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Fabrication and optical properties of silicon nanowire/Cu_2O nano-heterojunctions by electroless deposition technique

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ABSTRACT

Si NWs/Cu_2O nano-heterojunctions were prepared by adopting electroless deposition technique to deposit Cu_2O nanocrystallines on the surface of silicon nanowire arrays (Si NWs). Raman spectra of the composite structures demonstrate that the infrared (IR) active mode originated from the defects in the crystal lattice and is activated in Cu_2O nanocrystallines. Photoluminescence (PL) spectra of the nano-heterojunctions suggest that the as-prepared Si NWs/Cu_2O composite structures present a new luminescence wavelength after the formation of nano-heterojunctions. In addition, the PL peak of Si NWs in the composite structure exhibits a little red-shift and becomes broad in comparison with that of the pure Si NWs. The radial Si NWs/Cu_2O nano-heterojunction structure would have promising applications in many fields such as heterojuncion solar cell, photocatalysis, and water splitting hydrogen generation.

1. Introduction

Cuprous oxide has been regarded as one of the most promising materials for optoelectronic applications. Nanostructured Cu_2O with at least one spatial dimension less than 100 nm is more prefered for the quantum size effect. Many methods have been developed to fabricate various morphology of Cu_2O [1–3]. As an important liquid phase synthesis method, electroless deposition technique has been employed extensively in the fabrication of nanostructured metal and semiconductor material because of the simplicity of operation, cost effectiveness, high throughput, and lack of elaborate equipment [4–6].

Semiconductor heterojunction structures play an increasingly important role in modern material and device physics since they often present novel properties that originate from the synergies between the components [7–10]. However, few researches have been carried out on Cu_2O-based heterojunction nanostructure for the limitation of preparation method. In this letter, we employed electroless deposition technique to synthesize Cu_2O nanocrystallines on Si NWs in alkaline electrolyte to form radial nano-heterojunctions. In addition, the Raman and photoluminescence properties of the as-prepared nano-heterojunctions were studied further.

2. Experimental details

Highly ordered Si NWs were prepared on single crystalline n-type Si (100) wafer (10–20 Ω cm resistivity) by wet-chemical etching method at room temperature [11,12]. The etching time was 45 min.

The Si NWs/Cu_2O radial nano-heterojunctions were constructed by depositing Cu_2O nanocrystallines on Si NWs via electroless deposition in alkaline electrolyte. 50 ml 0.2 M $KNaC_4H_4O_6 \cdot 4H_2O$ was added to 100 ml 0.15 M $CuSO_4 \cdot 5H_2O$ solution under constant stirring. After ten minutes, 5 ml 1 M HCHO solution was added drop by drop to the mixed solution. Then, 2 M NaOH solution was added slowly to regulate the pH value between 12.5 and 14. After that, the mixed solution was put into a constant temperature bath to heat to 45 °C, then, the as-prepared Si NWs was dipped into it for different time durations; the nano-heterojunctions were finally obtained after washing them with deionized water.

The morphology of Si NWs and the as-prepared Si NWs/Cu_2O nano-heterojunction samples were observed using a Field Emission Scanning Electron Microscopy (FE-SEM, Philips Sirion 200, Philips, Netherlands). The structure and crystal orientation of Cu_2O nanocrystallines on Si NWs were analyzed with X-ray diffraction (XRD, D8 DISCOVER X-ray diffractometer, Bruker, Germany) with Cu Kα radiation ($\lambda = 1.5406$ Å). Raman and PL spectra of Si NWs and the as-prepared Si NWs/Cu_2O composite structures were obtained using the Jobin Yvon LabRam HR 800 UV system at room temperature. A laser wavelength of 514.5 nm was used as the excitation source.

