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RESEARCH PAPER

Effect for hydrogen, nitrogen, phosphorous, and argon ions irradiation on ZnO NWs

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Abstract Zinc oxide (ZnO) nanowires (NWs) are exposed to energetic proton (H^+), nitrogen (N^+), phosphorus (P^+), and argon (Ar^+) ions to understand the radiation hardness and structural changes induced by these irradiations. High-resolution transmission electron microscopy is utilized to see the irradiation effects in NWs. Multiple doses and energies of radiation at different temperatures are used for different set of samples. The study reveals that wurtzite (crystalline)-structured ZnO NWs experience amorphization, degradation, and morphological changes after the irradiation. At room temperature, deterioration of the crystalline structure is observed under high fluence of H^+, N^+, and P^+ ions. While for ZnO NWs, bombarded by Ar^+ and P^+ ions, nano-holes are produced. The ZnO NWs surfaces also show corrugated morphology full of nano-humps when irradiated by Ar^+ ions at 400 °C. The corrugated surface could serve as tight-holding interface when interconnecting it with other NWs/nanotubes. These nano-humps may have the function of increasing the surface for surface-oriented sensing applications in the future.

Keywords ZnO nanowires · Ion irradiation · Amorphization · Nano-holes · Nano-humps

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Introduction

The structure evolvement of nanowires (NWs) by ion irradiation is quite interesting both from theoretical and experimental points of view (Bettge et al. 2012). Recently, the phase transformation by kilo-electron-volt (keV) ion irradiation on a number of nano-materials has been studied (Dee et al. 2011a, b; Ishaq et al. 2009; Andrievski 2011). Numerous irradiation studies using electrons or ions on a different type of nano-materials have demonstrated the use of irradiation to alter the electronic, structural, and optical properties of the nano-materials (Ishaq et al. 2009;

Ni et al. 2009; Yan et al. 2011; Ishaq et al. 2011; Bettge et al. 2012; Bal et al. 2012; Borschel et al. 2011). With those demonstrations, ion and electron beam irradiation has proven its capability of tailoring and functionalized nanomaterial (Dee et al. 2011a, b).

Zinc oxide (ZnO) is a unique material that can demonstrate semiconducting, piezoelectric, and pyroelectric multiple properties and it can be synthesized as nanocombs, nanorings, nanobows, nanobelts, nanowires, and nanocages by varying growth conditions (Wang 2004). ZnO can have both n- and p-type ZnO nanowires which can be useful in a variety of applications, for instance, optical and sensing devices, transistors, spintronics, nanogenerators, and microscopy. In spintronics applications, dilute magnetic semiconductors can be prepared by doping ZnO with magnetic atoms, such as manganese and cobalt, where one possibility for doping is ion implantation or irradiation. The development of nano-devices and nano-circuits using nano-materials is an emerging technology for space applications, where heavy ion irradiation offers an opportunity to understand the behavior of nanomaterials under such harsh conditions (Shaw et al. 2005).

Compared to carbon nanotube (CNT), which consists of empty core, ZnO NWs were expected to interact with the ion beams in a different way. This is due to its solid core and higher density substance. Interaction of ions and electron after collisions of CNT lattice with ion beams has already been studied previously (Krasheninnikov and Banhart 2007). The irradiation-induced structural transformation from crystalline to amorphous for ZnO NWs, generated by H^+ ion irradiation, is caused by defects concentration in/between the crystal planes resulting from the cascaded collision (Dee et al. 2011a, b). However, the consequence of the structural transformation of ZnO NWs under different types of ion beam irradiation and also the power of resilience or inversely the thermal-assisted irradiation deterioration at elevated temperature is still not extensively investigated. Generally, ion beams traversing through a material introduce various modifications and changes in the properties of the target material. These material modifications depend on the type of ion, their energy, and fluence of ions.

