

Fabrication and photosensitivity of ZnO/CdS/Silica nanopillars based photoresistor

Jing Liu (✉ liujing1987@ihep.ac.cn)

Institute of High Energy Physics Chinese Academy of Sciences <https://orcid.org/0000-0002-1964-1639>

Yuanze Xu

Institute of High Energy Physics Chinese Academy of Sciences

Futing Yi

Institute of High Energy Physics Chinese Academy of Sciences

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Abstract

A kind of Zinc oxide (ZnO)/Cadmium sulfide (CdS)/Silica nanopillars structure is fabricated to photoresistor for the first time. The silica wafer with countless nanopillars is used as the substrate for photoresistor. CdS and ZnO film are deposited by frequency (RF) magnetron sputtering onto the silica nanopillars surface to form ZnO/CdS/Silica nanopillars structure. The ZnO nanowires also can grow on the CdS surface by the hydrothermal reaction to ZnO nanowires/CdS/Silica nanopillars structures. The X-ray diffraction curves show that the ZnO and CdS film both on the planar silica and nanopillar silica surface are well-crystallized. The ZnO film deposition can reduce the reflection and increase the absorption of the incoming light, especially for the light with a wavelength less than 350 nm. And the ZnO/CdS heterojunction structure can retard the recombination probability of the photon-generated carries and prolong the lifetime of the photon-generated carriers, which leading to a remarkable photocurrent improvement. The photosensitivity property testing results show that the ZnO nanowires/CdS/Silica nanopillars structure has the best photosensitivity response of 135 for the white light with 10 mW/cm² illumination.

1. Introduction

Cadmium sulfide (CdS) with a bandgap of 2.4 eV is an important II-VI semiconductor compounds semiconductor, and it has excellent optoelectronic properties in the visible light region, so it is widely used in electronic and optoelectronic devices such as solar cells [1, 2] light emitting diodes [3], photoresistors [4, 5], and so on [6, 7]. For the CdS based photoresistor, when it is exposed to light with a certain wavelength, the resistance of the photon-sensitive material will be decreased sharply for the photon-generated carriers. When the light is removed, the resistance will be recovered gradually. For the photoresistor, many methods are adopted to increase the sensitivity, for example making the CdS nanostructures to increase the sensitivity surface, such as nanowires, nanorods, nanoflowers, and so on [8–10]. And it was proved that the photocurrent to the dark current ratio of the CdS based photodetectors can be further enhanced through the formation of heterojunctions [11, 12]. Zinc oxide (ZnO) is a functional semiconductor with the bandgap of 3.37 eV, and the conduction band and valence band of the ZnO are 0.2 and 0.8 eV lower than those of CdS respectively, therefore the ZnO/CdS heterojunctions might be a promising structure for the photosensitive resistor of visible light [13, 14].

In the previous study, we reported the preparation and photosensitive property of CdS film on silicon nanopillars surface, which proved that the nanopillars with the large high aspect ratio as the substrate can improve the photosensitive property of CdS material [15, 16]. In this work, we fabricated the ZnO/CdS heterojunction on the silica nanopillars substrate for photoresistor application. Firstly, we deposited a layer of CdS film on the silica nanopillars surface by radio frequency (RF) magnetron sputtering, and then deposited a layer of ZnO film by RF magnetron sputtering or grew ZnO nanowires on the CdS surface by hydrothermal reaction to form ZnO/CdS heterojunction. This ZnO nanowires/CdS/silica nanopillars structure was used for the photoresistor application for the first time, and the testing results revealed that

this structure can improve the photosensitive performance of the CdS layer based photoresistor for white light.

