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# Influence of Beam Energy of Ions on Properties of Nickel Nanowires

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## Abstract

Electrical conductivity and optical transmittance of Nickel Nanowires (Ni-NWs) networks was reported in this work. The Ni-NWs was irradiated with 3.5 MeV, 3.8 MeV and 4.11 MeV proton ($H^+$) ions at room temperature. The electrical conductivity of Ni-NWs networks was observed to increase with the increase in beam energies of $H^+$ ions. With the increase in ions beam energies, electrical conductivity increases and this may be attributed to a reduction in wire-wire point contact resistance due to the irradiation-induced welding of NWs. Welding is probably initiated due to $H^+$ ions-irradiation induced heating effect that also improved the crystalline quality of nanowires (NWs). After ion beam irradiation, localize heat is generated in nanowires due to ionization which was also verified by SRIM simulation. Optical transmittance is increased with increase in energy of $H^+$ ions. The Ni-NWs networks subjected to an ion beam irradiation to observe corresponding changes in electrical conductivity and optical transparencies are promising for various nano-technological applications as highly transparent and conducting electrodes.

**KEYWORDS**: Ni-Nanowires, $H^+$ ions irradiation, Nano-welding, Electrical conductivity, Optical transmittance

## 1. Introduction

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For streaming of charge carriers in many new technologies, strongly conductive networks of metal nanowires (MNWs) are required for the flow of charge carriers in many new nano-technological applications [1]. In 2008, it was found by P. Peumans et al. [2] that MNWs mesh based transparent electrodes appeared to be most important contenders in the industry of transparent conducting electrodes. Revenue from MNWs based transparent electrodes will go beyond $255 million according to estimation of nano-market. A good percolation path is offered by MNWs networks to the flow of charge carriers which is accredited to intrinsic metallic nature of MNWs. In MNWs networks, nanowire-nanowire junction point is the main resistance point which needs to be welded [3]. For NW-NW junction welding, several techniques have been introduced by several researchers such as: cold welding [4], pulse laser processing [5], Joule heat welding [6, 2, and 7]. Besides, welding obtained by exposing nanomaterials to energetic ions is an important approach for fabrication of nanowire-nanowire junction through welding. This technique is applicable to variety of other nanomaterials [8-14]. Outburst of structure of nanomaterials as a result of exposure of nanomaterials to energetic ions is a general misconception but the other positive aspect is to tailor the electronic, structural, optical and magnetic properties of nanomaterials through ion beam irradiation [8, 9, 11, 15 and 16]. In one of previous report, Bari et al reported the increase in electrical conductivity of Ag-NWs networks through ion beam irradiation technology. Similarly, in another report, we found increase in electrical conductivity of Ag-NWs [14] networks by MeV $H^+$ ions. After successful modification of electrical conductivities of Ag-NWs through ion beam irradiation technique, we tried to implement this technique to modify conductivity of various types of metallic NWs.

In this report, we prepared the drop casted networks of Ni-NWs and irradiated these samples with beams of energies 3.5 MeV, 3.8 MeV and 4.11 MeV $H^+$ ions. To the best of our knowledge, this is first time we reported the influence of beams of $H^+$ ions of various energies on the properties of Ni-NWs. Drop casting is found to be an economical and simple approach to provide randomly distributed NWs networks on glass substrate which then can be followed with ion beam irradiation for welding at contact points and modification in electrical and optical properties.

## 2. Experimental Section

For present study, Nickel Nanowires were purchased from PlasmaChem (GmbH) (Product ID: PL-NiW200). The diameters of pristine NWs were in the range ≈ 300-500nm and having lengths ≈ 100-200 μm. Initially, it was obtained in form of wool-like fibre which was later converted to an aqueous solution. To prepare the solution, we used 5mg of Ni-NWs fiber in 1mL of ethanol. The finally prepared solution of Ni-NWs was deposited on a glass substrate using drop casting method. The schematic representation of transferring solution to a glass substrate can be seen in Figure 1 (a-b).

