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Preparation, structural and electrical properties of zinc oxide grown on silicon nanoporous pillar array*

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Polycrystalline thick film of zinc oxide (ZnO) is grown on a unique silicon substrate with a hierarchical structure, silicon nanoporous pillar array (Si-NPA), by using a vapour phase transport method. It is found that as-grown ZnO film is composed of closely packed ZnO crystallites with an average size of $\sim$10 μm. The film resistivity of ZnO/Si-NPA is measured to be $\sim$8.9$\Omega\cdot$cm by the standard four probe method. The lengthwise I-V curve of ZnO/Si-NPA heterostructure is measured. Theoretical analysis shows that the carrier transport across ZnO/Si-NPA heterojunction is dominated by two mechanisms, i.e. a thermionic process at high voltages and a quantum tunnelling process at low voltages.

Keywords: silicon nanoporous pillar array (Si-NPA), ZnO/Si-NPA heterostructure, thermionic process

PACC: 7340L, 8160C, 7210B

1. Introduction

Since the observation of its strong red photoluminescence,[1] porous silicon (PS) has been thought to be one of the most prospective candidates for realizing silicon-based optical electronic integrated circuits. In the past decade, the optical and electrical properties of PS have been extensively studied, and several kinds of PS-based prototype devices, such as light emitting diodes[2] and photo-electrical detectors,[3] have been proposed and developed. However, the problems of low quantum output and optical stability of the electroluminescence (EL) from PS diodes remain to be solved,[4] and the carrier transport mechanism is still debating.[5,6] PS possesses a complicated surface structure, and it is believed that metal electrodes made in a common mode cannot provide an efficient carrier injection. By replacing the metal electrodes with transparent conducting films, the carrier injection efficiency and thereby the EL efficiency can be greatly enhanced because of the filling of conducting materials into the pores.[7−9] Zinc oxide (ZnO) is a highly transparent compound semiconductor with the advantages of direct, wide band gap ($\sim$3.3 eV) and high tolerance to reducing atmospheres, and the ZnO film is expected to be an ideal candidate for improving the electric properties of PS based devices.[4,10−13] Therefore, the investigation of the deposition technique, microstructure, and electrical properties of ZnO film on various PS substrates has aroused much attention in the past several years.[14] In this paper, we report that by using a vapour phase transport method, a compacted polycrystalline ZnO film is grown on a novel patterned PS substrate, which has been proved to possess a hierarchical structure and named silicon nanoporous pillar array (Si-NPA).[15,16] The electrical properties of ZnO/Si-NPA are investigated and the carrier transport mechanism of the heterostructure is discussed based on the experimental current–voltage data.

2. Experiments

Si-NPA substrates were prepared by hydrothermally etching p-type, (111) oriented single crystal silicon (sc-Si) wafers in the solution of hydrofluoric acid containing ferric nitrate, which has been described in detail elsewhere.[15,16] The resistivity of the initial silicon wafers is 0.015 $\Omega\cdot$cm. As-prepared sample is

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named Si-NPA to stress its unique structural characteristics which are different from those of traditional sponge-structured PS.[16] For comparison, the ZnO films were deposited on two kinds of substrates, i.e. Si-NPA and sc-Si wafers, which had been slightly pretreated in diluted hydrofluoric acid before they were loaded into the deposition chamber. These samples were denoted as ZnO/Si-NPA and ZnO/Si accordingly. These substrates were all 1 cm × 1 cm in size. ZnO was deposited on these substrates by using a vapour phase transport method. In the process, the powder obtained by mixing ZnO and graphite with a mass ratio of 1 : 1 was used as a source material. Two quartz boats, one with the source material and the other with the substrates, were located in a horizontal furnace. There was a separation of 1.5 cm between the two boats and the boat with substrates was situated at a downstream position. A little water was placed in the furnace as an oxygen source. The furnace was heated up to 1000°C and then maintained at the temperature for 90 min. High-purity nitrogen gas was blown into the furnace in the whole preparation process. After ZnO growing procedure had been over, the furnace was quickly cooled down to 500°C in 30 min, and then to room temperature naturally.

The structural and morphological characterizations were carried out by using an x-ray diffractometer (XRD) and a field emission scanning electron microscope (FE-SEM). The electrical properties were investigated through an electrical group system mainly composed of SOURCEMETER-2400 and NANOVOLTMETER (Keithley).