In this study, we have investigated the structural changes caused by the irradiation of energetic H^+, N^+ (dopant), P^+ (dopant), and Ar^+ ions. The selection of these ions and their energies has been made on the basis of their masses (lightest of heavier) and their energy transfer mechanism. Ion beams of lighter elements mainly produce ionization in the target material, whereas heavier elements cause structural damage. The ions with different fluences are bombarded on ZnO NWs at room temperature and at an elevated temperature of 400 °C, and high-resolution transmission electron microscope (HRTEM) is used to observe the structural changes in ZnO NWs before and after the irradiation.

Experimental

ZnO NWs were synthesized on a silicon substrate using vapor transport deposition (VTD) technique in a mini-furnace by vapor solid (VS) mechanism (Dee et al. 2008). The ensemble of as-grown ZnO NWs were entangled and cross-linked on top of substrate. The NWs were separated out by sonication in the ethanol-based dissolver bath. With the help of field emission scanning electron microscope (FESEM), it was confirmed that the ZnO NWs have diameters in the range of 80–200 nm. The NWs-contenting ethanol was then dispersed on the holey carbon micro-grids. A 5MV pelletron accelerator, present at National Centre for Physics, Islamabad, was utilized to generate high-energy H^+ and P^+ ion beams to irradiate the as-grown ZnO NWs placed on the copper grid with different doses in the range of $\sim 10^{15}$ ions/cm^2 at an energy of 1 MeV. In addition, a 100 keV electromagnetic isotope separator (EMIS) was used to generate 70 keV N^+ and Ar^+ ion beams, which were bombarded on separate as-grown NW samples with ion fluences ranging from 5×10^{15} to 1×10^{17} ions/cm^2. The chamber pressure for these irradiations was kept at $\sim 10^{-4}$ Pa. The structural changes produced as a result of these irradiation in NWs were studied by HRTEM (JEOL 2010).

Results and discussion

Figure 1a, b show FESEM image of as-grown ZnO NWs and HRTEM image of single NW, respectively. It has been observed that most of these NWs have uniform diameter and are longer than 10 μm. The diameter of these NWs is in the range of 60–120 nm.

HRTEM image shown in Fig. 1c reveals that the crystalline lattice spacing is about 0.254 nm.

Figure 2a shows HRTEM images of ZnO NWs that has been completely and homogeneously converted to amorphous structure after irradiation by 1 MeV H^+ with a fluence of 3×10^{15} ions/cm^2. It can be seen from the image that there has not been any catastrophic destruction (such as formation of cracks and holes) that happened after the 1 MeV H^+ irradiation. The energy of ion beam used is almost 15 times the energy we have used in our previous experiment (Dee et al. 2011a, b). A high-resolution image of the structure, shown in Fig. 2b, reveals that the energy used in this experiment has not strongly affected the existing structure of the material. Compared to a previous experiment, where similar types of NWs were irradiated using high-energy electron beam, the formation of nano-holes was observed due to the sputtering effect (Ahmad et al. 2012). Selected area electron diffractions (SAED) ring pattern, shown in the inset of Fig. 2a, confirms the amorphous nature of the structure as a result of H^+ irradiation. A comparison of NWs before (Fig. 1c) and after (Fig. 2a) H^+ irradiation shows a complete conversion of crystalline ZnO NWs to amorphous NWs. On the same sample, sputtering effect, which is expected to displace the atoms from the lattice by H^+ ion during the irradiation, was not clearly observed. It can be indicated by the equal amount of residues and debris on the outer surface of the NWs before and after the irradiation (The nuclear displacement is always expected to deposit knock-out atoms on the outer surface of the NWs). We can conclude that highly energetic H^+ ions produce negligible sputtering on the ZnO NWs. The same phenomenon was also observed for multi-walled CNTs under H^+ ion beam at 70 keV of energy (Ishaq et al. 2009). Furthermore, high-energy H^+ ions cause bond breakage and localized heating in the

