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ARTICLE

Lateral Growth of ZnO Nanowires Network Based on the Micro-electrode

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Abstract: Using the substrate with the unique nanometer column arrays, the two dimensional ZnO nanowires network circuit was realized by CVD method without catalyst. This work not only removed the catalyst contamination, simplified the process and reduced the cost of nanowire's production, but also offered the new technical reference for breaking through the nano electronic devices limit.

Key words: nanowire network; CVD; catalyst-free; lateral growth

As a promising semiconductor, ZnO, has a large exciton binding energy of 60 meV, and a wide band gap of 3.4 eV at room temperature, high mechanical and thermal stabilities [1].

Vapor deposition and hydrothermal method are two most commonly used methods of synthesis of ZnO nanowires. Due to the low growth temperature of hydrothermal method, nanowires usually have a lot of defects so that they are easy to be polluted by catalyst, leading to the bad electrical and mechanical performance[2]. However, vapor deposition method, tends to use a kind of precious metals, e.g. Au, as a catalyst, at high temperature (900 ℃) to induce the growth of nanostructures.

Regarding with horizontal growth of nanowire arrays, researchers have used sputtering or the deposition in anisotropic deposits a layer of ZnO seed crystal substrate via catalyst-free CVD[3-5] in recent studies, but there are complex catalyst layer preparation, catalyst pollution and the synthetic efficiency of lateral growth, and hence the quality are not ideal.

It is a challenge to produce the large scale ZnO nanowire network by means of catalyst-free CVD. In order to achieve this goal, ZnO nanowires network must grow in the side of the micro/nano electrodes, rather than the substrate. Unfortunately there are very few papers about this until now.

In this paper, we report a novel method to realize catalyst-free growth of ZnO nanowires network directly on SiO_2/Si wafer with the independent designed nanometer column array by CVD method. Compared with reported catalyst-free growth of ZnO nanowires on SiO_2/Si substrates, our proposed method is much simpler, safer, cheaper, and more controllable[3,6].

1 Experiment

The SiO_2/Si wafer was cleaned with acetone, ethanol and deionized water in turn with the help of ultrasound, and then the wafer was dried with compressed nitrogen. The substrate is heated for 2 min at 100 ℃ being coated with S1818 photoresist in a spin coater at 3500 r/min. Then, the periodical square pillar microstructure with a top area size of 10 mm×10 mm and a height of around 1 mm was fabricated on substrate surfaces by RIE (Magnetic Enhanced Reactive Ion Etching, SF6:CHF3= 10:40) after a UV lithography process.

The synthetic process of ZnO nanowires network used mixture of ZnO and graphite powder with molar ratio of (1:4) gas-solid (VS) mechanism[7-10] different from the vertical TEM and placed them in a quartz boat, which was placed at the center of a ceramic tube in the vacuum tube furnace (BTF-1200C, BEQ). The substrate with the nanometer column array was cleaned and placed top down, right above the source material. Then, the whole system was pumped down to 20 Pa using an oil

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pump. 100 mL/min nitrogen and 2 mL/min oxygen were introduced into the chamber to bring the system pressure back to 3×10^7 MPa. By keeping a constant pressure of 3×10^7 MPa, the system then was heated up to 900 ℃ at a rate of 20 ℃ min^{-1}. After keeping at peak temperature for 30 min duration, the furnace was shut down and naturally cooled to room temperature.

The ZnO nanowires networks were characterized by high-resolution transmission electron microscopy (HRTEM, Zeiss LIBRA 200 FEG operated at 200 kV), field emission scanning electron microscope (FESEM, JEOL-7800), and X-ray diffractometer (XRD, X'Pert Powder) with Cu Kα radiation.

2 Results and Discussion

2.1 Growth mechanism of the lateral growth of ZnO nanowire nanonets

The characterization results of the as-synthesized ZnO nanowire network on the edge of the columnar electrode are shown in Fig1. Further XRD pattern and TEM images indicate the typical ZnO wurtzite structure and that (002) peaks are the main peak, which demonstrates that all of the ZnO nanostructures have a highly preferred [002] orientation.

The growth mechanism of the lateral growth of ZnO nanowire without catalyst coating in the substrate surface, was growth nanowires mechanism (VLS) in the substrate surface[11].

