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Characteristics of SiO_x-cored composite nanowires with Ag shell layers

Mesfin Abayneh Kebede, Hyoun Woo Kim *, Hyo Sung Kim

Division of Materials Science and Engineering, Inha University, Incheon 402-751, Republic of Korea

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ABSTRACT

This paper reports the preparation of Ag-coated SiO_x nanowires and analyzes changes in the structural properties and photoluminescence (PL) spectra induced by a thermal annealing process. The thermal induced changes in the sample morphology, generating Ag nanoparticles on the core of SiO_x nanowires and crystalline structures were affected, facilitating the generation of the Ag_2SiO_3 phase. The overall shape of the PL spectrum was changed significantly by both the Ag-coating and the subsequent thermal annealing. Possible emission mechanisms were discussed. This study gives insight into the annealing process regarding various coaxial one-dimensional materials, particularly with metal shell layers.

1. Introduction

Owing to their specific physical and chemical properties, thin nanowires have attracted considerable attention. Among them, silicon-based nanostructures and, more precisely, silicon oxide (SiO_x) nanowires have potential applications in nano-scale optical devices due to their excellent photoluminescence (PL) properties [1]. On the other hand, metal nanostructures have attracted considerable attention from materials scientists on account of their application to many areas of fundamental and technical importance [2]. Among all metals, silver (Ag) is particularly interesting due to its highest electrical and thermal conductivities [2].

In this paper, Ag layers were sputtered onto as-fabricated SiO_x nanowires, demonstrating the first fabrication of SiO_x-core/Ag-shell nanowires. The fabrication of coaxial nanocables will modify or improve the properties of individual materials. Ag nanoparticles on core SiO_x nanowires were fabricated via thermal annealing. Ag nanoshells or nanoparticles may possibly find a variety of applications, including heterogeneous catalysis, gas sensing, optics, and optoelectronics [3]. The structural and photoluminescence (PL) characteristics of these materials were also investigated.

2. Experimental

The core SiO_x nanowires were prepared using a tube furnace. The substrate temperature was set to 1000 °C for 2 h to anneal the Ag (approximate thickness = 10 nm)-coated Si substrates. During the experiment, a mixture of Ar and O_2 gases flowed at a pressure of 2 Torr. After that the furnace was cooled to room temperature and the substrates were transferred to a turbo sputter coater (Emitech K575X, Emitech Ltd., Ashford, Kent, UK) [4]. A circular Ag target was used during the sputtering process at room temperature. With the DC sputtering current set to 65 mA, the sputter time was set to 1 min in high-purity argon (Ar) gas (99.999%). The as-fabricated samples were annealed for 30 min at temperatures ranging from 300 to 700 °C in N_2 ambient.

The samples were analyzed by X-ray diffraction (XRD) (Philips X'pert MRD diffractometer with CuKα radiation), scanning electron microscopy (SEM) (Hitachi, S-4200), and transmission electron microscopy (TEM) (Philips, CM-200). The PL spectra were recorded at room temperature under excitation by a He–Cd laser (325 nm) in the UV region.

3. Results and discussion

Fig. 1a and b shows SEM images of the as-synthesized and annealed core/shell structures, indicating that the product consists

* Corresponding author. Tel.: +82 32 860 7544; fax: +82 32 862 5546.
E-mail address: hwkim@inha.ac.kr (H.W. Kim).

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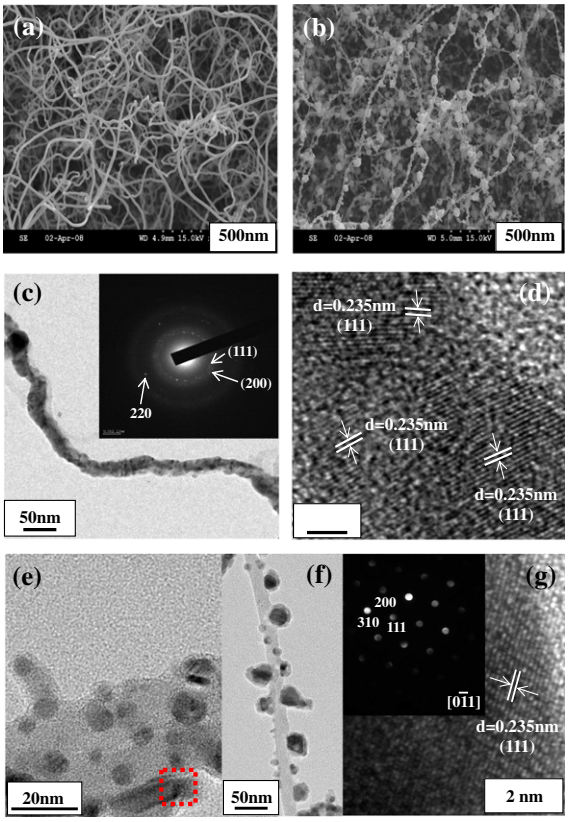

Fig. 1. SEM images of the core/shell structures (a) before and (b) after the thermal annealing at 700 °C. (c) TEM image of an as-synthesized SiO_x-core/Ag-shell nanowire. The corresponding SAED pattern image is shown in the inset. (d) Lattice-resolved TEM image. (e and f) TEM images of a SiO_x-core/Ag-shell nanowire annealed at 500 °C. (g) Lattice-resolved TEM image enlarging an area enclosed by the dotted box in (e). The corresponding SAED pattern image is shown in the inset.

