Current Applied Physics 14 (2014) 1304–1311

Contents lists available at ScienceDirect

Current Applied Physics

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

Low temperature crystallization behavior of multi-walled carbon nanotubes/$Pb(Zr_{0.52}Ti_{0.48})O_3$ nanocomposite thin films through annealing in various atmosphere and duration control

Jin Kyu Han, Jin Ho Kwak, Jong Ok Kim, Sang Don Bu*

Department of Physics, Chonbuk National University, Jeonju 561-756, Republic of Korea

ARTICLE INFO

Article history:
Received 3 April 2014
Received in revised form
23 June 2014
Accepted 1 July 2014
Available online 10 July 2014

Keywords:
Carbon nanotubes
$Pb(Zr_{0.52}Ti_{0.48})O_3$
Nanocomposites
Oxides
Sol–gel methods

ABSTRACT

We report a successful fabrication of 300 nm thick carbon nanotubes and $Pb(Zr_{0.52}Ti_{0.48})O_3$ (CNT–PZT) nanocomposite thin films with annealing temperature as low as 500 °C in H_2/N_2 atmosphere. Realizing the thickness of CNT–PZT nanocomposite thin films down to few hundred nanometers is one way to reduce the operating voltage of its application to micro- or nano-electromechanical system. The field emission scanning electron microscopic and atomic microscopic analysis revealed that the nanocomposite thin films annealed in H_2/N_2 atmosphere exhibits the most favorable surface morphology with adequate perovskite (111) reflection of PZT based on X-ray diffraction analysis. The measured dielectric constant and loss tangent of the nanocomposite thin films show that the annealing duration of 30 min promotes the optimum dielectric properties of the nanocomposite thin films. Our observations suggest that the annealing atmosphere and duration are important parameters in controlling the crystallization behavior hence the dielectric properties of the nanocomposite thin films, which can be readily applicable to other nanocomposite thin films.

1. Introduction

Graphene or carbon nanotubes (CNTs) embedded in ferroelectrics matrix have attracted a considerable attention in recent years because of their possible applications to the development of nonvolatile memory devices, nanogenerators, and charge storage capacitors [1–5]. Baeumer et al. reported that the ferroelectric polarization in the $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thin film was reversibly switched by the graphene in the graphene/PZT nanocomposite [1]. They found that the polarization of PZT can alter the carrier type and density in graphene field-effect transistors (FET). Paruch et al. reported a controllable memory switching behavior of ferroelectric-FET consisting individual single-walled CNTs and ferroelectric films and the reversible remnant polarization of the ferroelectric film made such switching possible [3]. Mendoza et al. fabricated ferroelectric nanotubes using CNTs as a positive template by pulsed laser deposition [4]. They suggested that the registered array of nanostructures may provide a new class of micro- or nano-electromechanical systems (MEMS/NEMS) devices. Park et al. presented a nanocomposite generator consisting CNTs and ferroelectrics nanoparticles dispersed in polydimethylsiloxane, which was fabricated by mixing them at room temperature [5]. They demonstrated that their nanocomposite generator could convert the mechanical movement into electric energy whose output voltage is about 3.2 V. Among various CNTs embedded in ferroelectrics matrix, CNT-ferroeletric composites are noteworthy for their expected synergy effect in MEMS/NEMS between CNTs, having high electrical and mechanical properties, and ferroelectrics, having piezoelectricity with non-volatile polarization switching properties. However, the previously reported CNT-ferroelectric composites so far have been fabricated in bulk ceramic [5,6] or thick film [7] which needs a large operating voltage. One way to reduce the operating voltage of a device is to decrease the thickness of the film down to few hundred nanometers. Chemical solution deposition (CSD) method of CNTs-dispersed ferroelectric sol–gel precursor using spin-coating is so far the only way to realize the CNTs-ferroelectric nanocomposite films in such thickness, which was presented in our previous work [8]. The nanocomposite thin films of 300 nm thick films consisting of multi-walled CNTs (MWCNT) and PZT (denoted by CNT–PZT) was successfully prepared by using the CSD with spin-coating and conventional annealing process in O_2 atmosphere. Yet, a field-emission scanning