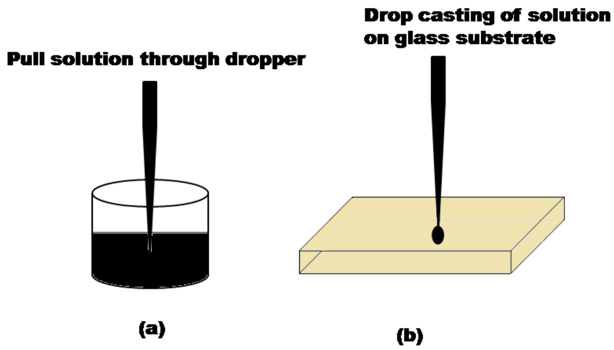


**Figure 1:** Experimental scheme of drop casting of solution on glass substrate.

The samples were thereafter exposed to energetic beams of $H^+$ ions of fluence $1x10^{16}$ ions/$cm^2$ and having energies i.e., 3.5 MeV, 3.8 MeV, 4.1 MeV and 4.4 MeV at room temperature ($R_T$) using a 5 UDH-Pelletron accelerator at~ $10^{-7}$ Pa. The Stopping Range of Ions in Matter (SRIM) simulation was carried out to obtain information about implantation of $H^+$ ions into Ni-NWs during irradiation and generation of localize heating effect in NWs. The structural and morphological information of Ni-NWs was obtained using transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques. Electrical conductivity and optical measurements were conducted using four-point probe techniques and UV-VIS Spectroscopy respectively. The voltage potential "V" in the probe is measured using the expression in equation 1 [14].

$$V = {}^{1}/_{2\pi SiG} \qquad (1)$$

Where G is "surface conductivity" and *S*i is "distance between current and voltage probes" and I is "current".

## 3. Results and Discussions

The pristine Ni-NWs deposited via drop casting technique on glass substrate are shown in Transmission Electron Microscopic images of Figure 2 (a-c). It is shown from these networks that NWs are self-assembled by Vander Waals forces with NWs density well above the percolation threshold. The diameters of pristine Ni-NWs ranges between 300-500nm (see Figure **2** (a)). These Ni-NWs have polycrystalline in nature and it is verified from HRTEM image of Figure **2**(b) which is further confirmed through SAED image of Figure 2 (c). An EDX spectrum of un-irradiated Ni-NWs is shown in Figure **2** (d). It shows trace elements of Ni and Cu. It is seen in Figure 2 (d) that main trace element is Ni and Cu is also appeared which might be due to copper grids that employed during TEM analysis of un-irradiated sample. For TEM analysis, solution of Ni-NWs was deposited on copper grids. After irradiation of Ni-NWs with beam energy 3.5 MeV with beam fluence $1x10^{16}$ions/$cm^2$, joining of NWs was observed as shown in Figure 2 (e). It is seen from TEM results that morphology of NWs is also preserved after irradiating Ni-NWs with beam of $H^+$ ions of energy~3.5 MeV.

