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## Tailoring the properties of copper nanowires by ion beam irradiation

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## HIGHLIGHTS

- Ion irradiation-induced changes in copper nanowires have been examined.
- Nanowires were prepared using template method.
- A variation in XRD peak intensities of irradiated nanowires was observed.
- Ion beam irradiation caused severe damage to grain size.

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## ABSTRACT

In the present paper, we investigated the change in the properties of copper nanowires under the irradiance of 80 MeV Si<sup>7+</sup> ion beam. The nanowires were electrodeposited in the cylindrical pores of the track-etched polycarbonate membranes. The phase, morphology and optical absorbance of the fabricated nanowires were characterized by powder X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and UV–visible spectroscopy, respectively. The XRD study showed a face centered cubic crystal structure of copper nanowires. Further measurements with FESEM revealed that nanowires were continuous, aligned with uniform diameter having high aspect ratio. The XRD spectra of irradiated nanowires indicated an improved crystallinity at low ion fluences while it declines at higher ion fluences. The optical absorbance properties of the irradiated copper nanowires were also examined. The absorption spectra exhibited a peak at 568 nm which was attributed to the surface plasmon resonance. A significant increase in absorbance after irradiation accounts for the possibility of defects formation. The electrical properties measured from I–V characteristics showed an increase in resistivity of irradiated nanowires.

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## 1. Introduction

Recently, there has been an intriguing interest in studying the interaction of ion beam irradiation with low-dimensional structures (Avasthi and Pivin, 2010; Krashennikov and Nordlund, 2010; Kuriakose et al., 2015; Li et al., 2014a, 2014b; Pivin, 2005; Schrimpf et al., 2011). Ion beam irradiation has been extensively studied in bulk materials. With low-dimensional structures being omnipresent, the concept of ion beam irradiation of nanostructures has become forefront area of research. Renewed interest has originated from the use of ion beams to synthesize and modify physical and chemical properties of the nanostructures for various applications (Abedini et al., 2012; Borschel et al., 2009; Chen et al.,

2010; Gokulakrishnan et al., 2012; Jeet et al., 2012; Jun et al., 2009; Patel et al., 2015; Romano et al., 2009; Ronning et al., 2010, 2007; Tuboltsev and Raisanen, 2009). Irradiation effects in low-dimensional structures often differ substantially from that observed in bulk materials. As a consequence, exciting potential applications have opened up. Further, ion beam irradiation of low-dimensional structures may lead to intriguing behavior and rich physics that can provide insight into the fundamentals of ion–solid interactions at nanoscale regime and helps in mechanizing the benefits of irradiation in favor of mankind. It also helps in predicting the reliable operation of nanodevices in different radiation environments. The energy deposited by the ion beam irradiation produces a wide variety of defects in the nanomaterials, which includes displacement, interstitials, vacancies and dislocations etc. These defects affect the physical and chemical properties of nanomaterials such as structure, optical absorbance and electrical transportation

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(Ahmad et al., 2010; Gautam et al., 2014; Zhao et al., 2013). The irradiation damages may be explained on the basis of elementary collision cascade theory (Christie et al., 2015). The primary knocked out atoms as freely migrating vacancies and interstitials play a significant role in the formation and evolution of secondary irradiation defect pairs. Only a fraction of these freely migrating defect pairs would be stable and rest would either annihilate by mutual recombination or absorbed by different sinks available in the material itself (Doan and Martin, 2003). Often, the ion beam irradiation deteriorates physical properties of the nanomaterials leaving a negative impact however, in certain circumstances they could be detrimental and beneficial (Borschel et al., 2011; Dee et al., 2011; Park et al., 2009).

Nanowires represent smallest dimension structure for efficient transport of charge carriers and have incredible significance in the realization of futuristic integrated circuits based on interconnects. The copper has high accessibility; superior electrical and thermal conductivity at a cost much less than other metals, which make it the best material for interconnects. Nanoscale copper wires exhibits enhanced non-linear optical properties due to surface plasmon resonance, which could lead to several applications in optical devices and non-linear optical materials (Pang et al., 2003; Duan et al., 2009). Numerous techniques have been developed for the preparation of copper nanowires over the years (Jiang et al., 2014; Li et al., 2014; Mayousse et al., 2014; Peng and Chen, 2013; Tan and Balela, 2015; Ye et al., 2014; Yin et al., 2014; Zhao et al., 2012; Monson and Woolley, 2003). But, filling the nanopores of polycarbonate membranes using electrochemical deposition provides an inexpensive, versatile and controllable technique for producing uniform copper nanowires (Chakarvarti, 2009; Duan et al., 2010; Toimil-Molares, 2012). Polycarbonate membrane is particularly used because of its high mechanical strength and easy dissolution after the deposition in order to characterize the wires. Ion beam irradiation may cause unexpected and challenging reliability problems in nanodevices which are designed using these nanowires. Thus, study of the behavior of nanowires under ion beam irradiation is of crucial importance, especially for realizing their applications in higher radiation environment.

