Fabrication of CdS Nanorods on Si Pyramid Surface for Photosensitive Application

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ABSTRACT: It is the first time that cadmium sulfide (CdS) nanorods have been fabricated on silicon (Si) pyramid surface by the hydrothermal reaction method. In our work, the Si pyramid morphology is able to increase the adhesion between the CdS seed layer and Si wafer. Hence, it is critical for CdS nanorods to grow successfully. During the fabrication process, the glutathione is used as the complexing agent for the formation of the CdS nanorods. By continuously adjusting the experimental conditions, the thickness of the CdS seed layer, the concentration of the glutathione, and the temperature and time of the hydrothermal reaction, the optimal condition for CdS nanorods growth on Si pyramid surface is 80 nm seed layer, 0.2–0.3 mmol glutathione, 200 °C, and 1.5 h. The Cd and S elements have a ratio of 1:1.03 from the energy-dispersive spectroscopy test, which is in agreement with the stoichiometric composition of CdS. The CdS nanorods have a bandwidth of 2.22 eV through the optical absorption spectra. The photosensitivity response test results reveal these CdS nanorods on the Si pyramid structure have an obvious photosensitive effect. From the analysis, the CdS nanorods can grow on any morphological Si surface if the adhesion between the CdS seed layer and the Si surface is strong enough.

INTRODUCTION

One-dimensional nanostructures have emerged as one of the most promising candidates for optoelectronics field due to their reduced optical reflection, high light-emitting surface, and so on. CdS with a direct band gap of 2.42 eV is a kind of important material in optical, electronic, and optoelectronic fields. To prepare CdS nanostructures with different morphologies, such as nanorods, nanospheres, and nanoflowers, various methods have been employed, including the hydrothermal method, chemical vapor deposition process, thermal evaporation, vapor–liquid–solid-assisted process and template method. However, most of the CdS nanostructures prepared with these methods are powder, which are difficult to fabricate on some substrate surface. Also, the powder of the CdS nanostructure cannot be used for element directly. To solve this problem, researchers have successfully fabricated the CdS nanostructures on an ITO glass substrate, fluorine-doped tin oxide coated glass surface, Al2O3 surface, and so on. Silicon (Si) is one of the most important semiconductor substrate; however, the fabrication of CdS nanostructure on the Si surface is rarely reported due to the poor adhesion between the CdS nanostructure and the polished Si surface. In our previous work, we fabricated countless nanopillars on the Si surface to increase the roughness, and the CdS nanorods have been synthesized on the Si nanopillars surface successfully, but the fabrication of Si nanopillars is costly and time-consuming. The Si pyramids, which are used widely for commercial Si solar cells as an antireflective layer, can be easily obtained by the anisotropy corrosion of monocrystalline silicon using an alkaline...
solution. Also, various kinds of nanostructures, such as Si nanowires, nanoporous, and nanopillars, are fabricated on the Si pyramid surface to micro-nano-surface texture.

In this work, the CdS nanorods have been prepared on the Si pyramid surface for the first time. The Si pyramids about 2−4 μm are brought in to increase the roughness of the surface. The CdS nanorods grow on the Si pyramid surface via the hydrothermal method with the assistance of glutathione. The glutathione is used as a complexing agent during the fabrication process, which plays an important role in the formation of the CdS nanorods. The fabrication condition of the CdS nanorods is optimized, and the composition and photosensitive properties of this structure have been researched. We also found that the adhesion between the CdS seed layer and the Si surface is the key to the growth of CdS nanorods.

RESULT AND DISCUSSION

The thickness of the seed layer is one of the important factors for the growth of CdS nanorods. According to our experiments, the CdS nanorods fail to grow on the Si pyramid surface due to poor adhesion. We change the sputtering time from 2 to 6 min, corresponding to the seed layer thickness from 40 to 120 nm. Figure 1 records the morphology of the CdS nanorods with different seed layer thicknesses under the same growth conditions of 0.3 mmol glutathione, 200 °C for 1 h: (a, b) 40 nm, (c, d) 80 nm, and (e, f) 120 nm.

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Figure 1. Top-view and cross-sectional SEM images of the CdS nanorods with different seed layer thicknesses under the same growth conditions of 0.3 mmol glutathione, 200 °C for 1 h: (a, b) 40 nm, (c, d) 80 nm, and (e, f) 120 nm.

Figure 2. Top-view SEM images of the CdS nanorods with different glutathione concentrations under the same growth conditions of the 80 nm seed layer, 200 °C for 1.5 h: (a) 0, (b) 0.1 mmol, (c) 0.2 mmol, (d) 0.3 mmol, (e) 0.4 mmol, and (f) 0.6 mmol.

