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Magnetic properties of carbon nanotubes filled with ferromagnetic metals

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ABSTRACT

Carbon nanotubes (CNTs) encapsulating Fe nanowires were prepared by the chemical vapor deposition (CVD) method using ferrocene as a precursor. The influence of the addition of Pt to an Fe catalyst, which is required for growing CNTs by CVD, on the magnetic properties of the resulting CNTs was examined from the viewpoint of enhancing coercivity. Our results showed that the addition of a Pt layer on the Fe catalyst deposited on a substrate increased the coercivity of the Fe-filled CNT. This increase is due to changes in the easy magnetization axis of the Fe nanowires in the CNTs. This result indicates that the magnetic properties of the Fe-filled CNTs can be tuned by the controlling the growth conditions, which is suitable for applications in areas such as magnetic recording media and medicine.

1. Introduction

CNTs filled with ferromagnetic metal show shape anisotropy owing to the presence of magnetic particles having a high-aspect ratio [1] and the anticorrosivity resulting from the protection of the encapsulated metal by a layer of graphite. Therefore, such CNTs are expected to have applications in magnetic recording media [2] and therapeutic modalities such as hyperthermia therapy [3–5]. For these applications, the appropriate control of the magnetic properties is desired. Numerous studies have been reported regarding the magnetic properties of CNTs filled with ferromagnetic metals and grown by the thermal chemical vapor deposition (T-CVD) [6–10] and plasma enhanced CVD methods [1,11]. However, the growth mechanism and the method for controlling the magnetic characteristics of ferromagnetic-metal-encapsulated CNTs have not yet been completely understood. Furthermore, clarifying the influence of the shape and crystallographic structure of the encapsulated metal on the magnetic properties of CNTs is important for the applications described above.

Recently, it has been reported that nanoparticles of an FePt alloy have extremely high coercivity [11–13]. Therefore, it was expected that the addition of Pt to the Fe encapsulated in the CNTs could enhance coercivity and varying the amount of Pt enables tuning the magnetic properties. In this study, we have investigated the magnetic properties of Fe-filled CNTs synthesized by the T-CVD method that uses a ferrocene precursor. In addition, the influence of Pt addition to Fe was examined to enhance coercivity.

2. Experiments

The substrate used for inducing CNT growth was composed of silicon (100) single crystal wafers cut into 10 × 10 mm squares. For cleaning, the substrate was sonicated in acetone and methanol. After cleaning, it was heat treated at 1000 °C (1 atm) for 2 h to form a silicon oxide layer (100 nm in thickness). Subsequently, an Fe thin film (2.0 nm in thickness) was deposited onto the substrate by DC magnetron sputtering at 0.80 Pa and 100 mA × 280 V. The Fe thin film formed on the substrate serves as a catalyst for CNT growth. It is expected that the Fe film is partially encapsulated into the CNTs from the root. To investigate the influence of the addition of Pt on the magnetic properties, a Pt layer was formed on the Fe layer with the thickness of 0.6–1.4 nm. The Pt layer was deposited by sequential DC-sputtering (0.80 Pa and 30 mA × 280 V) after the Fe deposition.

Fig. 1 shows a schematic of the T-CVD apparatus. This apparatus is a hot-wall-type CVD reactor comprising a system for introducing gases (Ar and ferrocene), a quartz tube reactor heated by an electric furnace, and a mechanical rotary pump. Ferrocene [$Fe(C_5H_5)_2Fe$], which was used as a precursor, was previously heated in the reservoir at 150 °C for 2 h under an Ar atmosphere in order to promote sublimation.

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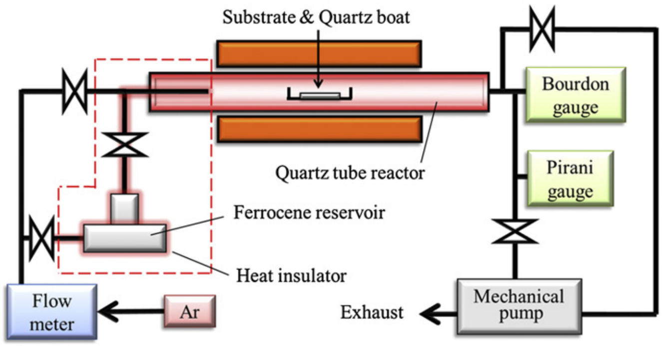

Fig. 1. Schematic of the T-CVD apparatus.

The CVD procedure is as follows: First, the substrate was introduced into the CVD reactor. Next, the reactor was evacuated to approximately 2 Pa, and the pressure was re-equilibrated to atmospheric pressure by introduction of Ar. The temperature of the reactor was then increased to 785 °C (the CNT growth temperature) under a flow of Ar (120 sccm). When the temperature of the reactor reached 785 °C, ferrocene was introduced into the reactor and CVD was performed for 10 min. Subsequently, the introduction of ferrocene was discontinued, and the reactor was cooled to 80 °C under a flow of Ar. After cooling, the substrate was removed from the reactor.

