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Large enhancement of ultra-violet photoresponse of silicon-nanoparticle-embedded porous silicon thin films by rapid-thermal-oxidation treatment

Kuen-Hsien Wu *, Chong-Wei Li, Jung-Hsuan Liu

Department of Electro-Optical Engineering, Southern Taiwan University of Science and Technology, No. 1, Nan-Tai Street, Yungkang Dist., Tainan City 710, Taiwan

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ABSTRACT

The ultra-violet (UV) photoresponses of silicon-nanoparticle-embedded porous silicon thin films that were prepared from electrochemical-etching silicon substrates in an anodization process had been greatly enhanced by rapid-thermal-oxidation (RTO) treatment. Experimental analysis demonstrated that the optical bandgap energy of the formed nanoporous silicon (NPS) films increased from 1.6 eV to 3.5 eV after the RTO process. It was supposed that this bandgap-widening effect resulted from the size shrinking of Si-nanocrystals embedded in the oxidized NPS films and led to the large increase in UV responses. With RTO treatment of 90 s, the oxidized NPS films exhibited high UV photoresponses for incident light of wavelength between 300 nm and 400 nm, with peak photoresponsivity of 78 mA/W at 375 nm. In addition, under illumination of 350-nm UV light, the photodiode based on these RTO-treated NPS films got a 370-time larger photo-to-dark current ratio (PTDR) than that of one fabricated without RTO treatment. Therefore, oxidized NPS materials prepared by RTO treatment after the electrochemical-etching of Si wafers have high potential for development of Si-based UV photodetectors.

1. Introduction

Ultra-violet (UV) photodetectors have attracted increasing attention because of their extensive applications in monitoring UV intensity in atmosphere, nuclear reactors, paint curing, semiconductor processes, and biosensing systems [1]. Most of the solid-state materials currently investigated for the use of UV detection are focused on wide-bandgap compound semiconductors such as gallium nitride (GaN), silicon carbide (SiC) and zinc oxide (ZnO) [2]. However, fabrication of these devices requires high production cost due to the involved complex processes and expensive equipments. Besides, they are difficult to integrate with silicon circuits monolithically, thus limiting their commercial applications. Therefore, Si-based photodetectors fabricated by a simple and compatible process with a standard microelectronic technology is of high priority.

Nanoporous silicon (NPS) is a composite material in which nanocrystalline Si particles are embedded in the porous structures. According to the bandgap widening effect coming from the quantum-confinement phenomena in nano-structures, NPS is regarded as a wide-bandgap semiconductor and as a good candidate for development of Si-based short-wavelength optoelectronic devices [3]. For effective UV detection, the optical bandgap energy (E_g) of a material has to be larger than 3 eV to absorb UV light. Based on the theory proposed by Suemune et al. [4], the size of Si-particles in a NPS material must be reduced down to less than 2 nm to reach such a value of bandgap energy. Unfortunately, it is difficult to get uniform and stable NPS films with nano-structures of such small sizes from traditional electrochemical etching methods. Therefore, there had been few published literatures about NPS-based devices for UV detection.

Oxidized porous-silicon (OPS) formed by oxidizing PS films is an alternative silicon-based material for device applications. In various reports, photodetectors based on OPS obtained higher sensitivity than their unoxidized counterparts [5,6]. However, the UV responses of these OPS-based devices are quite low. It was thought that the sizes of the residual crystal-Si in these oxidized microporous structures were not small enough to absorb UV photons. On the other hand, another oxidized silicon-based material, silicon-rich oxide (SRO) that is a material with silicon nanocrystals embedded in a silicon-oxide matrix, has recently received much interest in applications of optical-sensing devices because of its high UV photoconductive properties [7,8]. UV-induced carriers transport in this material by multi-tunneling processes between silicon and silicon-oxide nanoparticles to generate photocurrent [9]. Nevertheless the fabrication process of SRO is basically Si-compatible, the synthesis technology for SRO thin films is also quite difficult.