3. Results and discussion

The most important distinction of the Si-NPA from the traditional PS is the formation of a regular pillar array as shown by Fig.1. We have previously proved that this array has a micron superstructure imposed on a PS-like nanoporous structure, and is composed of a large number of well-separated, quasi-identical porous pillars.[15,16] The similarity between the porous structures of Si-NPA and traditional PS implies that the physical and chemical properties of Si-NPA surface should be similar to those of PS, except for the effects which might be caused by the regular pillar array.

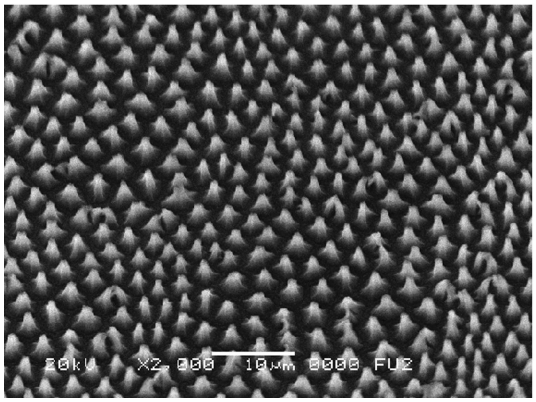


Fig.1. Typical surface morphology of Si-NPA obtained by FE-SEM.

The experimental XRD patterns of ZnO/Si-NPA and ZnO/Si are presented in Fig.2, showing that polycrystalline ZnO are grown on both Si-NPA and sc-Si substrates. From the typical surface morphology of ZnO/Si-NPA obtained by FE-SEM (Fig.3(a) and (b)), it can be found that the film is composed of ZnO crystallites with obvious geometrical shapes and relatively large dimensions. All the observed ZnO crystallites are polyhedrons with well-defined facets, from which the crystallographic features of hexahedron structure corresponding to wurtzite ZnO are distinguishable. It can be found by judging both the plan-view image (Fig.3(b)) and the lateral-sectional image of ZnO/Si-NPA (Fig.3(c)) that the stacking of these ZnO crystallites is highly compacted and no micro-cavities exist all over the sample surface. The average cross-sectional size of these ZnO crystallites is evaluated to be ∼10 μm. The thickness of the film is uniform and measured to be ∼7.7 μm, a little smaller than the average cross-sectional size of the observed crystallites, ∼10 μm.

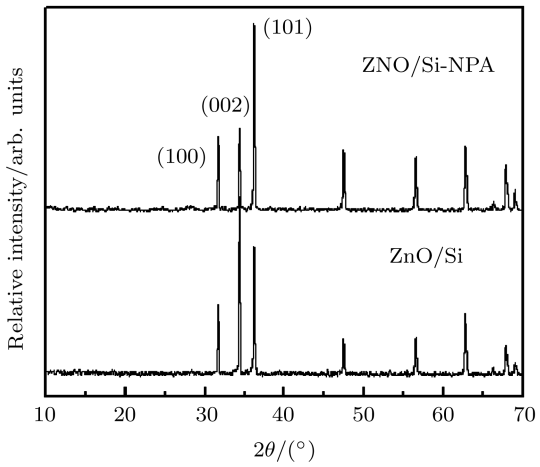


Fig.2. XRD patterns of ZnO/Si-NPA and ZnO/Si.

