Chapter

Ion Implantation in Metal Nanowires

Shehla Honey, Asim Jamil, Samson O. Aisida, Ishaq Ahmad, Ting-kai Zhao and Maaza Malek

Abstract

Ion implantation-induced materials modifications are the recent scope of research. A detailed recent experimental research on the effect of low- and high-energy ions implantation-induced morphological and structural changes in metal nanowires (MNWs) is being presented in this chapter. These morphological and structural changes in metal nanowires are discussed on the basis of collision cascade effects and ion beam-induced heats produced along the ion tracks. Various technical aspects of implantation of low energy ions in MNWs, their advantages, and drawbacks are also discussed in this chapter. Furthermore, detailed overview of implantations of ions in MNWs is also discussed.

Keywords: metal nanowires, ions implantation, morphology, structural defects, collisions of nanowires

1. Introduction

Metal nanowires (MNWs) such as silver, copper, nickel, and gold nanowires have a large value of conductivity and transparency. It could be replaced by ITO, but yet these MNWs networks or grids or meshes need more research and development (R&D) consideration from the scientific community in order to make them proficient for successful applications in recent transparent electrodes (TEs) industry. This can be realized by synthesizing MNWs using simple and economic solution-phase techniques and then transferring these MNWs into coating source. That coating source will be used to coat a transparent substrate with a film of MNWs. Even though silver (Ag) (approximately \$766/kg) is costly than indium (In) (approximately \$601/kg) [1–3], but these silver nanowires (Ag-NWs) can be synthesized using roll-to-roll inexpensive solution coating methods. Because of their economic processing expenditure, the stipulation of Ag-NWs is rising for their appliance in touch sensors as TEs.

Some researchers have reported the scalable synthesis of Cu-NWs via solution coating techniques to make TEs with performance equivalent to ITO [4]. This is inspired by the insight of combining the low cost and simple deposition techniques of Cu-NWs; since Cu is more copious (~1000 times) and less expensive (100 times) than Ag or In.

Recently, Cu-NWs have presented the transmittance of ~96% and sheet resistance of ~100 Ω/sq. However, a major challenge for the successful application of Cu-NWs as TEs is to protect it from oxidation while maintaining its performance equivalent to ITO. As discussed above, here are various substitutes available for ITO, but the successful candidate is MNWs networks or meshes which are capable of showing performance equivalent to ITO due to ease of synthesis via solution coating techniques. Moreover, MNWs networks or meshes are more flexible and stretchable as compared to ITO [5]. These nanowires based transparent conducting electrodes based devices or individual metal nanowires based nanodevices will be used under the harsh environment such as the upper space radiation environment. Therefore, radiation effects study on these metal nanowires is important.

Damage to the structure of nanomaterials on contact to high energy ion beams has been the general perceptive, but recent research has made known it to be as a tool to tailor electronic, optical and field emission properties and to change the structure of nanomaterials in an excellent controllable way [6–10].

Ion beam radiation effects on MNWs have been recently studied [11–16]. In literature, protons ions irradiated bismuth nanowires (Bi-NWs) were reported and found that electrical conductivity decreased with an increase in protons beam fluence due to crystal structural damage, while see-back coefficient remained unaffected. It was concluded that the crystal structure of Bi-NWs destroyed under protons irradiation, which consequently decreased mobility, whereas carrier concentration was unchanged [17]. Molecular dynamics simulations study was reported to examine a damage profile in Cu-NWs that occurred during exposure to ions beam having low energies [18]. A similar study has been done employing molecular dynamics simulations and found that mechanical properties of Cu-NWs are devastated due to ion beam irradiation [19]. Moreover, enhancement in conductivity of Cu-NWs is reported after their irradiation with gamma rays [20]. In addition, Co-NWs were irradiated with gallium (Ga^+) Ions and found that the propagation field of domain walls is modified within the magnetic channels [21]. Moreover, interconnections through welding of various nanomaterials have also been built using different ion beams, which lead to enhance electrical conductivity [22–24].