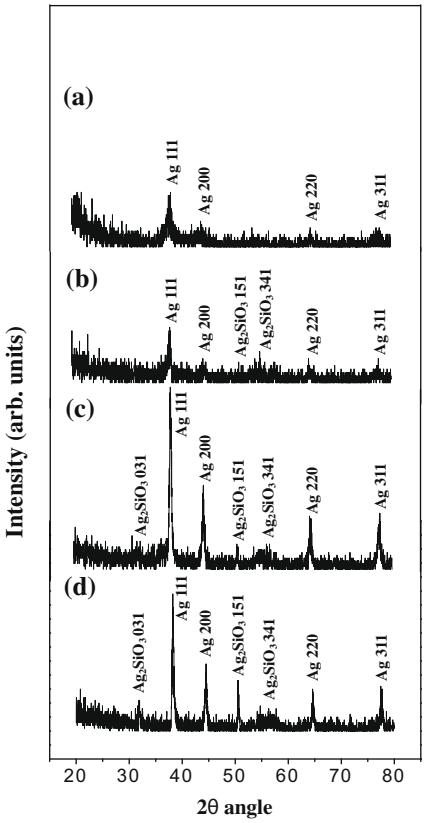

Fig. 2. XRD patterns of SiO_x-core/Ag-shell nanowires (a) as-synthesized as well as annealed at (b) 300 °C, (c) 500 °C, and (d) 700 °C.

of one-dimensional (1D) structures. However, it is noteworthy that the surface of the nanowires became rough after thermal annealing at 700 °C. Fig. 1c shows a TEM image of an as-fabricated SiO_x-core/Ag-shell nanowire. As shown in the inset, the pattern shows a halo as well as weak diffraction rings. The highly dispersed pattern is ascribed to the amorphous SiO_x core, whereas the diffusive rings correspond to the (1 1 1), (2 0 0), and (2 2 0) planes of cubic Ag, respectively. In a lattice-resolved TEM image (Fig. 1d), the interplanar spacings are approximately 0.235 nm, which is consistent with the (1 1 1) plane of cubic Ag. The figure clearly shows that the nanowire is poly-crystalline. Fig. 1e and f shows TEM images of a SiO_x-core/Ag-shell nanowire annealed at 500 °C. By comparing Fig. 1f with Fig. 1c, the Ag films appear to have been transformed into nanoparticle-like structures as a result of the thermal annealing process. Fig. 1g is a lattice-resolved TEM image enlarging the area enclosed by the dotted box in Fig. 1e. The spacing of the adjacent lattice plane is 0.235 nm, which is consistent with the separation of Ag (1 1 1) crystal planes. The upper left inset shows the associated SAED pattern. The set of electron diffraction spots corresponds to cubic Ag, revealing its single crystalline nature.

Fig. 2a–d shows XRD patterns of SiO_x-core/Ag-shell nanowires. The as-prepared nanowires, nanowires annealed at 300, 500 and 700 °C, respectively are shown in a succession of figures. Most of the peaks correspond to the Ag cubic structure reflection with a lattice constant of $a = 4.0862$ Å (JCPDS File No. 04-0783). An XRD peak-broadening analysis was performed, in which the recognizable diffraction peaks corresponding to the (1 1 1) and (2 0 0) indices were extracted. The full-width-at-half-maximum (FWHM) values of the Ag (1 1 1) peak at the nanowire samples annealed at 300 °C, at 500 °C, and at 700 °C decreased with the temperature increasing. The FWHM values of the Ag (2 0 0) peak at the nanowire samples annealed at the above mentioned temperatures similarly decreased. Accordingly, the Ag-associated peaks become sharper and thus the Ag grain size becomes larger as the annealing temperature increases [5]. The result is in good agreement with the TEM investigation, in which the degree of crystallization of the Ag shell increased after thermal annealing (Fig. 1). Apart from the Ag-associated peaks, in the annealed samples there exist diffraction peaks corresponding to orthorhombic Ag_2SiO_3 (JCPDS No. 12-0648). For a discernible peak of Ag_2SiO_3 (1 5 1), it was observed that its relative intensity increased with increasing of the annealing temperature from 300 to 700 °C. Moreover, the Ag_2SiO_3 (0 3 1) peak became clearer when the annealing temperature increases. It is assumed that Ag reacts with SiO_x, forming a Ag_2SiO_3 phase on the Ag/SiO_x interface and obviously this process will be favored at higher temperatures.

