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Carbon Ion-beam-induced Modification in Structural and Electrical Properties of ZnO Nanowires

(Alur-ion Karbon Teraruh terhadap Modifikasi Struktur dan Sifat Elektrik Nano Wayar ZnO)

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ABSTRACT

Zinc oxide nanowires (ZnO NWs) have an efficacious place in nanoworld due to their tremendous properties and applications. In the present work, structural and electrical properties of ZnO NWs have been modified by carbon (C) ions- beam irradiation. With ion-beam energy of 0.8MeV, the physical behaviors of NWs have been studied under different doses from 1×10^{12} to 1×10^{14} ions/cm^2. The microstructural and Raman spectroscopy studies showed that the wurtzite crystal structure of the ZnO NWs has been changed into disordered amorphous one under high C ion doses. Whereas, the XRD results showed that Zn nanoparticles are fabricated at high C ion-beam irradiation on ZnO NWs. Scanning electron microscopy (SEM) depicts the formation of cross junctions and parallel junctions between ZnO NWs after C ion irradiation. DC conductivity measurements have confirmed that the conductivity of NWs decreases with increase in C ion doses. It is concluded that the lattice defects significantly contribute to decrease in the conductivity of ZnO NWs.

Keywords: Electrical conductivity; ion-beam irradiation; lattice defects; ZnO nanowires

ABSTRAK

Nano wayar zink oksida (Zn NWs) telah mendapat perhatian di dalam dunia nano kerana sifat dan kegunaannya yang pelbagai. Dalam kajian yang dilakukan, struktur dan sifat elektrik Zn NWs dimodifikasi dengan radiasi alur-ion karbon. Kelakuan fizikal NMs telah dikaji dengan menggunakan tenaga alur-ion sebanyak 0.8 MeV, pada julat 1×10^{12} sehingga 1×10^{14} ion/cm^2. Kajian mikrostruktur dan spektrum Raman pada dos C yang tinggi menunjukkan struktur hablur wurtzit ZnO telah bertukar kepada amorfus yang tidak tersusun. Manakala keputusan XRD menunjukkan nanozarah Zn, terbentuk di atas Zn NWs apabila dikenakan pancaran alur-ion C yang tinggi. Mikroskop elektron imbasan (SEM) menunjukkan kehadiran simpang silang dan simpang selari antara Zn NWs selepas radiasi ion C. Pengujian kekonduksian DC mengesahkan kekonduksian NMs berkurangan dengan peningkatan dos ion C. Sebagai kesimpulan, kecacatan kekisi yang ketara telah menyebabkan penurunan kekonduksian ZnO NWs.

Kata kunci: Kecacatan kekisi; kekonduksian elektrik; nano wayar Zn; radiasi alur-ion

INTRODUCTION

One-dimensional nanomaterials have attracted much attention recently due to their potential as building blocks for nanostructures devices (Yang et al. 2002). One-dimensional nanomaterials are essential both as interconnects and function units in the fabrication of electrochemical, electronic, optoelectronic and electromechanical nanodevices (Zhang et al. 2012). Among one-dimensional nanomaterials, ZnO nanowires are of utmost importance in today's nanotechnology research (Wang 2009). ZnO is a semiconductor with 60 meV high exciton binding energy, good chemical and thermal stability and large wide band gap energy (E_g = 3.37 eV) (Wang 2009). Due to these tremendous properties ZnO nanowires are applicable as building blocks for complex nano- and microdevices. ZnO nanowires are also applicable in many other areas of science and technology like field-effect transistors, solar cells, lasers, biological and chemical sensors, photodiodes and optoelectronics (Ozgur et al. 2005; Von et al. 2006; Xiang et al. 2007; Zhang et al. 2001).

