Research Article

γ -Rays Irradiation Induced Structural and Morphological Changes in Copper Nanowires

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This contribution reports on the effect of γ -irradiations on the structural and morphological properties of copper nanowires (Cu-NWs) within the γ doses varying from 6 to 25 kGy. At 9 kGy, the Cu-NWs started welding, forming perfect X-, V-, II-, and Y-shaped molecular junctions. Further increasing the γ dose up to 15 kGy caused the Cu-NWs to fuse and form larger diameter NWs. At the highest dose of 25 kGy, the nanowires converted into a continuous Cu thin film. However, X-ray diffraction (XRD) results showed that the structure of the Cu-NWs remained stable even after converting into a thin film. The formation of the Cuprite (Cu_2O) phases was observed at higher γ dose. The mechanism of forming welded networks of Cu-NWs and Cu thin films is explained via the short and high energy γ -ray wavelengths which act on Cu-Cu molecular covalent bonds isotropically.

1. Introduction

Metal nanowires made of gold, silver, or copper are promising candidates for future nanodevices as interconnecting circuits which provide electrically conducting paths in view of increasing the device density for future integrated chips [1–6]. Moreover, such metal nanowires are also strong candidates for electrically conductive and transparent electrodes for solar cell applications equivalent to doped zinc oxide [7]. Among other metal nanowires family, the Cu-NWs system is a likely contender for the above optoelectronic applications due to its cost-effective and electric performance. While copper ($\rho = 1.59 \text{ n}\Omega \text{ m}$) has an electrical conductivity comparable to that of silver ($\rho = 1.67 \text{ n}\Omega \text{ m}$), it is far cost-effective and more crest-abundant than silver or indium [8, 9]. In addition, Cu has a significant presence in the modern semiconductor electronic circuitry. Recently, within the ongoing

miniaturization, Cu is being considered as an electronic interconnector of choice in the nanoscaled devices [10, 11]. Therefore, Cu-NWs are attracting considerable interest and are expected to be an essential component of nanoelectronic devices and nanocircuitry in the near future. In space technology, where the environment is generally harsh, such Cu nanocircuitry has to exhibit an optimal threshold of radiation damage. Consequentially, total radiation dose hardness tolerance testing of future Cu-NWs based electronic nanodevices, sensors, circuits, and solar cells working in harsh conditions is an emerging field explored by a broader scientific and engineering communities geared towards space applications. Over long periods of operation, the performance of solar cells and particle detectors in satellites deteriorates when they are exposed to energetic radiations. Considerable effort has been made to study radiation hardness of nanodevices and solar cells [12–15]. Recently, it was shown that MeV

carbon ions irradiations on silver NWs (Ag-NWs) induce significant damage on their structure while on the contrary they are stable under MeV proton beams [16, 17]. Cu-NWs are potential future integrated electronic components in nanodevices which require hardness tolerance testing. Therefore, our aim is to systematically study the effects of radiation on the properties of Cu-NWs. There is currently limited information in the broader literature dealing with the radiation effects on Cu-NWs especially γ -radiation [18, 19]. As for the protons from deep space radiations, γ -photons are also abundant in upper space which may cause ionization and radiation damage on embarked Cu-NWs based nanodevices. The study of γ -radiations effects on Cu-NWs is therefore necessary. In this paper, γ -radiations effect on the structure and morphology of Cu-NWs is discussed systematically.

2. Experimental

The Cu-NWs used in this work were purchased from the Guangzhou Jiechuang Trading Co. Ltd., China. Cu-NWs were dispersed in isopropanol with concentration of 20 mg/mL and then spray-coated on glass substrates placed on a hot plate at 170°C for rapid evaporation of isopropanol. Cu-NWs networks were formed on glass substrate and cut into $1 \times 1 \text{ cm}^2$ dimensions to ensure that all samples have the same physical properties. For TEM study, few drops of Cu-NWs solution were dispersed on a copper grid. All samples were then exposed to 5 MeV γ -photons at various doses of 6, 9, 12, 15, and 25 kGy using a Co^{60} source at room temperature and under atmospheric pressure. The dose rate of the γ -source was 38 Gy/min. The time of exposure for different doses was calculated from the activity of the source, as given in Table 1.

