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Calcination induced phase transformation of TiO_2 nanostructures and fabricated a Schottky diode as humidity sensor based on rutile phase

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ABSTRACT

The effects of annealing treatment on growth of TiO_2 nanostructures (Ns) on the structural and morphological properties were studied. The phase transformation also investigated in this study. TiO_2 Ns were fabricated on p-type (111)-oriented silicon substrates. Chemical bath deposition (CBD) method was employed to grow TiO_2 Ns on the Si substrate at different annealing temperatures (without annealing, 350, 550, 750, and 950 °C). The sample prepared at an annealing temperature of 550 °C had a high crystallinity. A metal–semiconductor–metal type humidity sensor device was fabricated by depositing Pt contacts on top of the optimal sample (the sample annealed at 550 °C) and the device working at room temperature, environmentally friendly features, and uncomplicated low-cost fabrication.

1. Introduction

Given the high stability, low cost, photo-active properties, and wide band gap (3 eV) of rutile TiO_2-based semiconductors, they are receiving significant interest and are considered as some of the most promising materials for optoelectronic devices characterization of rutile nanorods grown of p-Si (111). Rutile exhibits higher dielectric constant, high chemical stability, high hardness, excellent mechanical strength, high refractive index, transparency in visible region, and UV ray absorption rate [1,2]. The heat treatment of TiO_2 Ns had a great effect on its crystalline phase composition, grain size, surface morphology, and optical properties. Therefore, many studies have been done to understand the effect of annealing temperature on TiO_2 Ns. Elfanaoui et al. [3] grew TiO_2 thin films on glass substrates via CBD with $TiOSO_4$ as a precursor of Ti. The films were then annealed at a high temperature (500 °C–700 °C) in air for 1 h. The results showed that anatase-rutile transformation took place after annealing at 700 °C. Gao et al. [4] studied the effect of annealing temperature on the photoresponse of TiO_2 films prepared via the sol–gel process under nitrogen and oxygen at room temperature. The results showed that the anatase–rutile transformation partly took place at 550 °C, and anatase retained its structural stability until 500 °C.

Water vapor present in the atmosphere is defined as humidity which is highly variable and changes according to seasons, sea and land, etc. The controlling of humidity is significant for human comfort, industrial process control and storage of various goods [5], therefore the design and manufacture of humidity sensors has become one of the most active research fields. Metal oxide semiconductors such as TiO_2, SnO_2, ZnO, and Fe_2O_3, usually representing a property that the electrical conductivity varies with the composition of the gas atmosphere surrounding them, are the common and helpful sensing materials for gas and offer the potential for developing portable and inexpensive gas sensing device [6]. Among these metal oxide sensors, most of the progress work is focused on TiO_2 material due to its working at room temperature and adaptability to sense different gases after dopant addition [7]. This study aims to investigate phase transformation of TiO_2 Ns and the effects of annealing treatment on its structural and morphological properties. CBD was employed to grow TiO_2 Ns on the Si substrate at different annealing temperatures (without annealing, 350, 550, 750, and 950 °C). In addition, we proposed a novel type of humidity sensors based on the optimal sample.

2. Experimental details

The seed layers of TiO_2 were prepared with radio frequency (RF) reactive magnetron sputtering on p-type Si (111) substrates for 80 min, with a thickness of approximately 100 nm ± 5 nm. The target of TiO_2 is a disk with high purity (99.99%, 3 in diameter). To clean the TiO_2 disk surface, the target was presputtered for 5 min before deposition. Prior to the seed layer deposition, the Silicon substrates were cleaned with wet chemical etching using the RCA cleaning method that described in our previous work [8]. The substrates were deposited onto a heated substrate at 350 °C at an average deposition rate of 0.2 Å/s. Then, these seeded substrates were annealed at 550 °C for 1 h in air to improve crystallinity. The seeded Si substrates was cleaned in an

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ultrasonic bath with acetone solution, rinsed with distilled water, and dried with nitrogen gas. CBD was used to synthesize TiO_2 NRs by heating an acidic solution of $TiCl_3$, which contained an immersed seed layer of TiO_2-coated substrates. The growth conditions of TiO_2 NRs followed our previous procedure [8–12]. During the precipitation that initiated in the bath, a heterogeneous reaction occurred, and TiO_2 was deposited onto the substrate. The substrate coated with TiO_2 NRs was removed after 3 h, rinsed with distilled water, and dried with nitrogen gas. Then, these prepared samples were annealed at different annealing temperatures (without annealing, 350, 550, 750, and 950 °C) for 2 h in air to improve crystallinity and to decompose $Ti(OH)_4$ into TiO_2 [13]. The surface morphology and structure of the prepared TiO_2 NRs were characterized and analyzed with FESEM (Leo Supra 50VP, Carl Zeiss, Germany) equipped with an energy-dispersive X-ray (EDX) system and XRD (PANalytical X'Pert PRO MRD PW3040) with CuK_α radiation ($\lambda = 1.541$ Å). The optical properties were measured at room temperature with a Raman spectrometer (Horiba Jobin Yuon HR 800UV, Edi-son, NJ, USA) with Ar^+ as the excitation source operated at a wavelength of 514.55 nm (20 mW). The current–voltage measurements of the fabricated device were obtained using a computer-controlled integrated source meter (Keithley 2400) at room temperature.

