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Solution-grown ZnO Nanorods on Femtosecond Laser-microstructured Si Substrates

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High density ZnO nanorods were prepared on femtosecond laser-restructured Si substrates by the simple and facile sol-gel and chemical bath deposition combination technology. ZnO nanorods, preferentially oriented along the c-axis, were of the hexagonal wurzite structure. The investigation shown that the ultrafast melting and ablation can change the lattice constant during the formation of Si surface microstructure after laser irradiation, which can result in the surface of Si destroyed and rebuild. As a result, the strain between ZnO nanorods and Si can be effectively decreased. The influencing mechanism of laser-restructured Si surface on the characteristics of ZnO nanorods was further analyzed.

Keywords: ZnO; nanorods; laser-restructured Si; Strain

1. INTRODUCTION

One dimensional (1D) nanostructures have attracted much attention in the past years owing to their special properties and potential applications in electronic and optoelectronic nanodevices. ZnO has a wide direct band gap of 3.37eV at room temperature and a large exciton binding energy (60meV) [1]. As for the practical application, a key issue in this field is how to realize the high-density arrays of 1D ZnO nanostructure to obtain the desired gain and efficiency. It is necessary to fabricate high density ZnO nanostructure on the substrate surface. In a conventional filmlike nanorods or nanowires arrays structure, the density of ZnO nanorods may be difficult to improve. Some efforts have demonstrated the formation of high-density regular arrays of nanometer-scale Si rods using femtosecond laser irradiation of silicon surface immersed in water [2]. Cheng et al. developed a

method to fabricate highly ordered treelike Si/ZnO hierarchical nanostructures in a large scale by combining two common techniques [3]. Zhao and his coresearchers reported that hierarchical tree-like ZnO arrays with increasing branching order and complexities have been grown on zinc plates by a hydrothermal oxidation approach [4].

Owing to the promising applications, various ZnO nanostructures such as nanoribbons, nanowires, and nanopins have been fabricated by means of catalyst assisted vapor-phase transport [5], non-catalytic vapor-phase epitexy [6], and electrodeposition baths with three electrodes[7], but they are complex procedures, costly, or sophisticated equipment. Pulsed laser-assisted etching offers an attractive route to fabricate the micrometer-scale structures [8-11]. However, the size of such structures is typically larger than the laser wavelength. The facile solution procedures have been the popular preparing large-scale and well-crystallized ZnO 1D nanostructures way due to their simple and cheap properties. If the ZnO nanorods were grown directly on to the surface of Si substrate, serious strain would be generated between ZnO and Si due to the large lattice mismatch, which can lead to various edge dislocations introduced [12-14]. The defect can play an important role in the optical characteristics of ZnO nanorods prepared by solution method. We believe that the strain can be decreased by introducing the buffer or appropriate changing of substrate surface in order to obtain the high-quality and well-aligned ZnO nanorods on the Si substrates. On our previous investigation, depositing appropriate thickness ZnO on Si substrate by the sol-gel technology can effectively decrease the biaxial compressive stress [15]. Thus, high quality and density vertically aligned ZnO nanorods arrays prepared on femtosecond laser-microstructured Si substrates can be achieved by the simple and facile sol-gel and chemical bath deposition combination technology.

In this letter, we report a simple process for large-scale fabrication of single-crystal ZnO nanorods arrays on femtosecond laser-microstructured Si substrates. Effect of the strain on the optical and structure properties of ZnO nanorods films were investigated by Raman and XRD. The influencing mechanism of laser-restructured Si surface on the characteristics of ZnO nanorods was also analyzed.

2. EXPERIMENT

A regenerative Ti:Sapphire amplifier system with a central wavelength of 800 nm, pulse duration of 125 fs, and repetition rate of 1 kHz is used in the experiments for fabricating large area nanostructures.