2. Experimental And Section

In this work, polished (100) monocrystalline silicon wafers with resistivity $> 2000 \Omega \cdot \text{cm}$ and $400 \mu\text{m}$ thickness are chosen as substrates for photoresistors. Firstly, the Si nanopillars are fabricated by cesium chloride (CsCl) self-assembly and dry etching, which is low-cost and suitable for mass production. The fabrication process of the Si nanopillars includes the following four steps: CsCl film deposition, development to nanoislands, ICP etching, and CsCl nanoislands removal, which are recorded in Ref. 17 and 18 in detail. Secondly, to avoid the effects of silicon on heterojunctions, the Si wafer is heated at 900°C for 1 hour in the O_2 atmosphere to form a layer of silica film on the Si nanopillars surface. Thirdly, a 150 nm thickness CdS film as the photosensitive layer is deposited on the planar or nanopillars silica surface by radio frequency (RF) magnetron sputtering. The RF sputtering condition is that: CdS target with 99.99% pure, $1 \times 10^{-4} \text{ Pa}$ base pressure, 0.2 Pa working pressure, 20 sccm Ar , 40 W RF power, and 8 mins. Fourthly, two methods are adopted to fabricate the ZnO film on the CdS film surface. The one is that: a 70 nm thickness ZnO film layer is directly deposited by RF magnetron sputtering with 99.99% pure ZnO target, $1 \times 10^{-4} \text{ Pa}$ base pressure, 1 Pa working pressure, 20 sccm Ar , 120 W RF power, and 15 mins. The other one is that: 20 nm ZnO film layer is deposited by RF magnetron sputtering as the seed layer, and then the ZnO nanowires grow on the seed layer surface by the hydrothermal reaction method with 0.05 M zinc chloride and 0.05 M hexamethylenetetramine in 80 ml deionized water, and at 95°C keeping 30 mins in a water bath [19]. Finally, the Ti/Ag interdigitated electrodes with $100 \mu\text{m}$ width and $1 \mu\text{m}$ thickness are deposited onto the surface by the thermal evaporation method to the photoresistor.

The six different kinds of structures are fabricated to CdS based photoresistors, which are revealed in Fig. 1. Sample A is CdS layer on the planar silica surface, sample B is ZnO/CdS/planar silica structure, sample C is ZnO nanowires/CdS/planar silica structure, sample D is CdS/ silica nanopillars structure, sample E is ZnO/CdS/ silica nanopillars structure, and sample F is ZnO nanowires /CdS/ silica nanopillars structure.

CdS and ZnO film is deposited by a magnetron sputtering system (JGP-450, made by SKY Technology Development Company, Chinese academy of sciences). Ti/Ag electrodes are deposited by a vacuum coating machine (DM-300B).

3. Results And Discussion

The morphologies of ZnO/CdS/Silica structures are examined by scanning electron microscope (SEM, Hitachi-S4800), shown in Fig. 2. Fig. 2a and 2b are the polished Si wafer and Si nanopillars after oxidation, and the nanopillars are about 200 nm average diameter and $1 \mu\text{m}$ height. After RF magnetron sputtering, the CdS layer is about 150 nm thickness on the planar silica surface and the thickness is uniform shown in Fig. 2c. From the Fig. 2d, the CdS layer fabricated by RF magnetron sputtering

deposition can cover both the top and side-wall of the silica nanopillars tightly. After the ZnO film deposition, the film on the planar silica surface increases to 220 nm shown in Fig. 2e, which reveals that the ZnO layer is about 70 nm. Fig. 2g to 2h are the ZnO nanowires grow on the CdS surface, the nanowires on the planar silica surface is about 50 nm width and 500 nm high, while the ZnO nanowires growing on the silica nanopillars surface are about 20 nm width and 200 nm high. The ZnO nanowires are thick on the planar and nanopillars silica surface.

The crystal structure of the ZnO nanowires/CdS/silica nanopillars structure is determined by X-ray diffraction (XRD) using a Rigaku diffractometer with CuK X-rays from 20° to 65° and a scan step of 0.02°, which are recorded in Fig. 3. The peaks of the Si substrate, CdS, and ZnO film are marked by “circle”, “square”, and “triangle” respectively. After 150 nm CdS film covered on both polished and nanopillars silica surface, new peaks are observed at 24.9°, 26.5°, 28.2°, and 43.8°, which could be assigned to the CdS (100), (002), (101), and (110) according to the standard spectrum of JCPDS: 65-4314. After 70 nm thickness ZnO deposition and ZnO nanowires growing on the planar silica surface, only a new strong peak around 34.7° is appeared, which is the (002) peak of the ZnO from JCPDS: 36-1451. The one peak indicates that the ZnO film and ZnO nanowires have a high orientation with the c-axis vertical to the substrate surface. On the silica nanopillars surface, three ZnO diffraction peaks (100), (002), and (101) appear at 31.9°, 34.7°, and 36.3°, which means the ZnO film and nanowires grow at different crystal orientation on the silica nanopillar surface. Both the CdS and ZnO structures on the polished silica and silica nanopillars surface are well-crystallized gotten from the XRD curves.

