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Anneal effect on multipeak photoluminescence properties of porous silicon pillar arrays

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ABSTRACT

Porous silicon pillar array (PSPA) samples with broad photoluminescence (PL) from ~380 to ~800 nm were prepared by a hydrothermal etching method and found to be a hierarchical structure of silicon. The broad PL of PSPAs, which arises from four separate origins, could be tuned by varying annealing temperature and protective gas. In addition, the elemental compositions and their valence states change with annealing temperature and ventilation conditions. The results show that as the numbers of Si-H_x and Si-Si-Si bonds in the PSPAs decreased, different change of the intensities of red and pink PL bands. Moreover, at high annealing temperature, the PSPA samples contained only Si–O–Si bonds and only green and blue PL bands were observed. We attribute the pink and red PL bands to quantum confinement and quantum confinement/luminescence center emissions caused by the Si nanodots, and the blue and green emissions to two different luminescence centers associated with oxygen vacancies.

1. Introduction

Since the strong visible luminescence of porous silicon (PS) prepared by electrochemical and chemical dissolution method was first observed in 1990 [1], it has greatly stimulated interest in the optoelectronics. The preparation methods, structures, morphologies and optoelectronic properties of PS have been improved enormously over the past two decades [2–6]. For example, Chen et al. prepared PS with a uniform surface by a hydrothermal method and observed red and blue emission before and after annealing in air [3]. Peng et al. and Kotaro et al. prepared PS on silicon substrates at room temperature by localized chemical etching which exhibited two photoluminescence (PL) bands with peaks at ~635 and ~705 nm [4,5]. Lin et al. reported the vertical and single crystalline porous silicon nanowires and obtained a double-peak red PL band from ~600 to ~950 nm when excited by Ar laser [6]. Proposed applications of PS include light-emitting diodes, battery anodes, solar cells, sensors and biomedicine, which will have more influence for the future life [7–11].

Even though the phenomenon of as-prepared PS exhibiting red PL and annealed PS showing blue PL is commonly observed, the origins of these PL signals are still not fully understood [12,13]. Extensive experiments on this topic suggest that the red emission should arise from Si nanodots, because the red emission disappears when the Si nanodots in PS are removed by annealing [3,13,14]. To date, several PL emission models have been proposed to explain this luminescence phenomenon of fresh PS. Canham et al. and Proot et al. advanced the quantum confinement (QC) model, attributing the red emission to QC effect of Si nanodots, and calculating the change in emission induced by this QC effect [1,15]. Koch et al. used a surface-state model to interpret the red emission, proposing that surface states play the main role in this PL phenomenon [16]. Qin et al. propounded the quantum confinement luminescence center (QCLC) model and attributed the red emission to luminescence centers (LCs) in the oxygen layer [17]. In the QCLC model, the excitation of electron–hole pairs occurs mainly in the Si nanodots, and most of the excited electrons and holes are transported to the LCs where they recombine. Blue emission is typically observed from annealed PS samples, and the origin of this emission has been investigated experimentally and analytically [18–20]. For example, Chen et al. observed a blue PL band at ~430 nm along with an ultraviolet component at ~370 nm after rapid thermal oxidation of PS in air [3], and Xu et al. found the blue PL band has two peaks at ~420 and ~465 nm after the Si nanoporous pillar array was annealed in air at 700 °C [13]. But it still seems difficult to contrive a unified model to explain the physical mechanism of the emission of PS.

In this paper, we described the optical characterization of porous silicon pillar arrays (PSPAs), which are hierarchical Si composites in large-area structural regularity with blue, green and red emission bands. PSPAs were prepared by a hydrothermal etching method. To better understand the mechanism of PL in the

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PSPAs, we annealed PSPA samples at different temperatures under ventilation with N_2 and O_2.

2. Experiment

Heavily boron-doped, (111)-oriented single crystal Si wafers with a resistivity of 0.015 Ωcm were used here. PSPAs were prepared by hydrothermally etching the Si wafers in a solution of hydrofluoric acid (14 M) containing ferric nitrate (0.04 M) at 140 °C for 40 min. After etching, the wafer was copiously rinsed in deionized water and dried under N_2 gas at room temperature (sample A). Thermal annealing was performed in a tube furnace under a flow of dry N_2 gas at 200, 400, 600 or 800 °C for 3 h to get sample B, C, D and E, respectively. For comparison, a completely oxidized wafer was prepared by annealing in a tube under dry O_2 gas at 800 °C for 3 h, which is denoted sample F. The morphology and microstructures of samples were characterized by field-emission scanning electron microscopy (FE-SEM; JEOL, JSM-6700F), transmission electron microscopy (TEM; Philips, CM 200 FEG) and X-ray photoelectron spectroscopy (XPS; Axis Ultra, Kratos). Fourier-transform infrared transmission measurements (FTIR; Perkin Elmer, Paragon 1000) were carried out for samples A–E. PL spectra were recorded at room temperature on a Raman spectrometer (LabRAM, ARAMIS) with 325-nm laser excitation.

3. Results and discussion

Typical surface morphology of PSPA and high-resolution of the top of porous silicon pillar FE-SEM images of sample A are shown in Fig. 1(a and b), respectively. Different magnification TEM images of a single porous silicon pillar are shown in Fig. 1(c and d). The high-resolution TEM of pore walls reveal the presence of Si nanodots and oxygen layers (Fig. 1(e)). Sample A is a regular array composed of micron-sized, quasi-identical Si pillars. All the Si pillars and the transitional layer are densely nonporous structure. The average height of these well-separated Si pillars is ~3.6 μm and the average top-to-top distance is ~4.2 μm. The sizes of Si nanodots in the pore walls ranged from ~1.5 to ~4.5 nm (Fig. 1(e)). The average size of the Si nanodots calculated from high-resolution TEM investigation was ~2.96 nm (Fig. 1(f)).