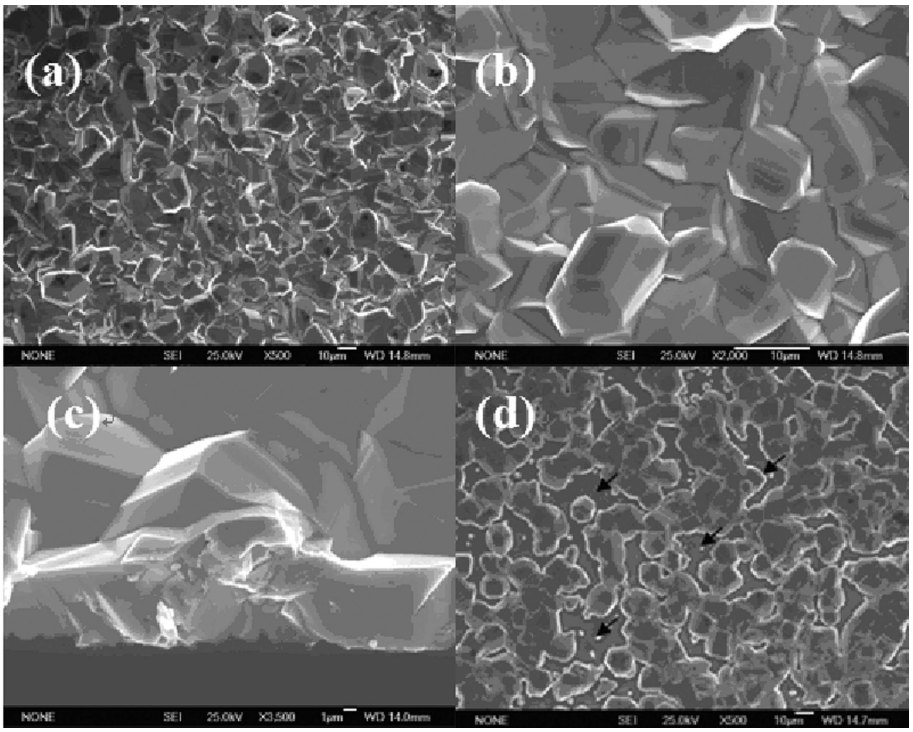


Fig.3. (a) and (b) plan-view, (c) lateral-sectional FE-SEM images of ZnO/Si-NPA, and (d) plan-view of ZnO/Si.

To reveal the roles played by Si-NPA substrate in the growing process of ZnO/Si-NPA, ZnO/Si was prepared by using sc-Si as a substrate under identical preparation conditions. The corresponding XRD pattern described by the bottom line in Fig.2 indicates the formation of ZnO film, and Fig.3(d) shows the surface morphology of ZnO/Si. Comparison of the surface morphologies of ZnO/Si-NPA given in Figs.3(a)–(c) shows that there exists an apparent difference. There are a large number of naked areas where no ZnO was deposited as indicated by arrows in Fig.3(d). The sizes of these naked areas range from several microns to several tens of microns. Therefore the continuity and compactness of as-deposited ZnO films on sc-Si substrate are poor. Furthermore, from the XRD patterns of ZnO/Si-NPA and ZnO/Si given in Fig.2, it can be found that ZnO crystallites grown on Si-NPA are more preferentially (101) oriented, while those on sc-Si preferentially (002) oriented. Because the deposition conditions adopted in preparing ZnO/Si-NPA and ZnO/Si are identical, the final structural difference between ZnO/Si-NPA and ZnO/Si can be attributed only to the difference in surface status between the two substrates.

As is known, the lattice mismatch between bulk wurtzite ZnO and silicon is as large as ∼16.6%, and the thermal expansion coefficient difference is also very big. Therefore, the growth of ZnO film on sc-Si substrate would be blocked by the strong stress caused by the lattice mismatch, which results in a main obstacle to the designing and fabricating of ZnO-related integrated photoelectrical devices.[17,18] The large lattice mismatch between ZnO and sc-Si substrates can lead to randomly dispersed initial nucleations and islands growth of ZnO. This growing mode is directly reflected by the final morphological features observed in Fig.3(d), where a large number of islands which are composed of ZnO crystallites and separated by numerous naked areas can be clearly distinguished, while in the case of Si-NPA, the regular pillar array and the intrinsic nanoporous structure form a flexible layer with a thickness of several microns. When ZnO was deposited on Si-NPA, the interfacial stress produced between ZnO and Si-NPA could be easily released by the nanoporous layer and therefore a highly compacted ZnO film with a uniform thickness was formed.

The exploration of the electrical properties of ZnO/Si-NPA was performed by measuring its film resistivity and longitudinal current–voltage curve (I–V curve). The film resistivity was detected at room temperature by the standard four probes method, with four silver electrodes being parallel-arranged on the surface of ZnO/Si-NPA. From the I–V curve presented in Fig.4, it can be found that the voltage varies

linearly with the applied current. This proves the ohmic contact between the silver electrodes and ZnO film. The film resistivity is calculated through the formula

$$\rho = 2\pi \times S \times \frac{V}{I} \times \frac{1}{B},$$

where S represents the thickness of ZnO film, B is the corrected factor to erase the boundary effect. In the present experiment, S and B are 7.7 μm and 18.5630, respectively, which are determined from the FE-SEM image (Fig.3(c)) and the geometry parameters of the sample shape and electrode arrangement. The slope of the I–V curve given in Fig.4 is $3.34 \times 10^{-2}\,\Omega^{-1}$. Therefore the film resistivity of ZnO/Si-NPA sample is calculated to be $\sim$8.9 Ωcm, which is much smaller than that achieved in other ZnO/PS systems.[19] The low film resistivity should be attributed to the strong electron translation ability resulting from the highly compacted and well crystallized ZnO film of ZnO/Si-NPA.

