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Self-purification model for metal-assisted chemical etching of metallurgical silicon

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ABSTRACT

Metal-assisted chemical etching (MaCE) of metallurgical-grade silicon (MG-Si) has improved the purity of MG-Si (~99%) to close to solar-grade (~99.9999%) by removing metal impurities during the successful preparation of porous silicon nanowires (SiNWs). A new etching principle is proposed to explain the different levels of chemical reduction between various metal impurities with pore formation during etching. This model provides chemical insights into the relationship between dissolved metal ions and pores evolved during the formation of SiNWs.

1. Introduction

Semiconductor nanowires (NWs) with a diameter range ≤200 nm have been under intensive study in the past decades [1,2]. Substantial efforts have been devoted to investigating their distinct physical [3,4] and chemical [5] properties derived from the confined size and/or geometry. Some novel properties make semiconductor nanowires attractive for a broad spectrum of applications in solar cells [6], photodetectors [7], and sensors [8]. Recently, new methods for enhancing the optical/electrical/chemical activities of NWs have focused on integrating nanoscale morphological features, e.g. surface roughness [9], particle decoration [10], and pores [11]. Generating pores inside NWs, for instance, greatly improves the stability/capacity of lithium ion batteries because porous NWs can accommodate a large amount of the mechanical strain developed during repeated charge/discharge cycles while providing a large surface area for full lithiation [11]. The presence of pores also suppresses phonon propagation, further reducing thermal conductivity of NWs, which is beneficial for thermoelectric applications [12].

To date, metal-assisted chemical etching (MaCE) has mostly received attention for its simplicity, room-temperature processing, and industry-friendly benefits [13–15]; moreover, porous SiNWs have only been obtained from ultrapure, electronic-grade Si (EG-Si, purity >99.999999%) [16,17]. We have reported that the MaCE of metallurgical Si (MG-Si, purity ~99%, ~US$ 2/kg) produced porous SiNWs which were improved to near solar-grade (SG-Si, purity ~99.9999%) by removing impurities inside MG-Si [18]. This is normally not possible by traditional acid leaching methods [19]. Understanding the specified etching mechanism is therefore crucial for the possibility to rationally design/control porosity in the formation of MG-SiNWs and replace the costly 'Siemens' process [20] for purifying MG-Si. Here, we propose a new chemical etching model to explain different reduction levels among various kinds of metal impurities and their impacts on the formation of SiNWs after dissolving into the etchant.

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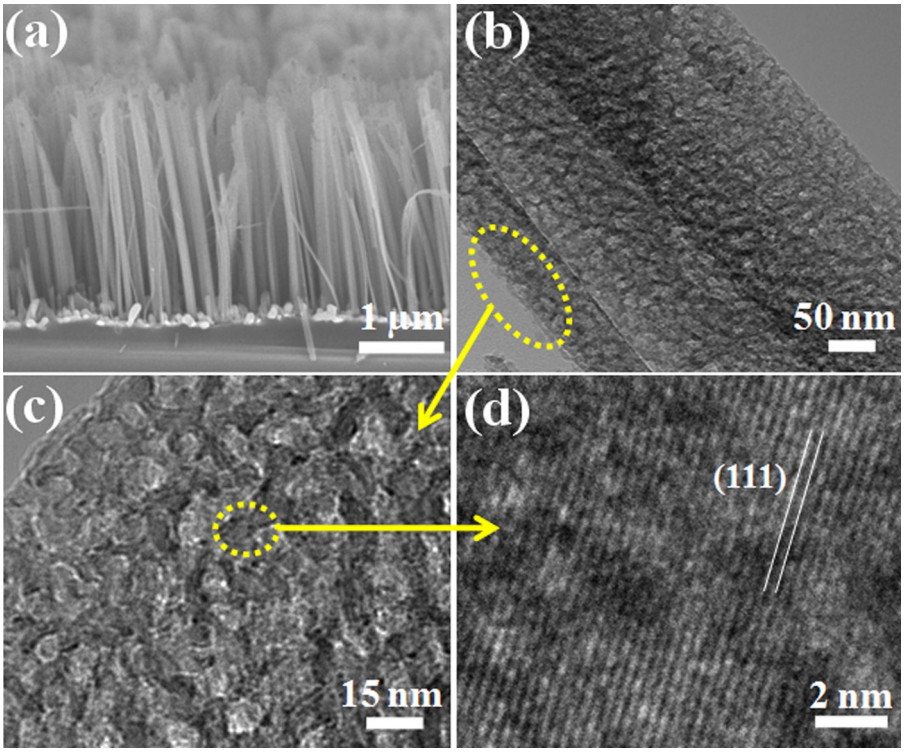

Fig. 1. (a) SEM image showing MG-SiNWs fabricated by MaCE, (b) TEM image of MG-SiNWs (MaCE followed by HNO_3 treatment). (c, d) are the magnified views.

