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Hydrofluoric acid free synthesis of macropores on silicon by chemical vapor deposition and their photoluminescence

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Abstract

A novel hydrofluoric acid (HF) free atmospheric pressure chemical vapor deposition (APCVD) method has been developed to synthesize macropores on silicon. Field emission scanning electron microscopy (FESEM), X-ray powder diffraction (XRD) and energy-dispersive X-ray (EDX) spectrum indicate that the composition of macropores with the diameters of several hundred nanometers is silica. Moreover, the mechanism of the formation of the macropores has been preliminarily discussed. The photoluminescence (PL) spectrum of the macropores shows a broad violet emission band with the peak position at 402 nm, which is related with the defects of silica.

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Keywords: HF free; Macropores; APCVD; PL

1. Introduction

Since the macroporous silicon was first reported in 1990 by Lehmann and Foll [1], great attention has been focused on it due to its significant applications such as electronics, photonic crystals and biomedical devices [2–8]. Among them, the photoluminescence (PL) of porous silicon is the one that has attracted most of the attention [9,10]. Red, green and blue emissions could be obtained by adjusting the erosion process of porous silicon. Numerous models have been proposed to explain its PL, including quantum confinement [11], surface state [12] and defects in the oxide [13]. Previously, the macroporous were usually synthesized by anodic etching of silicon in a hydrofluoric acid (HF)/H_2O electrolyte under backside illumination [1,14–18]. However, it is inevitable to use very toxic HF as electrolyte. Recently, Liu and Wang reported a HF free hydrothermal etching approach to synthesize porous silicon using $Bi(NO_3)_3$ and ammonia as reactants [19]. As a whole, the previous reports for the synthesis of macroporous silicon were based on the wet chemistry route with the disadvantages of toxicity and contamination for environment.

Herein, we develop a simple and novel approach for the synthesis of macropores on silicon by an atmospheric pressure chemical vapor deposition (APCVD). To our best knowledge, it is the first report for the synthesis of macropores on silicon by the vapor phase route. Moreover, the PL of macropores on silicon has been investigated.

2. Experiment

The experiment was carried out in an alumina tube. SnO_2 and C powders with the molar ratio of 2:1 were put into an alumina boat and then the boat was positioned in the center of the alumina tube. An n-type (1 1 1) silicon wafer with a resistivity of about 0.01 Ω cm was first cleaned by the standard RCA process and then placed in the downstream with a distance of about 10 cm from the source materials. Furthermore, a stream of pure Ar was passed through the tube at a flow rate of 1000 standard cubic centimeters per minute (sccm). Meanwhile, the furnace was heated to 1200 °C at a rate of 5 °C/min, and maintained at

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this temperature for 3 h. Finally, the furnace was cooled down to room temperature at a rate of 5 °C/min. For comparison, the same experiment at 1150 °C was also carried out.

The obtained samples were characterized by X-ray powder diffraction (XRD) using a Rigaku D/max-ga X-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The images of the samples were obtained by a field emission scanning electron microscope (FESEM, FEI SIRION) with an energy-dispersive X-ray (EDX) spectrometer. PL examination was measured with a detector PMT and ACTON SpectraPro 2500i using a He–Cd laser with a wavelength of 325 nm as the excitation source.

3. Results and discussion

Fig. 1a shows the FESEM image of the sample prepared by APCVD at 1200 °C. From the image, many macropores with the diameter of several hundred nanometers have been observed on the surface of the silicon wafer. And the morphology of the macropore is regular circle. The EDX spectrum of macropores is shown in Fig. 1b. Three peaks for Si, O and Sn are found in the spectrum. Fig. 1c shows the cross-sectional view FESEM of the macropores. As can be seen, the depth of the macropore is about 500 nm. Furthermore, several particles have also been observed in the macropores. Three elements Si, O and Sn are also detected by EDX performed on the particles as shown in Fig. 1d. Fig. 1e shows the FESEM image of the sample subsequently treated by 5% HF. As can be seen, the macropores are disappeared, which indicates that the composition of macropores is SiO_2 combined with the results of EDX spectra as shown in Fig. 1b and d. Moreover, there are many small particles on the wafer. The EDX spectrum of the particles as shown in Fig. $1f_1$ reveals that two elements Si and Sn are detected. However, there is only one element Si to be found in the EDX spectrum as shown in Fig. $1f_2$, which is performed on the margin of the particle. Fig. 1g is the XRD pattern of the as-grown sample, there are two components: Si (the substrate) and Sn. As a result, the composition of the particle should be Sn.