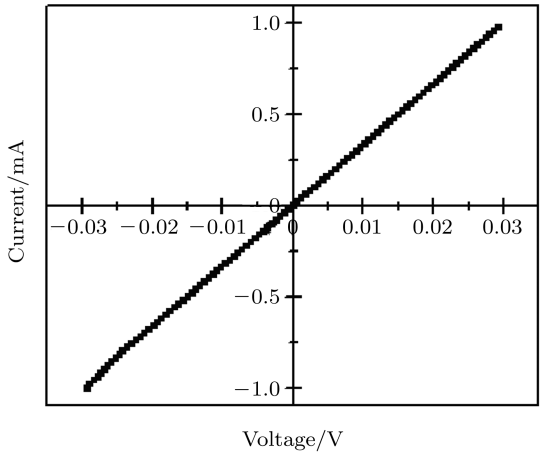


Fig.4. Planar I–V curve of ZnO/Si-NPA measured by using the standard four probes method.

Considering the fact that ZnO is a typical n-type semiconductor and the initial sc-Si wafer used in the experiment is a p-type semiconductor, a heterostructure of n-ZnO/Si-NPA/p-Si was formed after the deposition of ZnO. Naturally, the carrier transport behaviour across the heterostructure could play an important role in determining its photoelectrical performance. To clarify the transport mechanism of the heterostructure, the longitudinal I–V curve of n-ZnO/Si-NPA/p-Si was measured, and the experimental results are presented in Fig.5. From the I–V curve given in the inset of Fig.5, it can be found that n-ZnO/Si-NPA/p-Si possesses the excellent rectification characteristic, with a turn-on voltage of $\sim$0.54 V and a rectifying ratio of over 13 at an applied bias of 1V. Theoretically, the I–V relation of a p–n junction can be generally described as a thermionic process:[20,21]

$$I = I_0 \exp \frac{q(V - IR_S)}{nkT}, \tag{1}$$

where I_0, n and R_S represent the saturation current, diode ideal factor and series resistance of the junction, respectively. R_S is the resistance originating from the hindrance-to-hole transport due to the porous layer and any other structural factors introduced during the preparing process.[21,22] According to the theory on thermionic process,[21] I_0 is determined mainly by the potential barrier of the heterojunction and the temperature of the measuring environment, and n depends on the transport process of carriers across the junction. Experimental results disclose that there is no distinct rectification characteristic in the junction formed by Si-NPA and nc-Si substrate, and therefore the rectification characteristic observed in the inset of Fig.5 should be attributed mainly to ZnO/Si-NPA heterostructure. By employing the value of the differential resistance obtained according to the linear section of forward I–V curve at relatively large applied voltages (curve (a) in Fig.5), the series resistance is evaluated to be $\sim 3.8 \times 10^3\,\Omega$. Replacing V–IR_S in Eq.(1) with V_M, which represents the true voltage applied to the heterojunction, expression (1) can be rewritten as

$$I = I_0 \exp \frac{qV_M}{nkT}. \tag{2}$$

The transferred I–V_M curve below 1 V is depicted as curve (b) in Fig.5, where an obvious modification brought by the series resistance can be found. This

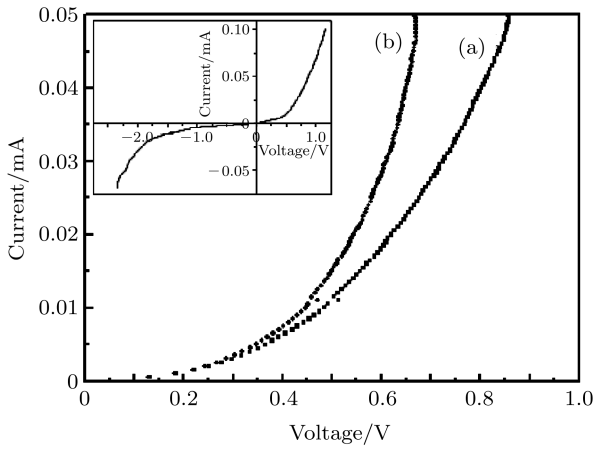


Fig.5. Experimental I–V curve (a) and corresponding I-V_M curve (b) of ZnO/Si-NPA heterostructure with applied bias voltages less than 1 V. Inset: I–V curve demonstrating the rectification characteristic of ZnO/Si-NPA.

is very helpful for analysing the carrier transformation mechanism across the heterostructure.

