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AMORPHIZATION OF ZnO NANOWIRES BY PROTON BEAM IRRADIATION

CHANG FU DEE[*,§], ISHAQ AHMAD[†,‡,¶], LONG YAN[‡,‖], XINGTAI ZHOU[‡,**] and BURHANUDDIN YEOP MAJLIS[*,††]

[*]*Institute of Microengineering and Nanoelectronics (IMEN)*
Universiti Kebangsaan Malaysia (UKM)
Bangi, Selangor 43600, Malaysia

[†]*Experimental Physics Laboratories*
National Center for Physics
Shahdra Valley Road
Islamabad, 44000, Pakistan

[‡]*Shanghai Institute of Applied Physics*
Chinese Academy of Sciences
Shanghai 201800, P. R. China

[§]*cfdee@ukm.my*
[¶]*ishaq_ah@yahoo.com*
[‖]*yan@sinap.ac.cn*
[**]*zhouxingtai@sinap.ac.cn*
[††]*burhan@vlsi.eng.ukm.my*

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We report the effects of 70 keV proton (H^+) irradiation on the structure of zinc oxide nanowires (ZnO NWs) for a wide range of irradiation doses at room temperature. It was found that at low dose 5×10^{15} ions/cm^2 of protons, few defects were created in ZnO NWs and the defects' density was increased with an increasing proton irradiation dose. After the irradiation dose was increased to 2×10^{17} ions/cm^2, the crystal structure of the ZnO NWs was almost completely damaged and the crystalline wurtzite structure of the ZnO NWs could be transformed into a disordered amorphous structure. Structural changes in the ZnO NWs upon bombardment with 70 keV protons were characterized by high resolution transmission electron microscopy (HRTEM).

Keywords: ZnO nanowires; proton beam irradiation; amorphization.

1. Introduction

Low-dimensional nanowires (NWs) have attracted more and more attention, due to their potential application as building blocks for complex nano- and microdevices.[1,2] As one of the important members of the group of available 1D nanomaterials, the excellent properties of ZnO NWs have drawn considerable attention regarding their potential future applications. Nevertheless, alteration and modification of their properties are important, to make them suitable as functional devices. Different means have been used to alter and

manipulate the properties and behaviors, such as doping,[3,4] alloying,[5] ion beam engineering,[6–9] cosynthesizing/compositing with other materials/NWs,[10] surface modification,[11] and plasma treatment.[12]

Ion beam engineering of materials has been performed for plenty of years. Starting in 1981, Merkle and Jager used Bi and Au ions with energies of 10–500 keV to fire at the Au surface and study the craters formed after bombardment by employing TEM.[6] English and Jenkins studied the effect of Mo surfaces after irradiating Mo, W and Sb ions. In 1995, Donnelly *et al.* performed a study of the population's changes in helium bubbles in gold and aluminum induced by 400 keV Ar ion beam irradiation.[13] The recent progress in ion beam engineering shows that the electrical properties of carbon nanotubes (CNTs) could be tuned by high energy beam irradiation.[14] Transformation of the graphite structure of CNTs into amorphous structure has been studied by Ishaq *et al.*[15] The electrical conductivity of CNTs was also studied by the same authors in 2009.[16] To the best of our knowledge, the irradiation effect of the high energy proton beam of ZnO NWs has never been studied so far. Understanding the effect of proton beam irradiation on nanoscaled structures and devices will bring forth a new avenue in proton-beam-mediated engineering.

Studies of luminescence and resonant Raman scattering have shown that nanostructure materials exhibit outstanding radiation hardness against high energy heavy ion irradiation as compared to bulk layers. The study of the phase transformation of nanostructures under electron and proton beam irradiation could potentially lead to application in phase change memory devices. Due to the repeatability, stability and controllability of the proton beam in recent years, the study of the interaction mechanism and effect of proton beam on nanoscaled materials is fundamentally important, especially for the emergence of nanomanufacturing, where the circuits, devices and interconnections are more fragile and vulnerable under energetic proton beam irradiation. High resolution transmission electron microscopy (HRTEM) has become one of the essential methods for studying the nanostructured materials because of its capability of providing images up to the atomic scale, as well as structural and chemical information.[17–20] Selected area electron diffraction (SAED) has been used to follow the change from crystalline to amorphous structure.

