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Silicon nanorods prepared by glancing angle catalytic chemical vapor deposition

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ABSTRACT

Vertically oriented amorphous and microcrystalline Si nanorods grown on different substrates were successfully obtained by Cat CVD with the glancing angle incident silane flux at low temperatures. The influences of the substrate type, substrate temperature, post treatment and hydrogen dilution on the microstructure of Si nanorods were investigated. The density and diameter of nanorods are varying with the substrates. The hydrogen dilution of silane dominates the crystallization of Si nanorods rather than high substrate temperature at 550 °C and annealing at 900 °C in nitrogen for 6 h. The crystallized Si nanorods with crystalline volume fraction, Xc, of 0.55 were achieved under a low substrate temperature of 140 °C.

1. Introduction

Silicon nanorods as a one-dimensional semiconductor material have attracted considerably attention for the potential application in nanoscale electrical devices, bioanalytical sensors and nanoscale solar cells [1–4]. The Si nanorods prepared by different technique approaches such as vapor–liquid–solid (VLS) process, nanoscale lithography, catalytic electrochemical process, molecular beam epitaxy and glancing angle deposition (GLAD) etc. have been extensively studied [3–6]. Most of the above techniques require high temperature or complicated processes. In this paper, we developed a new technique by combining catalytic chemical vapor deposition (Cat-CVD) with GLAD to prepare crystallized silicon nanorods at low temperatures.

During the GLAD process, the incident vapor flux, from thermal source, electron beam, sputtering and pulsed laser, impinges the substrate from an oblique angle (>60°), which leads to the atomic-scale shadowing effect [5]. The nanorods and isolated nano-columnar structures of metals, semiconductors and oxides etc., can be designed and sculpted by adjusting the oblique angle and the rotation of the substrate in GLAD process [3,5]. Amorphous Si nanorods can be prepared by physical vapor deposition (PVD) technique which restricts the application of Si nanorods to optoelectronic devices. The catalytic chemical vapor source, widely applied to the microcrystalline Si thin films preparation, is superior to the other sources of electron beam, sputtering and pulsed laser etc. in GLAD process because of the low temperature crystallization [8].

In this paper, we used the combination technique of Cat-CVD with GLAD to produce crystallized silicon nanorods at low temperature for the further application in radial pn junction nanorods solar cells. The influence of substrate type, substrate temperature, annealing treatment and hydrogen dilution ratio on the microstructure of the silicon nanorods are presented.

2. Experimental

Silicon nanorods thin films were deposited by the glancing angle catalytic chemical vapor deposition. The schematic structure is shown in Fig. 1. A spiraled tungsten wire with the 0.5-mm-diameter was assembled on the filament holder. The background pressure of the deposition chamber was 2×10^{-4} Pa. The filament temperature was fixed at 1950 °C. In order to get parallel incident flux, the tungsten wire was placed at 9.2–11 cm away from the substrate. Furthermore, to ensure the large mean free path of radicals and thus direct incident of Si flux to the substrate, the deposition pressure was controlled below 0.1 Pa. The rotation speed of the substrate is 15 rpm. The reaction gases of silane and hydrogen passed through the hot filament and generated the radicals flux with incident angle α about 80–85° arrived at the substrate. The c-Si (111), stainless steel, ITO glass and quartz were used as the substrates. The substrate temperature (T_s) was varied from 140 to 550 °C. The silane flow rate was fixed at 8 sccm. The hydrogen gas flow rate was varied from 0 to 30 sccm. The preparation parameters are listed in Table 1.

The morphologies of the silicon nanorods in top view and cross section structure were observed by field emission scanning electron

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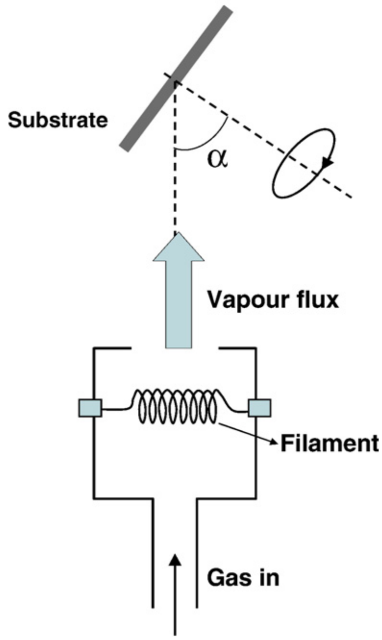

Fig. 1. Schematic of the glancing angle catalytic chemical vapor deposition method. α is the oblique angle.

microscopy (SEM, JEOL-JSM-7401F). Raman scattering spectra were measured by using HR800 (325 nm and 514 nm) to evaluate the film crystalline volume fraction.

