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Coaxial Multiferroic Nanorod Arrays

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We have developed a facile yet versatile method for fabricating coaxial nanowires of carbon nanotubes (CNTs) with multiferroic layers, such as $BaTiO_3$ and $CoFe_2O_4$. Oxide coatings were deposited by pulsed laser deposition, and a variety of deposition parameters were studied. Arrays of such multiferroic-coated CNTs offer a mean to design novel nanostructures with high surface areas.

I. Introduction

Because of their excellent dielectric and ferroelectric properties, $BaTiO_3$ (BTO) nanomaterials have recently attracted a great deal of interests.[1] Examples include single phase BTO epitaxial thin films deposited on various substrates to improve their piezoelectric properties.[2] If we integrate BTO nanoparticles/films with a magnetic phase, such as $CoFe_2O_4$ (CFO) or $NiFe_2O_4$, then we engineer nanocomposites with a product tensor property of magnetoelectricity (ME).[3–5] In recent years, there have been a number of investigations of two phases multiferroic materials in both multilayer[4,6] and self-assembled nanocomposite thin-layer films,[7,8] an important goal in both cases was to achieve higher ME coupling.[9] In order to effectively transfer strain from one phase to another, it was found necessary to have high interphase interface areas.

On the other hand, because of their unique one-dimensional (1D) nanostructure, large surface area, good chemical and thermal stability, and excellent mechanical properties,[10,11] carbon nanotubes offer a potential means by which to support BTO, CFO, or other multiferroic phases or oxides as coatings.[4] If one could coat vertically aligned carbon nanotubes (VACNTs) with such multiferroic oxides, then regular 2D thin film structures might be conformably transferred into a 3D nanorod structure. Accordingly, two-phase composites with large interphase interfacial structure could be created. In this study, we reported the use of VACNTs as a positive template by which to coat CFO and BTO layers by pulsed laser deposition (PLD).

II. Experimental Procedure

Aligned carbon nanotubes (CNTs) arrays were purchased from the Institute of Physics, CAS, China. The nanotubes were grown by chemical vapor deposition, via Fe nanoparticles as catalyst.

A PLD system was used to coat the CNT array with CFO and BTO. The outer shells were deposited by a KrF laser wavelength of 248 nm (Lambda 305i). A laser spot of 3 mm^2 in size and 1.2 J/cm^2 in energy density was rastered at a frequency of 10 Hz on stoichiometric target surfaces. The distance between the substrate and target was 8 cm, and the base vacuum of the chamber was 10^{-5} Torr. During deposition, the CNTs were first coaxially coated with CFO under a 10^{-5} Torr oxygen pressure for 6000 pulses: such low pressures were used to prevent the CNTs from oxidizing. Subsequently, the CNTs were coated by BTO under oxygen pressures of between 10 and 100 mTorr using a variable numbers of pulse. The deposition temperature was also varied from 650° to 900°C.

Scanning electron microscopy (SEM) images were obtained using a LEO (Zeiss, Peabody, MA) 1550 high-performance Schottky field-emission SEM. A Philips EM420 scanning transmission electron microscope (TEM) was used to obtain TEM images. Phase identification was determined by X-ray diffraction (XRD) using a Philips MPD system (Andover, MA). The electrical resistance was measured by an Agilent 4294A impedance analyzer (Santa Clara, CA).

III. Results and Discussion

Figures 1(a) and (b) show both SEM and TEM images for a typical CNT–CFO–BTO coaxial nanorod, respectively. From the TEM image we can identify each layer and its thickness. The diameter of the CNT was ~70 nm; and the thicknesses of the CFO and BTO layers were ~60 nm each. As the plasma first reached the tip of the tubes, the upper side of each coaxial nanotube was slightly larger than other parts: one potential solution is to use a rotatable substrate holder in the deposition process and increase the space between two CNTs in the array.

Here, we focused on the outer BTO layer as a representative study by which to determine how multiplies parameters affect the oxide layer. Because BTO is a typical and commonly used oxide, these conclusions can apply to other oxides including CFO: although the detail experiment parameters may vary.

