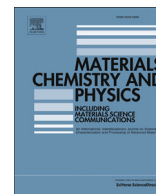




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## Influence of ion beam irradiation induced defects on the structural, optical and electrical properties of tellurium nanowires

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## HIGHLIGHTS

- 110 MeV Ni<sup>8+</sup> ion beam induced changes in tellurium nanowires have been examined.
- Nanowires were prepared using template electrodeposition method.
- Irradiation improved the electrical conductivity of tellurium nanowires.
- Mechanism for enhanced electrical conductivity of irradiated nanowires was discussed.

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## ABSTRACT

In this study, tellurium nanowires were electrodeposited into the polymer membranes from aqueous acidic bath containing HTeO<sub>3</sub><sup>+</sup> ions. The field emission scanning electron microscopy (FESEM) images confirmed the formation of uniform and straight nanowires. The influence of 110 MeV Ni<sup>8+</sup> ion irradiation induced defects on the structural, optical and electrical properties of as-deposited tellurium nanowires were examined using X-ray diffraction (XRD), UV–visible absorption spectroscopy and current–voltage (*I*–*V*) measurements. The XRD data depicted the hexagonal phase of tellurium nanowires and further revealed a variation in the intensity of diffraction peaks of ion irradiated nanowires. Williamson–Hall (WH) analysis is used for convoluting the size and microstrain contributions to the width of diffraction peaks. Tellurium nanowires exhibited a distinct absorbance band in the visible region at 686 nm, while this was absent in bulk tellurium. Electrical properties of nanowires are explored on the basis of *I*–*V* curves, which revealed a significant increase in the electrical conductivity of irradiated nanowires. A possible mechanism for the enhanced electrical conductivity is the increase in carrier concentration due to thermally excited defects. The defects produced by ion irradiation play a vital role in modifying the properties of semiconducting nanowires.

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## 1. Introduction

Nanowires of semiconducting materials have attracted significant research due to their widespread applications [1,2]. Tellurium (Te), a narrow bandgap *p*–type semiconducting material, has earned great attention because of its intrinsic photoconductive and piezoresistive properties, in addition to its thermoelectric, catalytic and nonlinear optical properties [3–14]. These properties make it a

useful material for a wide range of promising applications such as photoconductive detectors [15–19], sensors [20–24], photocatalysts [13], antiseptic agents [25–27], field emitters [28–30], field effect transistors [31], thermoelectric and piezoelectric devices [32–34]. The above-described facts make tellurium a fascinating material for synthesizing nanowires and exploring their structural, optical and electrical properties; and further examine how these properties can be modified by ion beam irradiation, doping and nanoengineering in order to use them in technological applications. C. Yan et al. studied the photocatalytic properties of ultra long Te nanowires prepared by hydrothermal method and observed that Te nanowires acted as potential catalysts to

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efficiently decompose organic toluidine blue O (TBO) dye [13]. B. Abad et al. studied the thermoelectric properties of electrodeposited Te films and found the figure of merit one order of magnitude higher than the bulk value [14].

Now a days, ion beam irradiation using high electronic excitation is one of the promising and effective methods used to engineer the size, shape and crystallinity in a controlled manner and hence the physical and chemical properties of nanostructured materials [35–39]. The exploration of nanostructured materials with ion irradiation provides immense opportunities and effective means to engineer the nanomaterials properties for various applications. The size constraints in one or more dimensions of nanostructured materials make ion irradiation effects different than that of the bulk. The nanostructured materials have exceptional irradiation resistance because of a large fraction of grain boundaries or interfaces that could absorb and annihilate mobile defects which are produced during irradiation [40,41]. Furthermore, the ion irradiation may lead to intriguing behaviors that can provide further insight into the fundamentals of ion–solid interactions at the nanoscale. The energetic ions passing through a solid dissipate energy in elastic and inelastic scattering with the target nuclei and electrons, respectively. The localized deposition of high energy by the passing energetic ions results in the evolution of defects and induces structural changes in target materials. This results in material modifications and thereby effects the properties of devices composed of these materials [42–45].

In semiconducting materials, ion irradiation deposits energy by generating the electron–hole pairs or through non-ionizing processes. The non-ionizing energy displaces atoms and creates defects in semiconductor regions. The defects caused by irradiation, serve as the traps that may serve as recombination centers. The defects in semiconductors play significant role in the performance of devices and modify the lifetime and mobility of charge carriers, change carrier densities and non-radiative transitions in optical devices [46–48]. The effects of ion irradiation on the properties of nanomaterials can be detrimental or beneficial [49,50].

Several efforts have been made by the researchers to elaborate the influence of irradiation on the nanostructured materials, but comparatively lesser number of research articles has been reported the irradiation effects on the nanowires. Zhao et al. [43] have irradiated ZnO nanowires, prepared by thermal oxidation method, with energetic X-ray radiations and studied the modifications in their structural and field emission properties. Yang et al. [51] studied the coupling effects of stress and ion irradiation on the mechanical behaviors of copper nanowires. The variation in the structural, optical and electrical properties of ion beam irradiated cadmium selenate nanowires was investigated by Rana and Chauhan [52].