To understand ion implantation effects on nanomaterials clearly, one must be aware of radiations and basics of ion solid interaction mechanisms. However, the unfavorable outcomes of radiations are termed as radiation-induced damage. In the next section, the general effects of irradiation on materials are discussed briefly.

2. Effects of ion implantation on materials

In ion beam implantation process principle is based on the extraction of beams of ions from the source and accelerate at a specific voltage often lies between 50 and 250 keV with a desired energy up to 10 MeV before transportation and impingement on the target or substrate [25]. The impingement causes the ions to interact with the specimen surface in which some are embedded in the specimen while some are scattered. Ion implantation is ingenious in surface modification of materials while retaining their bulk properties [25–27]. The beam implantation process, which can be static, broad and unidirectional, can either improve or cause a defect in the properties of materials like toughness, fatigue, wear, hardness, friction, dielectric, magnetic, electronic, resistive and superconductivity [25]. These effects are subjected to the applications of the prepared materials. This implantation can be done in materials like ceramics, insulators, semiconductors, metals, alloys and polymers. The magnitude of the defect caused in the materials depends majorly on the mass of the incoming ion to the specimen, the accelerating voltage used for the beam, the thermal properties of the point defects confining the cascade region and the crystal structure of the specimen [25–28].

The most characteristic feature in ion implantation of materials is the generation of lattice disordered, which can be enhanced using low dose energy of heavy ions. In optical materials, ion implantation often stimulates luminescence to analyze the purity and point defects in the materials. Also, electro-optic, birefringence, refractive index, optical waveguide, reflectivity absorption band, thermoluminescence, electrical conductivity, piezoelectric, an optoelectric, and acoustic wave can be controlled with the effect of ion implantation [26–28].

The ion implantation effect also creates luminescence in some crystal materials. The luminesces observed during ion beam implantation in materials give information on the dynamic defect states owing to the transient features by the passage of ions that are difficult to excite. The defects observed can then be sensed by ion beam-induced luminescence and give information about the decay, impurities, or growth of the inherent defect state of the sample [24, 29].

2.1 Ion beam-induced morphological changes in silver nanowires

The morphological image of un-implanted Ag-NWs is presented in **Figure 1(a)**. The morphology shows long-shaped Ag-NWs. After 5 MeV, carbon ions