In order to make a suitable applications of ZnO nanowires into the nanodevices, the modification of ZnO nanowires properties are important. Different techniques have been used to modify and manipulate the behavior and properties of ZnO using chemical routes, such as chemical doping (Shan et al. 2003; Zhu et al. 2007), alloying (Pan et al. 2007), compositing with other materials (Dutta & Busak 2009), plasma treatment and surface modification (Choi et al. 2008; Wu et al. 2007). On the other hand, ion-beam-induced modification study of ZnO NWs is limited. Only few reports are available (Ishaq et al. 2010, 2012; Merkle et al. 1981; Ni et al. 2007).

Ion-beam-induced engineering of nanomaterials is recently a hot issue to make functional devices through this technique. Moreover, ZnO NWs have tremendous applications in nanodevices, therefore ion-beam-induced modification in its properties may get some breakthrough for advance nanodevices. Few and limited attempts have been made to modify the characteristics of ZnO NWs through ion-beam technology (Ishaq et al. 2010, 2012, 2013; Merkle et al. 1981; Ni et al. 2007). These studies reveal that electron and ion-beam irradiations are powerful tool towards the successful tailoring of functionalized nanomaterials (Dee et al. 2008; Ishaq et al. 2012, 2013). In-addition, few analysis techniques were used to study ion-beam irradiation effects on ZnO NWs (Dee et al. 2008; Ishaq et al. 2012, 2013). A number of analysis techniques are highly desired to explore the effects of ion-beam irradiation on ZnO NWs.

In the present work, ZnO Nanowires (ZnO NWs) have been irradiated with high energy (0.8MeV) carbon ions. The effects of irradiation on the electrical and structural properties of ZnO NWs were observed. Use of these NWs as a basic building block in many applications is expected to bring revenue in carbon ion-beam-mediated engineering.

METHODS

The synthesis of ZnO NWs was carried out using the vapor-transport-deposition technique in a mini-furnace on silicon substrate through the vapor solid process as discussed elsewhere (Zhu et al. 2007). The as-prepared ZnO NWs having diameters in 80-200 nm range were mixed in ethanol. The homogeneous solution was achieved after continuous stirring for 40 min. This homogenous solution of ZnO NWs had to be dripped on a glass substrate to form films of ZnO NWs with homogenous thicknesses and whose diameters were about 1 cm. These prepared films were then irradiated with carbon ions of energy 0.8 MeV at room temperature and at different doses from 1×10^{12} to 1×10^{14} ions/cm^2 using a 5UDH-Pelletron accelerator. Four samples were prepared with tag numbers ZnO, C1ZnO, C2ZnO and C3ZnO, with ZnO un-irradiated and the rest carbon-irradiated with ion doses of 1×10^{12} ions/cm^2, 1×10^{13} ions/cm^2 and 1×10^{14} ions/cm^2, respectively. There was 10^{-4} Pa pressure in the target chamber during the irradiation process. The XRD, SEM, HRTEM, conductivity measurement and Raman spectroscopy techniques were used to study the comparison of ion-beam-irradiated and un-irradiated ZnO NWs.

RESULTS AND DISCUSSION

Ion-beam techniques can be used for the amorphization of NWs (Dee et al. 2008; Ishaq et al. 2013). Figure 1(a) depicts the HRTEM image of un-irradiated ZnO NWs which are highly crystalline with a typical growth direction along (0001). After irradiating with C ions at a dose of 1×10^{13} ions/cm^2, the nanosized defects are induced on the crystal lattice as marked by circles in Figure 1(b). By increasing the dose, the nano-defects has started to agglomerate. It has been found that the wurtzite hexagonal structure is transformed into disorder structure as observed in Figure 1(c). Amorphous structures of ZnO NWS have already been observed with H, N, P and Ar ion irradiations on ZnO NWs (Dee et al. 2008; Ishaq et al. 2013).

