The intensity of the peaks marked '*' is higher overall for annealed samples. While these observations were expected, more evidence and a better understanding of the kinetics of transformation of these iron phases in conjunction with the structural ordering of the MWCNTs are required.

All measurements were performed both at room temperature (~305 K) and at low temperature (~5 K), to investigate the hysteresis of the magnetic behavior. Anisotropy measurements in PPMS are facilitated by automated sample rotation; therefore, a magnetic field (H) is applied both parallel and perpendicular to the tube axis. Figs. 3 and 4 plot the resulting magnetic moment M and magnetic field H measured at ~305 K and 5 K, respectively of the *as-grown* and annealed MWCNTs.

Fig. 3(b) shows that there is an interface between ferromagnetic and anti-ferromagnetic materials in the annealed MWCNTs network, when magnetic field is applied parallel to the tube axis as a result the coercivity is not symmetric. The ferromagnetic behavior of the annealed MWCNT sample was apparently eliminated when magnetic field is applied perpendicular to the tube axis. We strongly believe that it is due to the formation of Fe-carbides and/or Fe-oxides upon high-temperature annealing. From Fig. 3(a) it is observed that the coercivity (H_c) of the *as-grown* MWCNTs exceeds ~750 Oe and is higher than that of the bulk Fe counterpart (0.9 Oe) [9] and/or Ni/Co-nano-wire arrays (200–500 Oe) [10,11] at the room temperature and is comparable with the reported values found in the literatures [12,13]. It is interesting to see, although the hysteresis loops look similar for parallel and perpendicular directions for the as-grown samples at the lowest recorded temperatures (5 K), but they differ significantly for the post-annealed MWCNTs establishing a high

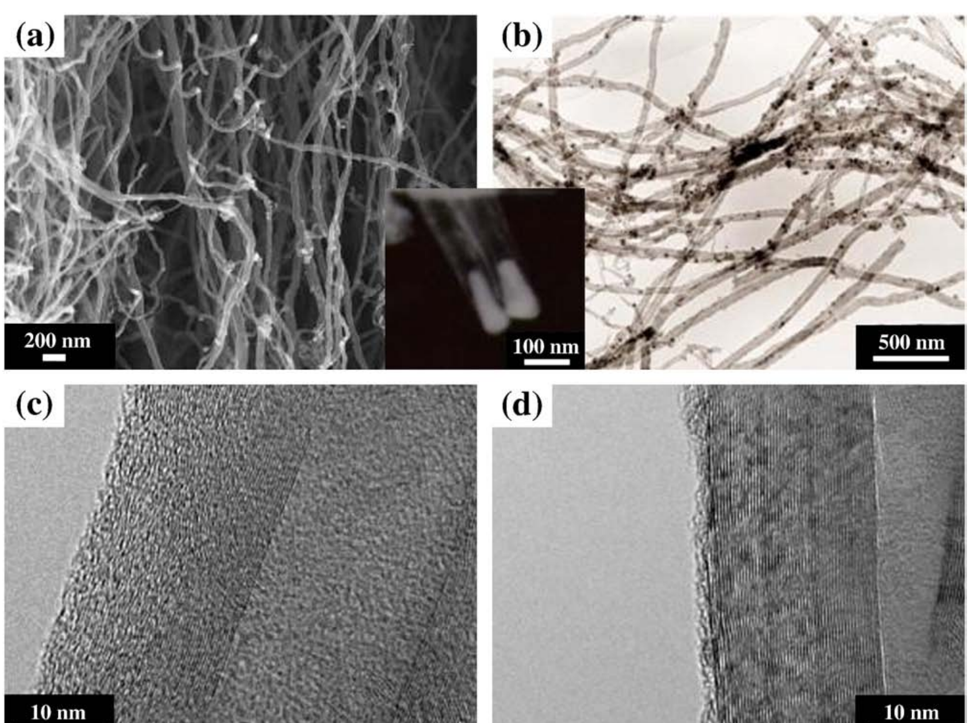

Fig. 1. (a) SEM and (b–d) HRTEM images of MWCNTs; insets in (a) and (b) show Fe nanoparticles at ends of nanotubes; HRTEM images of (c) *as-grown* and (d) annealed samples reveal apparent straightening of the tube walls.