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Modification of ZnO Nanowires Induced by Ion Irradiation for Device Applications

Research Article

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Abstract. ZnO nanowires grown by hydrothermal method were exposed to a beam of 50 keV argon ions at a fluence of 1×10^{16} ions/cm^2. The surface morphology of the nanowires has been investigated using high resolution electron microscopy. Raman scattering study has been carried out, which shows specific features resulting from argon ion irradiation. The post-irradiated nanowires exhibit high degree of surface roughness of dimension about few nm and tip of each nanowire is sharpened after this irradiation. The combined effect of surface roughening and tip sharpening are expected to enhance the aspect ratio as well as the effective surface-to-volume ratio. We invoked size and curvature dependent sputtering and defect dynamics to explain the observed features. We envisage that such increase of surface area and tip sharpening may enhance applications of these modified ZnO nanowires in the field of catalysis, gas sensing, field emission and photovoltaic.

Keywords. Nanowire; Ion irradiation; Surface modification, HRTEM

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1. Introduction

Energetic ions when incident on material surfaces produce a wide range of phenomena. If the incident ion has sufficient energy to penetrate the surface it loses energy in the medium via nuclear and electronic stopping processes. While the nuclear stopping is dominating for slow ions which suffer elastic collisions with the target atoms and the electronic stopping is effective for high energy ions which causes ionization and excitation of the target atoms in the solid. The ion induced surface modifications (such as nanohillocks, nanocraters, nanoripples etc.) have been studied extensively and are fairly well understood [1–3]. Ion induced phase transformation has been studied and realized by both experiment and theory in great detail for different metal alloys and metal oxide thin films and bulk solids where ion irradiation was found to trigger amorphization, crystallization and may produce different crystal phases [4, 5]. Recently numerous studies were focused on latent track formation in semiconductor [6–8] and metallic [9, 10] thin films induced by swift heavy ions.

All the above mentioned studies were performed in great detail for bulk materials or for thin films. Experimental studies and corresponding theoretical understanding on ion induced changes of structure and concomitant properties of nanomaterials with dimensions in the range of 1-100 nm are few. Nanomaterials of dimension 1 to 100 nm possess drastically different p roperties than their bulk counterpart due to their high surface-to-volume ratio and charge carrier confinement in specific dimensions. When the size of the nanostructures is comparable with the mean free path of the electrons or the wavelength of the light then the electronic and optical properties are strongly dependent on their size. At these small dimensions quantum size effects take a vital role leading to remarkable new properties. Among different nanostructures one-dimensional (1-D) structures, where carriers are confined in two dimensions have special advantage in terms of small diameter and long length yielding high aspect ratio and high surface areas. Manipulating structures in nanodimension for fabricating nanodevices has been a challenging task because of difficulty in handling structures at this tiny dimension. Attempts have been made through several theoretical [11] and experimental [12–15] studies on electron and ion beam irradiation techniques to produce multi-way junction formation of CNTs, which resulted in different types (such as X, Y, T etc) of junctions. Fluence dependent phase transformation and junction formation was studied on hydrogen titanate nanowires, which can be potentially used in the design of Li ion battery [16, 17]. The wetting property of Cu_2O nano-column arrays have been modified by low energy nitrogen ion irradiation [18]. Recently ion irradiation studies of ZnO nanowires yielded remarkable results [19]. For instance, ZnO nanowires showed excellent field emission upon bombarded with nitrogen ions [20]. In another work irradiation induced stress generation and bending in ZnO nanowires were achieved [21]. In this work we investigate the effect of argon irradiation on ZnO nanowires. The surface of nanowires are found be roughened to high degree and tips are narrowed down due to argon ion irradiation. Such roughening and tip sharpening may assist to enhance all surface related properties such as field emission, catalysis, gas sensing and photovoltaic.

2. Experimental

Array of ZnO nanorods were grown on silicon substrate by hydrothermal method. Silicon substrates were placed at the bottom of autoclave in an aqueous solution of 0.01 M zinc nitrate and 0.01 M hexamine. The autoclave was then heated at 95° C for 12 hr. After the reaction is over, the autoclave was cooled down to room temperature and ZnO nanorod coated substrates were taken out and washed thoroughly with deionized water. After this the samples were dried at 80° C. The sample was irradiated with Ar^{+2} ions of energy 50 keV and a fluence of 1×10^{16} ions/cm^2. The ion beam was obtained from ECR ion source at TIFR, Mumbai. The structural and optical measurements were performed on both the pristine and the irradiated samples. Detailed studies of the microstructures were performed using an eLiNE *Field Emission Scanning Electron Microscope* (FESEM) operated at 5 kV. The morphology and crystal structure of individual nanowires has been studied using a FEI Tecnai-20 transmission electron microscope (TEM) equipped with a LaB_6 filament and operated at 200 kV. The Raman scattering study was performed using a T64000 model of Horiba-Jobin.