The reflectivity of the ZnO nanowires/CdS/silica nanopillars structures is measured by an ultraviolet-visible-near-infrared spectrophotometer (Agilent Cary 5000) from 200 to 800 nm. For the planar silica surface in Fig. 4a, the bare silica wafer has a high reflectance above 45% for the whole wavelength. While after the CdS layer deposition, the reflectivity has a sharp reduction at the wavelength below 600 nm. With the ZnO film covering, the reflectivity for wavelength from 200 to 380 nm becomes much lower. After the ZnO nanowires growing, the reflectivity is suppressed to below 15% for wavelength from 200-60 nm. On the silica nanopillars surface in Fig. 4b, the reflectivity for the whole wavelength is below 15%. For the bare silica nanopillars surface, the reflectivity for wavelength from 300 to 800 nm is lower than 8%, for wavelength 200-300 nm, the reflectivity is much high. After the CdS layer covering, there is a slight increase in the reflectivity of wavelength 300-800 nm, and there is a low reflectivity for wavelength from 200-300 nm. With the ZnO nanowires growing, the reflectivity is lower than that without ZnO nanowires, especially for the wavelength below 400 nm. Compared with Fig. 3a and 3b, the reflectivity of the structure on the nanopillars based wafers is much lower than that on the planar silica wafer surface.

The photosensitive property of based ZnO/CdS/silica photoresistors is tested by a homemade instrument, including a dark box, a white light source, and a resistance measurer [20]. The illumination of the testing environment in dark is 1 $\mu\text{W}/\text{cm}^2$, while that of in white light is 10 mW/cm^2 . When the light incomes, the CdS material absorb the photons and the electron-hole pairs appear, and then the resistance declines instantaneously. When the light shuts off, the electron-hole pairs recombine gradually and the resistance increases gradually. The photosensitivity response (S) is defined as the resistance of the

photoresistor in dark dividing the resistance exposed to light. The photosensitivity performance is recorded in Fig. 5 and Table 1, and we can see that all the ZnO/CdS/silica based photoresistors have obvious photosensitivity properties. When the light turns on or off, the resistance declines or increases sharply without hesitating for all the photoresistors. Take the photoresistors with only the CdS layer as the example, on the planar silica surface, the resistance under 10 mW/cm^2 white light is $18 \text{ K}\Omega$, when the illumination of environment change to $1 \text{ }\mu\text{W/cm}^2$, the resistance restores to $1.35 \text{ M}\Omega$, so the response is $1.35 \text{ M}\Omega / 18 \text{ K}\Omega = 75$. With the same calculation method, the response for CdS layer on silica nanopillars surface is $2.1 \text{ M}\Omega / 23 \text{ K}\Omega = 91$, which is obviously higher than that of the planar based one. After 70 nm ZnO covering the CdS film, the S increase to 105 and 125 respectively, when the ZnO nanowires grown, the photosensitivity response further improves to 112 and 135, which indicates that the ZnO film covering can increase the photosensitivity response of the CdS based photoresistor both on the planar silica and silica nanopillars surface. On one hand, the ZnO film can reduce the reflection and increase the absorption of the incoming light, especially for the light with the wavelength of less than 350 nm . On the other hand, the conduction band and valence band of the ZnO are 0.2 and 0.8 eV lower than those of CdS respectively, when the light incoming, the photon-generated electrons of the CdS layer will be injected from the conduction band of CdS into the conduction band of ZnO, so the holes will transport along with CdS film, while the electrons will move along ZnO layer. As a result, the heterojunction structure between CdS and ZnO can prevent the recombination probability of the excess photon-generated carriers and prolong the lifetime of the photon-generated excess carriers, lending to a remarkable photocurrent improvement. Compared with the photosensitivity performance of sample A to F, we can see that the nanopillars based photoresistors have the higher response than that of the polished silica based one. The advantages of the nanopillars based wafer are that: (1) the nanopillars substrate has a larger surface radio, which is covered by the more sensitive material surface than the planar one. (2) The nanopillar substrate has a larger surface to contact with light and absorb the incident photons. Both the nanopillars morphology of the silica substrate and the ZnO layer covering can improve the photosensitivity performance of the CdS layer based photoresistors for white light. And the ZnO nanowires/CdS/silica nanopillars based photoresistors have the best photosensitivity performance of 135 for the white light with 10 mW/cm^2 illumination.