In the process of heating materials, source materials firstly ZnO powder and graphite powder chemical reaction between zinc steam, and then reaction generating gaseous zinc substrates in the columnar react with oxygen electrode chamfered edge into the nanometer array of ZnO crystal growth. The reaction is as follows:

First step:

$ZnO+C\rightarrow Zn+CO$

Or

$C+O_2\rightarrow CO$, $ZnO+CO\rightarrow Zn+CO_2\uparrow$

Second step:

$Zn+O_2\rightarrow ZnO$

According to the theory of Periodic Bond Chain (PBC)[12], there are a series of strong cycle repeatability of key chain within crystal, and the characteristics of the crystal are formed by the series of continuous strong key chain in the crystal lattice. Crystallization activation energy can be expressed as:

$$E_{hkl}^{cr} = E_{hkl}^{att} + E_{hkl}^{slice} \quad (1)$$

Where, E_{hkl}^{att} is (*hkl*) energy released each unit growth E_{hkl}^{slice} is surface energy.

In the experiments, the columnar chamfered edge is perfect K surface, which has a higher surface binding energy, very favorable for the nucleation and growth of ZnO. The key driving forces that guide the ZnO to nucleate and grow as nanowires on the edge instead of the surface is the local concentration of Zn vapor clusters and high binding surface energy at the top edge of the square pillar[13,14].

In the early of the growth, reactants generated zinc steam, and flowed upward to the substrate. Reaching the substrate, the zinc steam splits and flows along the square at the bottom electrode edge. Due to the nucleation occurring only in the right place,

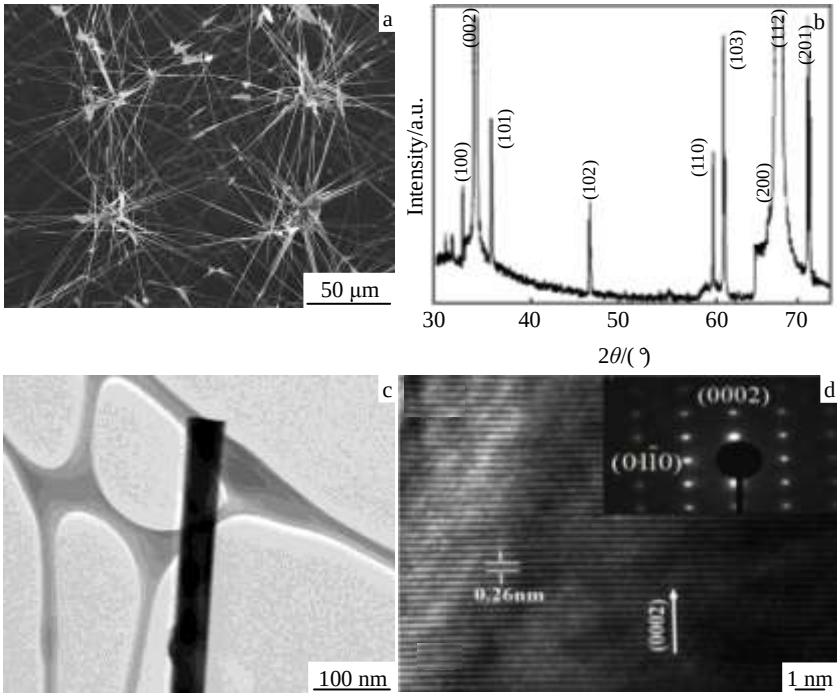

Fig.1 Characterization results for the as-synthesized ZnO nanowire network on the edge of the columnar electrode: (a) SEM image of ZnO nanowire network, (b) XRD pattern of the as-grown nanowires, (c) TEM image of a typical nanowire, and (d) high resolution TEM image of nanowire. (inset is the corresponding TEM diffraction pattern)