3. Results and Discussion

The overall morphology of as prepared ZnO nanowires was studied using *Field-Emission Scanning Electron Microscopy* (FESEM). Figure 1(a) represents plan view image of hexagonal Wurtzite crystal structure of ZnO. The average diameter of each nanowire is about 80-100 nm and length in the range of 1-2 μ m. The TEM image (Figure 1(b)) of individual nanowire shows highly crystalline structure with lattice spacing of about 0.28 nm which corresponds to (100) plane (JCPDS No 36-1451) running perpendicular to the axis of nanowire. The surfaces of the pristine nanowires are found to be atomically flat.

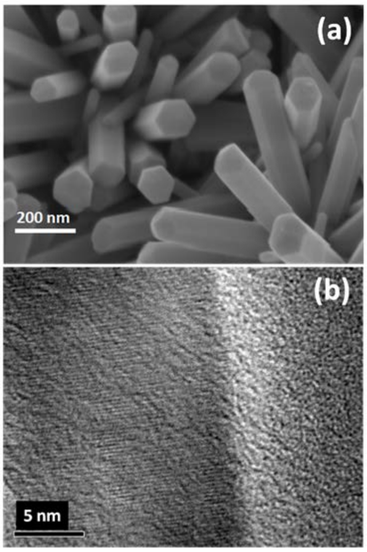

Figure 1. (a) Plan view SEM image of pristine ZnO nanowires. (b) TEM image of a pristine single crystalline ZnO nanowire. (100) plane is running through the axis of the nanowire.

TRIM [22] simulation yields that the longitudinal range of argon ions at 50 keV in ZnO is about 42 nm with a lateral projection of 14 nm. The ions mainly interacts in the surface layers of the nanowires. The consequence of argon irradiation at a fluence of 1×10^{16} ions/cm^2 can be observed in Figure 2(a). The SEM image apparently shows modification of tip morphology to a sharper structure. Under transmission electron microscope (Figure 2(b)) the individual nanowire shows a dramatic change due to ion irradiation viz. (i) a highly roughened surface, and (ii) a sharper tip compared to the pristine sample. The tip diameter is reduced by approximately 20 % of the initial diameter. The sharpened nanowires are potentially useful in the applications where large aspect ratio or small diameter of the tip plays crucial role. For instance, in an early study it was shown that the field emission of sharpened nanorod was dramatically enhanced than that of a flattened tip [23]. In another study gas break down voltage was found to be reduced for using nanowires with sharpened tips [24].

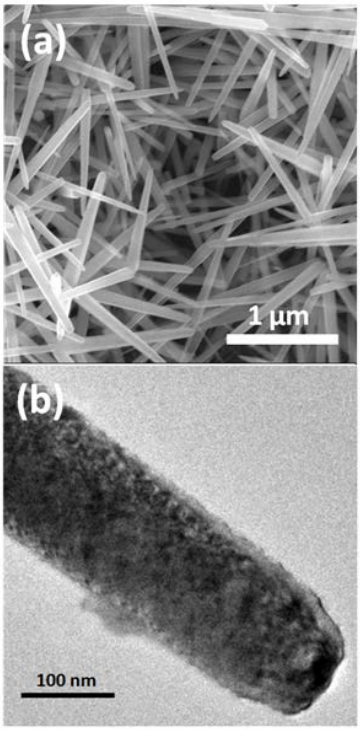

Figure 2. (a) Plan view SEM image shows apparent change in tip morphology of argon irradiated ZnO nanowires. (b) TEM image of irradiated nanowire shows high degree of surface roughness as well as tip sharpening.

Exact nature of the ion irradiated nanowires of ZnO is studied under high resolution TEM as shown in Figure 2. The surface shows roughness with height of about 2-5 nm and spread over almost uniformly throughout the nanowire surface. These nano-protrusions are contributing large specific surface area to each ZnO nanowire, which is likely to enhance the properties of ZnO that depend on the surface areas such as photo absorption, catalysis and gas sensing properties. The effect of ion irradiation on ZnO has been studied recently by Zhou et al. and found re-crystallization of amorphous surface layer of ZnO nanorods by N^+ ion bombardment and forming protrusions [25]. In a different synthesis technique by means of wet chemical method, titanate nanofibres were found to be covered by anatase nano-crystals of dimension 10 nm, which showed enhanced photocatalytic activity [26]. In this work we show that the ion bombardment as a useful tool to obtain at the same time a narrower tip and roughened but crystalline surface yielding large specific surface area. Interestingly, it is observed that even after argon ion irradiation, the crystalline structure is mostly retained. The lattice spacing of crystallites on rough surface is measured to be 0.28 nm, which corresponds to (100) planes of ZnO.