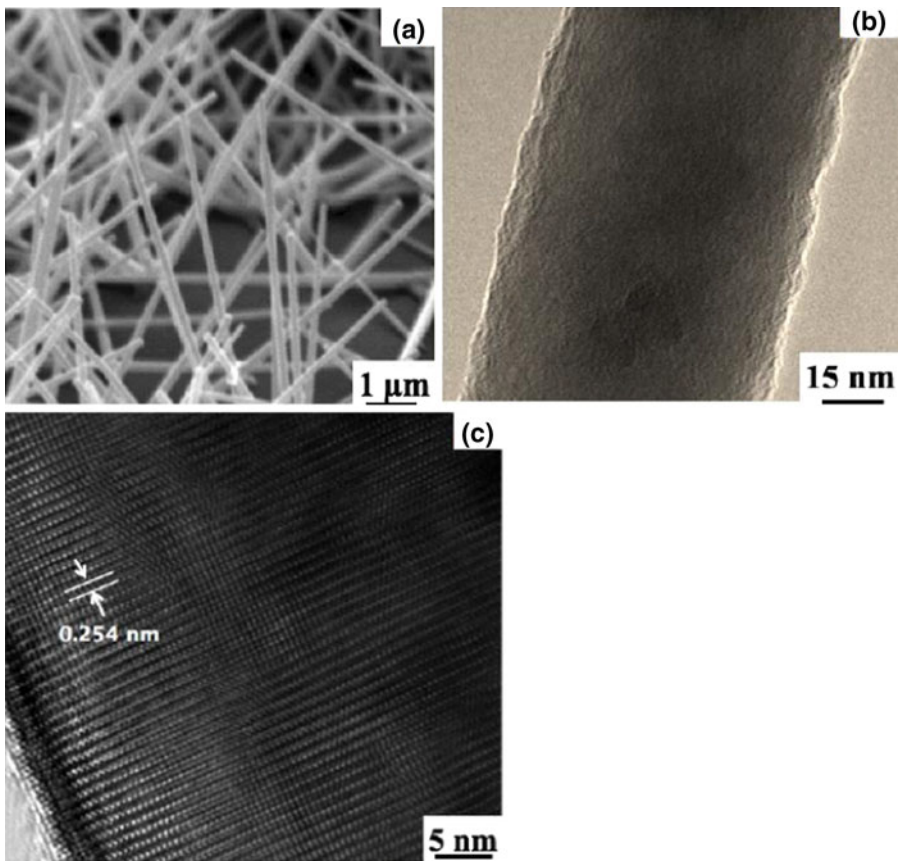

Fig. 1 **a** SEM images of ZnO NWs arrays prepared by VTD method. **b** TEM image of ZnO nanowires. **c** HRTEM image of the nanowire

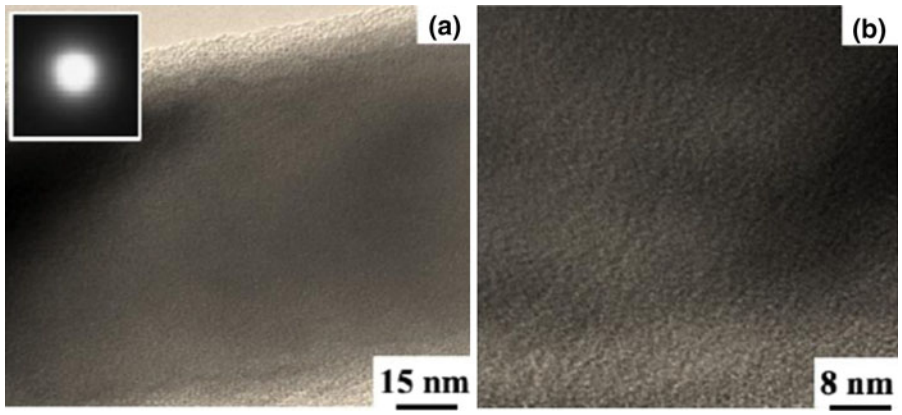

Fig. 2 HRTEM images of the ZnO NWs irradiated by 1 MeV H^+ ion beam at the doses of 3×10^{15} ion/cm^2 at room temperature. The *inset* is the corresponding SAED image

transformation process regarding crystal structure to amorphous one, due to nuclear stopping of the incoming ions.