2. Results and discussion

The fabrication process of MG-SiNWs has followed a two-step MaCE method suggested by Peng *et al.* [14] MG-Si pieces were first loaded with dense Ag nanoparticles (AgNPs) by galvanic displacement; then, they were etched in an HF and H_2O_2 solution to allow AgNPs to drill nanopores deep into MG-Si. SiNWs were spontaneously formed due to the contiguous Ag film. Meanwhile, metal impurities, such as silicides [21], were dissolved upon exposure to the acidic etchant solution. Fig. 1(a) shows a scanning electron microscopy (SEM) image of MG-SiNWs. The etching speed (0.1 μm/min) for the formation of MG-SiNWs is much slower than that for EG-SiNWs [0.36 μm/min, see Supporting Information (SI) Fig. S1]. Fig. 1(b,c) show transmission electron microscopy (TEM) images of MG-SiNWs after removing Ag catalysts by a HNO_3 cleaning step. The MG-SiNWs reveal a uniform distribution of pores in sizes of 8 – 15 nm. Fig. 1(d) confirms the presence of crystalline phase between pores.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was adopted to quantify the impurity levels inside MG-Si before and after etching. Three different treatments of MG-Si powders, i.e., MaCE, MaCE + HNO_3, and HF + H_2O_2/HNO_3 without Ag (acid wash), are compared in Fig. 2(a); the exact values of impurity concentration in non-treated and treated MG-Si powders are shown SI, Table S1. Simple acid washing (not MaCE) removed 60 – 95% of the original impurities for all kinds of metals such that the MG-Si purity was improved from 99.74 to 99.975% (see SI Table S1). For MaCE treatment, AgNPs penetrated into MG-Si particles with depths of 1 – 2.5 μm (see SI Fig. S2). Fig. 3(d) lists the reduction ratios of metal impurities between MaCE and MaCE + HNO_3 samples compared to the acid-washed samples. Most metals (from Ba to Ni) normally revealed a higher removal ratio than the acid-washed sample because large surface areas were exposed to the etchant, owing to the nanowire morphologies formed by MaCE. However, Ca is an exception because it reacts with HF to form CaF_2 precipitates, which were then trapped or absorbed into the porous MG-Si. In contrast, MaCE cannot effectively remove metals nobler than Pb. The Cu concentration in the MaCE sample is even higher than that in the acid-washed one. The additional HNO_3 cleaning step further purifies the MG-Si powders to 99.9884%, reaching near solar-grade. The purification enhancement by the HNO_3 step was remarkable for Ca, Pb, and Cu but was relatively weak for Zn, Cr, and Ni.

To understand the upgrading effect based on the relationship between the reduction of metals and formation of porosity in MG-SiNWs, there are several features to be considered. First, heterogeneous distribution of metal impurities is notable inside MG-Si. Different solid solubilities of impurity elements in Si mainly cause a non-uniform distribution of metal impurities. During solidification of Si from the molten state, impurities, e.g. Fe, with concentrations exceeding their low solid solubilities likely segregate along the grain boundaries [21,22]. Since the grain boundaries are morphological defects in the crystal structure, the nucleation of AgNPs preferentially occurs at these defect sites, which are energetically more favorable for etching. As a result, a higher Si dissolution rate is observed at grain boundaries than other areas (see SI, Fig. S3); the strong removal of Fe (see Table S1) is thus reasonable during MaCE.

Second, the effect of dissolved metal ions on MaCE of MG-Si should be understood in-depth. During the 'drilling' process of AgNPs, metal impurities are dissolved upon exposure to the acidic etchant. Fig. 3(a,b) show that many tiny metal particles spread over the surfaces of MG-SiNWs. Most nanoparticles were identified to be Ag using the energy dispersive X-ray spectrometer installed in the SEM (SEM-EDX) (see SI Fig. S4). Previous work has shown that Ag catalysts located around the bottom of the nanowire are partially dissolved, diffuse upward, and renucleate on the sidewalls of nanowires so as to initiate new etching pathways [17]. Since there are a large number of defective sites near the dopants in heavily doped Si ($10^{19} – 10^{20}$ cm^{-3}), many AgNPs renucleate at the NW surfaces. Here, the doping level of MG-Si is low (B: 6.6×10^{17} cm^{-3} and P: 3.0×10^{17} cm^{-3}). Therefore, it is reasonable that the metal