All chemicals used in this experiment, such as zinc acetate dihydrate $Zn(Ac)_2•2H_2O$, hexamethylenetetramine ($C_6H_{12}N_4$), 2-methoxyethanol, diethanol amine(DEA) are analytical grade regents and used as purchased without further purification. The fabrication of ZnO nanorods on femtosecond laser-microstructured Si substrate in this work was finished by using the two steps method. Seed layers were deposited on the substrates by the conventional sol-gel spin coating method and the rapid thermal treatment. The details of this procedure are as follows: 32.925g $Zn(CH_3COO)_2•2H_2O$ is dissolved to the 185.61 mL of 2-methoxyethanol under mild magnet stirring and then 14.39 mL of DEA is slowly added drop by drop as a sol stabilizer. The molar ratio of $Zn(Ac)_2•2H_2O$ and DEA solution is maintained at 1. The mixing solution is stirred at 60^oC for 2h to

form a transparent and homogeneous solution and then aged for 24h before pulling process. The pulling process on substrate is repeated 3 times. After each pulling, the film is dried at 100^{o}C for 10min in order to evaporate the solvent and remove the organic residuals. The resulting films are annealed at 500 ^{o}C for 1h to form the ZnO seed layers on surface of micrometer-sized silicon spikes.

The second step is preparing the ZnO nanorods on the as-prepared ZnO film by chemical bath deposition. The equimolar (1:1) mixed solution of $Zn(Ac)_2$•$2H_2O$ and hexamethylenetetramine (HMT) is used. 1.317g $Zn(Ac)_2$•$2H_2O$ and 0.8411g $C_6H_{12}N_4$ are first dissolved to 200mL deionized water under mild magnet stirring for 5 min at room temperature. The substrates with ZnO seed layers are immersed and suspended in the mixed solution respectively and stayed at 90^{o}C for 1.5h without any stirring. The obtained samples are rinsed with deionized water and dried in air before characterization.

The general morphologies of the ZnO thin films and thereon ZnO nanorod arrays were examined by scanning electron microscopy (SEM). The crystal phase and crystallinity were analyzed at room temperature by XRD using Cu Kαradiation. The room PL spectra of the as-prepared sample were measured using a Xe lamp with an excitation wavelength of 325nm. The Raman scattering was performed in the near backscattering geometry using an Ar^{+} laser and the power of 20mW.

3. RESULTS AND DISCUSSION

Fig 1 shows the typical top view SEM micrographs of the Si substrate acting by femtosecond laser and ZnO nanorods prepared on microstructure Si substrate, respectively.

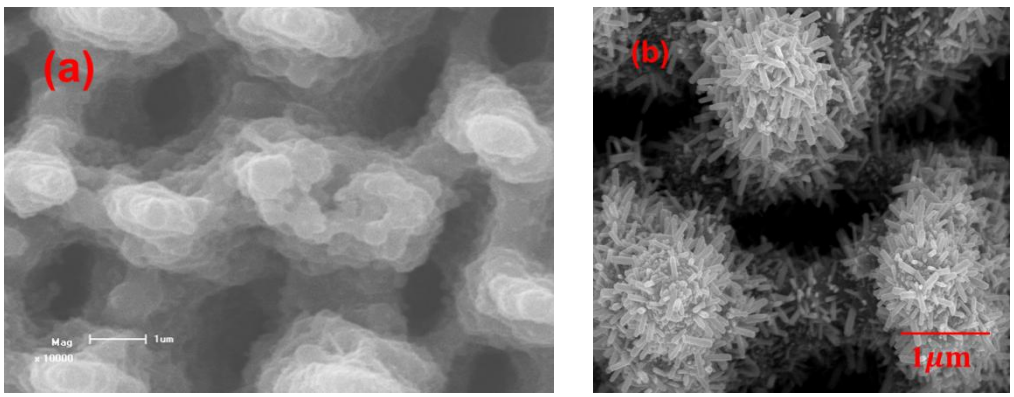

Figure 1. SEM images of (a) femtosecond laser-microstructured Si substrate and (b)ZnO nanorods prepared on microstructure Si substrate.

The polished Si surface has undergone melting and rebuilding after acting by the femtosecond laser with high energy. The micrometer-sized silicon spikes were formed and with several micron thickness and high, as shown in Fig 1(a). Fig 1(b) shows SEM image of the ZnO nanorods on surface of the femtosecond laser-microstructured Si substrate. The morphology-controlled synthesis of nanostructures is a key issue in nanoscience and nanotechnology. By changing the precoating layer thickness, the ZnO nanorod size and density can be easily controlled. It can be clearly seen that a

perpendicular growth of ZnO nanorods on the surface micrometer-sized silicon spikes and holes with an average length of several hundred nanometers and diameters of 40-60nm.

