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Effect of porous layer engineered with acid vapor etching on optical properties of solid silicon nanowire arrays

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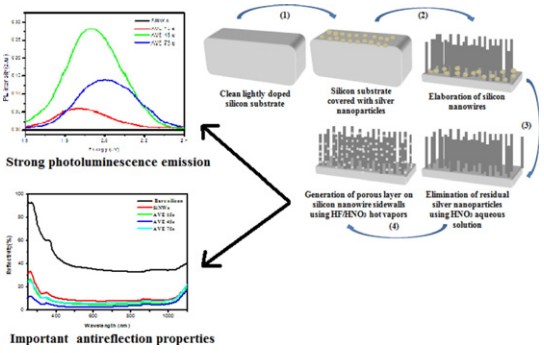
HIGHLIGHTS

- Fabrication of silicon solid nanowire arrays by silver assisted chemical etching.
- Generation of porous layer on solid silicon nanowires by acid vapor etching.
- Acid vapor etching treatment makes the Si nanowire highly photoluminescent.
- Si nanocrystallite (size and shape) and surface states determine the PL behavior.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, we report, for the first time, an investigative study involving the engineering of lightly doped porous silicon nanowire arrays (pSiNWs) by exposing solid silicon nanowire arrays (SiNWs) to an acid vapor emanating from HF/HNO_3 hot solution. SEM and TEM images exhibit vertically distributed SiNW arrays on the whole silicon (Si) surface with relatively smooth surface sidewalls. By submitting the SiNW arrays to Acid Vapor Etching (AVE), they become porous with a substantial decrease in their densities and lengths. Increasing etching duration leads to a higher porosity without affecting the wire diameter which remains almost constant nearly 100 nm. Exceeding a critical etching duration, a porous structure is observed superseding the SiNW structure. The morphological characterizations have been correlated to the optical properties. We note a blue shift of the strong visible photoluminescence (PL) bands after AVE treatment due to the decrease of the silicon quantum dots diameter (Si-QDs). UV–Visible measurement shows a decrease of the total reflectivity by 5% after AVE treatment.

1. Introduction

Silicon nanowires (SiNWs) have attracted much attention because of their unique optical and electrical properties compared to bulk Si. SiNWs are of great interest in various fields in the nanoscale essentially

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in electronics [1] catalysis [2] and solar cells [3]. Due to its simplicity and low expensiveness, the two step silver assisted chemical etching (Ag-ACE) method is the most used and studied technique to elaborate SiNWs on Si wafers having various properties [4]. The morphology of SiNWs can be affected by many parameters such as etching duration [5], HF/H_2O_2 ratio [6,7], Si orientation wafer [8], doping level [9,10] and temperature etching solution [11]. On the other hand, porous silicon (pSi) on flat [12–14] or textured wafers [15,16] has attracted a great deal of fundamental solid state physics studies since L. Canham discovered the visible room temperature luminescence in pSi [17]. Coated SiNWs with thin porous layer seem to be more interesting for optical applications due to the visible PL emission at room temperature. Obviously, it was found that the formation of porous structure on the SiNW sidewalls is strongly related to the doping level in the starting wafer. Backes and his collaborators state that the porous structure covers the wires only when silver-assisted chemical etching (Ag-ACE) treats highly doped samples exceeding 10^{16} cm^{-3} [9]. However, in our previous work, we found that SiNWs grooved in lightly doped monocrystalline Si (10^{14} cm^{-3}) exhibit relatively smooth sidewall surfaces without any PL emission [18]. The absence of such interesting optical properties hinders the route for SiNWs to be used as a starting material in optical devices. Recently some works have been conducted to overcome this impedes by submitting the solid SiNWs to post-treatments in order to generate a thin porous layer on their sidewalls. Ruey-Chi Wang et al. have fabricated uniform pSiNWs exhibiting a significant PL emission starting from lightly doped Si wafers having a resistivity ranging between 1 and 770 Ω·cm [19]. First, they synthesized a thin black layer of solid SiNWs using the Ag-ACE method. Afterwards, they submitted the obtained layers to the widely used electrochemical anodization technique for few minutes. Later on, Congli et al. [20] have founded that post treatment of solid SiNWs with the standard stain etching method in HF/HNO_3 solution leads to the appearance of the porous framework on the SiNW sidewalls. However, all these previous works have neglected the PL origin discussion. To understand the origin of the visible PL emission from pSi grooved on flat surface, many models have been proposed such as the hydrogenated amorphous Si [21], surface hydride [22], defects in amorphous Si oxide [23], interfacial oxide-related defects [24,25] and the quantum confinement [26]. Whereas, the interfacial oxide-related defects model proposed by Koch and developed by Prokes and the quantum confinement model proposed by Canham are still the most adopted models. On the other hand, Wolkin et al. have concluded that both quantum confinement effect and chemical surface passivation simultaneous determine the electronic states of Si-QDs and they have proposed a theoretical model that considers the effect of both QC and surface states [27]. Whatever the elaboration method, it is noticeable that the pSi layer is widely considered as SiNCs network forming a mix-up of Si-QWs and Si-QDs [28–33]. It has been shown in several previous works that the PL property of SiNCs is not only related to the size but also to their shape relative proportion where Si-QWs contribute to lower energy although they are smaller in diameter comparing to the Si-QDs. In a recent work, Ramirez-Porras et al. have refined the model suggested by Wolkin and they proposed the so-called "smart quantum confinement model" which allows them to correlate the shape (cylindrical or spherical) and size distribution to their contribution to the total PL emission [34,35]. Two different transitions are considered. The first is the band-to-band (B-B) transition originating from QC in Si-QWs and Si-QDs. The second corresponds to the localized-to-band (L-B) transition due to the presence of localized defect states within the band gap of the Si coming from NBOHCs in the interface Si/SiO_x [25].