3. Results and discussion

3.1. Silicon nanorods deposited on the different substrates

Fig. 2 shows the cross-section and top-view SEM images of A-1 series samples deposited on Si (a, b), stainless steel (c) and ITO (d) substrates with T_s of 140 °C in a same run with thickness of 600 nm. The vertical nanorods are well formed on silicon substrate shown in Fig. 2(a). The Si nanorods exhibit typical characteristic of columns prepared by GLAD technique with out pattern. The nanorods build up randomly. In the initial growth stage, some nanorods stopped growth at a certain length. On the other hand, the diameters of nanorods were broadened gradually during growth and some nanorods joined together but final nanorods are separated. These phenomena are due to the shadowing effect [5]. Shadowing occurs in the direction parallel to the incident flux. The short columns might be eventually ended as the high columns is near by and fall into the shadowed regions of the neighboring columns. The large incident angle will make the columns continue broadening until they chain together. As a

Table 1
Preparation parameters of Si nanorods thin films.

Name	Substrate	T_s (°C)	SiH_4 (sccm)	H (sccm)	α	Anneal (°C/h)
A-1	c-Si Stainless steel ITO glass	140	8	0	85°	
A-2	c-Si	300	8	0	85°	
A-3	c-Si	550	8	0	85°	
B-1	c-Si	140	8	0	80°	
B-2	c-Si	140	8	0	80°	900/6
C	c-Si, quartz	500	8	8	80°	
D	c-Si, quartz	140	8	16	80°	
E	c-Si, quartz	140	8	30	80°	

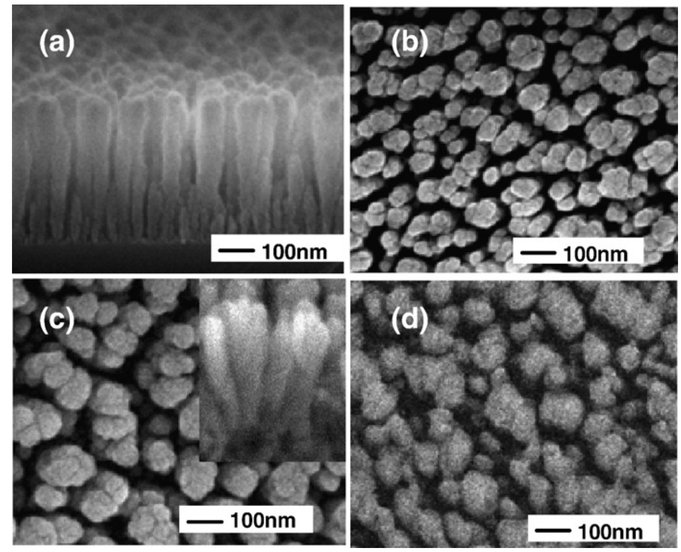

Fig. 2. SEM micrograph of Si nanorods grown on (a, b) c-Si, (c) stainless steel and (d) ITO substrates.

result, the diameters of the columns increase. The diameters of the columns vary between several tens and ~100 nm. The average diameter of nanorods is about 80 nm which is similar with that of the silicon nanorods deposited by electron beam evaporation at a glancing angle of 85° reported by Zhao etc [3]. The average density of the nanorods determined from Fig. 2(b) is about 3×10^{10} cm^{-2}.

The morphology of the nanorods is correlated with the initial nucleation condition. It is seen that the nanorods on the stainless steel (Fig. 2(c)) and ITO (Fig. 2(d)) exhibit the larger diameter and smaller density than that of on Si substrate. The average size and density of the nanorods on stainless steel and ITO are about 100 nm and 8×10^9 cm^{-2}, respectively. This is because that nucleation on the c-Si substrate is easy to happen. The similar phenomenon was observed on the microcrystalline silicon thin film grown [7].

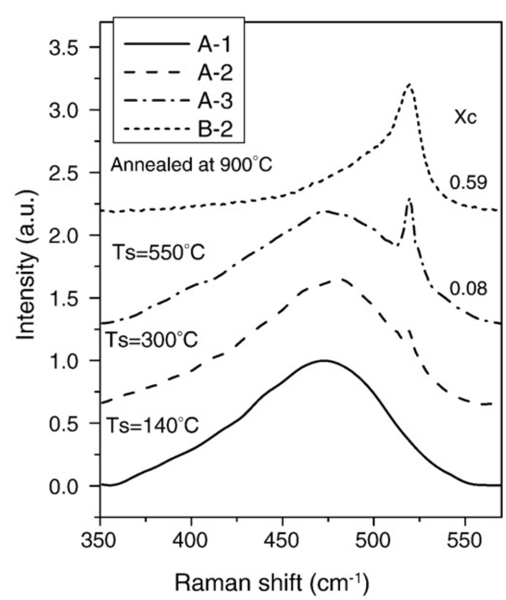

Fig. 3. The Raman scattering spectra for films deposited with different T_s. Sample B-2 annealed at 900 °C is also included.