The samples were characterized using multiple techniques such as high resolution scanning electron microscopy (HRSEM), EDX, high resolution transmission electron microscopy (HRTEM), and X-ray diffraction (XRD) techniques. The structural study of unirradiated and γ -irradiated samples with varying irradiation doses, that is, 6–25 kGy, was investigated by both qualitative and quantitative Rietveld refinement of the high resolution X-ray powder diffraction (XRD) data. The XRD data was collected in the 2θ angular range from 29° to 80° with an integration time of 2 s per 0.02 steps, employing a Bruker X-ray diffractometer with $\text{Cu}_{K\alpha}$ radiation (1.5409 Å). TOPAS program (version 4.1) is utilized for structural refinements using Rietveld refinement technique [19].

3. Results and Discussion

Structural study of unirradiated and γ -irradiated Cu-NWs was characterized by XRD technique. Figure 1 shows the XRD pattern of samples exposed at different doses. Figure 1(a) shows the XRD pattern of unirradiated Cu-NWs. The XRD pattern comprising one (111) peak at $2\theta = 44.2^\circ$ which is preferred crystal plan of Cu-NWs. Other two low intensities peaks at $2\theta = 52.4^\circ$ and 73.9° are corresponding to the crystal planes (200) and (220), respectively. These peaks and intensities show that Cu-NWs had a polycrystalline structure.

TABLE 1: Exposure time for different doses.

Dose (kGy)	Time of exposure
6	2 h 37 min 8 s
9	3 h 57 min 0 s
12	5 h 15 min 6 s
15	6 h 34 min 8 s
18	7 h 53 min 7 s
21	9 h 12 min 6 s
25	10 h 58 min 2 s

XRD results are confirmed with the HRTEM images shown in Figure 2(a).

X-ray powder diffraction patterns of unirradiated and γ -irradiated Cu-NWs samples were fitted using Rietveld refinements and the difference curves. There was no significant variation in lattice constant “ a ” and unit cell volume “ V ” for both unirradiated and γ -irradiated samples. The lattice parameter “ a ” of the Cu-NWs was found to be 3.610 Å for all the four samples as shown in Figure 2(b). The Rietveld refinement of unirradiated and irradiated Cu-NWs at a dose of 9 kGy shows that for the entire powder diffraction pattern no impurities were observed (Figure 1(b)). However, at higher irradiation doses (12 kGy and 15 kGy), surface microstructure evolutions start taking place and it turns out that, apart from standard Cu-NWs diffraction peaks, additional reflections started appearing, which can be indexed in terms of a mixture of metallic copper and cubic Cu_2O [20].

The weight percentages of both the phases are retrieved from program Topas 4.1 using quantitative multicomponent Rietveld analyses [21]. The Rietveld refinement results showed that a small fraction (15%) of impurity Cuprite phase (Cu_2O) (space group $Pn-3mS$, $a = 0.4265 \text{ nm}$) is also present in the XRD patterns of samples in Figures 1(c) and 1(d), apart from major (85%) face centered cubic (fcc) Cu (space group $Fm-3m$, $a = 0.3615 \text{ nm}$) phase. Moreover, as the dose increases, there is a slight increase in the intensity of (111) peak of fcc Cu lattice along with decrease in full width half maximum (FWHM) beckoning the increase in crystallinity of the sample. Recently, irradiation effects were studied on InGaN epilayer thin film and observed improvement of crystal quality [22].