Figure 3 indicates a subtle phase transformation of the single crystalline structure to the amorphous one for as-grown ZnO nanowires with an increase of ion irradiation. Figure 3a–c shows the corresponding HRTEM images when samples were exposed to 70 keV nitrogen ions at room temperature at fluences of 1×10^{15}, 5×10^{15}, and 1×10^{16} ions/cm^2, respectively. From Fig. 3a, it can be observed that, under N^+ ions irradiation, the spacing between the planes of the crystal decreases to form randomly oriented crystallites that are embedded in wurtzite and

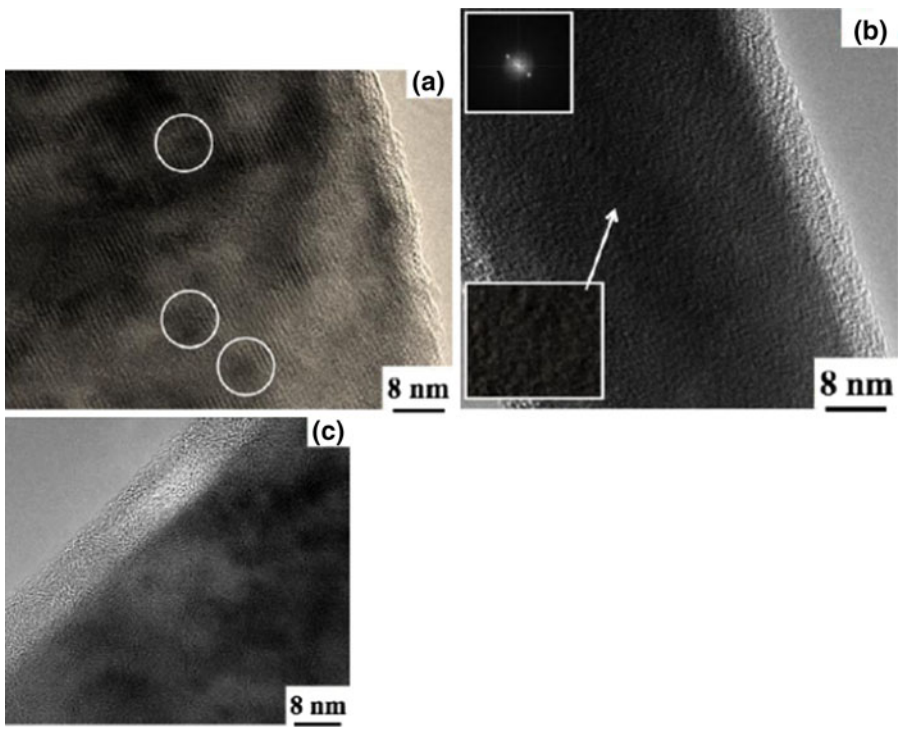

Fig. 3 HRTEM images of the ZnO NWs irradiated by 70 keV N^+ ion beam at room temperature at the doses of **a** 1×10^{15} ion/cm^2. **b** 1×10^{16} ion/cm^2, the *inset* is the corresponding SAED image. **c** 5×10^{16} ion/cm^2

amorphous matrices. With increasing dose of N^+ ions up to 1×10^{16} ions/cm^2 at room temperature, majority of the amorphous and crystalline locations of the NWs turn into minority. Although at this dose, few crystalline planes are still found in the amorphous matrix as is evident from the inset of Fig. 3b (SAED pattern). Furthermore, the increasing dose of N^+ ions converts the entire structure into amorphous one at the highest dose used, shown in Fig. 3c. A more uniform and homogenous conversion to amorphous structure has been observed in the N^+ irradiated ZnO NWs, because of the dominance of electronic stopping effect (Krasheninnikov and Nordlund 2010). Therefore, it can be expected that the internal heating generated by the electronic stopping in NWs at higher doses was contributing in a transformation of crystalline to amorphous phase of the crystal structure. This type of thermally induced phase change would normally give a more uniform conversion to amorphous phase throughout the whole NW. Irradiation by N^+ mostly results in nuclear collisions around the ion end range due to heavier mass of nitrogen. This type of collision will result in "thermal spike" or "heat spike" (Krasheninnikov and Nordlund 2010), which normally cause localized heating and conversion to amorphous structure. That is the reason why the irradiation by N^+ ions will normally cause incomplete localized conversion to amorphous structure, as can be seen in Fig. 3b.