Cds nanorods cannot be formed without glutathione, and a layer of CdS nanofilm is formed. Some CdS nanorods with irregular sizes begin to grow on the top and side of the Si pyramids at 0.1 mmol glutathione. The nanorods on the top of the pyramids are thicker than those on the side of pyramids. As the concentration of glutathione increases from 0.1 to 0.3 mmol, the CdS nanorods become strong and uniform. In Figure 2c,d, the nanorods are about 100−150 nm in diameter and 400−500 nm in length with a hexagonal section. When the concentration of the glutathione is more than 0.5 mmol, the nanorods become thin and short, even dissolved. In general, the glutathione under certain concentration is beneficial for the growth of nanorods. Nevertheless, once the concentration of the glutathione is too high, it will corrode the CdS nanorods. Therefore, the optimal glutathione concentration for the synthesis of CdS nanorods is 0.2−0.3 mmol.

The hydrothermal temperature is studied since it is a potential influencing factor in the CdS nanorod formation. As shown in Figure 3, the temperature ranges from 160 to 220 °C with a 80 nm seed layer, 0.3 mmol concentration of glutathione, and 1.5 h of reaction time. At 160 °C, there is no nanorod on the Si pyramid surface after 1.5 h of reaction.
time. When the temperature reached 180 °C, the nanorods began to grow, but the growth rate was slow. When the temperature increased to 200 °C, well-defined hexagon CdS nanorods with an aspect ratio of more than 3 were observed. However, when the temperature increased to 220 °C, the CdS nanorods became sparse and the morphology became irregular. Corresponding to the observation, 200 °C is the optimal growth temperature for the CdS nanorods.

To better understand the formation process of the CdS nanorods on the Si pyramid surface, the time of hydrothermal reaction is studied in this work. The seed layer is 80 nm thick, the concentration of glutathione is 0.3 mmol, the reaction temperature is 200 °C, and the reaction time is changed from 0.5 to 2.5 h. Figure 4 shows that after 0.5 h of synthesis, no CdS nanorod but a layer of CdS nanoparticles is deposited on the surface of the pyramids. When the reaction is sustained for 1 h, CdS nanorods with an average diameter of 70–80 nm and a height of 120–150 nm are detected, which appear to have a hexagonal morphology. When the reaction reaches 1.5 h, the nanorods become stronger and longer with an average diameter of 120 nm and a height of more than 400 nm. As the reaction time exceeds 2 h, the morphology of the nanorods becomes irregular, and the adjacent nanorods even adhere together. Therefore, 1.5 h is the appropriate growth time to ensure that the CdS nanorods are strong enough and maintain a well-defined hexagonal morphology. Form the above analysis, the optimized CdS nanorods growth condition is as follows: 80 nm seed layer, 0.3 mmol glutathione, 200 °C, and 1.5 h.

As shown in Figure 5, the crystal structure of the CdS nanorods was analyzed by X-ray diffraction (XRD, Rigaku). The peaks of the silicon pyramid substrate are marked by “circle”, and the peaks of the CdS are marked by “triangle”. In accordance with Figure 4b, the XRD pattern of 0.5 h growth time indicates no new peaks. However, a new peak appears at 28.2° regardless of the low intensity when the reaction time reaches 1 h. As the growth time reaches 1.5–2.5 h, the diffraction peaks appearing at around 28.2, 36.7, and 51.9° are well indexed to the (101), (102), and (112) crystallographic planes of the CdS, which are in accordance with the standard spectrum of JCPDS: 65-4314. From the XRD curves, we can see that the CdS nanorods grew on the Si pyramids at different crystal orientations.

The X-ray energy-dispersive spectroscopy (EDS) are used to characterize that the composition of the nanorods growing on the Si pyramids is CdS. As illustrated in Figure 6a, the Cd and S elements have an atomic ratio of 1:1.03, which is in accordance with the stoichiometric composition of CdS. The optical absorption spectra are obtained using an ultraviolet—visible—near-infrared spectrophotometer (Abs, Hitachi UV-4100). A sharp band edge is shown at 558 nm in Figure 6b,
indicating a bandwidth of 2.22 eV. The red shift of the absorption edge is attributed to the CdS nanorod morphology.

To realize the mechanism on the pyramid structure giving rise to the CdS nanorods growing on the Si surface, we attempted to grow the CdS nanorods on the polished Si surface with the same seed layer, glutathione concentration, hydrothermal temperature, and time. It is discovered that the seed layer will fall off as soon as immersed into the hydrothermal reaction solution so the CdS nanorods cannot be maintained on the polished Si surface despite a 40−120 nm thick seed layer covering the polished Si surface. From this perspective, the pyramid structure on the Si surface can increase the adhesion between the CdS seed layer and the Si surface. If the adhesion is enough, the CdS nanorods will grow perpendicular to the seed layer. During the process of growth of CdS nanorods, the glutathione concentration, the hydrothermal temperature, and the time are important factors, as shown in Figure 7.