4. Conclusions

In this work, it is the first time that ZnO/CdS heterojunction on the silica nanopillars substrate are fabricated for photoresistor application. 150 nm thickness CdS layer are deposited on the planar silica and silica nanopillars surface by the RF sputtering. Then, two kinds of ZnO structures are covered onto the CdS layer surface to form ZnO/CdS heterojunction, one is 70 nm thickness ZnO film deposited by RF sputtering, and the other is the ZnO nanowires grown by hydrothermal reaction method. Both the CdS and ZnO structures on the polished silica and silica nanopillars surface are well-crystallized gotten from the XRD curves. After the ZnO covering, the reflectivity can be reduced, especially for the wavelength less than 350 nm . With the ZnO nanowires growing, the reflectivity is much lower than that without ZnO nanowires. No matter with or without ZnO or CdS film, the reflectivity of the silica nanopillars wafer is

much lower than that of the planar surface. After the ZnO/CdS/Silica nanopillars photoresistor fabrication, the photosensitive property is tested and the results show that the ZnO/CdS structure can improve the photosensitive performance and the silica nanopillars can increase the photosensitivity response. The ZnO nanowires/CdS/Silica nanopillars structure has the best photosensitivity response of 135 for the white light with 10 mW/cm² illumination.

Declarations

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Table

Table 1 □ The detail of the resistance and response of the ZnO/CdS/silica based photoresistors.

	On the planar silica surface			On the silica nanopillars surface		
	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
R_1	18 K Ω	6 K Ω	17 K Ω	23 K Ω	8 K Ω	20 K Ω
R_d	1.35 M Ω	630 K Ω	1.9 M Ω	2.1 M Ω	1.0 M Ω	2.7 M Ω
S	75	105	112	91	125	135