The deposition conditions were found to notably affect the topography of the coaxial tubes. At low temperature and low oxygen partial pressure, the nanorods had very smooth surfaces (see Fig. 2(a)). After increasing the oxygen partial pressure from 10 to 100 mTorr, while keeping other conditions constant, the diameter of the nanorods increased notably to larger than 200 nm; however, the surfaces became more rough (see Fig. 2(b)). A possible reason for these changes is that BTO is better oxidized and crystallized at high oxygen atmospheres. If we continued to increase the deposition temperature to 700°C (Fig. 2(c)), the only difference we observed was that the surface roughness fur-

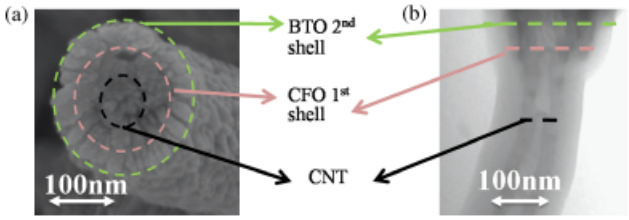

Fig. 1. (a) Scanning electron microscopy and (b) transmission electron microscope images of our coaxial CNT–CFO–BTO nanorod composite. CNT, carbon nanotube; CFO, $CoFe_2O_4$; BTO, $BaTiO_3$.

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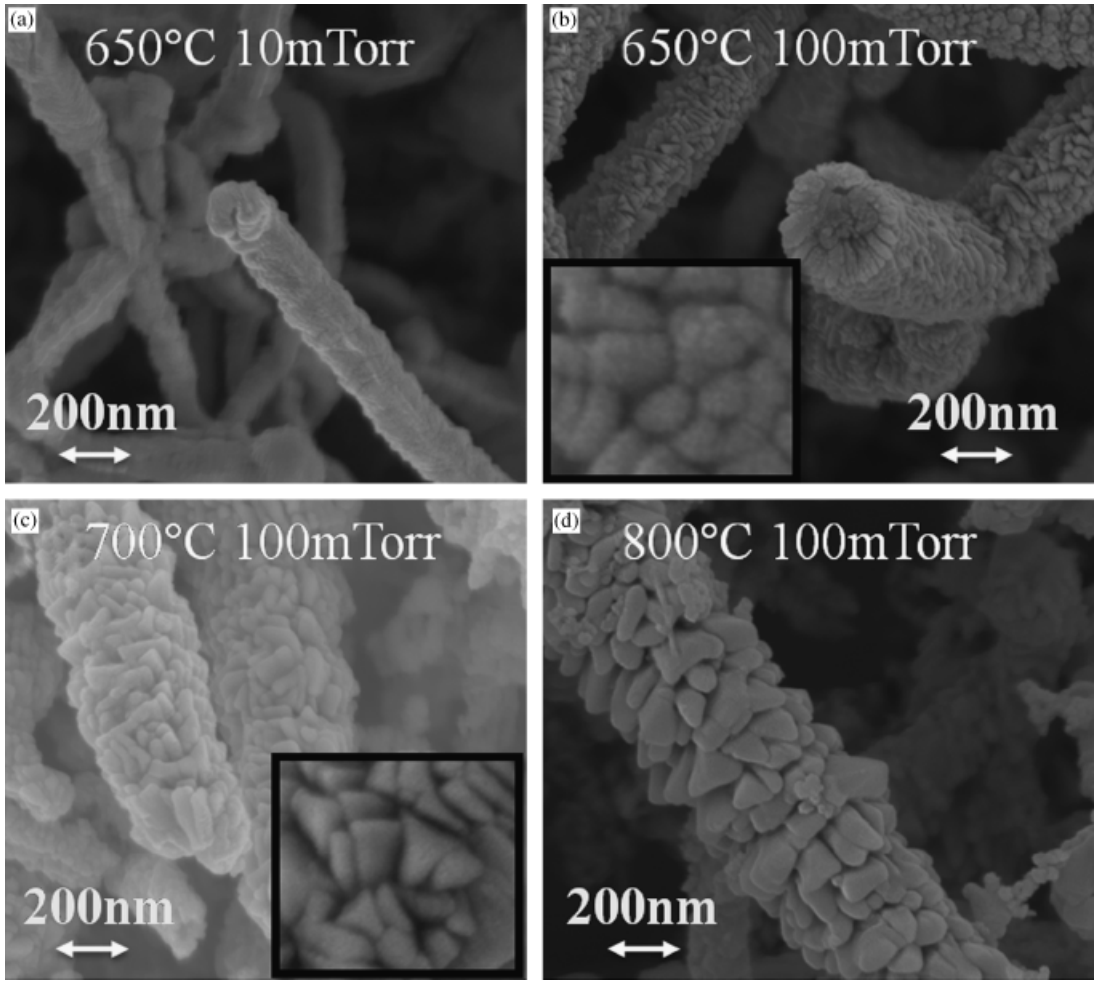