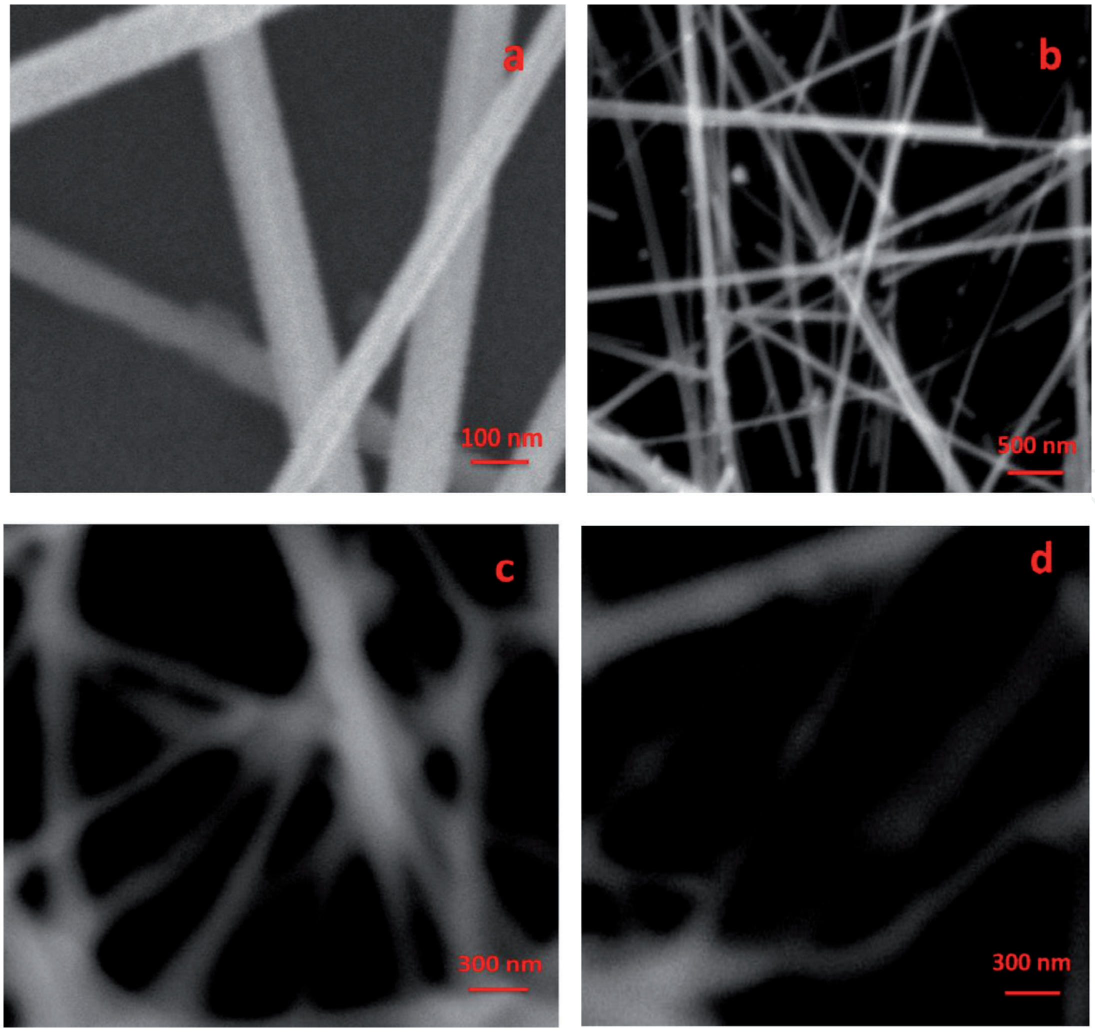

Figure 1.
(a) Un-implanted Ag-NWs, (b) 5 MeV carbon ions at the dose of 5×10^{14} *ions/cm*^{2}*, and (c, d)* 1×10^{16} *ions/cm*^{2} *(reuse after copyrights permission) [30].*

implantation at the dose of 5 × 10^{14} ions/cm^2, Ag-NWs diffused at the junction points, as shown in **Figure 1(b)** [30]. At high ion dose of 1 × 10^{16} ions/cm^2, Ag-NWs start to be sliced, i.e., reduce the diameter and finally cut the nanowires as shown in **Figure 1(c, d)**, respectively [30].

2.2 Ion beam-induced morphological changes in copper nanowires

The un-implanted Cu-NWs image is presented in **Figure 2(a)**, shows a long-shaped Cu-NWs. The diameters of un-irradiated Cu-NWs ranged from 100 to 150 nm. After 10 MeV Cu ions implantation at the dose of 5 × 10^{15} ions/cm^2, Cu-NWs diffused at the junction points, as shown in **Figure 2(b)**. At high ion dose of 1 × 10^{16} ions/cm^2, Cu-NWs start to be sliced, i.e., reduce the diameter and finally NWs are cut, as shown in **Figure 2(c)**.

2.3 Ion beam-induced morphological changes in Ni nanowires

The TEM micrograph before H^+ ions implantation of Ni-NWs is presented in **Figure 3(a)**. The Ni-NWs showed minor melting on the surface of the nanowires. After implantation with 2.75 MeV H^+ ions at fluence of 1 × 10^{16} ions/cm^2, Ni-NWs diffused to each other at junction points and seen in **Figure 3(b)**. The interconnections of Ni-NWs after H^+ ions beam irradiation are clearly shown by the TEM analysis. The reason for the interconnections between Ni-NWs might be heat induced due to H^+ ions beam irradiation, which leads to melt and fusing of Ni-NWs into each other at intersecting positions [13, 14].

