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Selective Growth of ZnONano-Porous Films by the Hydrothermal Technique

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Abstract: Well crystallized ZnOnano-porous films were selectively grown on the Al substrate using zinc nitrate(Zn $(NO_3)_2$) and hexamethylenetetramine ($(CH_2)_6N_4$) by the hydrothermal growth technique. We already reported the high-quality ZnO nanorods vertically grown on a GaN substrate owing to a good lattice match. However, in case of Al substrate, it was not a nanorods but a nano-porous film consisting of three dimensional 3D nanoflakes. The as-grown nano-porous films were highly crystalline, possessed a wurtzite hexagonal, confirmed from the X-ray diffraction (XRD) measurement. The proton induced X-ray emission (PIXE) experiment confirms the absence of any foreign element in ppm level in ZnOnano-porous film. It is suggested that the nanorod grows laterally on Al film and merges with the adjacent nanorods to form 2D nanoflakes. As the growth continues, the 2D nanoflakes are piled up to form 3D nanoflakes and finally a nano-porous film as seen under Scanning Electron Microscope.
Keywords: ZnONano-Porous Films, Hydrothermal Technique.

Introduction

Great variety of Zinc oxide nanostructures with one-dimensional (1D) and two-dimensional (2D) morphologies have been successfully developed, due to their outstanding properties piezoelectric, [1]pyroelectric,[2] and photoconducting[3] and potential applications in numerous fields, such as solar cells,[4] room-temperature ultraviolet lasers,[5] light emitting diodes,[6] field-emission devices,[7] gas sensors,[8,9] and photocatalysts[9] in recent days. Growth of nanostructures on metal films is useful to construct nano-electronic devices, piezoelectricdevices and different applications including sensors and detectors. The choice of substrate and thegeometry of the play an important role to develop various sensors and detectors. Moreover nano-porous surface are very important for different type of gas sensor application. These nanostructures are highly desired and widely studied because they can be considered as nanoscale building blocks for future optoelectronic devices. One of the interesting applications is an ultraviolet (UV) light-emitting diode (LED) [11] fabricated from n-ZnO and p-ZnO. However, improvement of the diode characteristic is expected by using ZnOnanorods, which usually have crystallinity better than ZnO thin films because of the 1D growth. The selective growth of ZnOnanorods is highly desirable for practical applications.There are number of methods have been devised and reported[1, 5-10] for Zinc oxide growth. However, the solution phase growth[6,8,10] has been demonstrated as one of the promising route rather than the vapor phase growth [1,5,7] techniques. Moreover, different types of substrate such as sapphire, GaN, soda-lime glass[4], different orientations of silicon[2,8,12], alumina[1,5], indium-doped tin oxide substrates, and steel alloy substrates[13] have been used to grow the ZnOnano-porous films, but the synthesis of ZnOnano-porous film on metal substrates has not been investigated rigorously. However, ZnOnano-porous film on highly conducting metal substrate have been regarded as one of the important issues for application in optoelectronic device fabrication process.The easy availability and the fact that they are cheap and easy use, makes Aluminum (Al) a good substrate candidate for the large scale synthesis of ZnOnano-porous film.

In this work, we report the synthesis and detailed characterization of ZnOnano-porous films on Al metal substrates by hydrothermal method. TheZnO films obtained on metal substrates shows selective growth and have wurtzite hexagonal structure with nano-porous films.

Experimental

The procedure to prepare ZnOnano-porous by hydrothermal growth technique is reported elsewhere.[14] Al-patterned Si substrates were used to study the selective growth of ZnOnano-porous film. The aqueous solution contains the mixture of zinc nitrate ($Zn(NO_3)_2$) and hexamethylenetetramine ($(CH_2)_6N_4$) with the concentration of 10 mM and the molar ratio of Zn:HMT being 1:1 for ZnOnano-porousfilm growth. The mixture was transferred into a stainless steel bottle with a screw cap with a filling capacity of about 80%. Subsequently, a piece of Al patterned Si substrate was placed vertically in the sealed autoclave and heated at a constant temperature of 90 °C for 4 h. Prior to ZnOnano-porous growth, 50nm thick Al films were deposited by vacuum evaporation on Si through a shadow mask to prepare Al-patterned substrates. Finally, the nano-porous films prepared on Al-patterned substrates were thoroughly washed with deionized water to eliminate residual salts, and dried in air. The scanning electron microscopy (SEM) micrographs of the as grown nano-porous films were obtained using a JEOL JSM-6340. The X-ray diffraction (XRD) spectra were collected using Phillips-X'Pert with Cu Kα X-ray source. The Elementalanalysis was made by proton-induced x-ray emission (PIXE).