The structural properties of the as-prepared ZnO nanorods were characterized by Rigaku X-ray diffractometer using Cu-radiation (λ=1.54178Å）. The diffraction angle was scanned from 20° to 80° at the scanning speed of 0.02° per second. Figure 2 shows the powder X-ray diffraction (XRD) patterns of the as-synthesized samples, where the main diffraction peaks can be attributed to the hexagonal wurzite ZnO with lattice constants of a=0.324nm and c=0.521nm, which results is quite close to that the bulk cubic ZnO. The diffraction peak intensity can further demonstrate a preferential growth direction along the c axis. The weak intensity of ZnO(002) can be ascribed to the irregular surface of the Si microstructures. The higher surface energy and thermodynamic metastable in the polar surface for ZnO results in faster growth along the (0001) direction, and thus, ZnO nanorods were formed [16, 17]. In contrast, the diffraction patterns of ZnO grown the Si substrate without laser irradiation shift to higher angles compared with the data of ZnO nanorods grown on Si microstructures, which can be result from the biaxial compressive stress within the ZnO films grown on Si(100). The ultrafast melting and ablation were play decisive roles during the formation of Si surface microstructure after laser irradiation, which can result in the surface of Si destroyed and rebuild. This is a possible explanation for why the XRD peaks of ZnO grown on Si microstructure is good agreement with the bulk cubic ZnO.

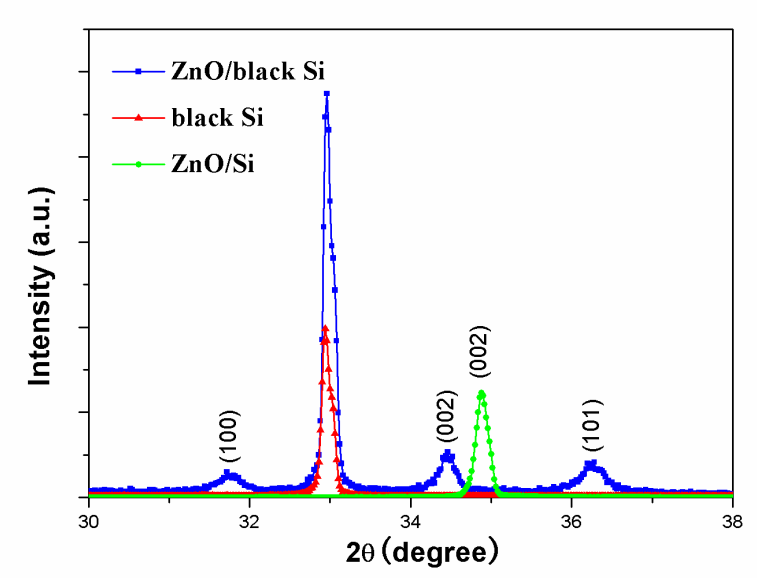

Figure 2. X-ray diffraction patterns of Si substrate (red line) and ZnO nanorods on femtosecond laser-microstructured Si substrate (blue line).

To understand the chemical bonding structure of as-grown ZnO nanorods, XPS was used to investigate the surface composition of the samples. Fig 3 shows the XPS survey spectra from as-grown ZnO nanorods on Si substrate and femtosecond laser-microstructured Si substrate, in which all of the peaks can be only ascribed to Zn, O, and C elements as labeled in Fig 3. It indicated that there were no

other impurities observed in both samples. We would like to mention that, in all the XPS spectra of ZnO nanorods, the binding energies have been calibrated by taking the carbon C1s peak (285.0 eV) as reference. The O1s state peak of ZnO nanopowder was fitted into two peaks as shown in Fig. 4 (c). The peak at 531.4 eV can be attributed to the O-Zn bond formation, while the peak at 532.8 eV can be due to the O-H bond formation [18]. The observed peak with binding energy of 1022.91±0.3 corresponds to Zn species (1022.73) in ZnO(OH) according to Ref.[19].