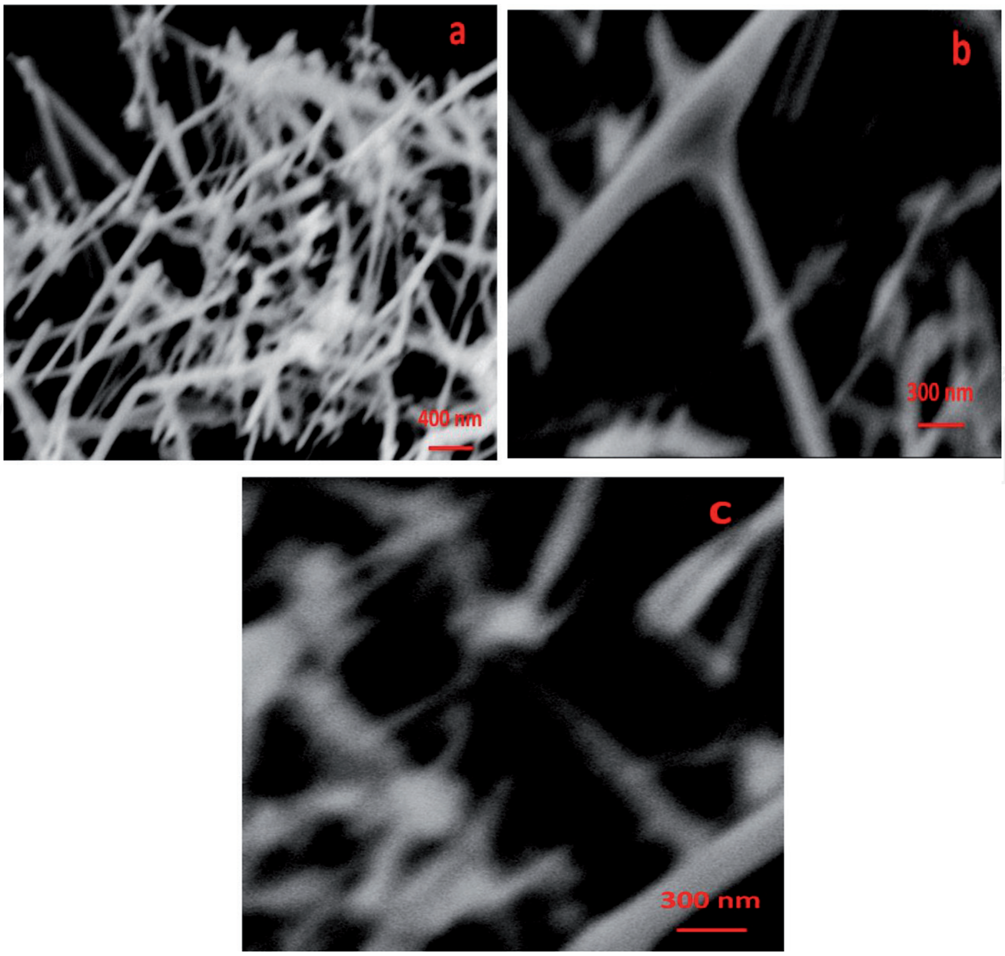

Figure 2.
(a) Un-implanted Cu-NWs, (b) 10 MeV Cu ions at 5 × 10^{15} ions/cm^2, and (c) 1 × 10^{16} ions/cm^2 fluence.