XRD patterns have been recorded in order to identify the crystalline phases and determine the crystallite size using Cu K_α (λ = 1.5418Å). All the diffraction peaks can be indexed to the standard ZnO diffraction pattern. The peak positions at 32, 34.8, 36.6, 47.6 and 56.8° are corresponded to the (100), (002), (101), (102) and (110) reflections of hexagonal wurtzite ZnO, respectively, as

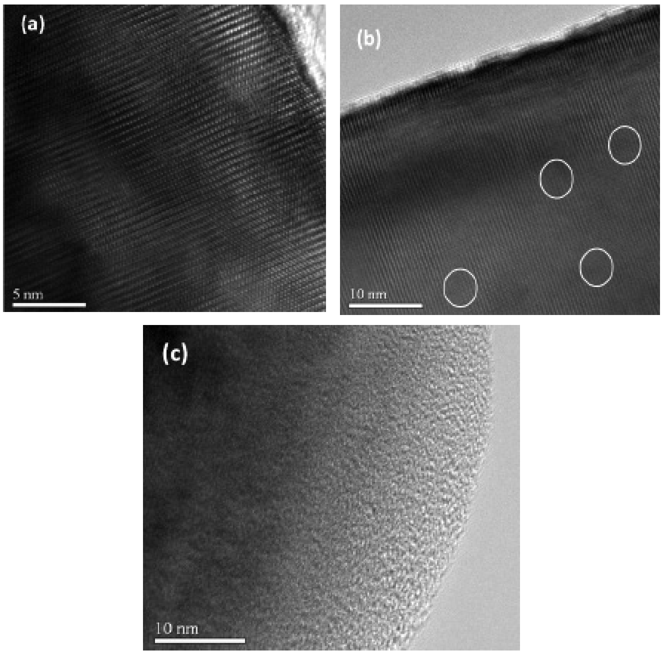

FIGURE 1. HRTEM images of the a) un-irradiated ZnO NWs b) C irradiated at the dose of 1×10^{13} ions/cm^2 and c) C irradiated at the dose of 1×10^{15} ions/cm^2

shown in Figure 2 (green color). There is no extra peak in case of as grown ZnO NWs, indicating purity of the sample. However, when these NWs are irradiated with carbon ions of dose 1×10^{12}ions/cm^2, an extra peaks appears at 38.6° which could be assigned to (102) reflection of Zinc element. When the ion-beam dose increases, the extra peak became more and more prominent as depicted in Figure 2. It has been found that by use of ion-beam technology, the Zn nanocrystallites can be made-up from ZnO NWs as seen in Figure 2. The formation of these crystallites may be due to the evaporation or sputtering of oxygen through ion-beam irradiation. Such kind of observation is one initial report for C ion-beam irradiated experiments on ZnO NWs.

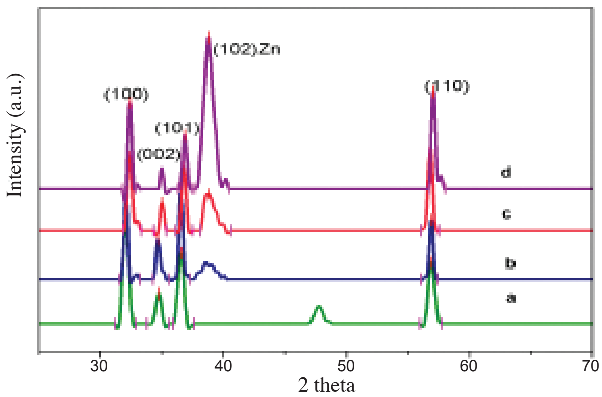

FIGURE 2. XRD patterns of carbon ion irradiated ZnO nanowires a) Un-irradiated ZnO nanowires, b) 1×10^{12}ions cm^{-2}, c) 1×10^{13} ions cm^{-2} and d) 1×10^{14} ions cm^{-2}

The decreasing trend in crystallite size with the enhancement in irradiation dose is observed and it may be due to difference in the atomic radii of C^+, Zn^+ and O^+ as shown in Figure 3. The average crystallite size is 128 nm which decreases with the increase in carbon ion implantation dose and becomes 65 nm at the dose of 1×10^{14} ions/cm^2. Furthermore, the lattice parameters of un-irradiated ZnO NWs (a = 3.2 Å and c = 5.2 Å) and carbon ion irradiated ZnO NWs (a=2.72 Å and c=1.82 Å) have been calculated from XRD pattern. The decrease in the crystallite size and lattice parameter show the substitution of smaller ionic radii C ions to larger ionic radii Zn^+ and O^- ions in ZnO NWs lattice.