Figures

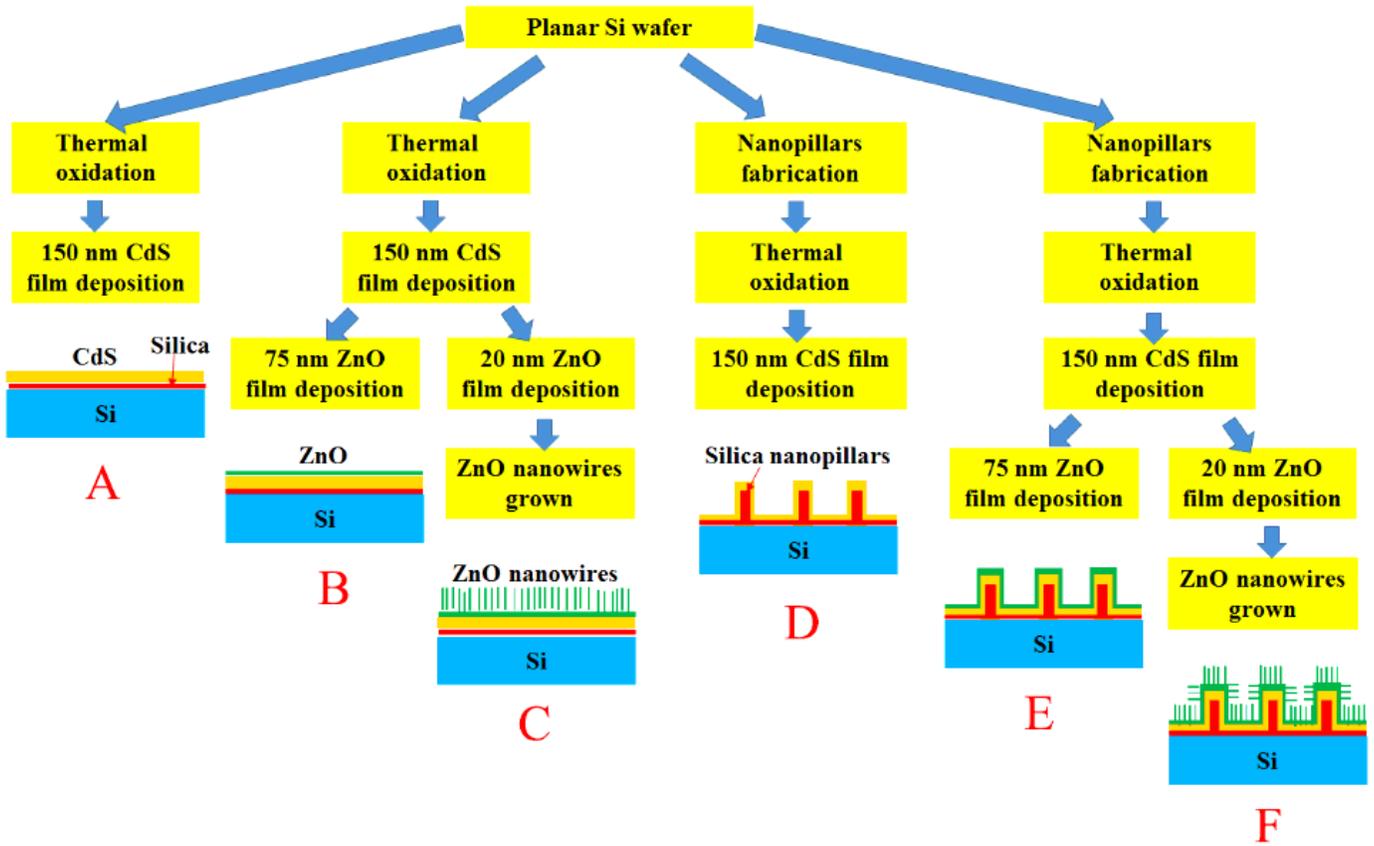


Figure 1

Fabrication process and diagram of the ZnO/CdS/Silica structures named Sample A-F respectively. CdS and ZnO film is deposited by a magnetron sputtering system (JGP-450, made by SKY Technology Development Company, Chinese academy of sciences). Ti/Ag electrodes are deposited by a vacuum coating machine (DM-300B).