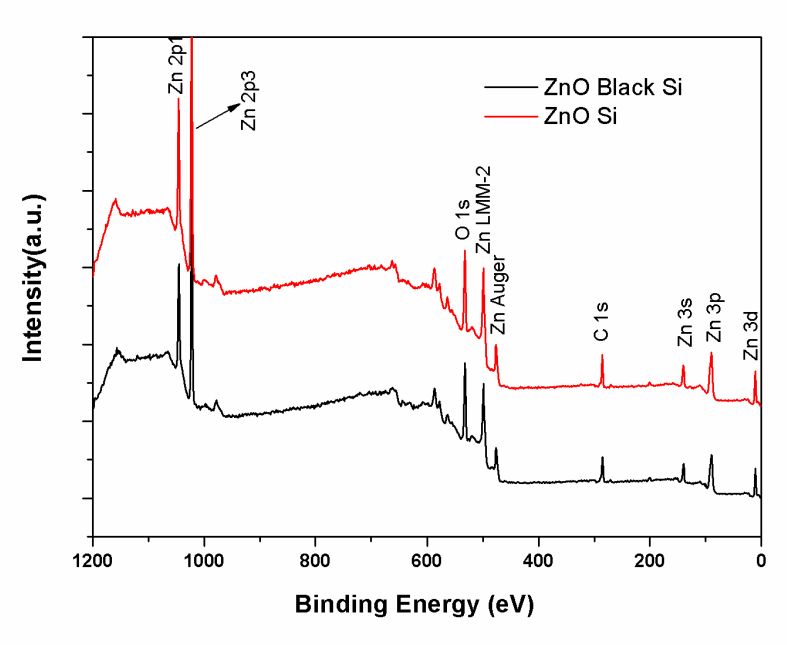

Figure 3. XPS survey spectra of as-grown ZnO nanorods on femtosecond laser-microstructured Si substrate.

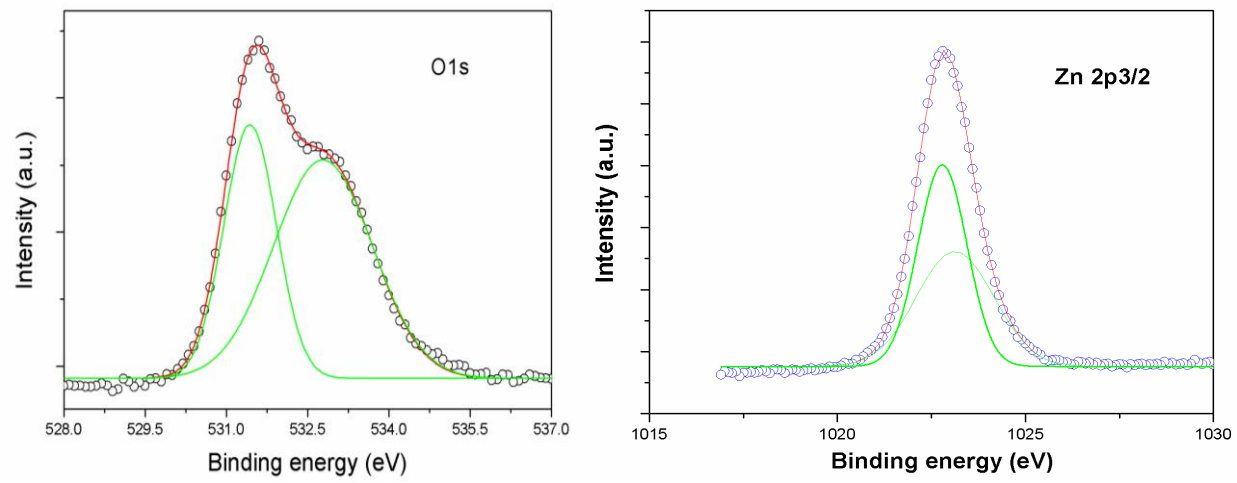

Figure 4. O1s XPS spectra (left) and Zn 2p3/2 XPS spectra (right) of as-grown ZnO nanorods, where two components (green curves) were used to deconvolute the experimental peak. The labels indicated the origins of the corresponding peaks.