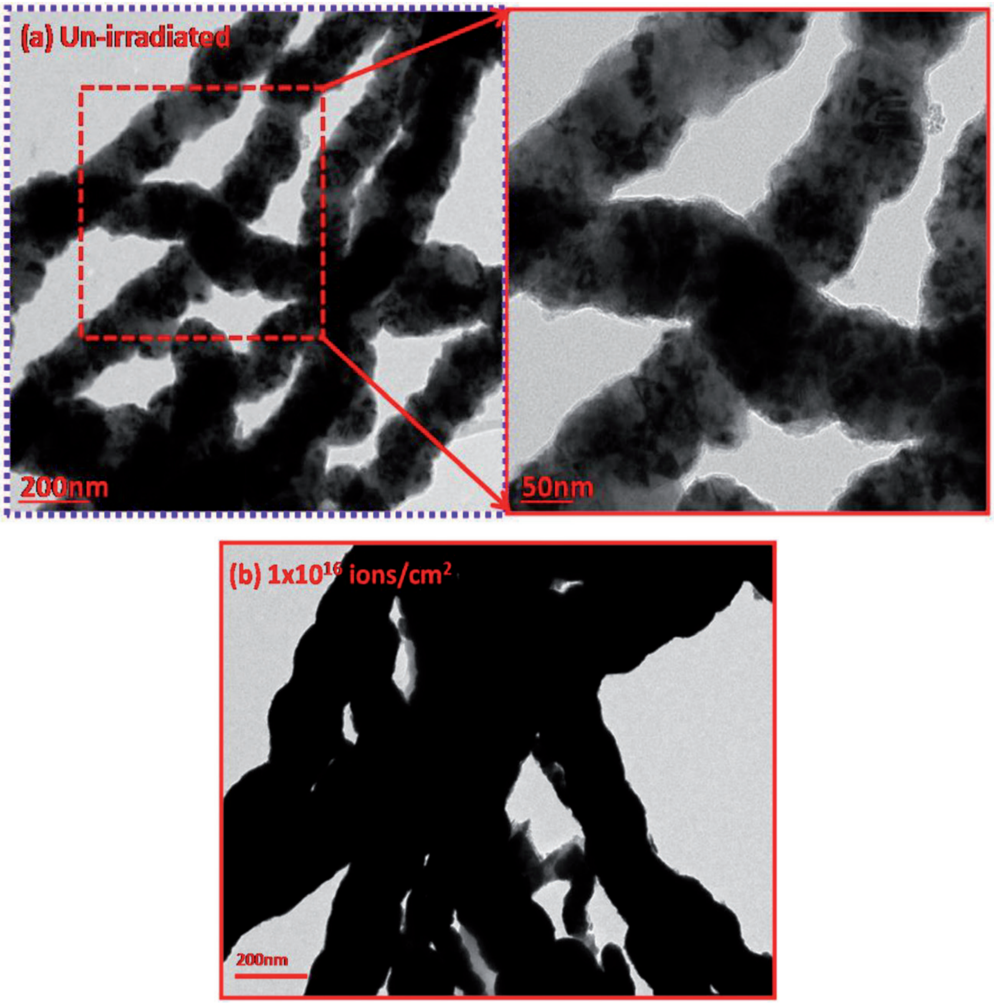

Figure 3.
(a) TEM image of Ni-NWs before H^+ *irradiation, and (b) TEM images of interconnected Ni-NWs after irradiation at a dose* 1×10^{16} *ions/cm*^{2}*.*

3. Discussion

The morphological changes of MNWs such as the reduction in the diameter of nanowires after ion beam implantation, slicing and cutting metal nanowires might be heat induced owing to the ions beam implantation along the track of ions which leads to the melt and fuse of MNWs into each other at intersecting positions [13, 14]. As mentioned above, the connection of metal nanowires might be because of localize heat induced due to interaction of ions with MNWs or due to accumulation of atoms sputtered from MNWs lattices due to collision cascade effect induced by ions beam irradiation.

In our previous reports, a similar mechanism of the interconnection of MNWs was also observed after the interaction of H^+ ions with Ag-NWs [13, 14]. In general, the interaction of ions with MNWs may be of two types: I-Columbic interaction in which energetic ions interact with electrons in the atoms of material or II-elastic interaction in which energetic ion strikes with nuclei of atoms in the material. If the collision between incident energetic ion and atom in the material would be of the elastic type, then an atom would be sputtered out from the lattice and lead to a secondary collision with another atom in the lattice. In this manner, the collision cascade effect would result in the ejection of atoms from NWs lattices. Usually, in case of low energy ions, the dominancy of the sputtering phenomenon would result in the accumulation of sputtered atoms on intersecting positions and lead to the interconnection between them. In the case of Columbic interaction, the generation of localized heat leads to the diffusion of atoms on the intersecting positions, which would result in the welding or joining of the intersecting positions.