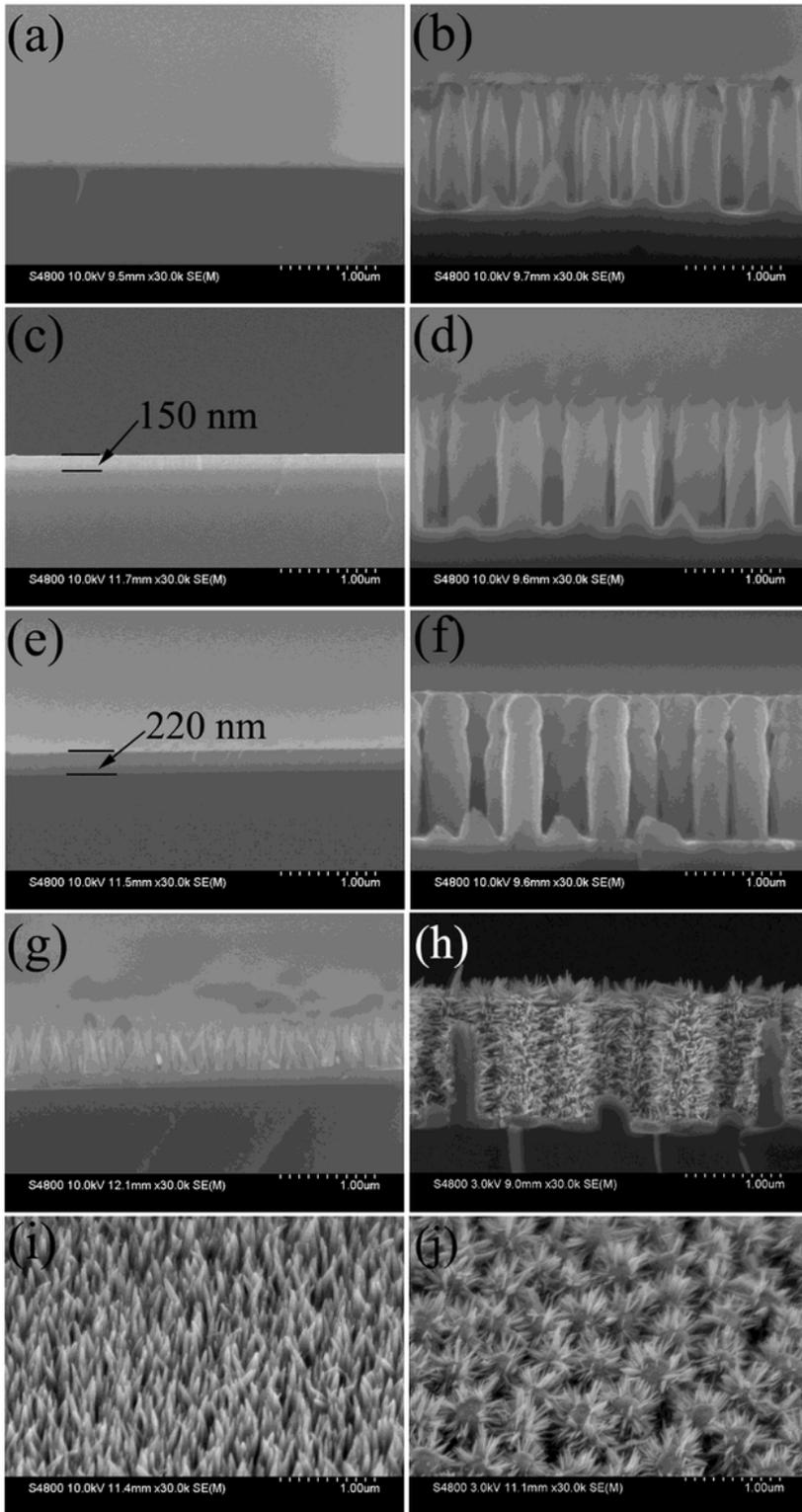


Figure 2

Cross-sectional and tilted top-view SEM images of structures: (a) planar silica; (b) silica nanopillars; (c) CdS layer on silica surface, Sample A; (d) the CdS layer on silica nanopillars, Sample D; (e) ZnO/CdS/planar silica structure, Sample B; (f) ZnO/CdS/ silica nanopillars structure, Sample E; (g) and (i) ZnO nanowires/CdS/planar silica structure, Sample C; (h) and (j) ZnO nanowires /CdS/ silica nanopillars structure, Sample F.