Result and Discussions

Figure 1 (a)depicts the morphology of ZnOnano-porous films grown on the silicon substrate coated with 50 nm Al film. As shown in Fig.1, SEM image, clearly depicts thenano-porous film consisting of three dimensional 3D nanoflakesmorphology of ZnO nanostructures. There is no deposition of ZnOnano-porous film on Si. However, the growth of ZnOnano-porous films are only on Al. Hence selective growthof ZnOnano-porous films are possible on Al metal surface. Fig 1(b) shows the high magnification part of theZnOnano-porous film. The width of the nano-porous wall found to be varied from 50 to 100 nm.

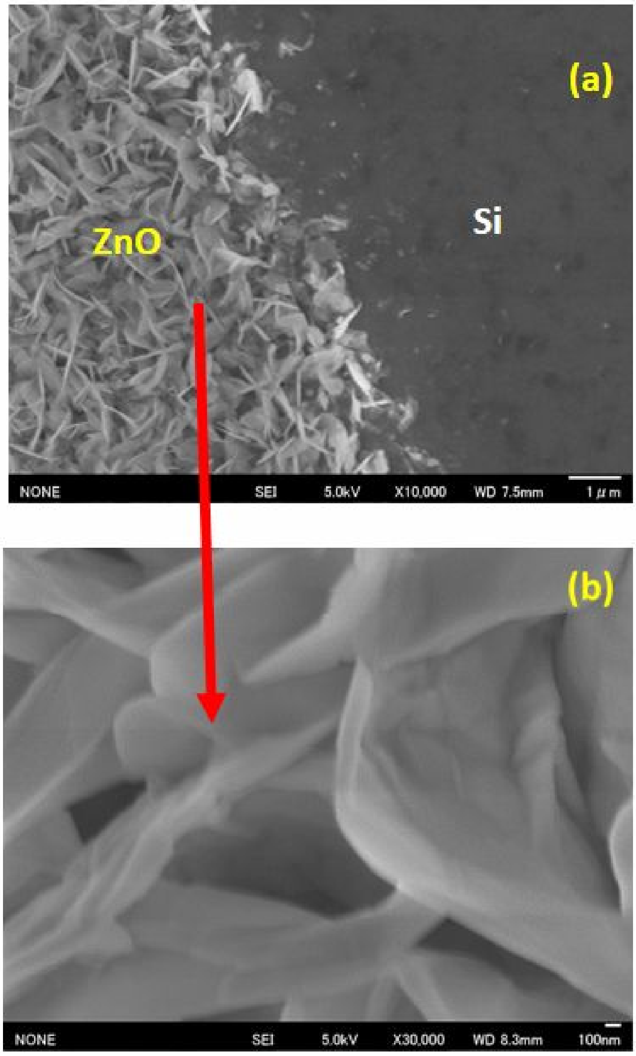

Figure 1. (a)SEM micrographs of ZnOnano-porous films grown on Al patterned Si substrate, (b) The high magnification part of the SEM micrographs of ZnOnano-porous filmsgrown on Al patterned Si substrate.

The as-grown ZnOnano-porous films on Al were investigated by XRD as shown in Figure 2. The wurtzite structure and polycrystalline nature was confirmed from the XRD diffraction pattern of the nano-porous film on Al as shown in Fig. 2. The spectrum clearly shows an a-axis texture of the ZnOnano-porous film, with intense (1100), (1101) and (1120) reflections. This result indicates that the film grew with a prism lateral plane lying in the film plane, i.e. with c-axis parallel to the Al substrate surface.

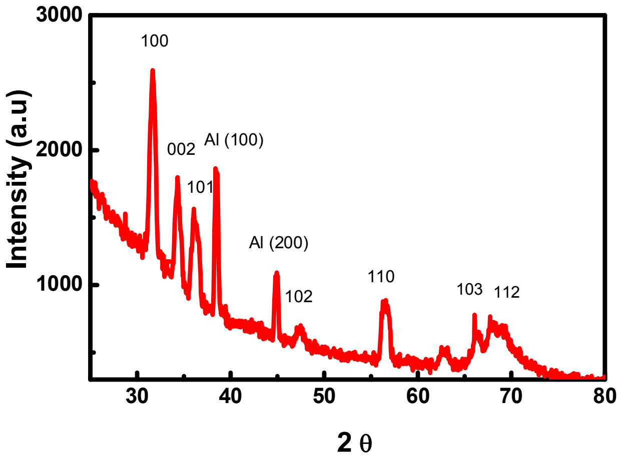

Figure 2. XRD spectra of ZnOnano-porous films grown on a Al substrate.