Raman spectroscopy is an extensively used for the study of defects, phonon shifts, phase transitions of one and zero dimensional ZnO materials such as nanowires, nanorods and quantum dots and as reported by several researchers (Alim et al. 2005; Javed et al. 2009; Lin et al. 2006; Sahoo et al. 2009). To study the defects created by C ions in ZnO NWs, Raman spectroscopy has been used. Figure 4 shows the Raman spectra of C^+ ion-irradiated ZnO NWs. The 330 cm^{-1} vibration mode has been observed which is known as fingerprint of ZnO wurtzite structure. This mode is raised from the zone boundary phonons E_2 (H) - E_1 (L). A wide band is formed at 619 cm^{-1} (combination of

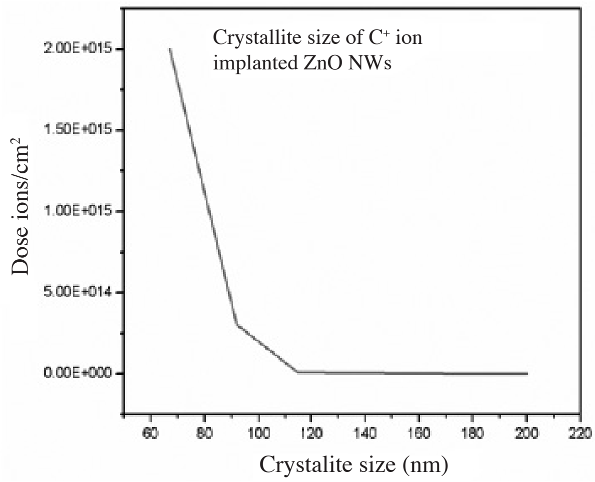

FIGURE 3. Crystallite sizes of C^+ ion implanted ZnO NWs

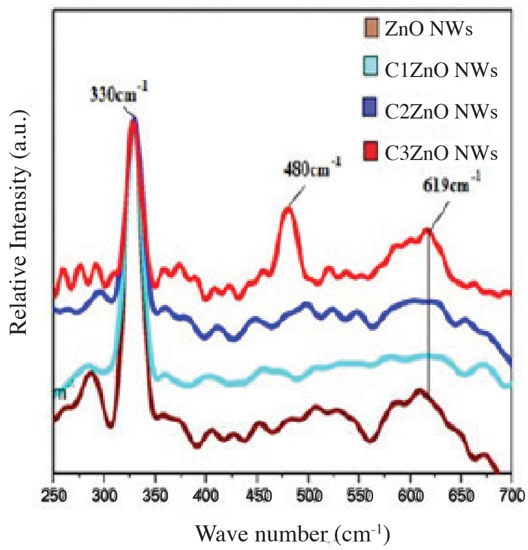

FIGURE 4. Raman spectra of C ion irradiated ZnO NWs

580 and 640 cm^{-1}) in carbon ion irradiated ZnO NWs and is attributed to Zn-C mode (Lin et al. 2006). The peak at 580 cm^{-1} has been assigned to E_1 (L) mode. This vibrational mode is due to the formation of oxygen vacancies in carbon ion irradiated ZnO NWs (Sahoo et al. 2009). The centered peak at 619 cm^{-1} has been assigned to E_1 (LO) mode which is related to defects such as vacancies. There is an appearance of additional peak centered at 480 cm^{-1} for the dose of 1×10^{14} ions/cm^2. This is basically a local vibrational mode corresponding to E_2 (High) and raised due to the introduction of carbon ions at Zn and O sites of ZnO lattice.