Figure 4 shows HRTEM images of the ZnO NWs irradiated by 70 keV Ar^+ ions at room temperature and with various doses. Deterioration of crystalline structure has been observed at a dose of 5×10^{15} ion/cm^2 as shown in the circular marks in Fig. 4a, b. A further analysis of the images reveals the production of nano-holes produced as a result of local heating and collision cascade effects under Ar^+ ion irradiation at a dose of 5×10^{15} ion/cm^2. A further increase in the ion

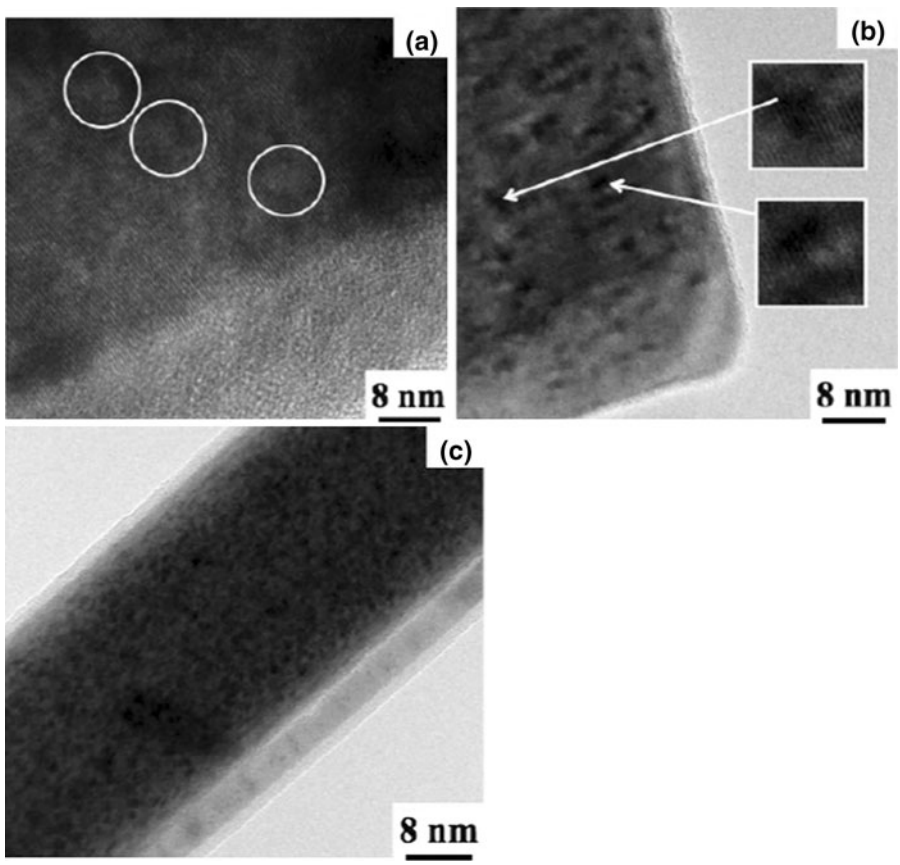

Fig. 4 HRTEM images of the ZnO NWs irradiated by 70 keV Ar ions at room temperature at the doses of **a** 1×10^{15} ion/cm^2, **b** 5×10^{15} ion/cm^2, and **c** 1×10^{16} ion/cm^2