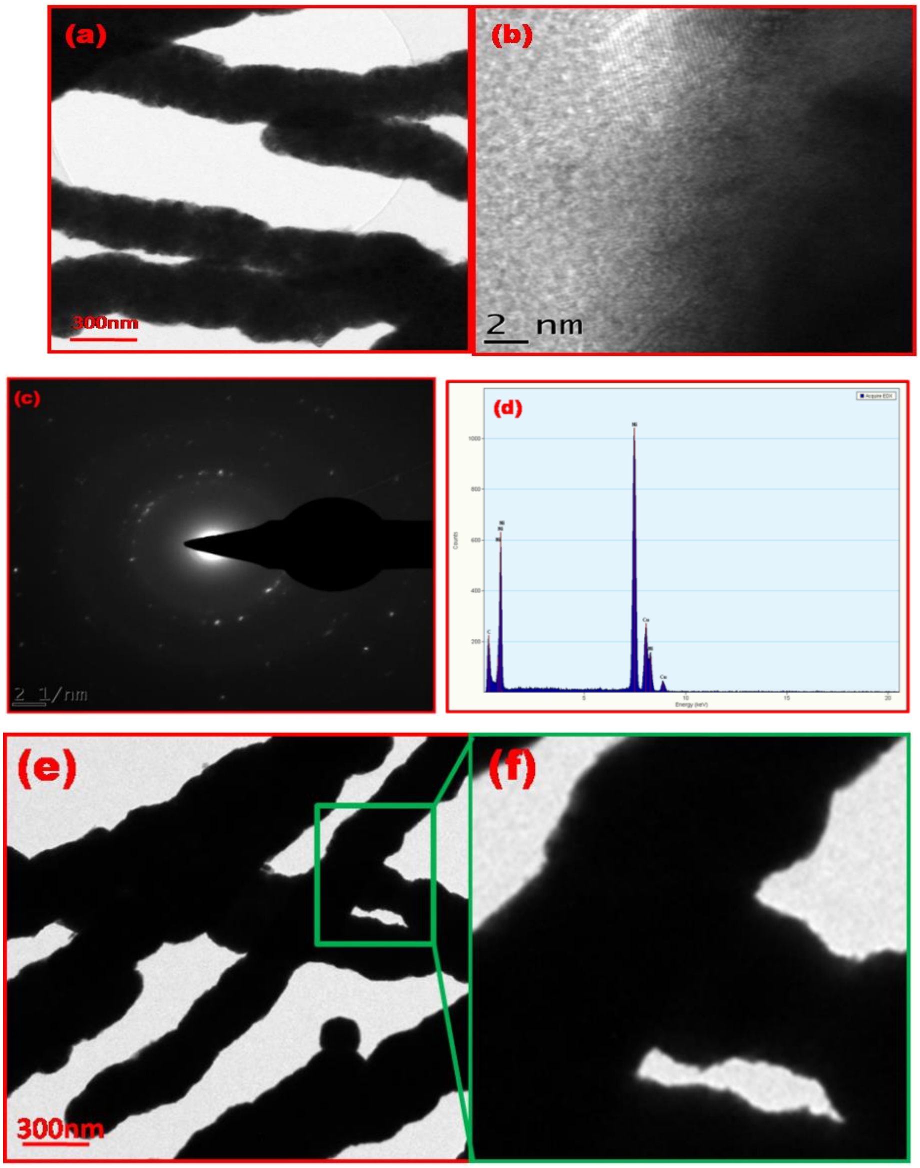


**Figure 2:** (a) Un-irradiated Ni-NWs (b) HRTEM of Ni-NWs (c) SAED image of un-irradiated Ni-NWs (d) EDX spectra (e) Ni-NWs network irradiated by $H^{+}$ ions (**3.5** MeV) at fluence $1x10^{16}$ ions/$cm^{2}$ (f) HRTEM image showing clear preview of interconnection or welding occurred between Ni-NWs after irradiation by $H^{+}$ ions of energy **3.5** MeV and fluence $1x10^{16}$ ions/$cm^{2}$.

The Ni-NWs are found to be welded or interconnected joined with each other after irradiating by ions of energy 3.5 MeV and beam fluence ~$1x10^{16}$ ions/$cm^{2}$ as seen in Figure **2 (e)**. The reason for welding or joining of these Ni NWs is due to ion irradiation-induced localized heat. The formation of junctions of Ni-NWs in various shapes such as cross and parallel shapes can be clearly seen in Figure **2(e)** due to $H^{+}$ ion irradiation-induced joining that might lead to form welded network of Ni-NWs. Furthermore, it can also be seen in TEM image of Figure **2 (e)** that morphology of NWs is still preserved. The clear preview of welded NWs of Figure 2 (e) can be seen in Figure 2 (f).