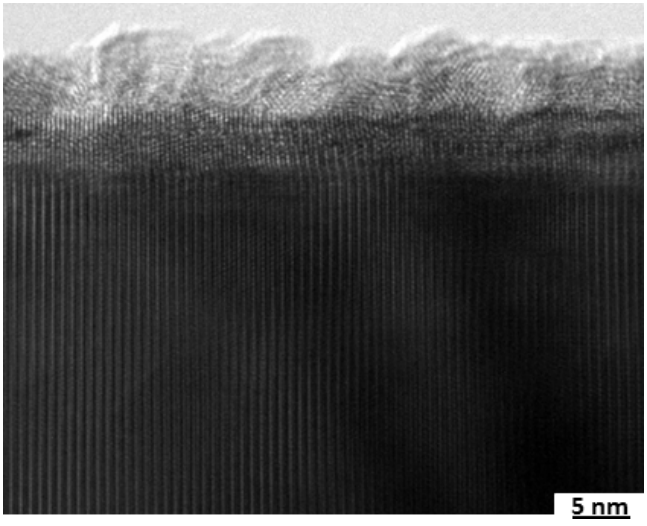
2. Experimental Method

ZnO NWs were synthesized by the method of vapor transport deposition (VTD) in a minifurnace through the vapor solid (VS) mechanism on silicon substrate.[21] The as-grown ZnO NW ensemble consisted of entangled and cross-linked NWs. It was sonicated in an ethanol-based dissolver bath. The ZnO NWs in ethanol, with diameters ranging from 80 to 200 nm, were dispersed on holey carbon microgrids and confirmed by a scanning electron microscope (SEM). Proton irradiation was carried out at room temperature with an irradiation energy of 70 keV for different doses, ranging from 5×10^{15} to 2×10^{17} ions/cm^2, using a 100 keV electromagnetic isotope separator (EMIS). During the irradiation, the chamber was maintained at a pressure of 10^{-4} Pa. The structural changes of unirradiated and ion-beam-irradiated ZnO NWs were observed through HRTEM (JEOL 2010). SAED was used for the determination of crystal/amorphous structures.

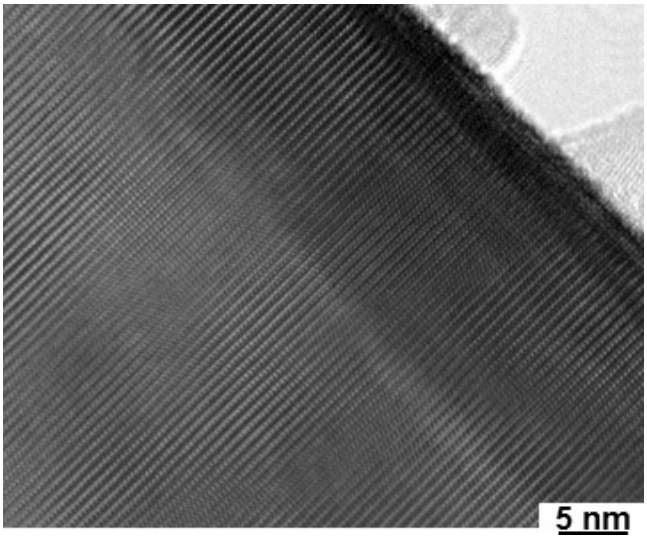
3. Result and Discussion

Figure 1 shows the HRTEM image of the as-grown ZnO NWs (unirradiated). The ZnO NWs had grown in the typical [0001] direction. The image shows that the NWs are highly crystalline. An amorphous layer could be observed in the outer part of the NW, as shown in Fig. 1(a). This contaminant was dominated by ZnO amorphous material.

After irradiating with 5×10^{15} ions/cm^2, amorphous nanodefects were created where the crystalline structures in those locations had been changed to amorphous structures. More amorphous spots were observed, as shown in Fig. 2, when the sample was irradiated with a proton beam with an intensity of 1×10^{17} ions/cm^2. The separate and isolated nanosized amorphous spots started to expand to form a bigger area of the amorphous region, as indicated in Figs. 3 and 4. They indeed showed that the amorphous structure of the irradiated ZnO continuously increased and the wurtzite structure decreased under high irradiation doses. Therefore, the proton-irradiation-induced wurtzite-to-amorphous structural transformation is considered to be the motion of the boundary, and the irradiation-induced structural transformation is a typical far-from-equilibrium process, where a thermodynamically stable structure under equilibrium conditions can continuously transform into a



(a)



(b)

Fig. 1. TEM images of the unirradiated ZnO NWs. (a) The surface of the NW is covered by an amorphous layer. (b) The inner core consists of nearly perfect crystalline lattice structure.

metastable structure along the boundary between the two structures.[22,23]

As the irradiation dosage increased, most of the areas in the NWs were dominated by amorphous and crystalline locations becoming a minority and therefore forming nanocrystalline dots in the amorphous matrix. This provides an alternative and indirect route for the formation of nanocrystalline structure in amorphous matrix. The phase transformation to amorphous structure or the defect formation process is expected as a result of direct