dose shows an enhancement in the density of nano-holes, which can be observed in Fig. 4c. In the same figure, a uniformly distributed porous structure, with pore sizes of 2–5 nm, produced due to Ar^+ irradiation can be seen along the length of the wire. These porous-structured ZnO NWs are very useful for many sensing and optical devices (Wang et al. 2012). A similar effect has been observed on boron nitrate nanotube under irradiation of 40 keV Ar^+ ion beam with dose of 1×10^{14} ion/cm^2. It is expected that the highly damaging Ar^+ ions produce Frenkel pairs, where vacancies are accumulated in the crystal and the interstitial defects quickly move to the surface. As mentioned by Bai et al. self-resilience will occur in the nanostructure materials at the boundary sites of the agglomerated nanostructures (Bai et al. 2010). But in this case, although it is a nanostructured material there was no contacted interface to form boundary sites similar to their work. Therefore, the interstitials may simply move to the surface and agglomerate there. A schematic diagram, shown in Fig. 5, illustrates the process of point defects creation and their accumulation for vacancies and surface agglomeration of interstitials (Ni et al. 2009). An already reported study has revealed that nano-holes can be generated by electron irradiation (Ishaq et al. 2011). Therefore, it can be concluded that ion beam technology can be successfully utilized to manufacture nano-holes in ZnO NWs on large scale and producing porous ZnO NWs. This study reports for the first time that ion irradiation can be used to produce porous ZnO NWs.

Figure 6 shows HRTEM images of the ZnO NWs irradiated by 1 MeV P^+ ions at room temperature with various doses. It can be observed from Fig. 6a that the irradiated ZnO NWs under 1 MeV P^+ ions irradiation and at a dose of 1×10^{15} ion/cm^2 exhibits reduced lattice plane spacing and random orientation of crystallites. However, ZnO NWs at the dose of 5×10^{15} ions/cm^2 reveal a transformed porous amorphous structure, as it can be seen in Fig. 6b. The melting and sputtering of the nanowires induced by energetic ions dominate under 1 MeV P^+ ions. Both the effects appear only for 1 MeV P^+ ions and 70 keV Ar^+ ions, where nuclear stopping of the energetic ions is dominant at the end of ion range, whereas 1 MeV H^+ ions do not show this behavior, where electronic stopping is a dominating process of energy transfer. Hence, the breakage of bonds by light ions is due to the complete ionization of the material and as a result it produces amorphous structure. On the other hand, heavy ions cause melting and evaporation of ZnO NWs molecules due to elastic scattering of incoming ions in the material and from the surface resulting in porous amorphous structure.

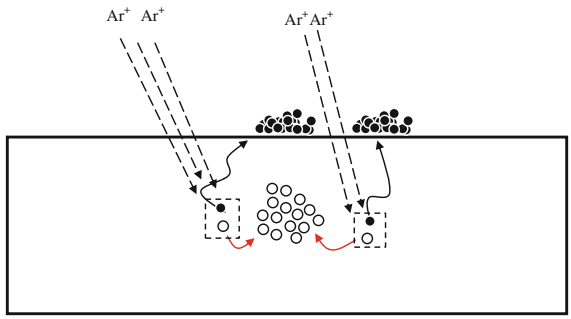

Fig. 5 A schematic diagram showing the generation, migration, and accumulation of interstitials and vacancies in ZnO NW under irradiation of 70 keV Ar^+ ion beam at room temperature