In the case of metals, the produced heat due to the ionization and increase in the temperature of the metal are all absorbed. This increment in temperature would result in the melting of MNWs and eventually interconnection is obtained between the melted NWs on intersecting positions in a better way. If the beam energy incident ion is high in MeV range, then more chances of production of localized heat rather than collision cascade effect will be observed and if the beam energy is low in keV range then the sputtering phenomenon would be dominant [14].

3.1 Ion beam-induced structural changes in silver nanowires

XRD measurements taken at room temperature were used to study the structural changes in pristine and Ag-NWs as shown in **Figure 4**.

The diffraction pattern of the pristine sample shows peaks at 2θ angles of 38.6° and 44.11°, which corresponds to (111) and (200) planes of face-centered cubic Ag-NW. However, when XRD patterns of C ion irradiated Ag-NWs were compared with the pristine XRD pattern, it revealed a slight shifting of 2θ positions of diffraction peaks. This shifting in the 2θ position might be due to strain, which is often produced from surface defects, grain boundaries, dislocations, etc. Moreover, it can be observed from **Figure 4** that XRD peak intensities decrease with an increase in ion beam fluence. This decrease in XRD peak intensities might be due to the production of irradiation-induced defects such as point defects, dislocations, and grain boundaries, which accumulated to form defect clusters and led to the formation of a few pockets of amorphous zones. The crystal quality of material degrades due to the presence of these amorphous zones [30].

3.2 Ion beam-induced structural changes in Cu nanowires

Structural changes by ion implantation in Cu-NWs were studied using the XRD technique. In this study, Cu-NWs were irradiated with 100 keV H^+ beam at

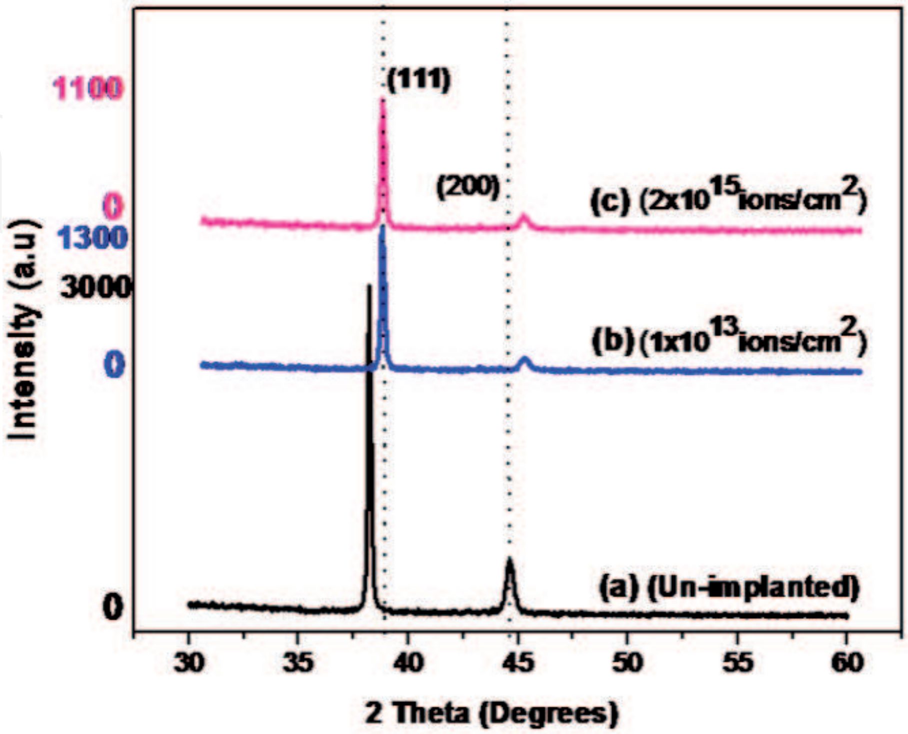

Figure 4.
XRD spectra of (a) un-implanted Ag-NWs, (b) 5 MeV C ions at the dose of (c) 2×10^{15} *ions/cm*^{2}.