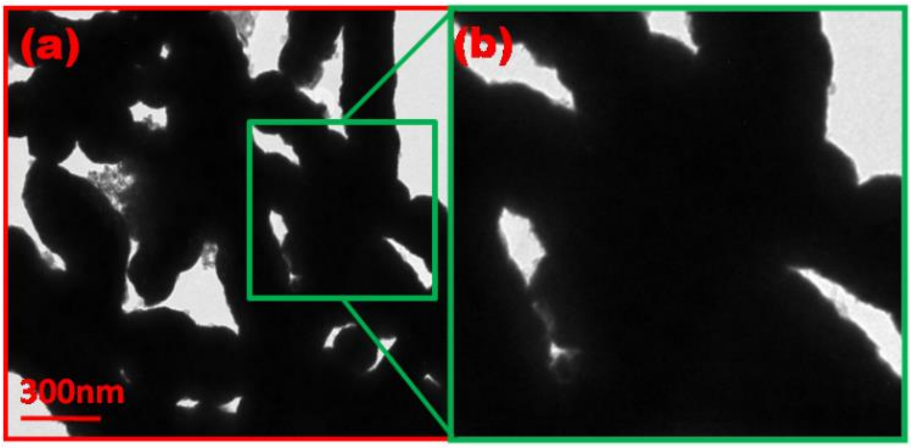


**Figure 3**: Ni-NWs network irradiated by **3.8** MeV $H^+$ ions at fluence $1x10^{16}$ ions/$cm^2$

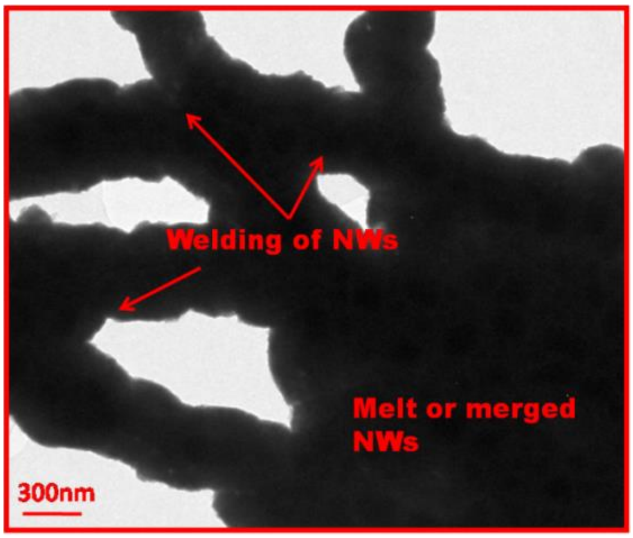


**Figure 4:** Ni-NWs network irradiated by 4.11 MeV $H^+$ ions at fluence$1x10^{16}$ ions/$cm^2$

With the increase of beam energy up to 3.8 MeV at beam fluence ~1 x $10^{16}$ ions/$cm^2$, welding of NWs is seen with stable morphology. The TEM images of the junctions that have been welded due to ion beam irradiation are presented in Figure 3 (a). Also, the corresponding HRTEM image of welded junctions is presented in Figure 3 (b). It is clear from Figure 3 that the morphology of Ni-NWs is still preserved at high energy. It is also seen in Figure 3 that NWs are perfectly welded to each other. With further increase in beam energy up to 4.11 MeV, welding is found between NWs with stable morphology as shown in TEM image of Figure 4. Figure 4 shows NWs are well-connected to each other in various shapes. However, it is found in case of high energy ions that some NWs are melted, fused or merged with each other. It is found from TEM results that welding between NWs is occurred at all beam energies and morphology of Ni-NWs is preserved at all energies.

Theoretical concept behind welding between nickel nanowires is explained by thermal spike model. For faster beam of proton ions (≥ 0.11 MeV), kinetic energy of the energetic ions is usually transferred to target electrons which would produce electronic energy losses (Se) due to ionization more dominantly. Therefore, Se may perhaps play an imperative role in the atomic transport process at the contact positions of individual Ni-NWs in case of high energy ions [17]. When beam of proton ions hits an individual Ni nanowire, ions might tend to lose a small fraction of their kinetic energy *by* columbic interaction with atomic electrons [18]. According to thermal spike's model, these excited electrons will remain in thermo dynamical equilibrium for the time interval of $10^{-15}$ s through electron–electron interactions and thereafter excited electrons discharge their energy to atoms in Ni lattice by electron–phonon coupling in time interval ̴ $10^{-13}$–$10^{-10}$ s. This energy is then deposited in form of heat to the Ni lattice along ions track and consequently produce localize spikes of heat or thermal spikes. It depends on potency of electron–phonon coupling that temperature along the ion's path may significantly enhanced up to melting point of the Ni material and a molten zone or a liquid cylinder of a few nm in depth is created at interface of crossing regions between two Ni nanowires [17]. This molten zone at intersecting positions is transitory and is formed up to several thousands of degree Kelvin which would result in atomic displacements and mass transport of two Ni-NWs into each other exactly on crossing positions. In a picoseconds time duration, proton or ion's tracks turn cool down and results in welding of Ni-NWs on crossing positions. With increasing in incident energy of ions beam, the localized heating effect of material also increases and results in the mass transport of Ni-NW's atoms into each other at contact position more efficiently. So, these MeV proton induced thermal spikes are localized in nature and increase with increasing incident beam energy cause to effectively weld Ni-NWs with each other [19]. Surplus or high ions beam energies and fluencies were avoided due to keep safe from damaging effect in NWs due to excessive power of ions. Similarly, in case of low beam fluencies, less heat is generated. This heat is insufficient to effectively weld NWs on overlapping positions. Therefore, medium dose and ions beam energies were selected to achieve optimized results [**20**].