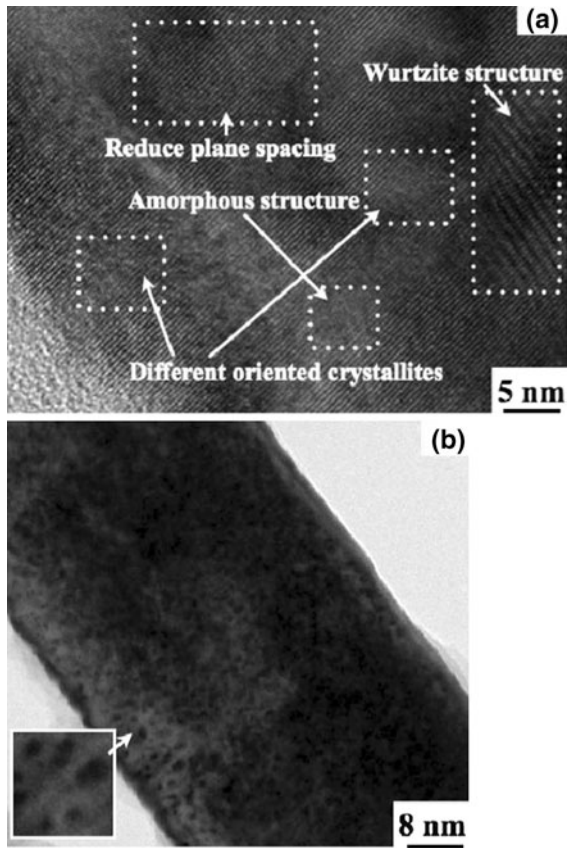

Fig. 6 HRTEM images of the ZnO NWs irradiated by 1 MeV P^+ ion beam at room temperature at the doses of **a** 1×10^{15} ion/cm^2 and **b** 5×10^{15} ion/cm^2

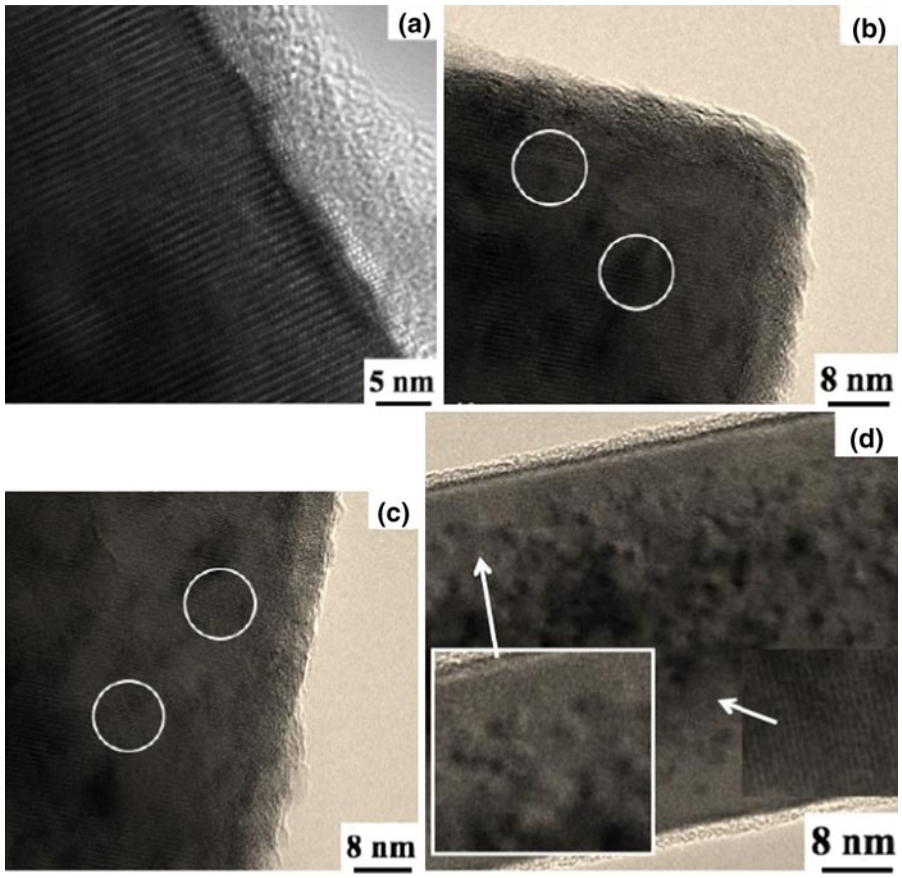

Fig. 7 HRTEM images of the ZnO NWs irradiated by 70 keV at 400 °C at the doses of 1×10^{16} ion/cm^2 by **a** H^+, **b** and **c** N^+, and **d** Ar^+ ion beams

Table 1 Summary of the effect of H^+, N^+, P^+, and Ar^+ ion beam irradiation on ZnO NW at room temperature