The CNTs grown on the substrates were observed by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The crystal structures of the metals encapsulated in the CNTs were examined using selected area diffraction (SAED) patterns. A resonating sample magnetometer (RSM) was used for the characterization of the magnetic properties.

Table 1
Dimensions of the CNTs and the nanowires encapsulated in the CNTs.

	Fe (2.0 nm)	Pt (1.0 nm)/Fe (2.0 nm)
Inner diameter	11.2 nm	10.6 nm
Filling rate	63%	63%
Length of metal nanowires	392 nm	492 nm

3. Results and discussion

Fig. 2 shows the SEM and TEM images of the CNTs grown by CVD. The CNTs grown on the substrates with Fe (2.0 nm) and Pt (1.0 nm)/Fe (2.0 nm) films are shown. Vertically oriented CNTs are presented on the substrates. More than half of the inner hollows of the CNTs are filled with the metal nanowires. The inner diameter and average filling rate (the volume ratio of the nanowire to the inner hollow of the CNT) of the individual CNTs grown on the Fe and Fe/Pt substrates are almost equal. On the other hand, the length of the metallic nanowires tends to increase in the sample with the added Pt layer. The dimensions of the CNTs and the encapsulated nanowires are summarized in Table 1.

Fig. 3 shows the results of the magnetic property measurements for the CNTs grown on the Fe (2.0 nm) and Pt (1.0 nm)/Fe (2.0 nm) layers shown in Fig. 2. A clear difference between the coercivities in the parallel and perpendicular directions is observed in the hysteresis curves. This result shows that CNTs have magnetic anisotropy that is dependent on the growth direction. The coercivities of the CNTs aligned perpendicular to the substrate are 87.5 kA/m and 175.1 kA/m for the Fe- and Pt/Fe-coated substrates, respectively. The coercivity of the CNTs grown on the Pt (1.0 nm)/Fe (2.0 nm) bilayer is two-fold higher than that of the CNTs grown without Pt addition, showing that coercivity is clearly increased by Pt addition.

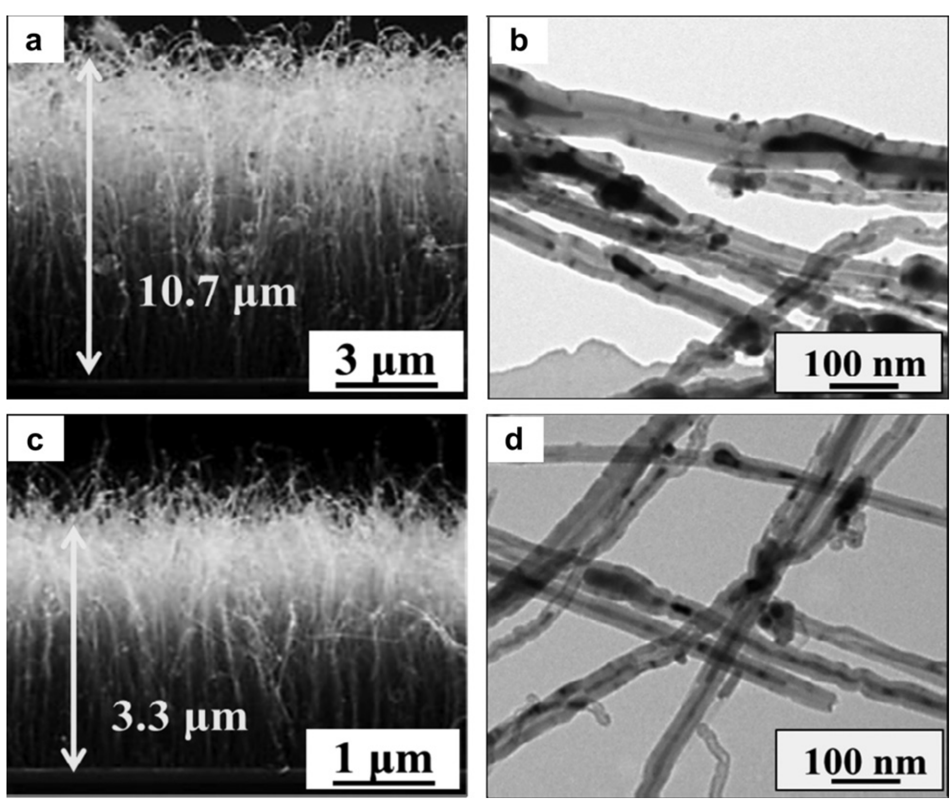

Fig. 2. SEM [(a), (c)] and TEM [(b), (d)] images of the CNTs grown by the CVD. (a), (b): Fe (2.0 nm) and (c), (d): Pt (1.0 nm)/Fe (2.0 nm).