Fig. 2. Scanning electron microscopy images of samples coated under different oxygen pressures and deposition temperatures. (a) 650°C and 10 mTorr oxygen; (b) 650°C and 100 mTorr oxygen; (c) 700°C and 100 mTorr oxygen; and (d) 800°C and 100 mTorr oxygen. Insets are high magnification images of surface details.

ther increased (see Fig. 2, insets). Other experiments have also shown that temperature and oxygen partial pressure play a very important role during PLD deposition,[12] however, what types of experimental parameters that should be chosen really depends on applications and needs.

Continued increase of the deposition temperature to 900°C resulted in notable changes in surface topography. BTO formed nanobelts of about 100 nm in width that covered the CNTs (Fig. 3(a)). Figure 3(b) shows a XRD pattern obtained from the sample shown in part (a): which confirms that BTO, CFO, and Carbon phases coexisted. In Fig. 3(c), for frequencies below 10 kHz, the real component of the resistance R can be seen to be much larger than the imaginary one X; i.e. the coaxial nanotubes appear as an ideal resistance. However, with increasing frequency in the range of 10 kHz$<f<$50 kHz, the value of X increased relative to R, reaching a maximum value near 40 kHz. In this case, the coaxial nanotubes appear near-completely hysteric: i.e., limited real component R, relative to the imaginary one X or loss.

The above samples all had BTO shells deposited using 6000 pulses: i.e., we kept this deposition condition as constant. We then tried to understand how the laser deposition pulse numbers affected the structure at a constant temperature of 700°C and a constant oxygen partial pressure of 100 mTorr. We increased the laser pulse numbers (i.e., prolonged deposition time at same frequency) to 12 000 pulses and then to 24 000. In this case, we found that the thickness of the BTO coating layer increased, 24 000 pulses are enough such as to fill the space between CNTs. Figure 4 shows the evolution with deposition time following this procedure. We can see from the initial case of aligned CNTs (see Fig. 4(a)), to CNTs–CFO–BTO coaxial rods (see Fig. 4(b)) using 12 000 pulses, and finally to CNTs within a BTO matrix (see

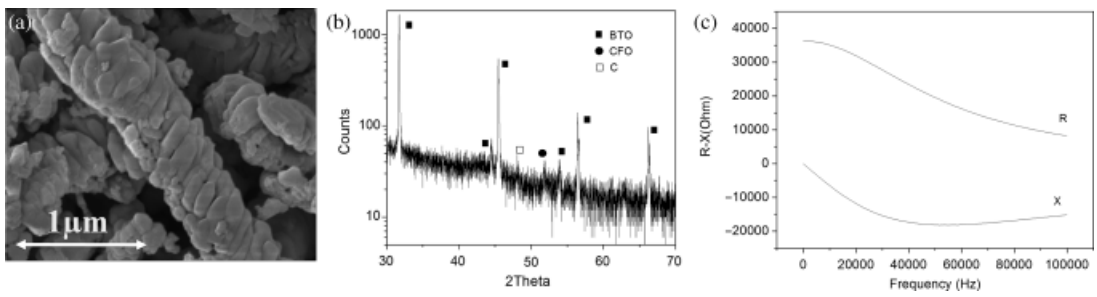

Fig. 3. Structure and properties of coaxial nanorods deposited at 900°C: (a) scanning electron microscopy image; (b) X-ray diffraction pattern; and (c) frequency dependent resistance (R–X) curve.