different fluence from 1 × 10^{15}ions/cm^2 to 5 × 10^{16} ions/cm^2, Cu-NWs was done by XRD technique and compared with the un-irradiated spectrum. **Figure 5** shows the XRD spectra of samples irradiated at different fluences. **Figure 5(a)** shows the XRD spectrum of un-irradiated Cu-NWs. The XRD spectrum comprised of one (111) peak at $2\theta = 44.2°$, which is the preferred crystal plan of Cu-NWs. The other two low intensities peaks at $2\theta = 52.4°$ and 73.9° are corresponding to the

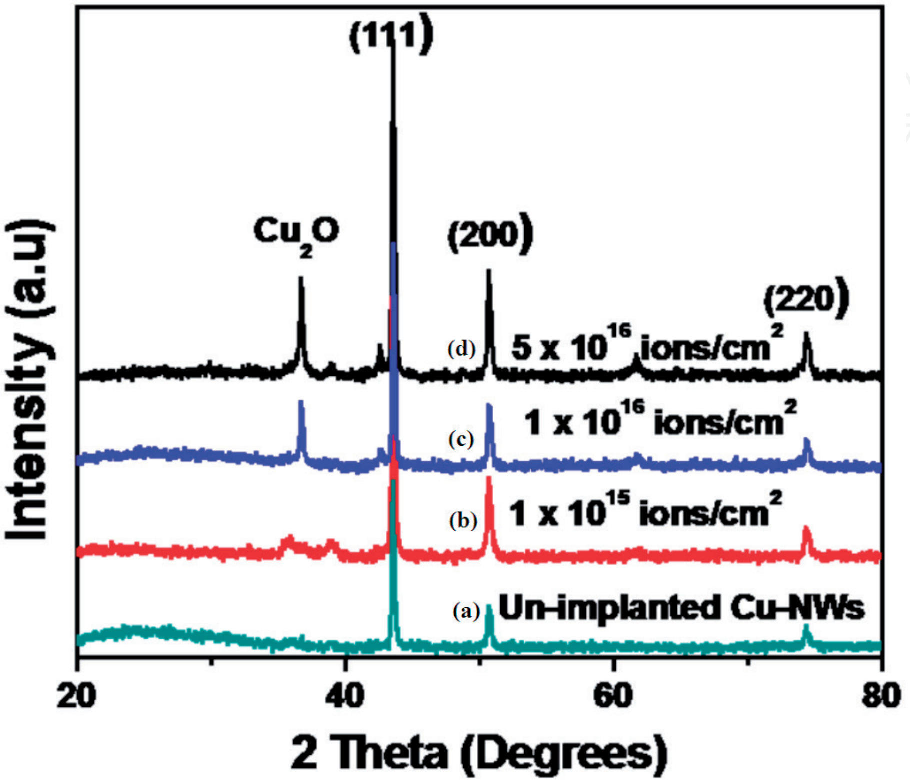

Figure 5.
XRD spectra of Cu-NWs (a) Un-implanted; (b-d) implanted with 100 keV H^+ ions at different doses.