* Corresponding author. Tel.: +82 63 270 4264; fax: +82 63 270 3320.
E-mail addresses: sbu@chonbuk.ac.kr, sbu@jbnu.ac.kr (S.D. Bu).

http://dx.doi.org/10.1016/j.cap.2014.07.004
1567-1739/

electron microscopy (FESEM) observation revealed that the MWCNTs were not observable at the surface and cross-section of the CNT–PZT nanocomposite thin films. MWCNTs are known to be oxidized when they are heated above 700 °C in the air [9] which suggests that the MWCNTs in our CNT–PZT nanocomposite thin films were oxidized when the film is annealed. The oxidation temperature of MWCNTs in the nanocomposites appears to be affected by the annealing condition. For example, annealing of TiO_2–MWCNTs sol–gel solution resulted in the decreased oxidation temperature of MWCNTs down to 565 °C [10]. In our previous work, the oxidation temperature of MWCNTs in CNT–PZT nanocomposite thin films in O_2 atmosphere decreases the oxidation temperature to about 500 °C [8]. In this study, we investigated the influence of annealing atmosphere and duration on the stability of MWCNTs and crystallinity of CNT–PZT nanocomposite thin films. The synthesis of a well-crystallized CNT–PZT nanocomposite thin film embedded with stable MWCNTs is the first goal in realizing its application to NEMS/MEME devices and it is made in this work by firing the CNT–PZT nanocomposite thin films in H_2/N_2 atmosphere.

2. Experimental

2.1. Pre-treatment of MWCNTs

MWCNTs (Carbon Nano-materials Technology, Korea) are oxidized and purified by thermal and acid treatments, respectively, to remove the impurities such as amorphous carbon and catalyst particles [11]. As-grown MWCNTs are oxidized at 550 °C in the air to remove the carbonaceous impurities. The oxidized MWCNTs are mixed in 6 M HCl solution and stirred at 30 °C for 3 h. Then, the MWCNTs are neutralized with deionized (DI) water using centrifugation technique and dried on the hot plate at 80 °C. The HCl-treatment results in shortened and well-dispersed MWCNTs in a liquid. Then, the MWCNTs are immersed in the mixture solution of HNO_3 and H_2SO_4 solutions and stirred at 80 °C, called the functionalization process [12]. The functionalization treatment can produce carboxylic groups (–COOH), which can facilitate the bonding between the metal oxide and the surface of MWCNTs [10]. Fig. 1 presents the morphological, optical, and thermal analysis of the functionalized MWCNTs. Fig. 1(a) is a histogram showing that the average diameter of about 14.8 nm and their typical morphology obtained from FESEM is shown in the inset. Their aspect ratio (length/diameter) is 300–1000. This broad variation of the aspect ratio comes from the non-uniform shortening by the HCl-treatment. A Fourier transform infrared spectroscopy (FTIR) of the MWCNTs is shown in Fig. 1(b), which is used to identify functional groups on the surface of the MWCNTs. The peaks observed at 3445 cm^{-1} and 1720 cm^{-1} account for the successful functionalization of the MWCNTs with carboxylic groups. Fig. 1(c) shows the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the MWCNTs, measured in air range from 25 °C to 800 °C. A 98% weight loss of MWCNTs is observed when the MWCNTs were heated up to 650 °C indicating that the MWCNTs are well purified.