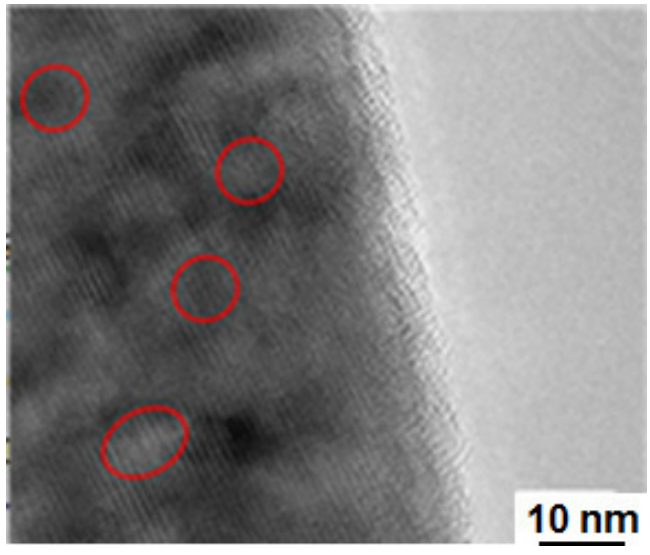


Fig. 2. After irradiation with a proton beam of 5×10^{15} ions/cm^2. Nanosized defects start to form on the crystal lattice (marked with red circles) (color online).

knock-on atom displacement and not because of the radiolysis or irradiative heating process. This is because the formation of amorphous structure or defects is not a uniform process throughout the whole area. It was found that the nanoamorphous defect formation was almost instantaneous after the irradiation of the proton beam proofs that the irradiation heating mechanism does not take part in the amorphous structure transformation.[24]

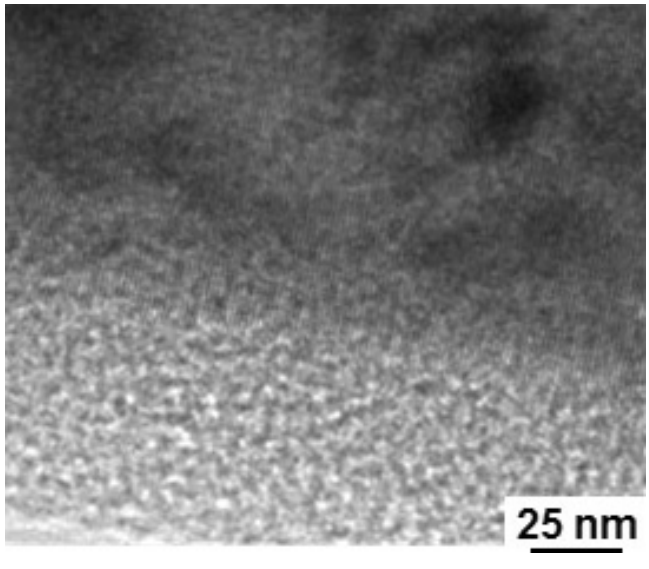


Fig. 3. After irradiation with a proton beam of 1×10^{17} protons/cm^2. Nanosized defects start to agglomerate to form a bigger area of the amorphous region.