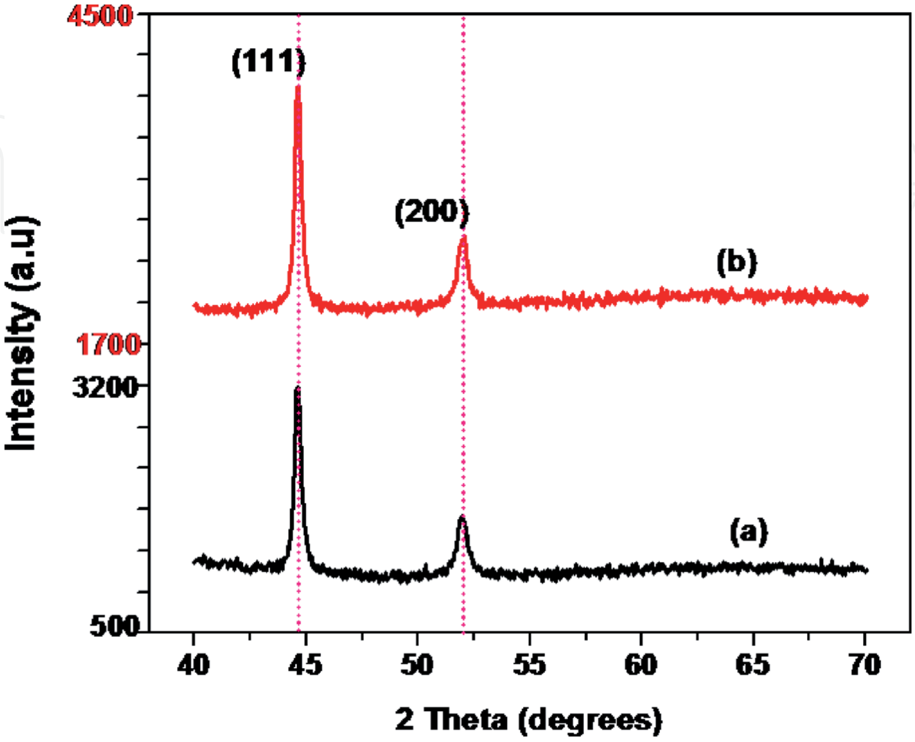

Figure 6.
XRD patterns of Ni-NWs (a) before irradiation and (b) irradiated with H^+ ions at fluence 1 × 10^{16} ions/cm^2.

crystal planes (200) and (220), respectively. These peaks and intensities showed that Cu-NWs had a polycrystalline structure. XRD results are confirmed with the HRTEM images as shown in **Figure 5(a)**. While if we observe XRD patterns of proton irradiated Cu-NWs, some new peaks appeared at low angle positions (see **Figure 5(b–d)**). These new peaks are of Cu_2O, showing that Cu nanowires might be oxidized due to oxygen atoms trapped into proton irradiation-induced defect sites in nanowire lattices.

These defects sites were observed by HRTEM study of ion irradiated in Cu-NWs. It was observed that at low ion irradiation, few point defects were created as the ion fluence increases, these point defects agglomerate to form large amorphous zones. These defects and amorphous zones give a path to O atom to form the Cu_2O phase in Cu-NWs.

3.3 Ion beam-induced structural changes in Ni nanowires

The XRD measurements taken at room temperature before and after exposure to the beam of H^+ ions on Ni-NWs are seen in **Figure 6**. The XRD patterns exhibit peaks of face-centered cubic planes (111) and (200) of Ni-NWs [20]. Changes in angle positions are not observed after proton irradiation; whereas, the intensities of the peaks were seen to increase after exposure to H^+ ions beam. The increase in peaks intensities might be associated with improvement in the crystalline structure of NWs. The crystalline structure might be improved due to the localized heating effect of Ni-NWs induced by H^+ ions beam irradiation.

Author details

Shehla Honey[1,2*], Asim Jamil[3], Samson O. Aisida[4,5], Ishaq Ahmad[5,6],
Ting-kai Zhao[6,7] and Maaza Malek[2]

1 Department of Physics, University of Okara, Okara, Pakistan

2 UNESCO-UNISA Africa Chair in Nanosciences/Nanotechnology, University of South Africa, iThemba LABS-NRF, Somerset West, South Africa

3 Department of Computer Science, University of Okara, Okara, Pakistan

4 Department of Physics and Astronomy, University of Nigeria, Nsukka, Nigeria

5 National Centre for Physics, Quaid-i-Azam University Campus, Islamabad, Pakistan

6 NPU-NCP Joint International Research Center on Advanced Nanomaterials and Defects Engineering, Northwestern Polytechnical University, Xi'an, China

7 School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, China

*Address all correspondence to: shehlahoney@yahoo.com

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