Usually, the hexagonal wurtziteZnOcrystals grows preferentiallyalong (001) direction due to the lowest surface energy of(002) facet, leading to the formation of nanorods. As the substrate is aluminum, nano-porousmorphology of ZnO crystal grows. It is suggested that the nanorod grows laterally on Al film and merges with the adjacent nanorods to form 2D nanoflakes. As the growth continues, the 2D nanoflakes are piled up to form 3D nanoflakes and finally a nano-porous film as seen under Scanning Electron Microscope as shown in Fig 1. We believe, aluminum substrate should be responsible for the suppression of ZnO growth along (001) direction.During the ZnO nanostructure growth, reaction of Zn $(NO_3)_2$ and HMT produces OH^{-}anions as shown in the chemical equation 3.

$$Zn(NO_3)_2 . 6H_2O \rightarrow Zn^{2+} + 2NO^{-}_3 \quad (1)$$

$$C_6H_{12}N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (2)$$

$$NH_3 + H_2O \rightarrow NH^{+}_4 + OH^{-} \quad (3)$$

$$2OH^{-} + Zn^{2+} \rightarrow Zn(OH)_2 \quad (4)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (5)$$

The OH^{-}concentrationcan slower the formation process of new Zn $(OH)_4^{2-}$ionsand suppress the crystal growth along [001] direction[15]. At the same time, aluminum can be dissolved into the solution under alkaline conditions in the presence of HMT and Al $(OH)_4^{-}$ ions are first formed by the reaction between OH^{-} and Al substrate. Then Al $(OH)_4^{-}$ bind to Zn^{2+} -terminated (001) surface more stronglythan to other nonpolar surfaces resulting suppression of growth along (001) direction and enhancing the growth along lateral direction.

PIXE is a highly sensitive tool for elemental analysis. It isan excellent technique to identify any defect or impurity in the samples in parts per million (ppm) level. The as-grown ZnOnano-porous films were characterized by PIXE analysis to probe the impurity in ZnOnano-porous films. In general, PIXE is an ion beam analysis technique commonlyused to perform elemental analysis with a detectionlimit of ppm for elements atomic number *(Z)*>10 in any material[16].The PIXE analysis were performed by using apelletron accelerator with 3.0 MeVproton beam situated at Institute of Physics, Bhubaneswar, Indiaand the results were showed in figure 3. Inthe PIXE spectrum, elements were identified based on theircharacteristic x-ray energy. Only Zn related peaks are seen in figure 3revealing the purity of ZnOnano-porous films. No other elements found in the spectra confirms the absence of any impurity in the ppm level.

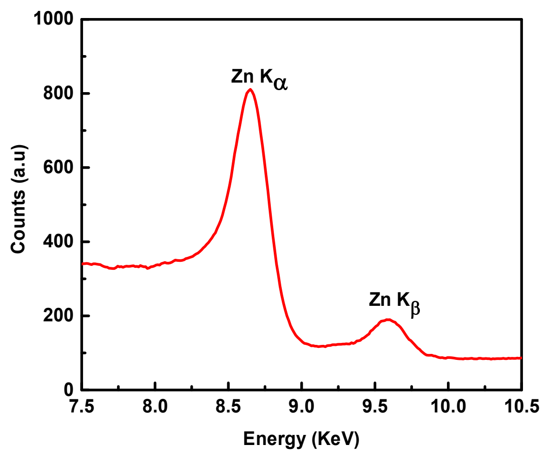

Figure 3.PIXE spectrum of ZnOnano-porous films.

Conclusions

In summary, the growth of ZnOnano-porous films through the hydrothermal method was studied using metal Al substrate. The nanostructures growth found to be selective for Alpatterned substrate. The as-grown ZnOnano-porous films were highly crystalline, possessed a wurtzite hexagonal structure. The proton induced X-ray emission (PIXE) experiment confirms the absence of any foreign element in ZnOnano-porous films in ppm level.

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