In this paper, we investigated the properties of tellurium nanowires irradiated with 110 MeV  $\text{Ni}^{8+}$  ions at different ion fluences in order to explore the possibility of using ion beam irradiation for material modification. The nanowires were prepared by a simple template-based electrodeposition method in potentiostatic mode. The structural, optical and electrical properties were analyzed to explore the ion irradiation effects in tellurium nanowires. Our results showed that ion irradiation leads to increase in the electrical conductivity of tellurium nanowires by the generation of charge carriers.

## 2. Experimental details

### 2.1. Synthesis of tellurium nanowires

Tellurium nanowires were electrodeposited from aqueous electrolytes containing  $10^{-4}$  M  $\text{TeO}_2$  at a constant potential of 1.2 V. The electrolyte was dissolved completely using 2.5 M  $\text{H}_2\text{SO}_4$ . The

$\text{TeO}_2$  (99.995%, Sigma Aldrich) dissolved as  $\text{HTeO}_2^+$  in an acidic medium. The deionized water was used to prepare the electrolytes. All the chemicals used in nanowires fabrication were of analytical grade and used as received without further purification. The electrodeposition was carried out using a two-electrode electrochemical cell in which template with copper substrate (3 M copper tape coated with conducting adhesive layer) served as the cathode and the platinum wire as an anode as described elsewhere in our previous work [53,54]. Commercially available polycarbonate track-etched membranes (Whatman) with cylindrical pores of size 100 nm, thickness 10  $\mu\text{m}$  and density  $10^6$  pores  $\text{cm}^{-2}$  (manufacturer's specifications) were used as templates. The electrodeposition process was carried out for 25 min at room temperature. The synthesis parameters used were optimized taking into considerations the preliminary experiments. The low solubility of tellurium dioxide in water resulted in the slow growth rate of the tellurium nanowires, causing long deposition times. To ensure pore wetting, the membrane was immersed in the electrolyte prior to the deposition process. The pore wetting improved the convection in the pores resulting in homogeneous deposition through the entire membrane. The length of the nanowires was controlled by adjusting the deposition time.

After completion of the deposition process, samples were removed and rinsed several times with deionized water, and then dried in the open air. For imaging with FESEM, nanowires were retrieved by completely dissolving away the polycarbonate template, which was accomplished by soaking the sample of polycarbonate template embedded with the tellurium nanowires in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) solution for 30 min at room temperature. The solution was then slowly removed using a syringe and cautiously replaced with deionized water to rinse the nanowires. The rinse process was repeated several times and then the nanowires were dried in the open air. It is to be noted that the tellurium nanowires were found to be almost vertically standing freely and parallel to each other because of the fact that their lower ends were adhered to the 3 M copper tape with the help of an adhesive conducting layer on the base.

### 2.2. Ion beam irradiation of tellurium nanowires

The in situ nanowires, embedded in polymer membranes as templates (without dissolution of the template in an organic solvent) were irradiated with  $\text{Ni}^{8+}$  ion beam of energy 110 MeV using Pelletron tandem accelerator at Inter University Accelerator Centre (IUAC), New Delhi, India. The samples mounted on a copper ladder were placed vertically at normal incidence of ion beam. The irradiation was carried out at room temperature. The vacuum during irradiation was approximately  $10^{-6}$  mbar and the ion beam current was maintained at 1 pA (1 particle nanoampere =  $6.25 \times 10^9$  ions/s) to avoid the thermal degradation of the membranes. The irradiation fluence was varied from  $1 \times 10^{11}$  to  $1 \times 10^{13}$  ions  $\text{cm}^{-2}$  for this particular study. The exposure area and exposure time was used to control the irradiation fluence. The ion beam was scanned in area of 1  $\text{cm}^2$  of sample by an electromagnetic scanner to ensure uniformity of ion irradiation. The  $\text{Ni}^{8+}$  ion beam deposits energy of  $\sim 16.21$  MeV  $\text{mg}^{-1} \text{cm}^2$  by electronic energy loss due to inelastic collisions and  $\sim 3.213 \times 10^{-2}$  MeV  $\text{mg}^{-1} \text{cm}^2$  by nuclear energy loss due to elastic collisions, as calculated from SRIM–2010 simulation code [55]. This ensures that the electronic energy loss is the dominant mode through which the Nickel ions lose their energy in the tellurium wires. From SRIM simulation, the projected range of the incident ion in the tellurium was found to be  $\sim 16.14$   $\mu\text{m}$ . This was much larger than the length of wires (10  $\mu\text{m}$ ), neglecting the probability of ion implantation in the nanowires. The ions get buried deep inside the Cu substrate.

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