Synthesis of ZnO Nanostructures on Silicon Wafer by Wet Chemical Method

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Abstract

The ZnO nanoflowers, nanosheets and nanoparticles were synthesized on silicon (Si) wafers by a wet chemical method at low temperature (~ 35ºC). The ZnO nanosheets and flowers have been grown without any catalyst and surfactant at low temperature just by solvent variation in the solution. While using the surfactant nanoparticles have been synthesized. The ZnO nanosheet with thickness 10 nm, were interwoven into network to form a nanosheet film on surface of Si substrate. The growth mechanism and an effect of surfactant on the morphology are also discussed in detail.

1. Introduction

Among various semiconductors, ZnO has many excellent properties such as direct band gap (3.37eV), transparent, piezoelectric and strong excitons energy (60 meV) [1-4]. Also, it has valuable characteristics, such as a large piezoelectric constant, excellent thermal and chemical stability, and an easily modified electric conductivity. Because of these properties it is considered as an attractive material for gas sensors [5], solar cells [6], light emitting diodes [7], transistors [8], nanolasers [9], photocatalysts [10], photodetectors [11] etc. The ZnO nanostructures can be synthesized by many methods [12-17]. Among these the wet chemical method is considered more prominent since it is a low cost method with a simple process set-up and enables large-scale production at low temperature synthesis.

So far the nanostructures are concern, various morphologies of ZnO such as nanorods [18], tubes and wires [19, 20], belts [21], disks [22], rings [23], cables [24], combs [25], tower-like [26], flower-like [27], tetrapods [28], nano-helices [29] etc. have been formed for various proposed applications [30]. In this work, we report formation of nanoflowers, nanosheets and nanoparticles on the surface of Si substrate by using chemical method. These nanostructures have been formed by varying the solvent as well as by the use of surfactant. The ZnO nanoflowers and nanosheet structures—have been formed without the use of any capping materials and catalyst at low temperature unlike to the reported studies [31-34] for the formation of sheet like structures. Also using capping material nanoparticles have been formed. We investigated the influence of solvent and surfactant on the ZnO structure and morphology. The synthesis has been carried out at low temperature. A growth mechanism for the formation of the as synthesized nanoflowers, *nanosheets* and *nanoparticles* has also been presented in brief..

2. Experimental

A. Synthesis of ZnO nanoflower, nanosheets and nanoparticles

For the synthesis of nanoflowers and nanosheets, 0.35 M solution of Zinc Nitrate Hexahydrate ($ZnNO_3.6H_2O$) (with a purity of 99.99%, Sigma Aldrich) and Sodium Hydroxide (NaOH) (with a purity of 98.00%, Merck) was prepared in two different mediums namely; distilled water (H_2O) and ethanol (C_2H_5OH), respectively. In the above prepared solution a $ZnNO_3.6H_2O$ solution was added drop wise to NaOH solution at 35^oC temperatures with continuous stirring. During the $ZnNO_3.6H_2O$ solution pouring process, Si wafers were hanged vertically with the help of a clamp. The reaction proceeds till a white precipitate of $Zn(OH)_2$ was obtained. After the reaction, the wafer was washed with deionised water, and dried at 60^oC temperature. In order to synthesize nanosheets, the solvent has been varied in the solution with all similar conditions as for nanoflowers.

In case of nanoparticles, 0.05M of cetyltrimethylammonium bromide (CTAB) (purity 99%, Sigma Aldrich) was added abruptly to the above aqueous solution.Thus synthesized ZnO structures were investigated by Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) pattern analysis for their morphological and structural characterization.

3. Results and Discussion

A. ZnO nanoflowers, nanosheets and nanoparticles

Figure 1 shows the SEM image of nanoflowers and nanosheets. The nanoflowers were formed in H_2O medium. Most of the nanoflowers are grown vertically over the Si substrate. These nanoflowers are composed of thin nanosheets network (figure 1(b)). The thickness of the nanosheets is around 10 nm while their width is up to 2μm (figure 1(b)). Some of the nanosheets seem to be interpenetrating to each other (figure 1(b)). Figures 1(c) and (d) show the FESEM images of nanosheets network on the surface of Si substrate which were synthesized in C_2H_5OH medium at 35^oC temperature for 3 h of reaction time. Figure 1(d) shows the higher magnification FESEM images of large scale nanosheets grown on the Si substrate. The XRD patterns for both the nanoflower and nanosheets formed at 35°C for 3 h show diffraction peaks corresponding to (100), (002) and (101) (figure 2(a) and (b)). These diffraction peaks are in accordance with the standard data of Joint Committee on Powder Diffraction Standards (JCPDS) (file no. 89-1397). .