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3. Results and discussion

The growth mechanism of Cu_2O nanocrystallines self-assembled on Si NWs via electroless deposition technique can be explained as follows [6]. Formaldehyde is used as the reducing agent. When the pH value of the solution increases to about 12.5, the concentration of OH^- increases and the following chemical reaction occurs.

$$2Cu^{2+}+H_2O+2OH^- \rightarrow Cu_2O+2H_2O$$

Fig. 1 shows SEM images of Si NWs (Fig. 1(a)) and Si NWs/Cu_2O nano-heterojunctions with different deposition time of Cu_2O and pH value. Because of the presence of sodium potassium tartrate tetrahydrate as a protecting agent, Cu^{2+} in alkaline solution are reduced to Cu^+, and the Cu_2O nanoparticles nucleated uniformly on the surface of Si NWs initially. As the time went on, these crystal nucleuses grew big gradually. When the deposition time increased to about 8 min, Cu_2O nanocrystallines presented inerratic cube morphology (Fig. 1(b)–(d), pH=12.5). In addition, the morphology of Cu_2O nanocrystallines was closely related with the pH value of the growth solution. It transferred from cube (Fig. 1(e)) to polyhedron (inset of Fig. 1(f)) when the pH value was changed from 12.5 to 13.5 (the deposition time are all 10 min). This probably can be attributed to the faster growth rate originated from the increase of OH^- intensity.

XRD patterns of Si NWs/Cu_2O nano-heterojunctions are given in Fig. 2(a). Several diffraction peaks in the 2θ range of 25–80° observed in the Si NWs/Cu_2O nano-heterojunction can be assigned respectively to the (110), (111), (200), (220), (311) and (222) planes

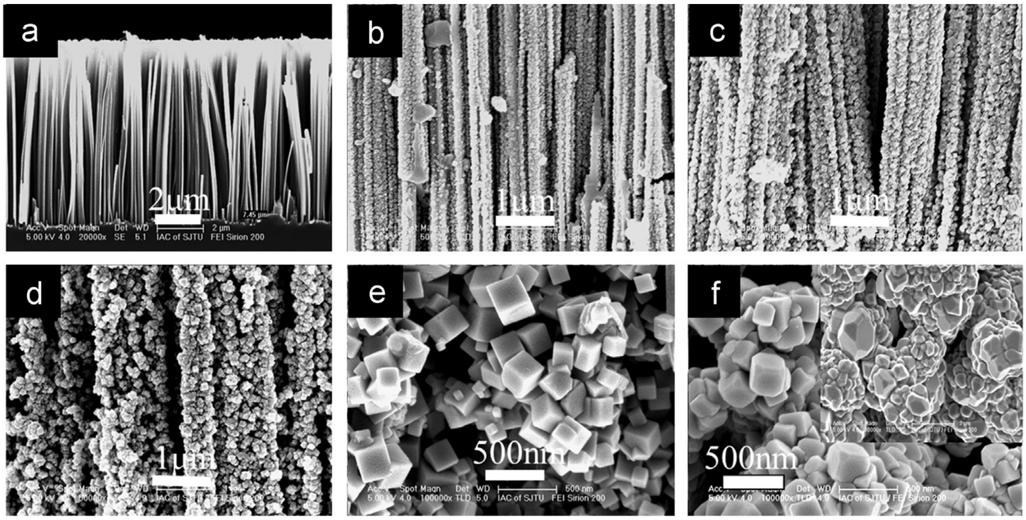

Fig. 1. SEM images of Si NWs (a), Si NWs/Cu_2O nano-heterojunction with different deposition time: 2 min (b), 5 min (c), 10 min (d) and morphology with 10 min deposition time at different pH value: pH=12.5 (e) and pH=13 (f).