A photoresistor is fabricated by depositing a 100 nm thick Ti/Ag interdigitated electrodes onto the CdS nanorod surface (80 nm seed layer, 0.3 mmol glutathione, 200 °C, and 1.5 h), and the photosensitive property is tested by a homemade instrument. When the light is irradiated, the CdS material absorbs the photons and produces electron−hole pairs, and then the resistance of the CdS film declines sharply. When the light shuts off, the electron−hole pairs recombine gradually and the resistance is restored to the original value by degrees. The photosensitivity response (S) is defined as the resistance value of the photoresistor in the dark divided by the resistance value in light.

In Figure 8a, five light on/off cycles are recorded in the curve, and the CdS nanorods on Si pyramid structure have a stable and repeatable light response performance in every cycle. Figure 8a shows that the resistance value of the CdS nanorods on the pyramid surface in dark (1 μW/cm²) is 357 kΩ, when a white light of 13 000 μW/cm² is irradiated, the resistance value of the CdS nanorods decreases to 17.8 kΩ instantaneously so S = 357/17.8 kΩ = 21. The response time of the CdS nanorods on the pyramid surface is too short to be calculated from this curve, which reveals that this structure is very sensitive to the incident light. In Figure 8b, the illumination of the incoming light is changed from 1000 to 13 000 μW/cm² gradually, and the resistance value is different under different illumination. The resistance value of the CdS nanorod tends to be lower under strong illumination. Furthermore, as the illumination intensity gradually increases, the resistance value of the CdS nanorods decreases step by step. When the light is shut off (1 μW/cm²), the resistance value restores to 357 MΩ immediately. From the above analysis, we can see that these CdS nanorods on the Si pyramid structure have a stable and quick photosensitive response to white light and is very sensitive to the changes in the illumination intensity of the incoming light.

In our previous work, we have covered 200 nm thickness CdS film on silica planar, silica pillar, and Si nanoscrew structure surfaces through radio frequency (RF) magnetron
sputtering, which has the photosensitivity response of 62, 137, and 141 respectively. In this paper, the CdS nanorods on the Si pyramid structure, which is fabricated by the hydrothermal reaction, are used for photosensitive applications for the first time. Compared with the CdS film photosensor, the photosensitivity response of the CdS nanorods on the Si pyramid structure is low, but the response time is short. Moreover, more work needs to be done for improving the photosensitivity response of the CdS nanorods on the Si pyramid structure photoresistors in the future.

## CONCLUSIONS

The CdS nanorods were successfully grown on the Si surface with the assistance of Si pyramids fabricated by wet corrosion to increase the adhesion between the CdS nanorods and the Si wafer. The CdS nanorods are able to form on the Si pyramid surface via the hydrothermal method with the addition of glutathione. The thickness of the CdS seed film, the concentration of glutathione, and temperature and time of the hydrothermal reaction are studied in this work, and the best conditions for the growth of CdS nanorods is 80 nm seed layer, 0.2−0.3 mmol glutathione, 200 °C, and 1.5 h. The elementary composition and bandwidth of this structure grown on the Si pyramids are studied by EDS and Abs, respectively, which show that Cd and S elements are present in the ratio of 1:1.03 and the CdS nanorods have a bandwidth of 2.22 eV. The photosensitivity response test shows that the CdS nanorods on the Si pyramid surface are sensitive to white light, which has great potential in the field of photoelectronics. From this work, we can see that if the adhesion between the CdS seed layer and the Si surface is strong enough, the CdS nanorods can grow on the Si surface with any morphology, even on the polished surface.

## EXPERIMENTAL SECTION

A 400 μm thick polished (100) monocrystalline silicon wafers are used as substrates. First, the Si wafers are soaked into NaOH (1.5 wt %) solution, Na2SiO3·9H2O (1.5 wt %) solution, isopropyl alcohol (IPA) (6.5%), and DI water (90.5%) at 80 °C for 25 min to form a pyramidal structure. Second, a 40−120 nm thick CdS film serving as a seed layer is deposited onto the Si pyramid surface by RF magnetron sputtering. The condition of sputtering is as follows: 20 sccm Ar, 0.2 Pa working pressure, 20 W RF power, and 2−6 min sputtering time. Third, 1 mmol of cadmium nitrate Cd(NO3)2·4H2O, 3 mmol of thiourea, and 0.1−0.8 mmol of glutathione are dissolved in 80 mL of deionized (DI) water to form a mixture solution. The solution is stirred by a magnetic stirrer for 10 min, and then transferred to a 100 mL Tellin-lined stainless steel autoclave. Meanwhile, the Si substrates are immersed in this solution vertically, and the autoclave is heated in an oven at 160−220 °C for 0.5−2.5 h. After being cooled to room temperature, the wafer is washed with DI water and dried in the air naturally.

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## ACKNOWLEDGMENTS

This work was supported by Projects 11605226 supported by the National Natural Science Foundation of China.

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