2.2. Fabrication of MWCNTs–PZT nanocomposite thin films

The CNT–PZT nanocomposite thin films are synthesized using sol–gel process and spin-coating technique. The CNT–PZT sol–gel solution is obtained by dispersing the functionalized MWCNTs in the PZT sol–gel solution, employing a 125 W ultrasonic treatment. The PZT sol–gel solution is synthesized from lead acetate trihydrate, zirconium *n*-propoxide, and titanium(IV) isopropoxide in 2-methoxyethanol as a solvent (Sigma Aldrich, USA) via sol–gel process [13–15]. The MWCNTs are added to the 2-methoxyethanol

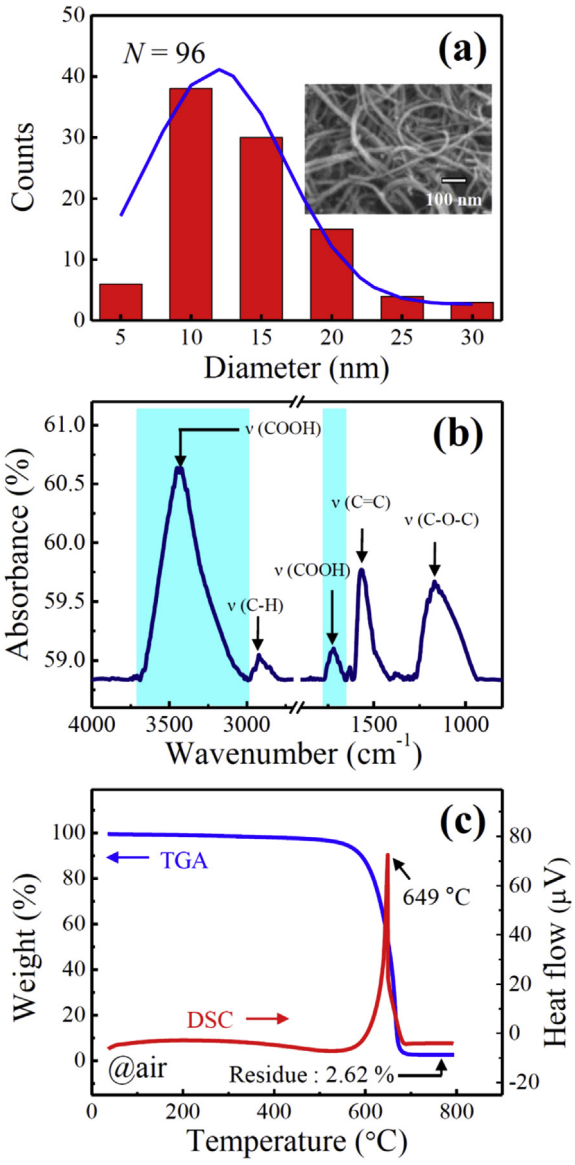

Fig. 1. (a) A graph of the MWCNTs diameterdistribution and inset image of FESEM images showing functionalized MWCNTs, (b) FTIR absorbance spectra, and (c) TGA and DSC spectra of functionalized MWCNTs.

with a ratio of 0.05 wt% and ultrasonicated for 1 h to prepare MWCNT solution. The MWCNTs solution is mixed with PZT sol–gel solution keeping the ratio of 10 wt% and dispersed by the ultrasonic method. No sedimentation or aggregation of the MWCNTs in the PZT sol–gel solution is observed at least for 48 h, which is a prerequisite for the well-dispersed MWCNTs in the PZT film. CNT–PZT sol–gel solution is spin-coated at 3000 rpm for 1 min on a Pt(111)/Ti/SiO_2/Si substrate. The coated CNT–PZT nanocomposite thin films is dried at 200 °C for 2 min and pyrolyzed at 400 °C for 5 min on a hot plate in the air. Then, the films is annealed at a 500 °C in a tube furnace under flowing atmospheres (N_2, H_2(4%)/N_2(96%), and O_2) at gas pressure of 1 MPa for various annealing duration from 5 min to 60 min.

2.3. Characterization of CNT–PZT nanocomposite thin films

The surface morphology of the CNT–PZT nanocomposite thin films was observed by FESEM and atomic force microscopy (AFM)