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Synthesis of nanopyramidal SnO_2 by hydrothermal method on nanostructured silicon substrate with some study about the effect of silicon morphology

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Abstract

In this study, we grew nanopyramidal SnO_2 hydrothermally at low temperature on both bare and nanotextured silicon substrates. Plasma etching of silicon is accomplished for the evolution of nanotextures on silicon substrate which are called silicon nanograsses. Comparing Scanning Electron Microscope (SEM) images of the synthesized SnO_2 nanopyramids on two bare and nanotextured silicon substrates, reveals that there are considerable differences between growth on these substrates such as better uniformity. Therefore, application of silicon nanograss substrates in the synthesis of SnO_2 nanostructures can improve growth process and this promotes various applications of this material in the different science fields. We also survey the effect of seed layer on growth of SnO_2 nanopyramid.

Keywords: SnO_2 nanopyramid; Silicone substrate; Silicon nanograss; Nanostructure; Hydrothermal synthesis.

1. Introduction

Because of unique electronics, optical and thermal characteristics, one-dimensional nanostructured metal oxides are very attractive. Among these nanostructures SnO_2, as a n-type semiconductor with a wide band gap (E_g=3.6 eV, at 300 K), has been used in many applications, such as catalyst and gas sensing [1-2]. Up to now, several growth methods such as thermal evaporation, anodic alumina membrane, laser ablation and hydrothermal synthesis have been used for the evolution of tin dioxide nanostructures [2].

Among these methods, hydrothermal or growing crystal from solutions is very attractive for a variety of materials and morphologies, because of its simplicity, low cost, ambient pressure, safety and less harmful for the environment (growth from aqueous solution instead of organic solvent). Another advantage is that, its synthesizing temperature is typically reasonable (moderate, under 200°C) and low reaction temperature allows fabrication of nanostructures on flexible plastic substrates which can be easily integrated with organic optoelectronic device [3].

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Arrangement of nanostructures on the substrate can be controlled by adjusting number of nucleation centers, which can be accomplished by deposition a seed layer on the substrate. Seed layer deposition can be done before growing films or nanostructures by hydrothermal method. In previous works, morphology differences between bare and seed-coated substrates are surveyed. Typically, seed layer promotes growth of dense nanorods because of supplying abundant nuclei for this process. Other results show that hydrothermally controlling density of grown nanorods is accomplished via a variety of the substrate pretreatments. Therefore, seed layer is a simple and convenient method for achieving adjusted and oriented growth of nanostructures. Obtained results depend on the properties of the seed layer, which can be affected by the fabrication process and condition of used substrate. In some cases, grain size and orientation are different due to fabrication of seed layers on different substrates [3]. In this paper we grow SnO_2 nanopyramids on nanotextured silicon substrate called silicon nanograsses. These nanograsses with height of about 2 to 3 µm and width of 30 to 100 nm, have a variety of applications such as solar cells, field-effect transistors, electrochemical sensors, increasing the effective area of the gas and biological sensors, etc [4].

We grow SnO_2 nanopyramids hydrothermally on a silicon nanograss substrate and investigate effect of this substrate on the growth process of SnO_2.

2. Experimental

2. 1. Materials and methods

All the chemical reagents used in this study were of spectroscopic grade and used as received without further purification. The morphology of the obtained materials was examined with a field emission scanning electron microscope (FE-SEM model KYKY-EM3200).

In this study, we use two substrates, one is bare silicon and the other is silicon nanograss substrate. After cleaning the substrate using RCA#1 solution (NH_4OH:H_2O_2:H_2O, 1:1:5), it is blow dried. Silicon nanograss formation is achieved by modification of a DRIE process which is reported elsewhere [5]. This DRIE process consists of successive steps of passivation and etching sub-cycles like Bosch process. Passivation sub-cycle is done in the presence of a gas mixture of O_2, H_2 and SF_6 with proper plasma condition while etching sub-cycle is performed in the presence of SF_6 with suitable plasma condition. Grass formation could be considered as the one of undesirable side effects of DRIE in the evolution of high aspect ratio features. The vertical etching process, however, can be adjusted to obtain grass-free structures at both micro and nanoscales with high aspect ratios. On the other hand, by using proper flows of gasses during the passivation and etching sub-cycles one can manipulate vertical or spaghetti-like Si nanograsses with a height of 2-3 µm and width of 30 to 100 nm with the aspect ratios of the order 50. For such structures, in the passivation step (Figure 1-a), a mixture of H_2/O_2 gases with typical flows of 100 and 85 sccm and a trace value of SF_6 is used, whereas for the etching step, SF_6 is used as the inlet gas with typical flows of 10–40 sccm (Figure 1-b).