The diode ideal factor n can be obtained directly by calculating the slope coefficient of $\ln(I)$–V_{M} curve given in Fig.6(a). Obviously, the curve exhibits a good linearity when the bias is higher than 0.3 V, and the corresponding n is calculated to be ∼5.7. The diode with a high ideal factor is often found in oxide semiconductor/silicon p–n junction diodes, and it is generally due to the interface states related to the interphase layer between silicon and oxide semiconductor.[20,23] Within the frame of this theory, the high n value of ZnO/Si-NPA indicates that there may be formed an interphase layer between silicon and ZnO, by which high density of interface states are produced. Therefore, the carrier transport across ZnO/Si-NPA heterojunction under high biases (>0.3 V) can be well described by the thermionic theory. But when biases are below 0.3 V, there appears an apparent deviation between the experimental $\ln(I)$–V_{M} curve and the straight fitting line. This deviation strongly suggests that the carrier transport at low biases may be dominated by other mechanisms rather than by thermionic process. One of the most possible mechanisms is the quantum tunnelling process suggested by Molnár *et al*[24] in studying the carrier transport of traditional PS, where the tunnelling current was described to be proportional to an exponential function $\exp(BV)$, with B being a constant. Fitting the experimental I-V curve by the function of $\exp(q(V - IR_{\mathrm{S}})/nkT)$ at $V > 0.3$ V and $\exp(B(V - IR_{\mathrm{S}}))$ at $V \leq 0.3$ V separately, a good agreement between the experimental and fitting curves is achieved as shown in Fig.6(b). Based on these results, it can be concluded that in as-prepared ZnO/Si-NPA, the carrier transport across the heterojunction is dominated by two processes, i.e. a quantum tunnelling process at low applied biases and a thermionic process at high applied biases.

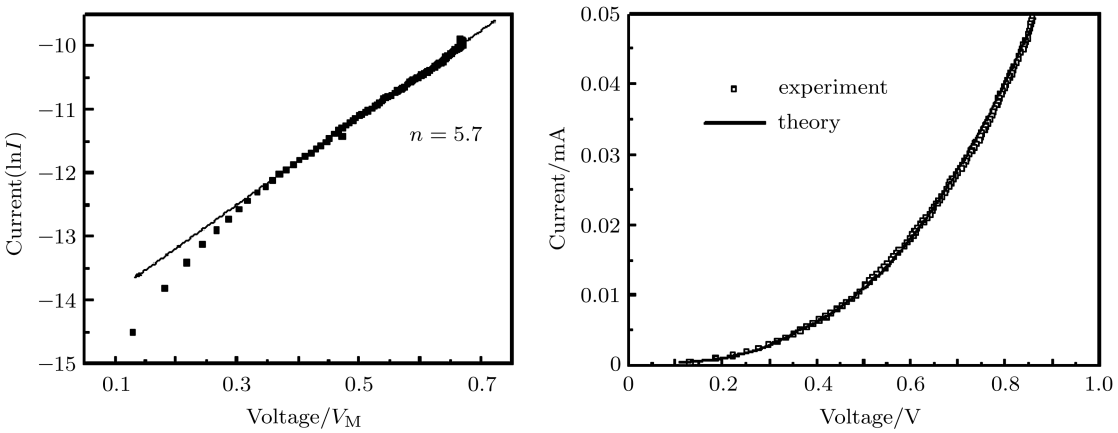


Fig.6. Experimental $\ln(I)$-V_{M} plot (a), and the experimental I–V curve and the combinational fitting curve by quantum tunnelling process and thermionic process of ZnO/Si-NPA (b).

4. Conclusion

A highly compacted and well crystallized ZnO thick film is grown on a Si-NPA substrate by using a vapour phase transport method. The growing process of ZnO on Si-NPA is analysed according to the structural characteristics of Si-NPA. Based on the data of experimental I–V curve, the diode ideal factor is calculated. Theoretical analysis shows that the carrier transport across ZnO/Si-NPA heterojunction is dominated by two mechanisms, i.e. a thermionic process at high voltages and a quantum tunnelling process at low voltages.

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