Limited efforts have been devoted to study the ion beam irradiation effects in nanowires and hence, the response of ion beam irradiation has not been well understood (Kumari et al., 2014; Xue-Qing et al., 2010; Yang et al., 2013). Kaur and Chauhan (2014) have irradiated Zn nanowires, prepared by template electrodeposition method, with  $\gamma$ -ray irradiations and studied the modifications in their structural and electrical properties. Li et al. (2013) studied the influence of ion irradiation-induced defects on mechanical properties of copper nanowires. The variation in the electronic transport through Cu nanowires induced by swift heavy ions was investigated by Gehlawat and Chauhan (2014). Here, we report the 80 MeV  $\text{Si}^{7+}$  ion beam irradiation-induced effects in the structural, optical and electrical properties of copper nanowires. The wires were prepared by template-assisted electrodeposition technique inside polymer membrane on copper substrate. The present study depicts that ion beam irradiation plays a significant role in tailoring the properties of the nanowires. The possible mechanism of irradiation-induced effects is also discussed.

## 2. Experimental details

### 2.1. Synthesis of copper nanowires

Copper nanowires were prepared using template-directed electrodeposition approach as described in our previous work (Kumar et al., 2014). In brief, commercial polycarbonate membranes manufactured by Whatman were used as the templates to

direct the growth of nanowires. The characteristics of the membrane were 10  $\mu\text{m}$  in thickness, 100 nm in pore diameter with a pore density of  $10^6$  pores  $\text{cm}^{-2}$ . The wires deposition was performed by using a two-electrode electrochemical cell in potentiostatic mode with a conical copper rod as counter electrode, and a conductor covered with a template as an overlay, serving as working electrode. The electrolyte used consists of 0.5 M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution with pH value adjusted to 1.6 using 0.1 M  $\text{H}_2\text{SO}_4$ . Prior to deposition, the membrane was immersed in the solution to ensure the porewetting. The wires were grown at a constant potential of 0.4 V for 12 min at 30  $^\circ\text{C}$ . On the completion of deposition process, the electrolyte was drained from the cell and the sample was removed cautiously. After this, the samples were rinsed several times with deionized water, and then dried in the open air. The as-deposited nanowires embedded inside the membrane were well protected from oxidation. The nanowires could be harvested by dissolving the polymer membrane into dichloromethane ( $\text{CH}_2\text{Cl}_2$ ).

### 2.2. Ion beam irradiation

The nanowires embedded in polymer membranes were irradiated with  $\text{Si}^{7+}$  ion beam of energy 80 MeV using a tandem Pelletron accelerator at Inter University Accelerator Centre (IUAC), New Delhi, India. The samples mounted on a copper ladder were placed vertically at normal incidence of the ion beam. The irradiation was carried out at room temperature in an ultrahigh vacuum chamber. The irradiation fluence was varied from  $1 \times 10^{11}$  to  $1 \times 10^{13}$  ions  $\text{cm}^{-2}$  for this particular study. The ion beam current was maintained at 1 pA (particle nanoampere) to prevent the blazing of membrane due to heating effects. The beam was scanned over the exposed area of sample with an electromagnetic scanner to ensure uniformity of irradiation. The projected range, electronic energy loss ( $S_e$ ) and nuclear energy loss ( $S_n$ ) of the incident ion in the copper as indicated through SRIM simulation were observed to be 10.9  $\mu\text{m}$ , 8.285 MeV/(mg/cm<sup>2</sup>) and  $7.455 \times 10^{-3}$  MeV/(mg/cm<sup>2</sup>), respectively (Ziegler et al., 2010). This ensures that the electronic energy loss is the dominant mode through which the silicon ions lose their energy in fabricated copper nanowires. The projected range of incident ions was much larger than the length of nanowire arrays (10  $\mu\text{m}$ ), neglecting the probability of ion implantation in nanowires.

### 2.3. Characterization

The morphology of as-grown nanowires was studied using JEOL, JSM 7100F FESEM at an accelerating voltage of 5 kV. Structural study was examined by Rigaku C/max 2500 X-ray diffractometer using graphite filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ), operated at 30 kV and current 15 mA, in the  $2\theta$  range of 20–80 $^\circ$  with the scan rate of 0.02  $^\circ/\text{s}$  at room temperature. The optical absorption spectra were recorded using Shimadzu, UV-1650PC double beam UV-visible spectrophotometer in the wavelength range of 300–900 nm. For this, the wires were left embedded in membrane and the back layer was removed. A pristine polycarbonate membrane was used as a reference. The Keithley 2400 series source meter was used for  $I$ - $V$  characteristic measurements. The probe tip which was used to make the precise contact with nanowires embedded in the membrane acts as one electrode, while the copper substrate acts as other during electrical measurements. The  $I$ - $V$  results shown here are corresponding to the integrated effect of parallel nanowires, which may be calculated from the pore density of the membrane.

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