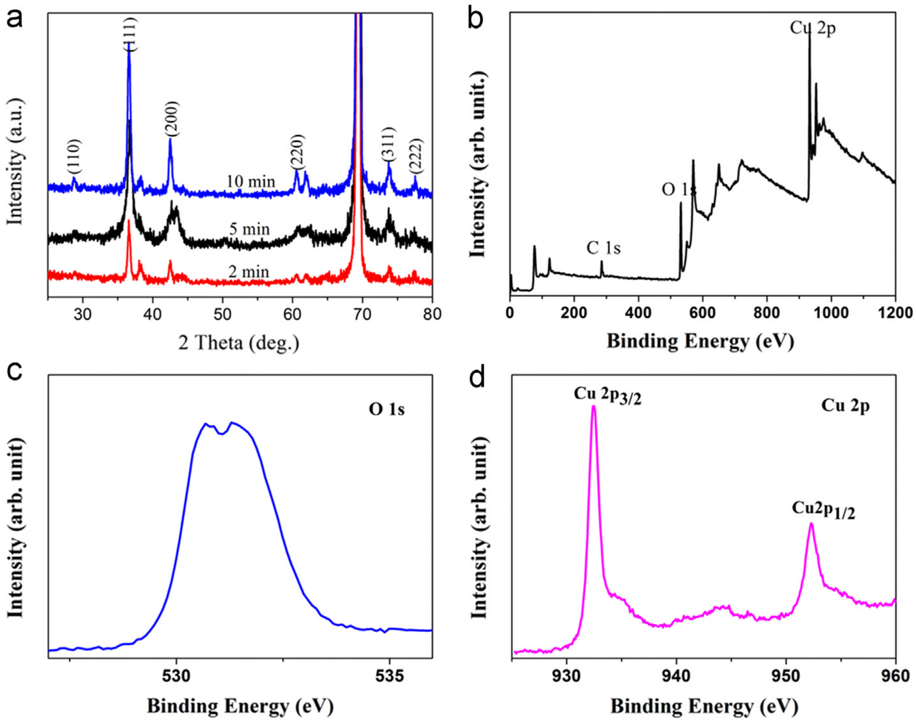

Fig. 2. XRD patterns ((a)) and typical XPS spectrum ((b)–(d)) of Si NWs/Cu_2O nano-heterojunction.

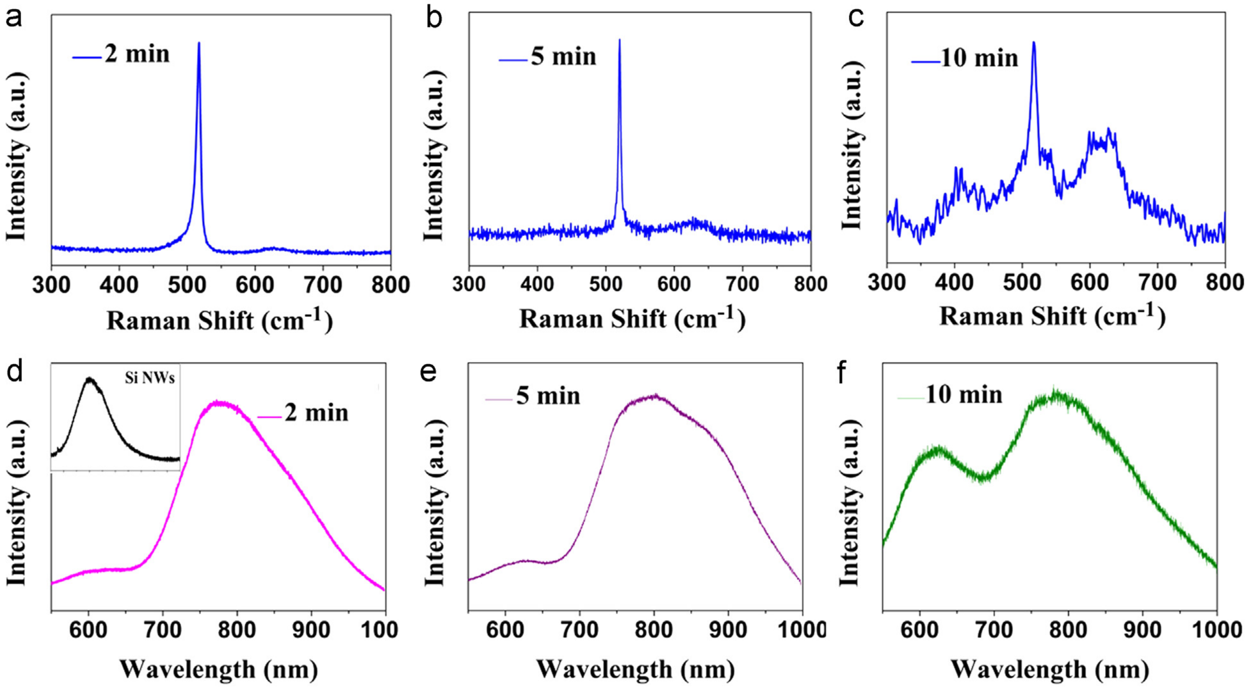

Fig. 3. Raman and PL spectra of Si NWs/Cu_2O nano-heterojunction with different deposition time of Cu_2O.