The elemental composition and valence state of sample A is analyzed by XPS at room temperature, which also implied the existence of Si nanodots and oxygen layers. In the spectrum in Fig. 2(a), five peaks at ~102, ~153, ~285, ~533, and ~979 eV are observed, corresponding to the binding energies of Si_{2p}, Si_{2s}, C_{1s}, O_{1s}, and C (Auger), respectively. Therefore, the elements present on the surface of sample A are mainly Si and oxygenium (O). To analyze the valance state of silicon, the Si_{2p} peak was re-depicted at the localized horizontal ordinate scale and was found to be an asymmetrically broadened peak ranging from ~97 to ~107 eV, as shown in the inset of Fig. 2(a). Gaussian deconvolution resolved three peaks at ~99.7, ~101.6 and ~102.9 eV corresponding to the valence states of Si°, Si^{2+} and Si^{4+}, respectively [21]. All results imply that the oxygen layers in sample A are not uniform. In other words, the oxygen layer contains different species that generate these different oxidation valence states.

To clarify the changes in the PSPA samples induced by annealing, FTIR absorption spectra of samples A–E, annealed in N_2 at different temperatures, are shown in Fig. 2(b). There are in each spectrum two constant peaks located at ~800 and ~1080 cm^{-1}, and six peaks with variable intensity located at ~610, ~650, ~700, ~885, ~920 and ~980 cm^{-1}. The peaks located at ~800 and ~1080 cm^{-1} correspond to Si–O symmetric vibration and Si–O–Si asymmetric vibration modes, respectively, which further confirm the presence of oxygen layers. The peak located at ~610 cm^{-1} is attributed to the vibration of the Si–Si–Si mode of Si crystals, while the remainders are attributed to Si–H_x modes. Compared with sample A, the intensity of Si–H_x bands for sample B does not change too much, but for sample C the intensity of these bands decreases considerably. The reason might be that the Si nanodots of the as-prepared PSPA are covered with numerous H^+ ions that forming Si–H_x bonds with the Si wafer during etching by hydrofluoric acid which shows a positive correlation with the dangling bonds for Si nanodots. As annealing temperature increases, these Si–H_x bonds and dangling bonds are oxidized gradually and entirely at the end. When annealing temperature is

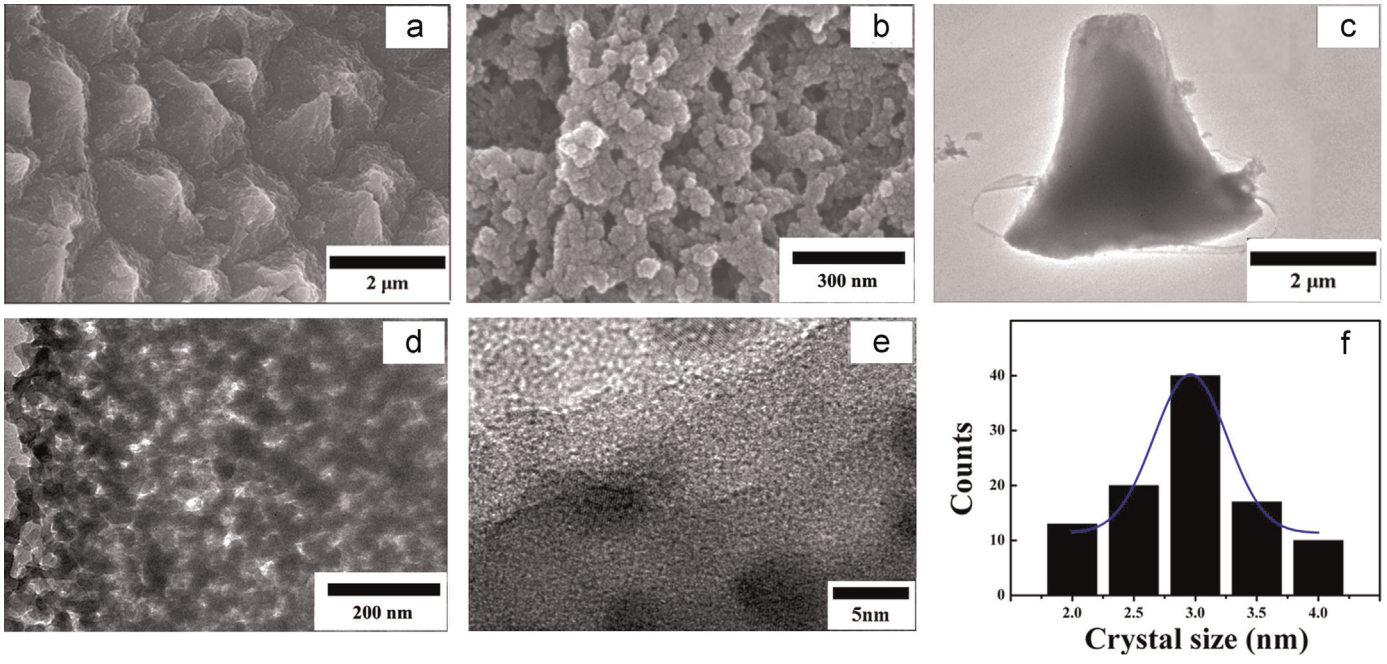

Fig. 1. (a) Typical surface SEM morphology of PSPA, (b) high-resolution SEM of a porous silicon pillar, (c) and (d) different magnification TEM images of a single porous silicon pillar, (e) high-resolution TEM image of pore walls with Si nanodots, and (f) size distribution of Si nanodots shown in (e).