In addition, the XRD patterns of unirradiated and γ -irradiated Cu-NWs samples were refined in the space group $Fm-3m$ with Cu at 4a 0, 0, 0, whereas the impurity phase Cu_2O was refined in space group $Pn-3mS$ with Cu residing at 4b 1/4, 1/4, 1/4 site and oxygen occupying the 2a 0, 0, 0 site. During the refinement, all atomic positions were fully occupied, and isotropic thermal vibration parameters and occupancies were found to be highly correlated. The weighted profile R factor (R_{wp} and R_{exp}) values show a good agreement between the experimental model and respective X-ray diffraction data. The R_{wp} values of Figures 1(a) to 1(d) are 5.84, 10.60, 3.61, and 2.79, respectively, while the R_{exp} values of Figures 1(a) to 1(d) show similar behavior and are 3.76, 4.44, 2.80, and 13 2.44, respectively.

FIGURE 1: XRD spectra of Cu-NWs (a) unirradiated, (b) irradiated at 9 kGy, (c) irradiated at 12 kGy, and (d) irradiated at 15 kGy.

The morphological changes of the Cu-NWs were studied after γ -irradiation. Figure 3(a) shows typical HRSEM images of unirradiated Cu-NWs. The diameters of unirradiated Cu-NWs range from 100 to 150 nm. Moreover, it can be observed from Figure 3(a) that the Cu-NWs are covered with an amorphous Cu structure on the outer sides. Figure 3(b) is the corresponding EDX of unirradiated Cu-NWs. The Cu-NWs were first irradiated with γ -irradiation to a dose of 6 kGy. It can be observed that coalescence of these NWs, called necking, commenced as shown in Figure 3(c). Further increase in γ dose up to 9 kGy resulted in nanowelding between two Cu-NWs and X-, Y-, II-, and V-shaped junctions between the Cu-NWs were formed by γ -irradiation induced coalescence (Figure 4) because as their molecular bonding

is broken, the spacing between atoms decreases; hence, their surface area increases. Schematic mechanism of the coalescence process is presented in Figure 5 where the process is started from necking to joining of Cu-NWs when subjected to medium γ -fluence and finally to complete coalescence of two NWs at high γ -fluence, forming single NWs with double diameter. Recently, coalescence of silver nanowires by carbon ion beam irradiation has been reported and formed X-, Y-, and II-shaped molecular junctions [16]. Formation of X-, Y-, V-, and II-shaped junctions is also confirmed from HRTEM images in Figure 6 (indicated by arrows). Welding of Cu-NWs became visible due to the strong and high energy short γ -rays induced, showing clearly the formation of junctions, which ultimately resulted in welded Cu-NW networks. However,

FIGURE 2: (a) HRTEM image of Cu-NWs. (b) Crystal structure with unit cell (orange sticks) of $3 \times 3 \times 3$ supercell of face centered cubic lattice of copper nanowire (space group $Fm-3m$, $a = 0.3615$ nm) viewed along the $[111]$ direction.

FIGURE 3: SEM images of Cu-NWs (a) unirradiated and (b) corresponding EDX spectra (c) irradiated at 6 kGy ions/cm².

the morphology and structure of the nanowires remained unchanged. It is clear from Figures 4 and 6 that, after γ -irradiation, different types of junctions are formed between Cu-NWs whenever these NWs overlap.

Further increase in γ -irradiation dose up to 12 kGy resulted in coalescence at junction positions and perfect

nanowelding of Cu-NWs is obtained and shown in Figure 7. HRTEM images are consistent with XRD results (Figure 8). Moreover, perfect nanowelding of crystalline structure was achieved by γ -rays induced, as shown in Figure 8. γ -irradiation induced nanowelding of Cu-NWs is a new approach to integrate any nanodevices or forming welded

FIGURE 4: SEM image of Cu-NWs irradiated at a dose of 9 kGy: X-, Y-, V-, and II-shaped junctions are observed.

FIGURE 5: Gamma irradiation induced coalescence process.

networks for solar cells. The welding of Ag-NWs has matured for fabrication of transparent electrodes for solar cells [16] while work on welded networks of Cu-NWs as a transparent electrode still needs to be explored. Our new approach to get welded conducting networks of Cu-NWs will be useful for solar cell designers and integration of nanodevices.