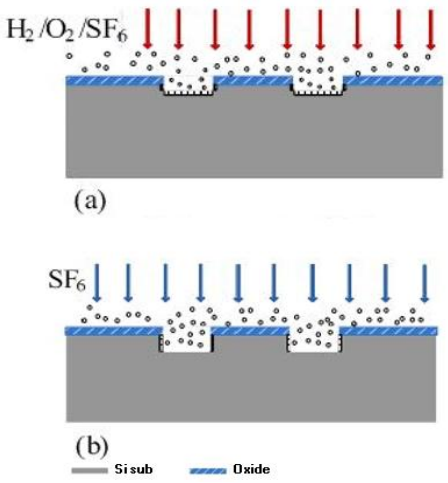


Fig. 1. DRIE different sub-cycles (a) passivation sub-cycle, (1-b) etching sub-cycle. These cub-cycles should be done successively several times.

The plasma power and duration of the passivation sub-cycle set at 150 W and 50 seconds and for the etching sub-cycle, we set them at 130 W and 10 seconds

respectively [4, 6, 7, 8]. In the next step, a thermal oxide with a thickness of 0.1 µm is grown on both bare and silicon nanograss substrates. Figure 2 shows the SEM image of silicon nanograss substrate.

Before hydrothermal synthesis, it is better to deposit a seed layer on the substrate. It can be done as follows: Stannic acid gel ($SnO_2.nH_2O$) is obtained by adding a $SnCl_4.5H_2O$ solution (1 M) to a $NaHCO_3$ solution (1 M) in a drop wise manner. Obtained white precipitate is collected and washed with sufficient amount of distilled water for removing chloride ions. Then we disperse this precipitate in distilled water and adjust pH of solution with ammonia solution to10.5 [9]. Then solution is spin coated 4 times on the silicon nanograss substrate and after each time substrate is dried at 30-40°C. At the end of process, annealing is done at 450°C for an hour.

Another method for creating gel for spin coating of seed layer is preparing a mixture of $SnCl_2.2H_2O$ (0.05 M) in 10 ml absolute ethanol. Then the mixture is stored on a hot plate at 40-50°C for 10-30 min. This process is done in seed layer of bare substrate and after spin coating of the gel, annealing is done for 2 hours. It can be noted that existing a seed layer is important, but production method of this layer is not so important.

SnO_2 nanopyramids were synthesized hydrothermally using a mixture of 4 ml $SnCl_4.5H_2O$ (0.5 mol/l), 10 ml NaOH (5 mol/l) and 80 ml ethanol/water solution. Then, this solution is stirred for about 10 min [10]. After preparing solution, samples are floating in it and kept at 90°C for 15 hours.

Equation (1) shows hydrothermal reaction. In this equation OH^- is produced from NaOH solution.

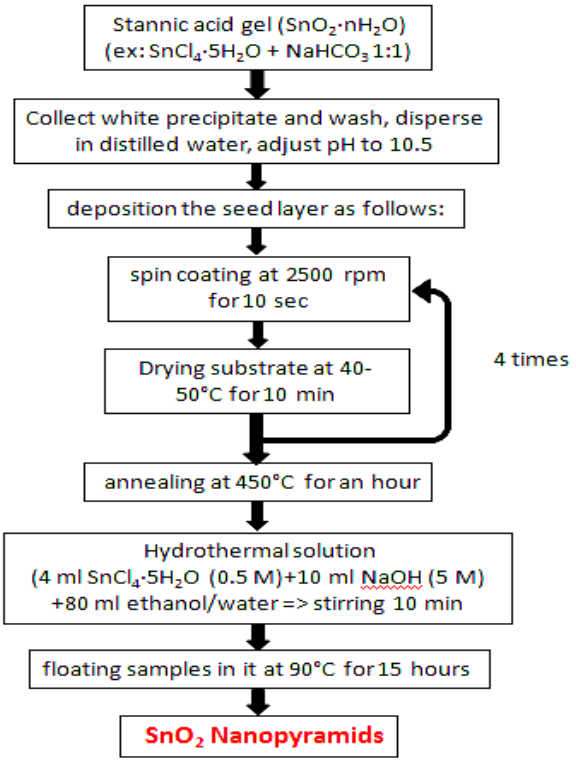
$$SnCl_4+OH^- \rightarrow [Sn(OH)_6]^{2-} \qquad (1)$$

$Sn(OH)_6]^{2-}$ is a gel and can be used as the hydrothermal solution for SnO_2 growth. In a hot oven, precipitate accumulates after a few hours and growth process completes. Time of growth process affects height and density of nanopyramids while temperature has an important effect on the size of nanostructures. All preparation steps of nanosized SnO_2 are shown in Scheme 1.

3. Results and Discussion

Figure 2 shows SEM image of a silicon nanograss substrate. Comparing with a bare substrate, effective surface area is highly increased.

Figure 3 shows SEM images of the synthesized SnO_2 nanostructures on two silicon substrates. It can be observed that, these nanostructures are pyramid shape. Part (a) of this figure shows synthesized SnO_2 nanopyramids on silicon nanograss substrate while part (b) shows these nanostructures on the bare silicon. As it is obvious from parts of this figure, SnO_2 growth on nanotextured silicon substrate is more regular.



