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Performance modulation of contact electrification nanogenerators by controlling the doping concentration of fluorine-doped tin oxide

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ABSTRACT

Contact electrification nanogenerators (CENGs) were fabricated, and their output performance was modulated by controlling the doping concentration of fluorine-doped SnO_2 (FTO) thin films. As the fluorine source content was increased from 0.8 to 1.2 mM during spray pyrolysis deposition, the electron concentration in the FTO thin film increased from 1.84×10^{20} to 5.22×10^{20} cm^{-3}, which is much larger than the Mott critical carrier concentration of SnO_2. The output voltage and current from the CENGs which were fabricated by the aluminium and FTO surfaces increased from 2.76 to 5.66 V and from 0.003 to 0.005 μA/cm^2 when controlling the electron concentration in the FTO layer from 5.22 to 1.84×10^{20} cm^{-3}. The modulation of the output performance of the CENGs originated from the change in work function of the FTO layer by Burstein-Moss shift.

1. Introduction

Harvesting energy from the environment has been a great concern for realizing the internet of things [1–3]. Among four main ambient energy sources, radiant, chemical, mechanical, and thermal energies, converting mechanical energy to electrical energy has received much attention because of the large available power density of about 10–1000 μW/cm^2, which can be obtained from abundant sources easily, regardless of environmental conditions [4]. Mechanical energy has been harvested using electromagnetic, magnetorestric, piezoelectric, and electrostatic mechanisms [5–9]. However, these methods have suffered from insufficient power conversion efficiency to operate wireless sensor networks, as well as complicated fabrication procedures based on micro-electro-mechanical system (MEMS) processes [4–8]. In addition, electrostatic energy harvesters need electret materials, which are difficult to fabricate and have short lifetimes [9].

Recently, triboelectric nanogenerators have been developed and have received much attention due to their incredibly large output voltage [10–12]. Triboelectric nanogenerators use a pair of electropositive and electronegative materials in triboelectric series [10–12]. However, most of these materials are organic materials, which have inherently poor reliability for long-term operation [12]. To circumvent these problems, mechanical energy harvesting using metals with a large difference in work functions [13]. When two metals with differing work functions are in contact, electrons can transfer from one to the other, and the opposite net charges grow larger and larger until the difference in electrostatic potential between the two metals reaches a particular value. This physical phenomenon is one of the contact electrification processes.

This mechanism could be used to fabricate the nanogenerators by pairing the materials with a large difference in work functions. The nanogenerators would have high reliability due to the robust nature of the inorganic materials. Therefore, we fabricated contact electrification nanogenerators (CENG) using pure aluminium metal and thin films of a degenerately doped metallic semiconductor, fluorine-doped SnO_2 (FTO). The output performance of the CENGs was modulated by controlling the work function of the FTO.

SnO_2 semiconductor was chosen because it has high mechanical, chemical, and thermal stability [14]. Especially, SnO_2 has a wide bandgap energy (E_g = 3.6–4.0 eV), and it is easy to control the charge carrier concentration by doping with fluorine or antimony [14]. The work function of the FTO thin film was controlled based on the Burstein-Moss shift by changing the doping concentration of the fluorine during the deposition of the FTO thin films by the spray pyrolysis method.

2. Experimental details

2.1. Experimental

To fabricate the performance-modulated CENGs, FTO thin films with variable doping concentration were deposited on a glass substrate using ultrasonic-assisted spray pyrolysis deposition. The source solution was prepared by dissolving 1.36 M of tin chloride ($SnCl_4$, Sigma

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Aldrich) in deionized (DI) water. Next, 0.8–1.2 mM of ammonium fluoride (NH_4F, Daejung Chemistry) was added as an *n*-type dopant to the solution. The solutions were stirred at room temperature for 24 h, which resulted in clear and homogeneous solutions. The glass substrates ($5 \times 5\ cm^2$) were cleaned with acetone, methanol, and DI water in an ultrasonic bath for 5 min and then loaded into a commercial ultrasonic-assisted spray pyrolysis deposition system (Nano SPD-TV500, Ceon, Korea). The FTO thin films were deposited at 430 °C using an N_2 carrier gas for 15 min.

To fabricate the CENGs, a 500-nm-thick Al thin film deposited on Si substrate was used as a counter electrode because Al has a low work function of 4.1 eV. Cu wires were attached to the Al and FTO surfaces to connect them with the measurement systems.

2.2. Characterizations

The structural properties of the FTO thin films were investigated using an atomic force microscope (AFM) and field emission-scanning electron microscope (FE-SEM). The optical and electrical properties of the FTO thin films were characterized using UV–vis spectroscopy and Hall effect measurements.

The output voltage and current from the CENGs were measured using a high-speed oscilloscope and picoammeter (Keithley 6485 Picoammeter). The contact and separation movement between two surfaces were carried out using an external mechanical strain system with a motorized cam. The output performance of the CENGs was investigated with respect to the applied strain frequency by controlling the rotation speed of the motorized cam in the range of 1–3 Hz. To avoid external noise from the environment, all of the output measurements were performed in a Faraday cage.