3. Results and discussion

3.1. Surface morphology

Fig. 1 shows the FESEM images (at two different magnifications) of the TiO_2 Ns on p-type (111)-oriented silicon substrates with a TiO_2 buffer layer. These TiO_2 Ns were synthesized via CBD at different annealing temperatures. Fig. 1(a) (as deposited) shows that the sample consisted

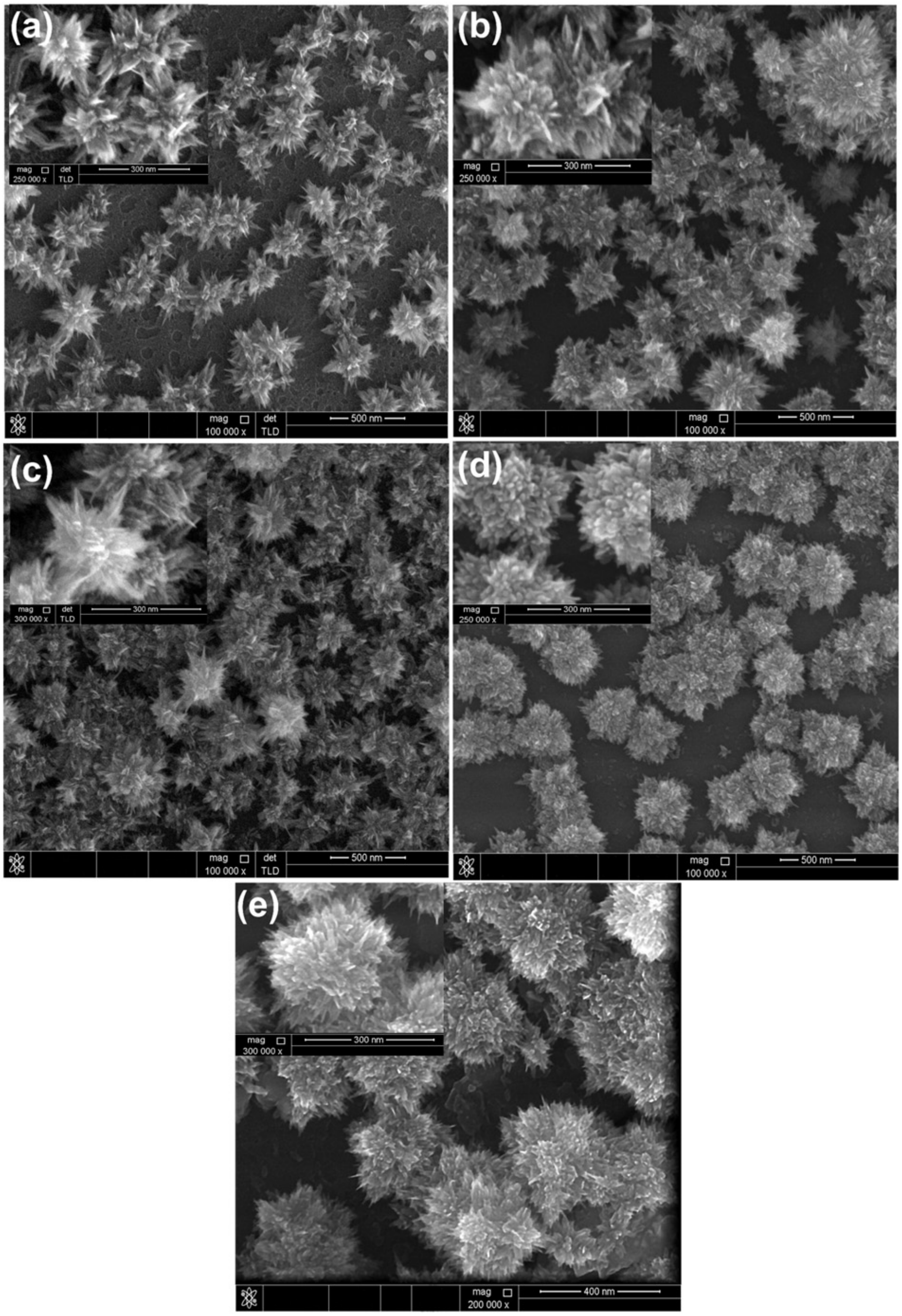

Fig. 1. FESEM image of the rutile TiO_2 Ns grown on silicon (111) substrate (a) as deposited, and annealed at (b) 350 °C, (c) 550 °C, (d) 750 °C and (e) 950 °C.