of Cu_2O structure according to their positions and the relative intensity (JCPDS card no. 5-667). According to the diffraction intensity in the corresponding XRD pattern, Cu_2O nanocrystalline mainly grow along (111) orientation, which indicates that there is a relatively slow growth rate along the (111) facet. In addition, the obtained Cu_2O nanocrystallines with (111) facet would have good photocatalytic activity [13]. Typical XPS spectrum of the Si NWs/Cu_2O sample is shown in Fig. 2(b)–(d). The XPS peaks of the Cu (2p) at 952.5 eV and 932.6 eV [14] for Si NWs/Cu_2O demonstrate the existence of Cu^+ (Fig. 2(d)). Furthermore, the characteristic peak for Cu^{2+} at 942 eV was not observed. This result confirms that the sample contains Cu^+ rather than Cu^{2+}.

Raman scattering at an excitation wavelength of 514.5 nm are shown in Fig. 3(a)–(c). The most prominent Raman peak at about 520.3 cm^{-1} in each picture corresponds to the Si NWs. Another remarkable Raman peak at about 614.9 cm^{-1} whose intensity increases gradually with the increase of deposition time of Cu_2O nanocrystallines can be identified to the $\Gamma_{15}^{-(2)}$(TO) mode of Cu_2O [15]. This mode is called infrared (IR) active mode, it results from the breakdown of the symmetry of the crystal lattice because of the presence of defects in Cu_2O nanocrystalline. These imported defects in crystal lattice of nanocrystalline, including the oxygen and copper site defects, may activate the silent mode. The Raman peak at about 412 cm^{-1} in Fig. 3(c) can be assigned to $\Gamma_{12}^{-}+\Gamma_{15}^{-(1)}$(TO) [15].

Fig. 3(d)–(f) represents the PL spectra of Si NWs and Si NWs/Cu_2O composite structure. For the pure Si NWs, there is only a single narrow PL peak at about 700 nm (inset of Fig. 3(d)). In the Si NWs/Cu_2O composite structure, the PL peak of the Si NWs exhibits a little red-shift and becomes broad compared with that of the pure Si NWs. The former phenomenon could be ascribed to the interface states of the excitons formed between Si and the oxide layer, while the latter could be attributed to the disorder potential at the interface and the extrinsic self-trapping of excitons with lattice distortion [16]. There exists another PL peak at about 615 nm in the Si NWs/Cu_2O nano-heterojunctions, the relative intensity increases gradually with the increase of the deposition time of Cu_2O. However, for Cu_2O, the direct band gap recombination transitions from 600 to 630 nm can only be observed in high-quality material or at very low temperatures (~2 K) [17]. With respect to the hetero-junction structure of Si NWs/Cu_2O, there is an energy band bending at the interface, which induces a new position of the energy level. In addition, the difference of the crystal lattice constant between Cu_2O and silicon brings interfacial defects, which can influence the band bending. Therefore, the peak at 615 nm may be attributed to the new built interfacial energy band transition in nano-heterojunction.

4. Conclusions

Si NWs/Cu_2O radial nano-heterojunctions were obtained successfully by electroless deposition technique. The morphology of Cu_2O nanocrystallines are closely related with the pH value of the growth solution. In Cu_2O nanocrystallines, the aggregation of small Cu_2O nanoparticles brings the structure defect, which lead to the symmetry breaking in nanocrystalline. So a peak corresponding to the IR active mode appears in the Raman spectra. In Si NWs/Cu_2O nano-heterojunctions, the PL peak of the Si NWs exhibits a little red-shift and becomes broad. More interestingly, a new PL peak at about 615 nm appears in the PL spectrum due to the formation of nano-heterojunctions.

Acknowledgments

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