In this work, we present a novel approach to generate porous layer on the sidewalls of lightly doped solid SiNWs. It consists to expose SiNW arrays to acid vapors emanating from hot HF/HNO_3 aqueous solution. In the remaining manuscript, we name this post-treatment as acid vapor etching (AVE). This approach is simple because it is an electroless technique, rapid since its processing does not exceed few minutes and inexpensive because it uses some cheap chemicals and beakers. Based on structural and optical characterizations, we present the effect of AVE exposure duration on the SiNWs morphology correlated to their room temperature PL emission. Since the pSi layer properties coated on the SiNW sidewalls are considered similar to that grooved on a flat surface, we adopt the smart quantum confinement model to interpret the room-temperature PL behavior.

2. Experimental

2.1. Synthesis of SiNWs

The substrates used here are Czochralski (Cz) solar grade, (100) oriented, p-type boron doped Si wafers, having a resistivity of 14–25 Ω·cm and a thickness of 450 μm, for the c-Si. The wafers were cleaned in CP_4 acid solution (HNO_3: 64%, HF: 16%, CH_3COOH: 20%) for 30 s, then rinsed with deionized water and dried. This step had removed approximately 10–15 μm of Si from both sides. SiNWs were prepared by the widely used two steps Ag-assisted chemical etching. First, the samples were immersed in an aqueous solution of 4.8 M HF (40 wt%) and 0.02 M $AgNO_3$ for 60 s to form Ag nanoparticles dendrites films. Then, the Ag-deposited wafers were etched to form the SiNWs in the mixture of 4.8 M of HF (40 wt%) and 0.1 M of H_2O_2 (30 wt%) solution for 5 min. Subsequently, the as-prepared dark-brown samples were immersed in concentrated nitric acid (HNO_3) during 5 min to remove silver particles, rinsed copiously with deionized water and dried. The color of the samples turns homogeneous black.

2.2. Engineering of pSiNWs arrays

The as-prepared black samples are exposed to acid vapors, issued from an acid mixture of HF/HNO_3. The HF/HNO_3 mixture was placed in a polypropylene container. The container was introduced in a thermostatic bath, wherein a Pt100 thermometric probe controls the temperature. The total volume of HF/HNO_3 solution used for the present investigation was 50 ml. The HF/HNO_3 volume ratio and etching temperature were fixed to 1/3 and 60 °C respectively. Silicon substrates were initiated at a height of 1 cm from the acid mixture. The etching duration varies from 15 to 100 s. Fig. 1 shows the experimental set-up of the HF/HNO_3 etching step. After etching, the samples are rinsed in deionized water then blown by nitrogen until they dried.

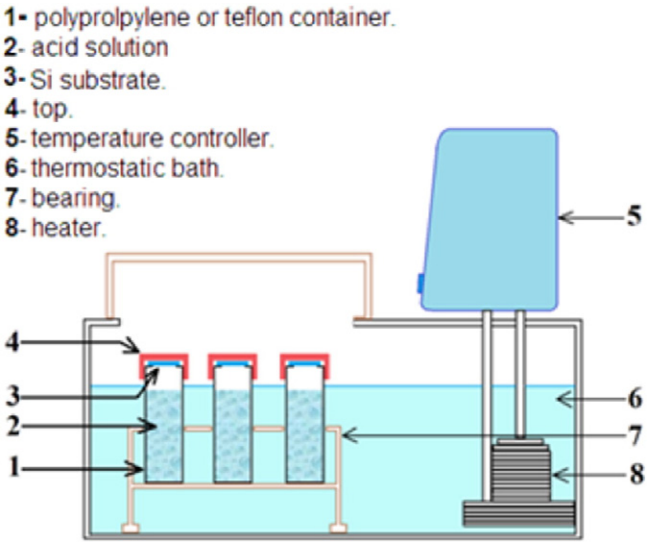

Fig. 1. Schematic illustration of the experimental set-up of the AVE technique.