After examining the Ni-NWs networks by TEM, the structural evaluation of Ni-NWs network before and after irradiation with 3.5 MeV, 3.8 MeV, 4.11 MeV $H^+$ ions was also carried out. Structural evaluation was made to observe changes in crystalline structure of NWs.

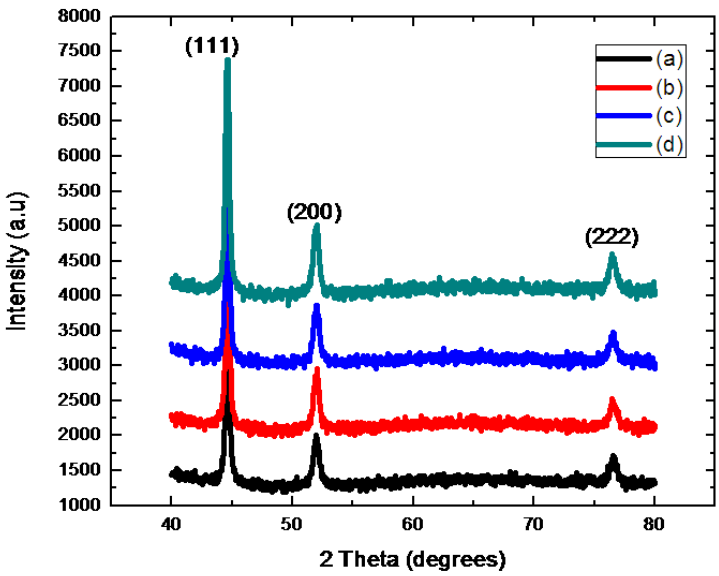


**Figure 5:** XRD spectra analysis of Ni-NWs network irradiated with 3.5, 3.8, 4.11 MeV of $H^+$ ions at $1x10^{16}$ ions/$cm^2$.

Structural information on $H^+$ ions irradiated Ni-NWs networks would also be supportive for examining the changes in conductivity of the material. In order to verify the structure of the pristine and the irradiated Ni-NWs networks, the XRD measurements were conducted at room temperature ($R_T$) and presented in Fig. 5. Un-irradiated sample is showing peaks of face centered cubic (fcc) structure of Ni-NWs [13]. After irradiation, shifting in the value of 2θ of the diffraction peaks is not observed in the XRD spectra when compared with the un-irradiated samples. We also observed that the peak intensities are increased with the increase in ion beam energies, as seen in Fig. **5.** The increase in intensity of XRD peaks is might be due to improvement in crystalline quality of NWs after irradiation [9, 14, 21].

After the TEM and XRD analysis of Ni-NWs, four probe methods was employed to determined the conductivity of samples before and after irradiation. The electrical conductivity was observed to increase at beam 3.5 MeV with respect to un-irradiated samples; which is further increased with increase in beam energy. This increment might be owing to local heating of Ni-NWs by the ion beam irradiation which improved the crystalline quality of NWs which lead to increase conductivity of NWs slightly [10].

The relative conductivity of un-irradiated samples is 1 which is increased to 2.74 at beam energy 3.5 MeV. The observed increase of relative conductivity after irradiation is similar to carbon nanotubes (C-NTs) and silver nanowires (Ag-NWs) networks already demonstrated in our previous report [14, 22]. As beam energy is increased to 3.8 MeV, Ni-NWs network becomes highly conductive. Fused, welded junctions between Ni-NWs at irradiation fluence 3.8 MeV were presented in TEM images of Fig. 2 (b). At this beam fluence, the electrical conductivity of Ni-NWs mesh was recorded and observed to increase by 3.98 times referred to un-irradiated sample. The increase in the value of electrical conductivity might be due to welding of NWs at junction positions which caused a decrease in resistance at contact points; hence a resistance free path is provided to electrons at junction locations. At high beam energy i.e., 4.11 MeV some NWs are fused and merged to each other which gives more rise to conductivity. TEM image of Fig. 4 is presenting this mutilation where these NWs were found to be melted and merged with each other. Variations of electrical conductivity in Ni-NWs are analyzed with irradiation energy of $H^+$ ions, a plot of relative conductivity versus irradiation energy is presented in Figure 6.