In this paper, we proposed an easy approach to producing SRO-like materials directly from rapid-thermal-oxidation (RTO) treated NPS films that are prepared by electrochemical-etching of Si wafers. These RTO-treated NPS films exhibited greatly enhanced UV photoresponses as compared to NPS films without RTO treatment. In addition, photodetectors based on these developed RTO-treated NPS films achieved lower

* Corresponding author.
E-mail address: khwu@mail.stust.edu.tw (K.-H. Wu).

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dark current and larger UV-induced photocurrent than those of devices based on non-RTO-treated NPS films.

2. Materials and methods

NPS films were prepared from electrochemical etching p^+-type (100) Si wafers (with resistivity of 1–5 mΩ-cm) in an anodization process. Samples were anodized in hydrogen fluoride (HF)–ethanol (C_2H_5OH) solution in a Teflon cell with a Pt electrode. The concentration of etching solution was $HF:C_2H_5OH:H_2O = 3:1:1$. Because the etching rate will be too high to control the nanostructures of PS when using high anodic current, low etching current density of 10 mA/cm^2 was used to obtain PS thin films with nanoparticles during the anodic process. An etching time of 4 min was used to get a 3.85-μm thick PS film with a estimated etching rate of about 16 Å/s. The HF concentration of the etching solution is the key parameter to control sizes and distribution of Si-nanoparticles in the NPS films. In order to get smaller sizes of Si-nanoparticles and higher reproducibility, the concentration of HF was set as 30% of the etching solution in this work. For HF-concentration higher than 30%, the formed NPS layers will be too fragile and be prone to peeling from the Si substrates.

After the anodization process, samples were rapid-thermally oxidized in pure O_2 ambient at 850 °C in a RTO furnace with a ramping rate of 150 °C/s for heating and 80 °C/s for cooling. Since the PS films tend to be completely oxidized in a few seconds for a RTO temperature higher than 900 °C [10], an oxidation temperature of 850 °C was chosen to gain partial oxidation. Because the longer the oxidation time the smaller the size of the residual Si crystal and the wider the energy bandgap of the nanoparticle, increase of oxidation time will help to enhance the short-wavelength photoresponses. On the other hand, a longer oxidation time will result in a thicker oxide capping layer that will reduce the tunneling probability of photocarriers and thus the photocurrent. Therefore, the oxidation time was set as the primary parameter to control the degree of oxidation of NPS films, which determined the structures and sizes of nanoparticles in the oxidized NPS films.

To explore the UV-detecting capability of the prepared thin films, metal–semiconductor–metal (MSM) photodiodes based the oxidized NPS films were fabricated by depositing 200-nm thick aluminum (Al) interdigitated electrodes on the surfaces of the formed films via a metal mask. The device has an active area of about 1 cm^2 and an electrode with metal fingers of 0.2 mm in width with a space of 0.5 mm between two fingers.

The morphological analysis of prepared films was undertaken using a field-emission scanning electron microscopy (FE-SEM) (JEOL; JSM-6701F) operated at 10 kV. The photoresponses of prepared films were measured with a spectrometer (TRIAX-320) and a potentiostat meter (AUTOLAB; PGSTAT12). Analysis of the current–voltage (I–V) characteristics of devices was carried out by a HP-4155A semiconductor parameter analyzer.

3. Results and discussion

Fig. 1 showed the SEM images of the cross-sectional views of the formed NPS thin films without and with RTO treatment. As shown in Fig. 1(a), thickness of the NPS layer without RTO treatment was about 3.85 μm. It can be observed that the NPS film was embedded with uniformly distributed Si-nanoparticles. The average size of Si-nanoparticles can be estimated from Fig. 1(b) to be about 12 nm. According to Ref. [4], the bandgap energy E_g of porous silicon (PS) can be expressed as