The surface roughness and tip sharpening can be understood by size and curvature

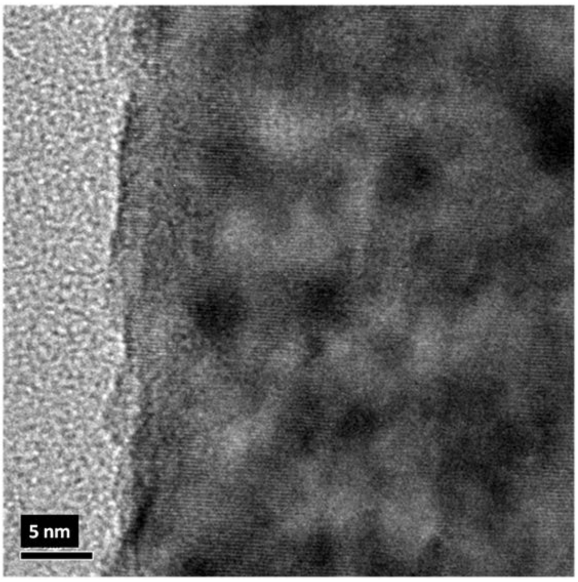

Figure 3. High resolution TEM of surface morphology of post-irradiated nanowire.

dependent sputtering and diffusion and dynamic annealing of defects on the surface. It is known that the sputter yield (Y) of nanowires is in general different from their bulk counterpart since "Y" strongly depends on particle size, or more precisely on the ratio of their size and the ion range. Since a nanowire has high effective surface area, therefore, sputter yield may be expected to be large. It was observed that the size of nanoparticles less than 150 nm show high sputter yield and it converges to the sputter yield of bulk at larger diameters [27]. Since ZnO nanowires of this work have diameters less than 100 nm, therefore, significant sputtering of its surface is expected to take place. The high sputter yield of ZnO nanowires leads to surface roughening. Since the tips of the nanowires are completely exposed to the ion beam, which eventually leads to tip sharpening. In order to understand the crystalline structure of roughened surface we invoke that ZnO has high iconicity of about 1.8, which favours annihilation of vacancies and interstitials. This leads to fact that ZnO is hard to amorphize and it may recrystallize or retain the crystalline structure [5]. Our result indicates that strong dynamic annealing occurs in the nanowire surface as the ion deposits its energy in a small cylindrical volume, which leads to local heating of the material at the surface. High temperatures can be reached due to the heat spike followed by annealing of the defects and interstitials [28]. In a nanowire, the typical annealing time is more than in bulk, since in bulk the thermal energy dissipates quickly (~ 0.1 ps) leaving no time for annealing. This is due to the fact that in a nanowire, the thermal energy can only dissipate in one dimension as the carriers are restricted in other two dimensions as opposed to three dimensional dissipation in case of bulk. Thus, there is more time for removal of defects and retaining crystalline structure in case of ZnO nanowires.

Raman spectra of both the pristine and Ar irradiated ZnO nanowires are shown in Figure 4. A characteristic E_2 (high) mode is observed at around 439 cm^{-1} for as grown ZnO samples. The Ar irradiated ZnO nanowires show a clear peak at around 576 cm^{-1}, apart from the E_2 (high) which can be attributed to A_1 (LO) mode of ZnO. This broad peak at 576 cm^{-1} appears due to

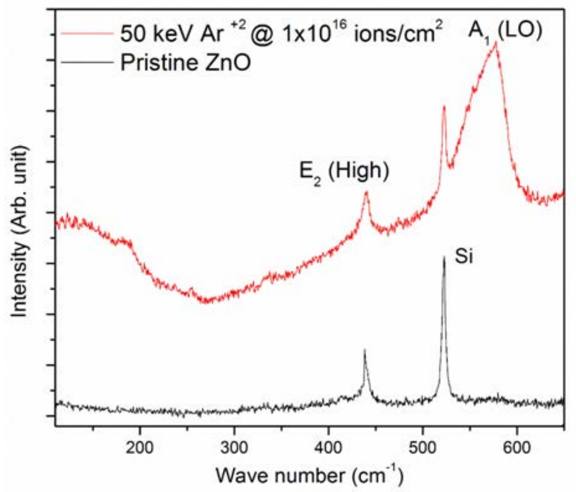

Figure 4. The Raman spectra of pristine and irradiated nanowires.

the density of phonon states of the high energy phonon branch [29–31]. Furthermore, the width of the E_2 (high) mode peak is increased and the intensity is decreased in case of irradiated sample compared to that of pristine, which arises because of possible presence of mild lattice defects and loss of translational periodicity.

4. Conclusion

In this work we report the modification of surface morphology of ZnO nanowires induced by argon ion irradiation. The surface of ZnO nanowire is highly roughened by ion impact, which are apparently crystalline in nature with dimension of about few nm and the rough structures are found to be distributed throughout the nanowire surface. In addition, the tip of ZnO nanowire is found to be sharpened by argon ion impact. Therefore, using ion irradiation as a tool, at the same time it is possible to enhance the surface area of the ZnO nanowire by roughening it and make a finer tip with large aspect ratio. Such aberration of ZnO nanowire surface and the tip may exhibit enhanced performance in those applications where large surface area and high aspect ratios are vital requirements. We envisage that these modified nanowires can be potentially used to make devices in applications such as field emission, catalysis, gas sensing and photovoltaic.

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Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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