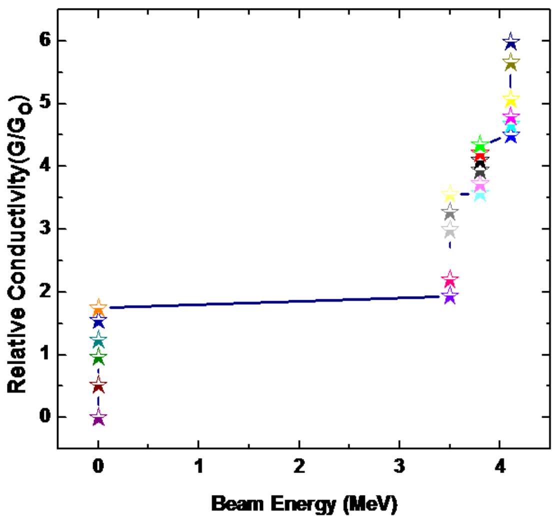


**Figure 6:** Electrical conductivity (relative i.e., $G/G_o$) of Ni-NWs meshes as a function of energy of $H^+$ ions.

G is conductivity of irradiated sample and $G_o$ is the conductivity of un-irradiated sample whereas $G/G_0$ is relative conductivity of samples. The obtained results are similar to Ag-NWs at different fluencies of $Li^{3+}$ ions

[14, 20]. A rise in conductivity value was clearly seen in Figure 6 which reaches a maximum value at beam energy 4.11 MeV as shown in Figure 6. The observed increase in conductivity might be due to reduction of defects caused as results of local heating induced fusion or coalescence of NWs.

The analysis improvement in value of conductivities of Ni-NWs after irradiation with $H^+$ ions of different energies have also been examined by Stopping and Range of Ions in Matter (SRIM) simulation program. The SRIM simulation program was run for parameters i. Incidet ions was 10000 ii. Incident angle was 0º iii. Layer thickness was 2000 Aº. The plots of ions tracks in the materials at various energies and collision events have been demonstrated in Figure 7 (a-f). In Fig. 7 (a-c), red colored dots are representing vacancies induced due to impact of 3.5 MeV, 3.8MeV and 4.11 MeV $H^+$ ions with a lattice of Ni layer respectively whereas Figure 7 (d-e) shows the collision events.