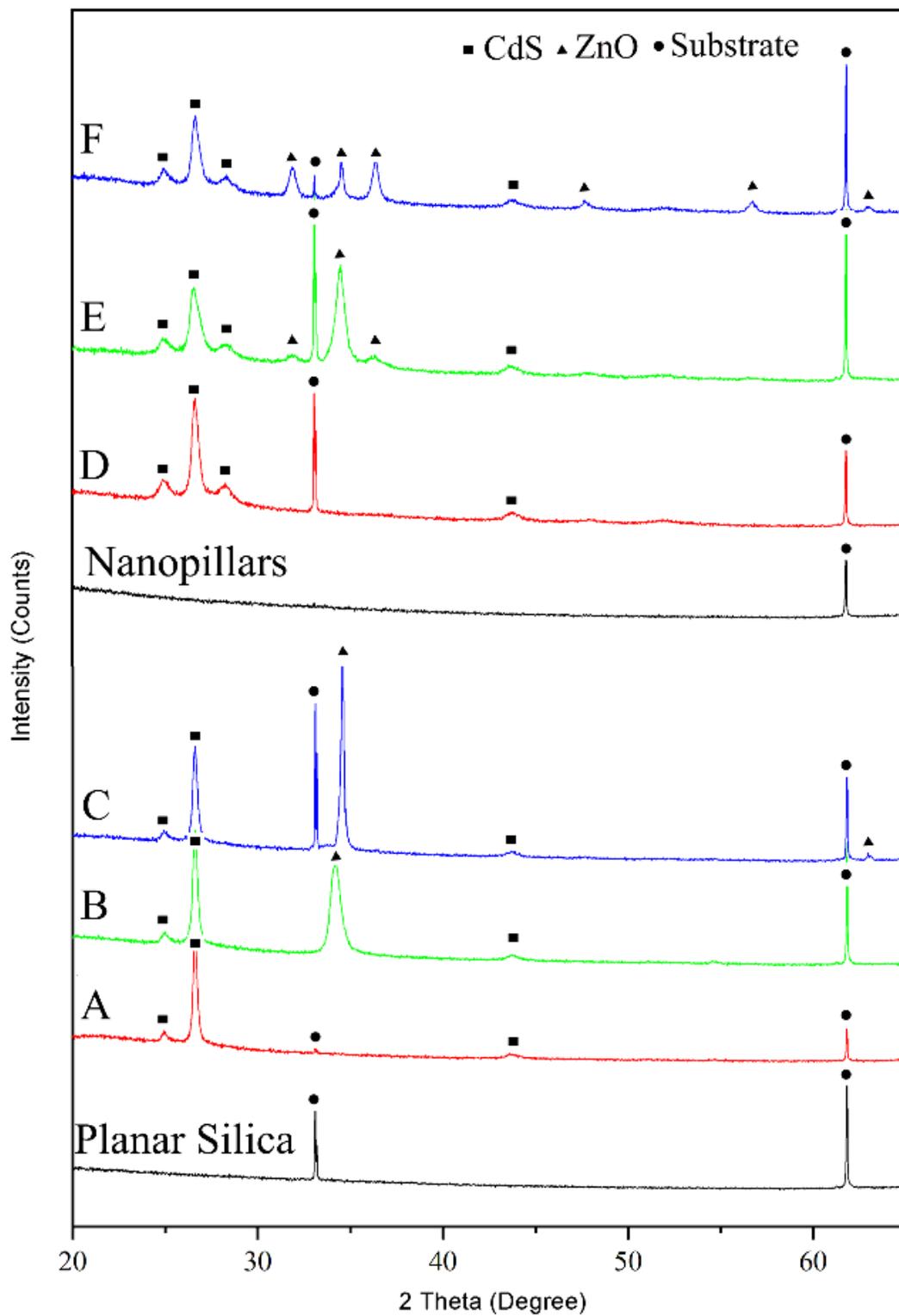


Figure 3

XRD patterns of the planar silica, nanopillars substrates, and Sample A-F.

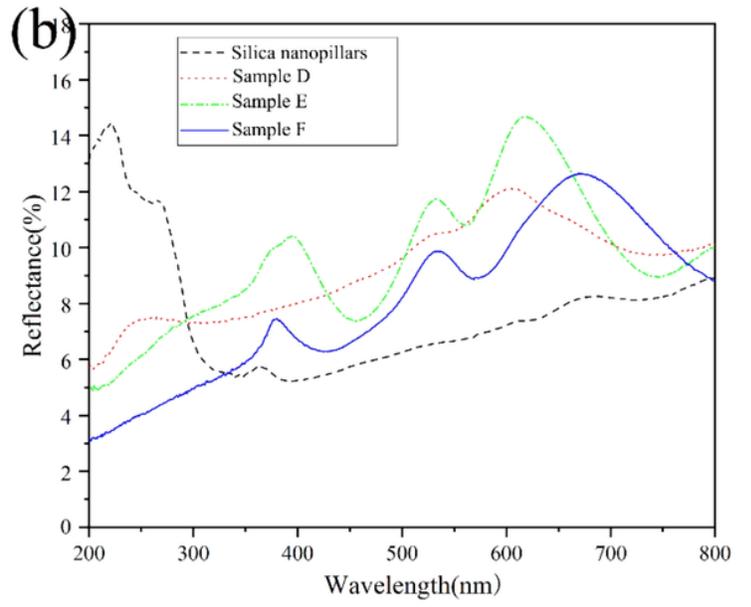
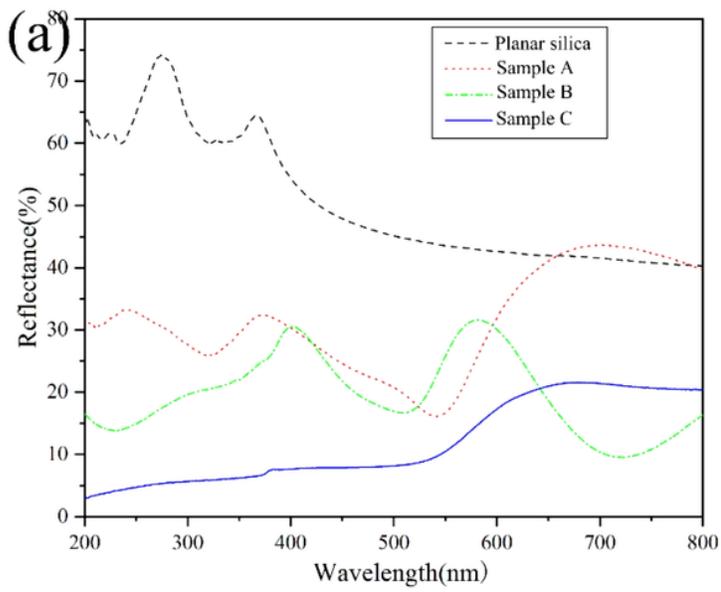


Figure 4

The reflectivity of ZnO/CdS/silica structures. (a) On the planar silica surface; (b) on the silica nanopillars surface.