The PL spectra of the as-prepared ZnO samples were measured using a Xe lamp with an excitation wavelength of 325nm at room temperature. Fig 5 shows the PL spectrum consisting of a weak green band at 375nm~425nm in wavelength and a very broad band located in the blue-red region. The band-edge emission is at 391nm, which can be ascribed to the free exciton recombination. The green band was generally explained by the radial recombination of a photogenerated hole with the electron in a singly ionized oxygen vacancy or surface states. Although high quality ZnO nanorods were prepared by the two-step method, a number of interface states were produced, which can result in the green-blue band emission increasing. It can be clearly seen that the overall features of the spectrum differ from the previous investigation results. The integrate intensity ratio of the deep level emission to the band edge emission have a large ratio value, which indicates that the films prepared by the two-step method contained a number of impurities and defects. It is generally acknowledged that excess zinc or oxygen vacancies, these defects can be introduced and act as nonradiative centers and reduce green light emission in low temperature solution deposition [14]. According to the effective mass approximation with considering the effect of Coulomb interaction energy, the quantum confinement effect of the ZnO nanorods can be analyzed quantity. For the nanorods with radius r=40-60nm, the effect of the quantum confinement on excitonic emission of ZnO nanorods can be negligible according to the simple calculation [15]. The investigation shows that the quantum confinement effect can only be observed from ZnO nanorods with a diameter of less than 20 nm [20]. Obviously, the strain from the substrate has few influencing on the optical properties of ZnO nanorods prepared by the solution method.

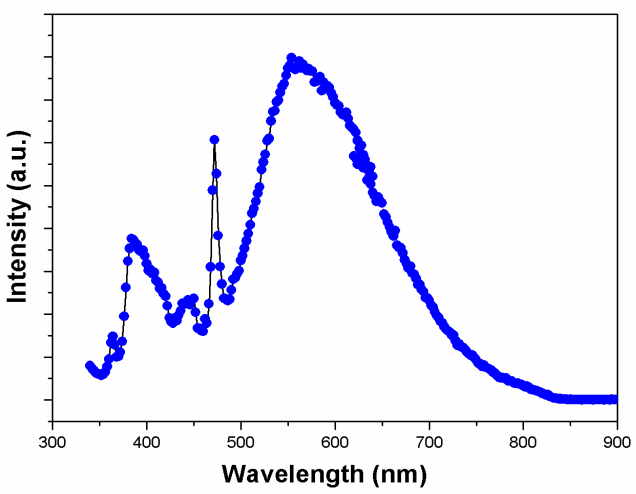

Figure 5. Room temperature PL of the ZnO nanorods on femtosecond laser-microstructured Si substrate.

This formation mechanism of ZnO nanorods can be analyzed as follow. When Si sample is ablated with a single femtosecond pulse, a large proportion of the absorbed energy is dissipated into the bulk of the sample, which can change the structure of Si surface due to the ultrafast melting and ablation after laser irradiation. When ZnO collosol was deposition on the surface of the femtosecond

laser-microstructured Si substrate, ZnO crystalline grains can be formed with the temperature increasing. The lattice constant can be affected by the structure of Si surface. In the process of the formation of ZnO nanorods, the ZnO crystalline grains act as the role of the nuclei. The size of ZnO nanorods can be mainly dependent on the size of crystalline grains, which can result in the nanorods with different diameters. As for the growth direction of ZnO nanorods, the surface attracted opposite charged ions on it and reacted to form ZnO nanorods owing to its anisotropic growth character because of the polar nature of positively or negatively charged ZnO surface [18]. The nanorods grew preferentially along (001) directions due to the high surface energy of (001) facets.

4. CONCLUSIONS

In summary, high density ZnO nanorods were prepared on femtosecond laser-restructured Si substrates by the simple and facile sol-gel and chemical bath deposition combination technology. ZnO nanorods, preferentially oriented along the *c*-axis, were of the hexagonal wurzite structure. The investigation shown that the ultrafast melting and ablation were play decisive roles during the formation of Si surface microstructure after laser irradiation, which can result in the surface of Si destroyed and rebuild. Laser-restructured Si substrates have few effects on chemical bonding structure of as-grown ZnO nanorods, which can show that the seed layer play a crucial role on ZnO nanorods growth.

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