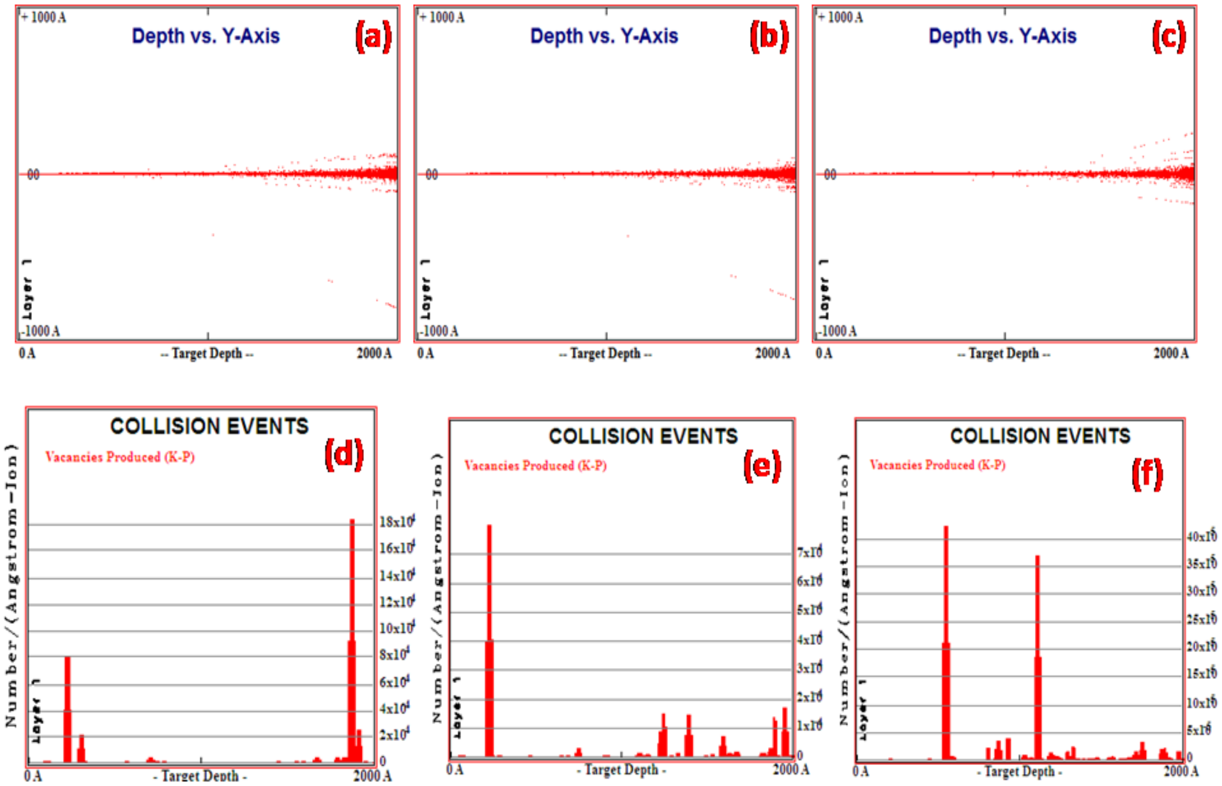


**Figure 7:** SRIM simulation results. Path of $H^+$ ions on Y-axis (a) 3.5 MeV ions (b) 3.8 MeV ions (c) 4.11 MeV ions (d-f) Collision impacts in Ni layer.

The simulation results of impact of $H^+$ ions with Ni layer are shown in Table 1. Simulations were carried out to obtain information about loss of energy of $H^+$ ions in the materials. Total damage was found using Kinchin-Pease method and recoils after impact of 3.5 MeV, 3.8 MeV and 4.11 MeV $H^+$ ions with materials. Incident angle was selected to be 0º. The term ionization gives us information about loss of energy of $H^+$ ions to target electrons. From Simulation results, it is found that no $H^+$ ions is diffused or implanted in Ni layer. The localize heat is produced in form of ionization in Ni layer which improves the crystalline quality of material and cause to increase the conductivity of Ni NWs. Simulation results are showing that no defects are produced in lattice due to diffusion of $H^+$ ions into Ni layer. Moreover, it is shown from Table 1 that ionization rate due to ions is increased to 99.93 from 99.90 as the energy is increased to 4.11 MeV from 3.5 MeV. Loss of energy of ions in producing phonons is 0.02 which is too small and constant at all energies. Therefore, it is seen from SRIM results that major part of ion's energy is contributing to production of heat due to ionization. The production of recoils is very small in the materials, however, recoils also contributing their energies in form of ionization and phonons. XRD and simulation results collectively represents the improvement in crystallinity of NWs due to ionization induced localized heat and production of lattice defects are too small within NWs after exposure to $H^+$ ions. However, induction of localize heat is dominant process as compared to creation of defects and it is verified from SRIM results.

**Table 1**: Simulation of $H^+$ ions interacting with Ni layer.

| **Energy of Ions (MeV)** | **Number of incident ions** | **Total Number of Vacancies/Ion** | **No of Transmitted ions** | **% of Energy Loss (Ion)** | | **% of Energy Loss (Recoil)** | |
|---|---|---|---|---|---|---|---|
| | | | | **Ionization** | **Phonons** | **Ionization** | **Phonons** |
| 3.5 | 10000 | 0.1 | 10000 | 99.90 | 0.02 | 0.02 | 0.06 |
| 3.8 | 10000 | 0.1 | 10000 | 99.92 | 0.02 | 0.01 | 0.05 |
| 4.11 | 10000 | 0.0 | 10000 | 99.93 | 0.02 | 0.01 | 0.04 |

After initiation of coalescence or fusion of NWs, contact resistance of NWs is reduced, path length is increased and consequently conductivity is increased. XRD and simulation results collectively represents that both phenomena such as coalescence of NWs due to heat and production of lattice defects are occurring concurrently within NWs after exposure to $H^+$ ions. However, induction of localize heat is dominant process as compared to creation of defects. If the beam fluence is low, coalescence process of NWs is dominant and increased path length; consequently, conductivity is increased. In case of high irradiation fluence $1x10^{16}$ ions/cm$^2$, both localize heating effect and generations of defects are appearing in the structure concurrently. Besides, less path length is occurred after exposure of NWs to high fluencies of $H^+$ ions which is due to cutting and slicing of NWs; consequently, reduces conductivity. On the basis of present experimental findings and previous experiments, it is found that changes of electrical conductivity of Ni-NWs have been occurred which could be tuned for numerous nanotechnology applications.