To study the radiation hardness of Cu-NWs under γ -rays with high dose, results are mentioned in Figures 9 and 10. At an irradiation dose of 15 kGy, the Cu-NWs start to

change their morphology and convert into a thin Cu film (Figure 9(a)). Figure 9(b) corresponds to HRTEM image which shows Cu-NWs coming closer to each other and converting into bulk material. Figure 10(a) clearly shows that molecular bond breakage of Cu-NWs results in intact bulk material. The corresponding TEM image is consistent with SEM as shown in Figure 10(b). Further increase of dose to 25 kGy converts the whole nanostructure to Cu thin film as shown in Figure 10(c). It can be concluded that Cu-NWs

FIGURE 6: ((a)–(c)) TEM images of Cu-NWs irradiated at a dose of 9 kGy: X-, Y-, V-, and II-shaped junctions are observed.

FIGURE 7: SEM image of Cu-NWs (a) irradiated at 12 kGy and (b) irradiated at 15 kGy.

based nanodevices or solar cells may not be suitable materials for use in harsh environment.

A detailed discussion of the observed nanowelding and conversion of Cu-NWs into Cu thin film appears hereunder. At a dose of 9 kGy, welding of Cu-NWs became visible due to the breakage Cu-Cu bonds by the γ -rays which are isotropically distributed, showing clearly the formation of junctions, which ultimately resulted in welded Cu-NW networks. However, the morphology and structure of the nanowires remained unchanged. Nanowelding process is discussed in schematic diagram as shown in Figure 5. The figure shows that, at low γ -fluence, necking between nanowires is started.

At medium γ -fluence, coalescence starts and at higher fluence Cu-NWs fused on each other. Finally, Cu-NWs form four types of molecular junctions (i.e., X-, Y-, T-, and II-shaped junctions). The breakage of Cu-NWs was conducted using the γ -irradiation which acted only on the covalent bonds leaving the structure intact as evidenced by the XRD. γ -Irradiation in MeV energy range interacted with target material and suffers significant electronic energy loss along its paths in the target material and this attracted addition of oxygen functional groups from the atmosphere resulting in the formation of Cu_2O material as evidenced by XRD (Figures 1(c) and 1(d)). Moreover, this γ -irradiation induced phase changes which

FIGURE 8: ((a) and (b)) SEM images of Cu-NWs irradiated at a dose of 15 kGy.

FIGURE 9: (a) SEM image of Cu-NWs irradiated at a dose of 18 kGy. (b) Corresponding TEM image.

FIGURE 10: SEM image of Cu-NWs (a) irradiated at 21 kGy. (b) Corresponding TEM image (c) irradiated at 25 kGy.

at room temperature do not disorientate the coordination of the Cu atoms due to breakage of bonds resulting in atomic closeness and mass movement at contact positions of Cu-NWs to reach their equilibrium stability and changing of position but maintaining the initial orientation of the Cu atomic structure resulting in a sheet-like surface area. Atoms are never displaced by γ -irradiation induced effect since γ -rays only act on bonds. As a preclusion, this study will be followed by the investigation of the effect of other radiations on similar samples using a similar approach as in other systems that we studied [23].

4. Conclusion

In conclusion, we have demonstrated a nanowelding technique in which large scale molecular junctions of Cu-NWs were formed by γ -irradiation. These nanowires were welded on each other due to isotropic γ -ray irradiated metal Cu-NWs. This technique is very useful for fabrication of large scale junction-like structures comprising welded Cu nanowires with FCC cubic phase with uniform diameters. It is believed that the synthesis of connections between metallic nanowires is very important in nanoelectronics and circuit industry. It can be concluded that Cu nanowires may not be suitable materials for use in harsh environment like nanodevices or solar cells for upper space applications because Cu-NWs in their pure form cannot maintain their nanoidentity under harsh environments.

Disclosure

Plagiarism test has been carried out via ID 555843245 (similarity index 09%) in Turnitin software.

Competing Interests

The authors declare that they have no competing interests.

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