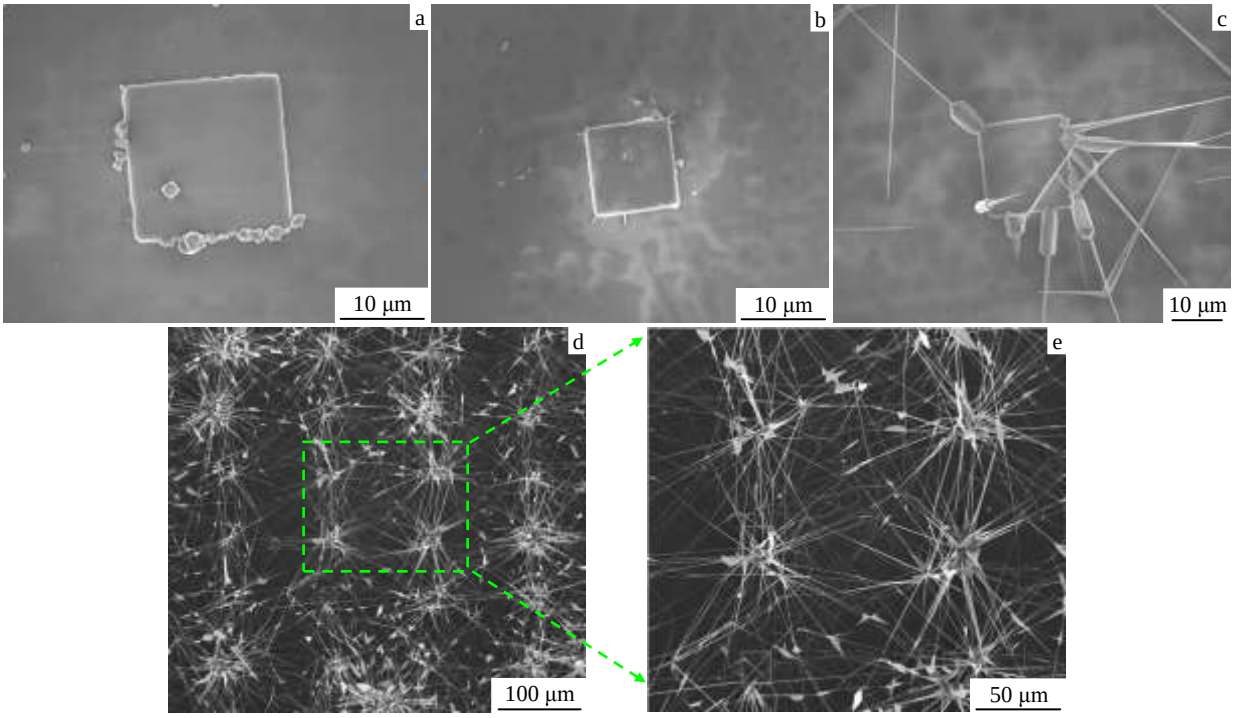

Fig.2 SEM images of ZnO nanowires grown on a bare silicon substrate with columnar electrodes: (a~c) growth result with a synthesis time of 10, 20 min; (d) low magnification SEM image of the growth result with a synthesis time of 30 min; (e) zoom in SEM image of the area with the red line indicated in Fig.2d

some zinc atoms adsorb at the edge for the high binding energy[15]. These zinc atoms can react with the oxygen atoms to form ZnO crystal nucleus. In the second stage, ZnO molecules tend to gathered near the crystal nucleus and precipitation formation of ZnO arrays.

2.2 Verification of the lateral growth mechanism

As shown in Fig.2a, some small bright spots growing on the edge of the cylindrical electrode edges after 1 min illustrate that there are some crystal nucleus on the edge of the substrate of cylindrical electrode edges. The bright spots are proved to be ZnO crystal nucleus by EDS spectrum diagram. With the increasing of the growth time, the ZnO deposits near the nucleation and forms small nanowires. Since ZnO forms nucleus only on the edge of the substrate of cylindrical electrode edges, ZnO nanowire arrays only in the edges of the electrode edges, as shown in Fig.2b. After the formation of the nanowire arrays, atoms tend to be deposited on the formed nanowires, making the diameter and length of nanowires increase over time, as shown in Fig.2c. It can be seen that the large area of the nanowires can be synthesized on the electrode. And most of the ZnO nanowires grow on horizontal or inclined to the electrodes on the electrodes, as shown in Fig.2d. Through the high times of SEM, the structure of the nanowires nanonets can be seen in Fig.2e.

3 Conclusions

The lateral ZnO nanowire network is fabricated successfully by placing the substrates over the source material, and controlling the steam flow and the cavity pressure. There are two main factors: one is that the edge of the electrode has high binding energy, while the other is that the concentration of the steam is higher at the edge of the square pillar electrode material.

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基于微柱状电极生长 ZnO 纳米线的研究

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摘　要：采用硅衬底电极无催化剂制备横向 ZnO 纳米线，实现了二维氧化锌纳米线网电路的制备。本研究涉及的技术一方面可以为突破纳电子器件制备极限提供新技术参考；另一方面，去除了纳米线生长过程中的金催化剂污染，降低成本，简化工艺。

关键词：纳米线网；CVD；无催化剂；横向生长

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