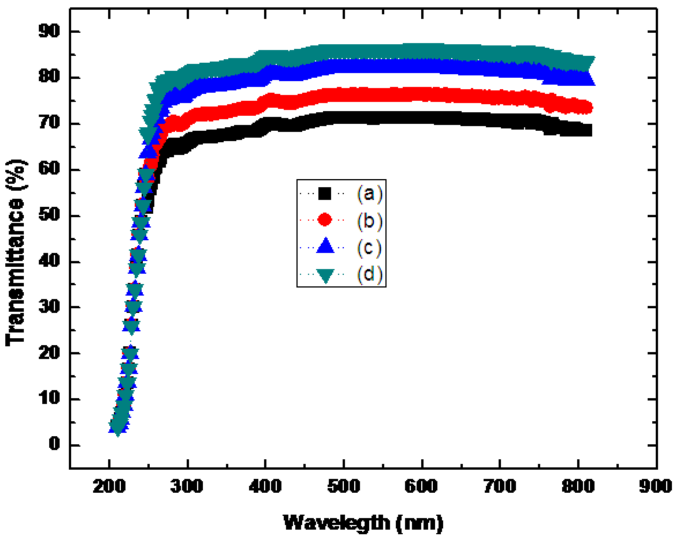


**Figure 8:** Transmittance spectra of random network of Ni-NWs (a) un-irradiated (b) 3.5 MeV ions (c) 3.8 MeV ions (d) 4.11 MeV ions

The optical properties of Ni-NWs networks are different as compared to bulk nickel and originated due to surface plasmonic resonance effect. Figure 8 (a-d) represents optical transmittance spectra of Ni-NWs networks. in the transmittance spectra of Figure 8 (a-d), strong absorption band is seen at around 375 nm which lies in ultraviolet region [23, 24, 25]. The absorption band appears at 375 nm which is in ultraviolet region due to surface plasmonic resonance effect which is missing in bulk nickel [25]. This absorption band might become visible due to an interaction of conduction band electrons with an electromagnetic field.

When electromagnetic field interacts with Ni-NWs network, oscillating electric field will be induced and this oscillating electric field perturbs conduction band electrons at the surface. Consequently, electron cloud is displaced with respect to nuclei of material. Later, the electron cloud oscillates are produced relative to the nuclei due to columbic force of attraction between electrons and material nuclei [25]. Collective effects of oscillations of conduction band electrons at the surface are called surface plasmonic resonance [25]. This resonance effect is might be the reason for reducing transmittance, enhanced scattering and absorption of light in UV region. In case of metal nanowires, these surface plasmonic bands lead to highly tunable and controllable properties which can be exploited in various nanotechnology applications. Moreover, it can be seen from Fig. 8 that transmittance of presented networks increased with increase in beam energy of proton ions which might be due to improvement of crystallinity of Ni-NWs occurred due to localized heating effect induced by ionization.

## 4. Conclusion

Welding of NWs is obtained by exposure to beams of energetic $H^+$ ions of various energies. Welding between NWs will cause to reduce the wire-wire junction resistance and due to and improve the electrical conductivity of NWs. The electrical conductivity of NWs is increased with the increase in beam energy of energetic ions. This increase is might be due to improvement in crystallinity of NWs with ion beam irradiation. Similarly, the optical transmittance is also increased with increase in beam fluence of $H^+$ ions which is might be due to improvement in crystallinity of material. SRIM simulation shows that ionization rate is increasing with the increase in beam energy of $H^+$ ions which is indication that localize heat is producing in the NWs and increasing with the increase in beam energy of ions. The present approach is superb for fabrication of highly conductive NWs networks. This study is useful in many current nanotechnology applications where high electrical conductivity and optical transmittance are required.

## 5. Acknowledgement

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