3. Results and discussion

Fig. 1 shows the evolution of the surface morphologies of the FTO thin films with different molar contents of fluorine. As shown in Fig. 1(a)-(e), the FTO thin films consisted of small granular domains with size of around 60 nm, which indicates polycrystalline structures. The nano-textured surface of the FTO can be beneficial for enhancing

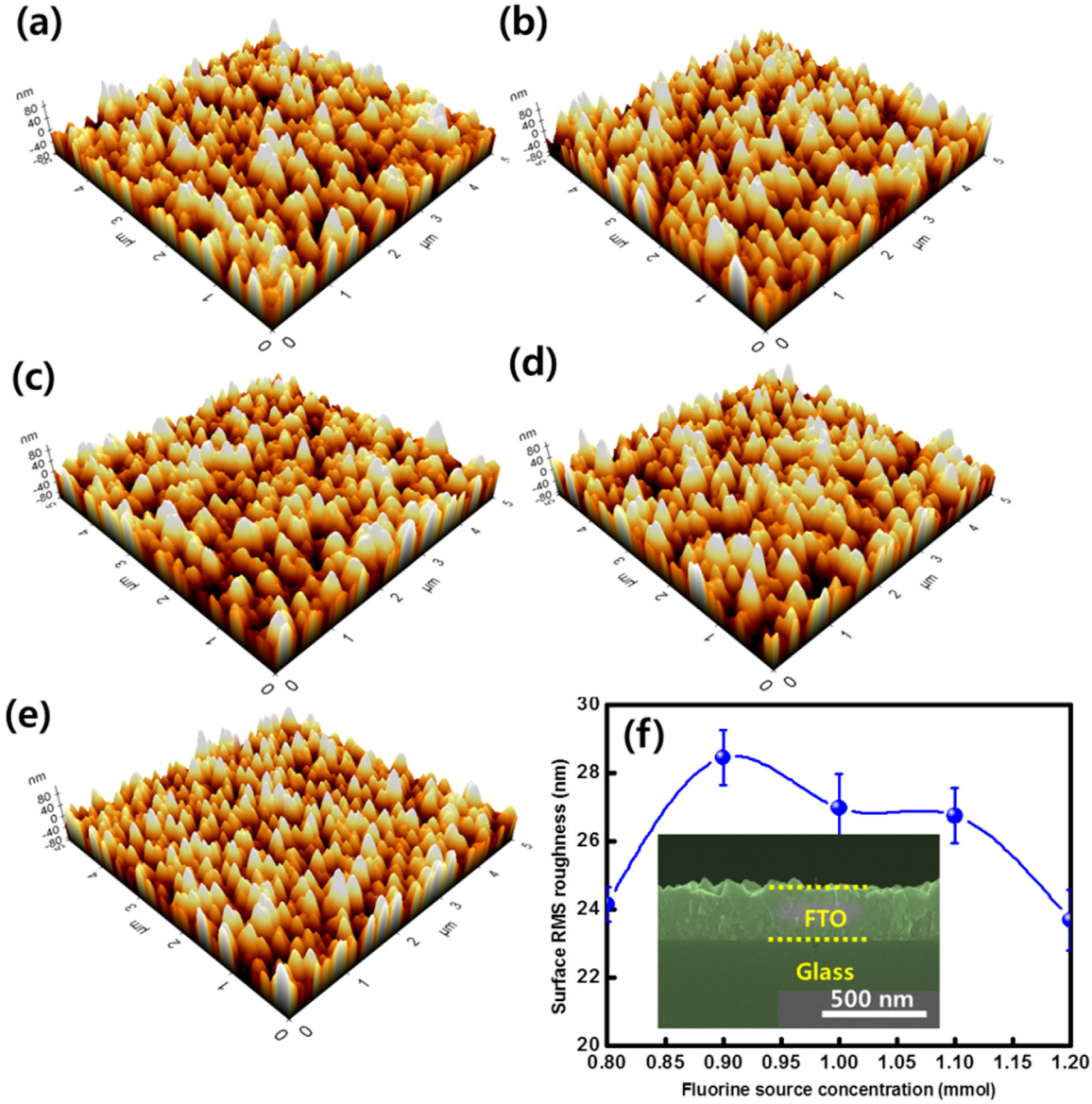

Fig. 1. AFM images of FTO thin film surfaces for different fluorine source content: (a) 0.8 mM, (b) 0.9 mM, (c) 1.0 mM, (d) 1.1 mM, and (e) 1.2 mM. (f) Surface RMS roughness of the FTO thin films with variation of the fluorine source contents. The inset shows cross-sectional images of the FTO thin films deposited by using 0.8 mM of fluorine source content on glass substrates.