Ions	Dose (ion/cm^2)	Energy	Temperature	Results
H^+	1×10^{15}	1 MeV	RT	Complete amorphization of the materials
P^+	1×10^{15}	1 MeV	RT	Reduced plane spacing and randomly oriented crystallites formation
	5×10^{15}	1 MeV	RT	Corrugated surface (formation of nano-holes) (structure transformed to amorphous)
N^+	1×10^{15}	70 keV	RT	Deterioration of crystalline structure (incomplete amorphous conversion)
	5×10^{15}	70 keV	RT	Deterioration of crystalline structure (incomplete amorphous conversion)
	1×10^{16}	70 keV	RT	Complete amorphization of the materials
Ar^+	1×10^{15}	70 keV	RT	Deterioration of crystalline structure (incomplete amorphous conversion)
	5×10^{15}	70 keV	RT	Low density nano-holes creation along the length of nanowire (entire structure stable)
	1×10^{16}	70 keV	RT	High density nano-holes creation along the length of nanowire (entire structure stable)

The ZnO NWs were also irradiated by H^+, N^+, and Ar^+ ion separately at an elevated temperature. Based on our previous study, we have optimized the substrate temperature of 400 °C to study the crystal stability under ion irradiation at 70 keV. For this, we have extended our study for 70 keV H^+, N^+, and Ar^+ ion irradiation on ZnO NWs' structure at an elevated target temperature of 400 °C at dose of 1×10^{16} ions/cm^2.

Table 2 Summary of the effect of H^+, N^+, and Ar^+ion beam irradiation on ZnO NW at 400 °C

Ions	Energy (ion/cm^2)	Dose (keV)	Temperature (°C)	Results
H^+	1×10^{16}	70	400	Stability of crystal structure
N^+	1×10^{16}	70	400	Randomly oriented crystallites formation
Ar^+	1×10^{16}	70	400	Corrugated surface (formation of nano-humps)

A comparison among H^+, N^+, and Ar^+ irradiations on ZnO NWs has been made and shown in Fig. 7. We have observed that at the dose of 1×10^{16} ions/cm^2 at the temperature of 400 °C under H^+, N^+, and Ar^+ ions, the ZnO NWs structure remains almost stable. Figure 7a confirms the stability of the structure of ZnO NWs under H^+ ion irradiation. The stability of the structure with these irradiations refers to the production of single vacancies and the least collision cascade at higher temperature. The uniform elevated temperature during irradiation will anneal the NWs and reduce defects such as vacancies in the NWs. This indicates that the ZnO NWs are able to recover damage induced by irradiation. However, in the case of N^+ and Ar^+ ion irradiation at 400 °C, the observations are different. In Fig. 7b, c, it can be seen that the space between the crystal planes of ZnO NWs is reduced under N^+ irradiation and randomly oriented crystallites embedded in wurtize matrices appear, which are marked by circles in the image. However, the entire crystal structure remains stable. On the other hand, Fig. 7d shows the corrugated surface after Ar^+ irradiation at 400 °C. In these irradiations, nano-humps are expected to form after the irradiation. The stability of the structure is clear from the inset of Fig. 7d. From these studies, it can be deduced that 400 °C is high enough to keep the crystalline structure of ZnO NWs. Nano-humps, being templates, on the surface of ZnO NWs can potentially be beneficial for the growth of further nanowires/nanotubes.

Conclusion

We have studied the effect of H^+, N^+, P^+, and Ar^+ irradiation at room temperature and at 400 °C, different energies, and doses on ZnO NWs. Different effects have been observed for different ions bombarding the ZnO NWs. A summary of the results obtained in these studies is shown in Tables 1 and 2. The results show that high-energy H^+ can be used to convert ZnO NWs from crystalline to amorphous structure. N^+ and Ar^+ ion beam in most of the cases will either cause incomplete conversion to amorphous structure or induce severe damage (nano-holes or nano-humps) in the structure. Therefore, ion beam irradiation is a useful tool to modify the structure of ZnO NWs in a controlled way. It states that the high energy impinging particles produced interstitial defects by breaking bonds in the lattice and also changed the structure in the ZnO NWs. In addition, this study reports for the first time that ion irradiation can be used to produce porous ZnO NWs.

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