Scheme 1. All preparation steps of SnO_2 nanopyramids

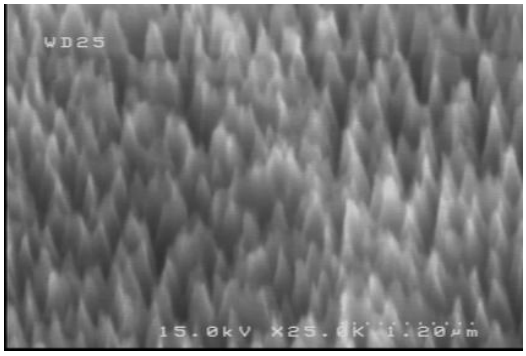
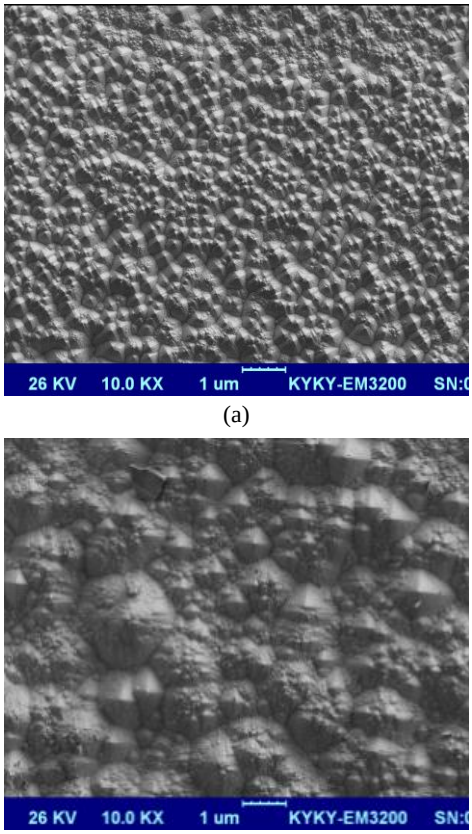


Fig. 2. SEM image of silicon nanograss substrate

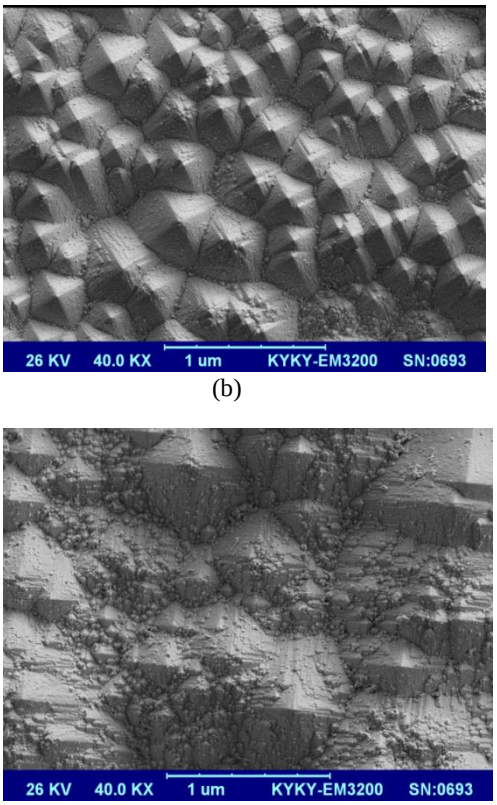
Figure 4 shows a higher magnification of Figure 3. Like the previous, part (a) of Figure 4 shows synthesized SnO_2 nanostructures on nanotextured silicon substrate and part (b) shows synthesize on the bare silicon. It can be seen in part (a), apex of nanopyramids is sharper while on each pyramid faces there are some other nanostructures, which enhance the performance and the effective surface of the substrate drastically. In part (b) of Figure 4, formation of nanopyramids is very erratic and is similar to a destroyed region. Therefore, application a nanostructured base, like silicon nanograss substrate, improves morphology of a growth nanostructure on it and this improves various applications of this material in the different science fields.



(a)

(b)

Fig. 3. SEM images of SnO_2 nanopyramids on (a) silicon nanograss substrate and (b) bare silicon substrate



(a)

(b)

Fig. 4. SEM images of SnO_2 nanopyramids on (a) nanograss silicon substrate and (b) and on bare silicon substrate

3. Conclusions

We successfully synthesized SnO_2 nanopyramids on two types of bare and nanograss silicon substrates using hydrothermal synthesize method. We used plasma etching of silicon for the evolution of nanograsses on the silicon substrate. Obtained results from synthesized tin dioxide (SnO_2) nanostructures indicated that growth on the silicon nanograss substrate is better and more uniform. It seemed that defects which are made during nanograss formation on silicon substrate, decreases mismatch between silicon and SnO_2 lattice, therefore formation of primary seed layer improves which leads to the more uniform SnO_2 growth. For high-quality growth of tin dioxide nanostructures, silicon nanograss substrates are good options to achieve this goal.

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