The electrical conductivity of C ion-beam irradiated ZnO NWs has been studied at room temperature. The behavior of electrical conductivity of ZnO NWs as a function of C ion irradiation dose is shown in Figure 5. It is observed that the electrical conductivity decreases with the increase in irradiation dose of C ions on ZnO NWs. This modification in conductivity of ZnO NWs by C ions

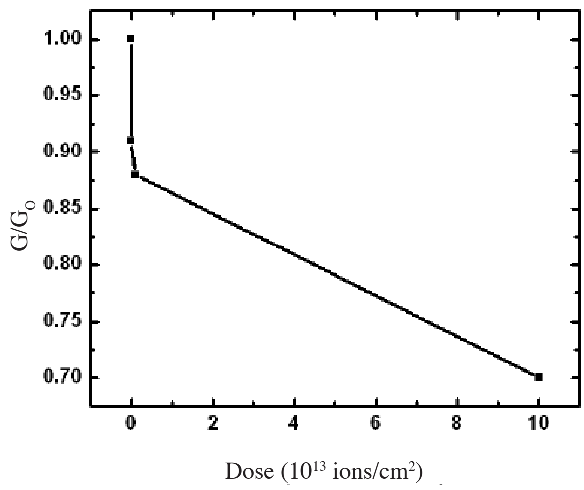

FIGURE 5. Electrical conductivity as a function of irradiation dose. G_o is reference conductivity of un-irradiated ZnO NWs

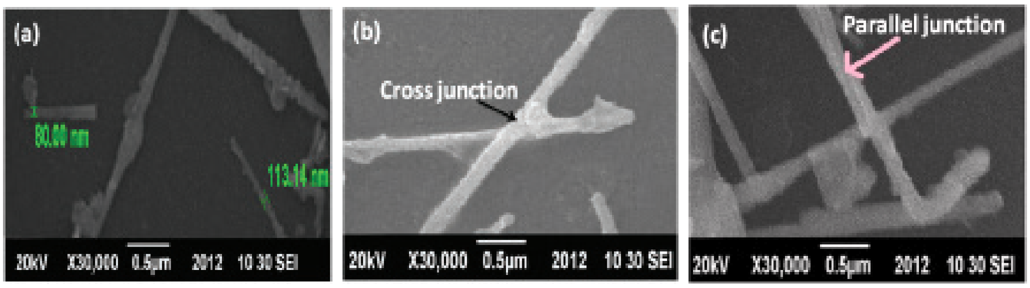

FIGURE 6. a) Un-irradiated ZnO nanowires, b) cross junction and c) parallel junction of carbon ion irradiated ZnO NWs

irradiation may be due to the creation of ion-beam-induced defects in ZnO NWs. The complimentary above techniques such as HRTEM and Raman have already confirmed that the structure of ZnO NWs become disordered by C ions irradiation which may cause a decrease in the conductivity.

The welding of NWs improves the quality of ICs for the miniaturization of electronics devices (Dee et al. 2011). The ion-beam engineering technique has been used for the welding of the ZnO NWs. SEM has been used to examine the morphologies of the as-grown and carbon ion irradiated ZnO NWs. Figure 6(a) shows the SEM image of as grown ZnO NWs having diameters in the range of 80 to 200 nm. The C ion irradiation of as-grown ZnO NWs for a dose of 1×10^{14} ions/cm^2 resulted in the formation of two types of junctions in the joints of the nanowires, i.e. cross junctions and parallel junctions as shown in Figures 6(b) and 6(c), respectively.

Conclusion

Structural and electrical properties of C ion-beam irradiated ZnO nanowires (NWs) at different doses have been discussed. The C ions implantations have significantly changed the wurtzite crystalline structure of NWs and transformed it into a disordered amorphous structure. The increase in ion dose has leaded to enhance the parallel and cross junctions of the NWs. The ion dose rate created numbers of defects in NWs are found to be responsible for the tuning of ZnO NWs conductivity. Furthermore, the Zn nanoparticles have been produced through carbon ion-beam irradiation, which may have potential for the future Zn nanoparticles embedded ZnO NWs system.

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