In order to clarify the formation mechanism of the macropores, the same experiment at 1150 °C was carried out. Fig. 2a shows the FESEM image of the sample prepared by APCVD at 1150 °C. From the image, lots of small balls with the diameter of several hundred nanometers have been observed on the surface of the silicon wafer. Fig. 2b shows the EDX spectrum of the sample. Three peaks for Si, O and Sn are found in the spectrum. The intensity of Sn in Fig. 2b is much higher than that in the previous spectrum. Moreover, the XRD pattern of the sample as shown in Fig. 2c indicates that the sample is composed of three components such as Si, Sn and SnO_2. After the treatment by HCl, it is found that all the balls are disappeared, and there are many macropores on the surface of the silicon wafer, as shown in Fig. 2d.

Fig. 3 is a schematic illustration of the process for the formation of macropores on silicon. It is believed that the process for the formation of the macropores can be divided into four steps. At the beginning, SnO_2 is reduced to SnO vapor by reaction (1) at 1200 °C (Fig. 3a). And then, SnO clusters are carried on the Si substrate downstream from the source materials by Ar flowing. As we known, SnO is metastable and can be decomposed into SnO_2 and Sn by reaction (2). Therefore, the Sn balls will be formed on the Si substrate (Fig. 3b):

$$SnO_2(s) + C(s) = SnO(v) + CO(v) \quad (1)$$

$$2SnO(v) = SnO_2(s) + Sn(1). \quad (2)$$

From the tin–silicon binary phase diagram, Sn–Si alloy will be easily formed from Sn ball and Si substrate due to the low melting point of about 232 °C. Then, the Sn–Si alloy may react with the residual O_2 in the alumina tube to form something that can be easily evaporated. Therefore, the macropores of silicon are synthesized due to the evaporation of Sn–Si alloy (Fig. 3c). Finally, the macropores of silicon are oxidized by the residual O_2 (Fig. 3d). To clarify it, quartz slice instead of silicon wafer is used as the substrate. There are no macropores to be found on the quartz slice. Furthermore, a 0.22 μm thick oxide can be formed on silicon under dry O_2 oxidation at 1100 °C for 3 h [20], and in our process there are much less O_2, so it cannot form a 0.5 μm thick oxide if there are no macropores. These evidences indicate that the macropores of silicon are first formed and then oxidized into silica. Moreover, with the decrease of the temperature (1150 °C), it may be difficult for the formation of something that can be evaporated. Certainly, the above explanation for the formation of silica macropores is somewhat conjectural and phenomenological, and extensive work is underway towards its further clarification.

The optical property of the sample prepared at 1200 °C is characterized by the PL using a He–Cd laser with an excitation wavelength of 325 nm. A broad violet emission band with the peak position at 402 nm can be observed, as shown in Fig. 4. The peak possibly originates from the weak O–O bonding of silica [21].

4. Conclusions

In summary, we have developed a one-step and HF free APCVD method to synthesize macropores with the diameter of several hundreds nanometers on silicon wafers. The formation and evaporation of Sn–Si alloy play the critical role on the synthesis of the macropores. Moreover, the macropores shows a broad violet emission band with the peak position at 402 nm, which is related with the defects of silica. The approach presented here is of scientific and technological importance for the synthesis of macropores on silicon wafers.