$$E_g \approx 1.12 + \frac{h^2\pi^2}{0.245\, m_e d^2}(eV), \tag{1}$$

where m_e is the effective mass of electron and d is the pillar size of PS. In this case, d was set as 12 nm and E_g was calculated to be about 1.5 eV, which corresponds to the light wavelength of 830 nm. For an oxidation time of 30 s, the overall thickness of the RTO-treated NPS layer was not obviously changed while some of the embedded nanoparticles apparently became bigger, as shown in Fig. 1(c) and (d). It was supposed that some of the Si-nanoparticles in the RTO-treated NPS layer were partially oxidized and were transformed to be with Si-core/SiO_x-shell structures [11]. We can also observe that the amount of defects in the oxidized NPS films became much less, as a result of thermal annealing in the RTO process. For an oxidation time of 90 s, sizes of the oxidized

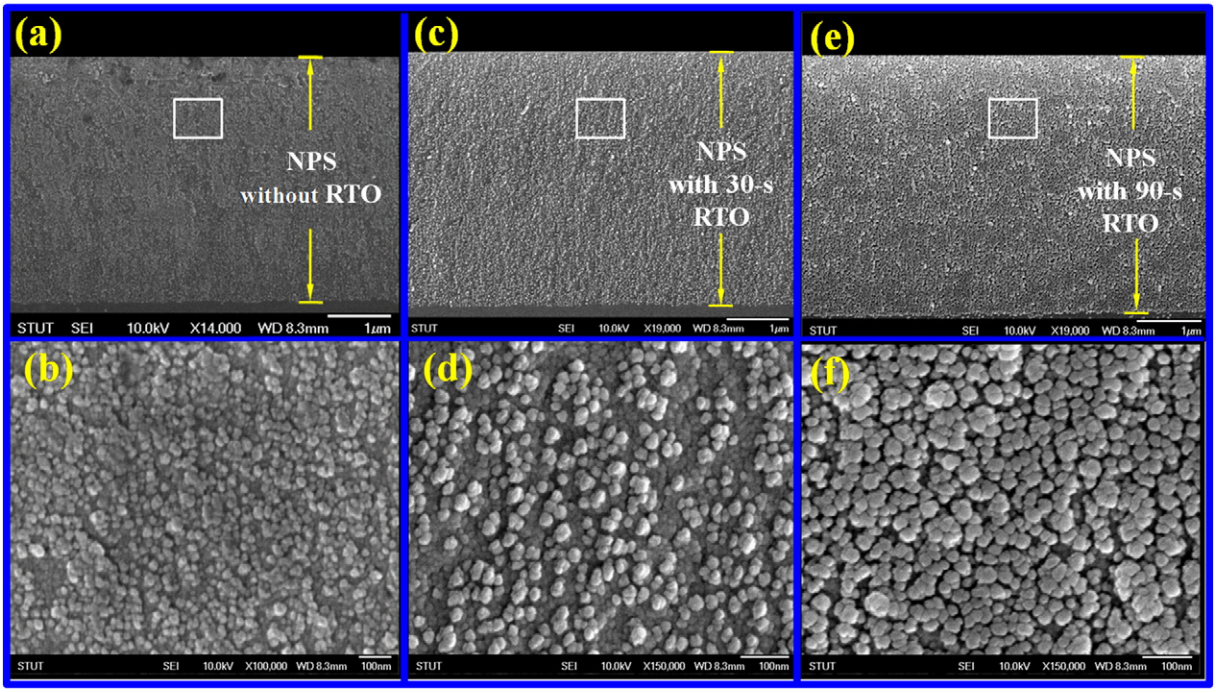

Fig. 1. SEM images of cross-sectional views of the nanoparticle-embedded porous silicon thin films prepared on Si substrates. (a) Without RTO treatment. (c) With 30 s-RTO treatment. (e) With 90 s-RTO treatment. Sub-panels (b), (d) and (f) show the zoom-in images of areas in the indicated white frames in Sub-panels (a), (c) and (e) respectively.