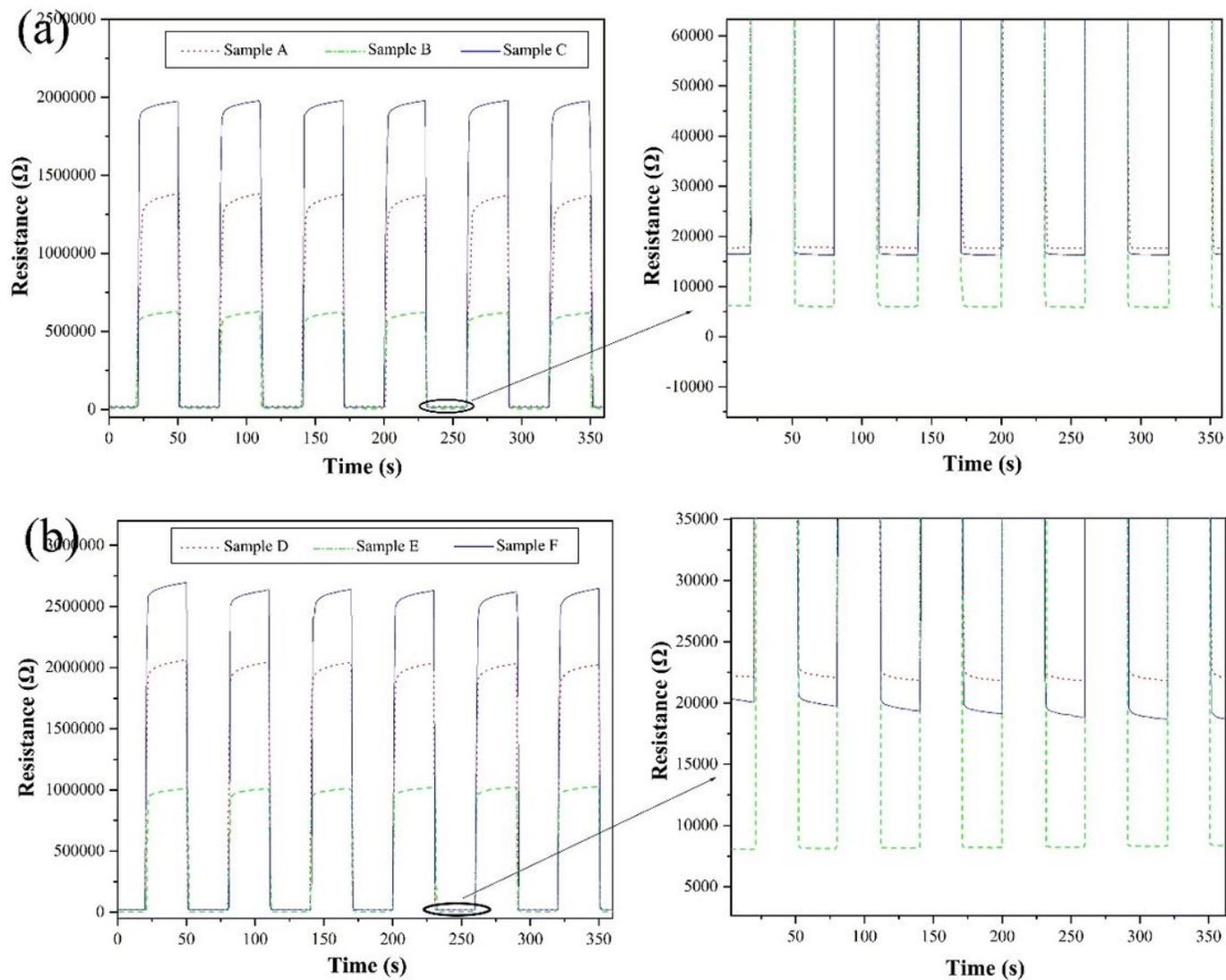


Figure 5

Resistance response curve of the ZnO/CdS/silica based photoresistors. (a) On the planar silica surface; (b) on the silica nanopillars surface.