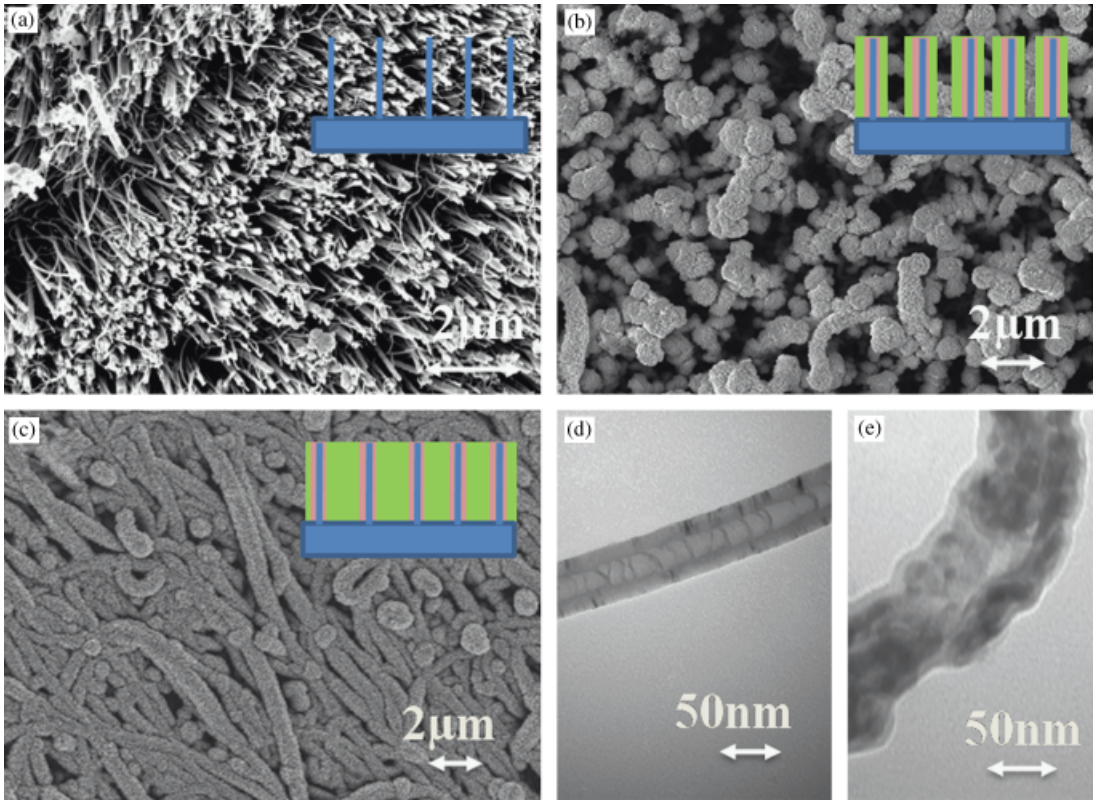

Fig. 4. Scanning electron microscopy images of (a) pure aligned carbon nanotubes (CNTs) arrays; (b) CNT–CFO–BTO coaxial rods (12 000 deposition pulses); (c) CNT–CFO–BTO composite fabricated at longer deposition time (24 000 pulses): the insets in (a)–(c) show schematic illustrations of the nanostructure; and (d and e) are transmission electron microscope images of a pure CNT nanotube and a CNT–CFO–BTO coaxial rod (taken from specimen in (c) via ultrasonic dispersion in ethanol), respectively. CFO, $CoFe_2O_4$; BTO, $BaTiO_3$.

Fig. 4(c)) using 24 000 pulses. Unfortunately, for thick coatings (24 000 pulsed), the CNTs no longer remained aligned. Schematics of corresponding nanostructures are shown in the insets of Figs. 4(a), (b), and (c). TEM images obtained from a pure CNT and a thick-coated CNT (separated from matrix via ultrasonic dispersion) are given in Figs. 4(d) and (e). These images clearly show after coating that the thickness of the tube was increased, and that the surface becomes roughened. We also observed in Fig. 4(e), that the coating was polycrystalline.

IV. Summary

We have successfully fabricated CNTs–CFO–BTO coaxial nanorod arrays, via PLD. The deposition conditions (oxygen pressure and deposition temperature) were found to affect the topography of the nanorod arrays considerably. Higher deposition temperatures and oxygen rich atmospheres improved the BTO crystallization, but made the surface nonsmooth. Longer deposition time (i.e., more laser pulses) filled the spaces between rods in the array, forming a BTO matrix with embedded CNTs–CFO fibers: a classical one to three composite structure.

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