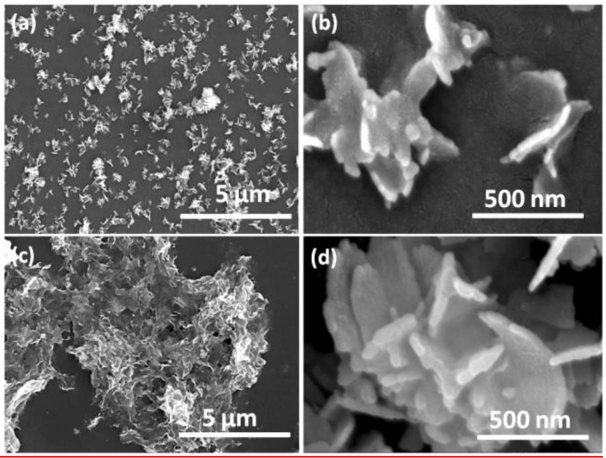

Fig. 1 FESEM image of (a) ZnO nanoflowers at lower magnification (b) at higher magnification shows consist of nanosheets (c) nanosheets network at lower magnification (d) nanosheets at higher magnification, on Si Wafer

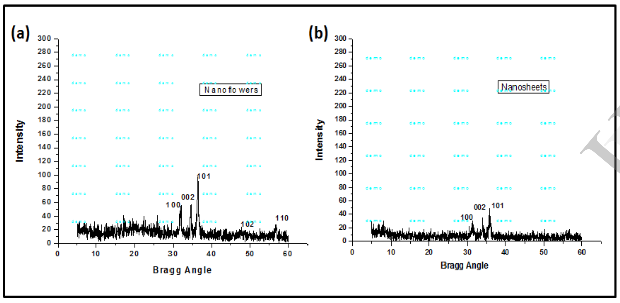

Fig. 2 XRD Patterns for (a) ZnO nanoflowers, (b) ZnO nanosheets network on Si wafer

The surfactant CTAB was used to synthesize the ZnO nanoparticles film on Si wafer (figure 3). The SEM images (figures 3(a) and 3(b)) indicate the formation of particles on Si substrate. As a rough estimation from SEM data, the size of nanoparticles is around 25 nm (figure 3(b)).

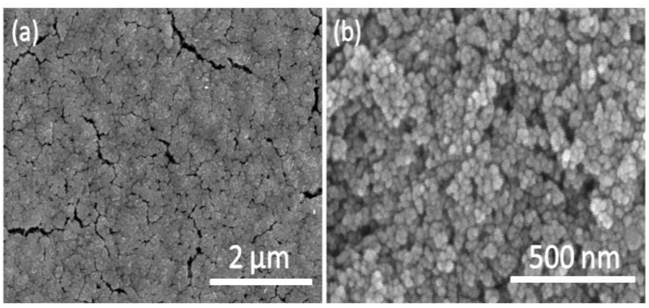

Fig. 3 FESEM images of ZnO nanoparticles synthesized in the presence of surfactant on Si wafer (a) at lower magnification (b) at higher magnification shows particles size of 25nm

B. Growth mechanism of ZnO nanoflowers, nanosheets and nanoparticles

It is expected that during the dipping of silicon substrate inside the reaction mixture at the high energy sites of Si substrate, the nuclei are formed, which with the passage of the process time grows further in the form of interwoven nanosheets. The surface of thus formed structures is not smooth as seen in figure 1(b). As the flowers are not grown uniformly on the Si substrate it is again probably due to the fact that the higher energy sites at Si substrate favours the accumulation of newly formed nuclei causing the reduction of overall system energy. In the growth process, the surface energy decreases due to the nucleation on the surface defects or active sites on the growth surface [35]. The inorganic ZnO polar nanocrystals growth is sensitive to the reaction solvents. Their morphologies can be controlled by the crystal solvent interfacial interactions and is largely directed by anisotropic growth of the initially formed aggregates, forming the sheet structure [1]. The catalyst free growth of ZnO nanoflowers and nanosheets at low temperature also depends on the physical and chemical nature of the solvents, which influences the nucleation and the oriented growth process of ZnO materials. In fact the $Zn(OH)_2$ dissociates to Zn^{2+} ions and OH^- ions, and the detachment of OH^- radical may activate the nucleation centers. ZnO nuclei can be preferentially formed on the coalescent sites by the Coulomb interactions between Zn^{2+} ions and O^- ions within the solution. As the time of growth increases more ZnO molecules will be attached to the initially formed nucleation centers. On these individually formed nucleation centers, bundles of ZnO nanosheets are aggregated in three-dimensional-array and flower-like morphology is expected to develop [36]. As using the different solution mediums i.e. H_2O and C_2H_5OH nanoflowers and nanosheets are formed on the Si substrate so it may be attributed to the solvent nature in a solution.

In general, the synthesis of the ZnO structures proceeds via the formation of $Zn(OH)_2$ which is formed due to the reaction of the base (NaOH or KOH) with $ZnNO_3.6H_2O$ precursor (in this study). Thus formed $Zn(OH)_2$, when reacts with OH^- ion, transforms into $Zn(OH)_4^{2-}$. The ZnO nuclei is the resultant of the dehydration of $Zn(OH)_4^{2-}$, which further converts into the crystal depending upon the process conditions such as the temperature, time and surfactant. The presence of the surfactant plays an important role on the growth of the nanoparticles. As mentioned earlier, in the formation of nanoparticles, we have used CTAB which works as the surfactant of the nanoparticles. For the used amount of CTAB, the obtained average size of ZnO nanoparticles is about 25 nm (figure 2(b). In general, the use of surfactant caps the surface of nanoparticles and prevents the particles from growing beyond a certain size. Therefore, while using CTAB, we note the ZnO nanoparticles are found almost spherical and smaller than the size of ZnO structures without surfactant. As stated earlier, in the case of nanoflowers and nanosheets, the solvent is an important factor which controls the growth of ZnO structures.

4. Conclusions

In a surfactant free growth medium, we have observed that the synthesis of nanoflowers and nanosheets on Si wafer is conjectured due to the reduction of the surface free energy. While using a surfactant, we have found that nanoparticles film with particles size of 25 nm is formed on Si wafer due the capping of the particle surface for further growth.

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