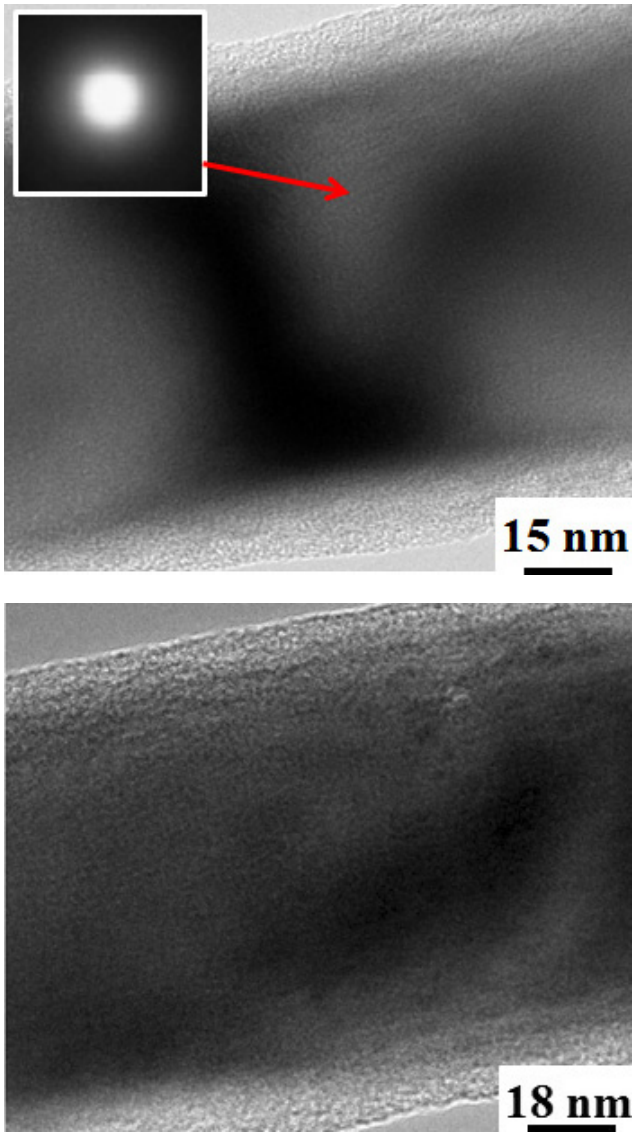


Fig. 4. TEM image of the ZnO NWs after irradiation with H^+ beam with an intensity of 2×10^{17} ions/cm^2. The inset is the corresponding SEAD image showing that the amorphous structure has dominated the whole nanowire.

Some mechanisms have been suggested to explain the path taken by the proton beam and the change in the structures of the NWs. During the irradiation process, a portion of the proton particles may penetrate the ZnO NWs, as shown in the schematic diagram in Fig. 5, due to the small diameter size. Some energy from the proton was absorbed to the NW to break the bonds if collision happens to the crystal lattice. The breaking process of bondings may further induce the formation of amorphous structure. A small portion of the proton particles would encounter the backscattering process and bounce back to the ambient.

Two possible amorphous formation mechanisms have been proposed for the irradiation process, as shown in Fig. 6. For the first mechanism, the high energy particles break the bonds in the lattice and cause interstitial defects in the lattice and also formation of nanoamorphous grains within the lattice structure in the "bulk" of the NWs. The coalescence of the amorphous grains after a high dose of irradiation will finally convert the whole crystalline NW into an amorphous structure. In the second mechanism, the irradiation-induced free atoms set near to the surface by the bond-breaking process and these atoms tend to agglomerate to form amorphous structures on the NW surface. Free atoms will experience migration and reabsorption on the surface to form amorphous hillocks. Therefore, the TEM image of the amorphous grains may be located inside or on the surface of ZnO NWs.

At an irradiation dose of 2×10^{17} ions/cm^2, it can be seen (Fig. 4) that the whole NW has been converted into an amorphous structure. SAED has given the supporting proof for the final conversion to an amorphous structure.

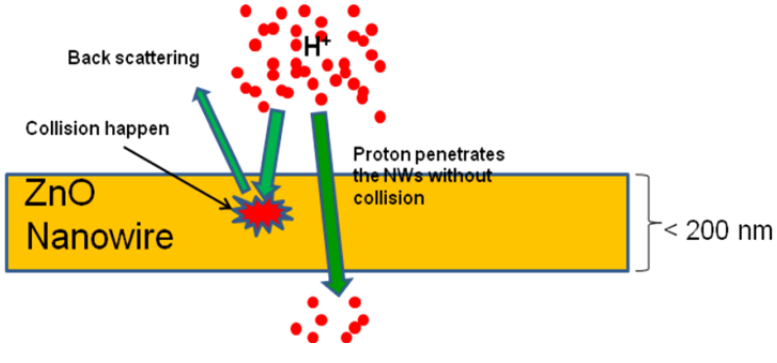


Fig. 5. Schematic diagram showing the possible paths which may have been experienced by the proton beam.

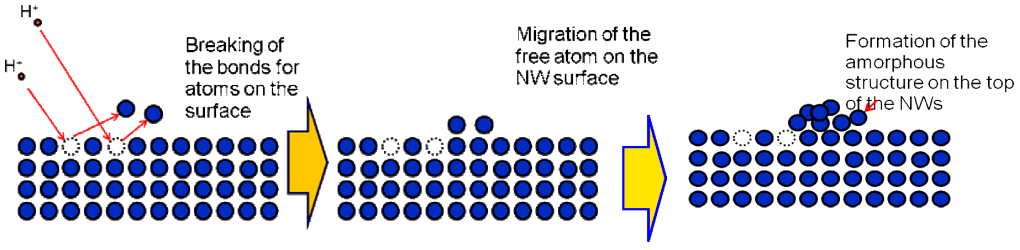


Fig. 6. Schematic diagram showing the two possible ways which may have been experienced by the NWs when irradiated with the proton beam.

4. Conclusion

The effect of proton beam irradiation has been studied under HRTEM. The irradiation process has eventually completely converted the crystalline ZnO NWs into amorphous structures. Two ways for the amorphous formation have been proposed. From the experiment, the dose of proton irradiation for complete change of the ZnO NW crystalline structure to a disordered amorphous structure has been estimated to be around 2×10^{17} ions/cm^2. The major effect of the proton irradiation was found to be due to displacement damage by direct or indirect knock-on collisions and not radiolysis or irradiative heating.

Acknowledgments

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