The PL spectrum of SiO_x nanowires prior to Ag coating is shown in Fig. 3a, which has a band maximum value of 2.88 eV. It exhibits an emission band with a main peak at approximately 2.9 eV in the blue region and a shoulder peak at approximately 2.3 eV in the green region. Fig. 3b shows the PL spectrum of Ag-coated SiO_x nanowires prior to thermal annealing. By comparing Fig. 3b with Fig. 3a, the relative intensity of 2.3 eV-peak to 2.9 eV-peak is shown to become higher due to the Ag coating, suggesting that this result stems from the overlapping of new emission bands (~2.3 eV) in connection with the Ag shell layer. Furthermore, Fig. 3b–d shows that the relative intensity of the peak at 2.3 eV to that at 2.9 eV increases as the annealing temperature increases. The mechanism of both the green and blue bands in SiO_x is mainly associated with oxygen deficiency [6,7], which cannot explain the temperature-induced change in their relative intensities.

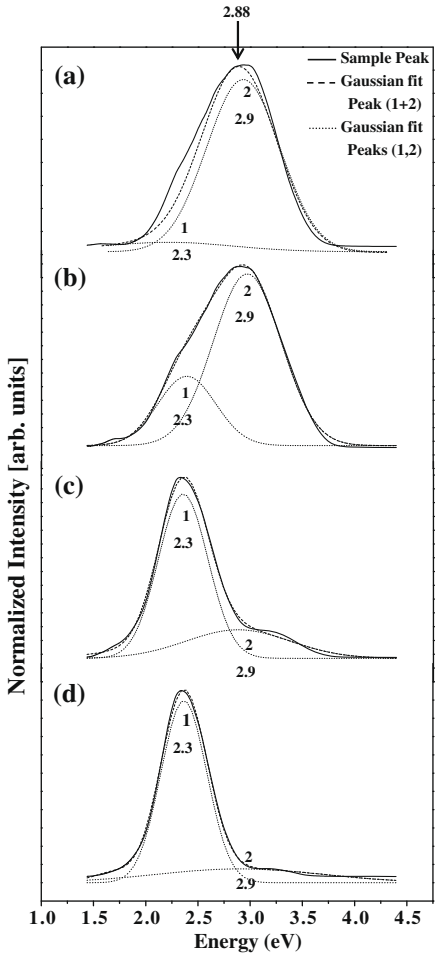

Fig. 3. PL spectra of (a) core SiO_x nanowires prior to Ag coating, (b) Ag-coated SiO_x nanowires prior to thermal annealing, (c and d) Ag-coated SiO_x nanowires which were annealed at (c) 500 °C and (d) 700 °C.

In some instances, green emission from Ag is attributed to Ag_2O with an optical band gap of 2.25 eV [8,9]. However, the XRD spectrum does not exhibit an Ag_2O-related peak, negates the presence of the Ag_2O phase in the present work. It is possible that the green emission is ascribed to a pure Ag shell layer. Green PL emissions were previously reported for Ag nanoparticles [10], and it is due to plasmon resonance [11,12]. Accordingly, annealing at higher temperatures will influence the structure and morphology of the Ag shell, eventually enhancing the peak emission at 2.3 eV. Further systematic study is in progress.

4. Conclusions

In summary, SiO_x-core/Ag-shell nanowires were fabricated and the effects of thermal annealing on the structural and optical properties were investigated. XRD, SEM, TEM, and PL spectroscopy were used to characterize the samples. Thermal annealing was found to contribute not only to the formation of crystalline Ag nanoparticles, but also to the generation of the Ag_2SiO_3 phase. The relative intensity of the 2.3–2.9 eV bands in the PL spectra is increased by Ag coating as well as by subsequent thermal annealing. This suggests that the change in PL spectrum is associated with structural and morphological changes in the Ag shell.

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References

[1] H. Nishikawa, T. Shiroyama, R. Nakamura, Y. Ohiki, K. Nagasawa, Y. Hama, Phys. Rev. B 45 (1992) 586.
[2] J.-Q. Hu, Q. Chen, Z.-X. Xie, G.-B. Han, R.-H. Wang, B. Ren, Y. Zhang, Z.-L. Yang, Z.-Q. Tian, Adv. Funct. Mater. 14 (2004) 183.
[3] D. Barreca, A. Gasparotto, C. Maragno, E. Tondello, S. Gialanella, J. Appl. Phys. 97 (2005) 054311.
[4] H.W. Kim, S.H. Shim, J.W. Lee, Carbon 45 (2007) 2695.
[5] B.D. Cullity, Elements of X-ray Diffraction, Addision-Wesley, 1978.
[6] D.P. Yu, Q.L. Hang, Y. Ding, H.Z. Zhang, Z.G. Bai, J.J. Wang, Y.H. Zou, W. Qian, G.C. Xiong, S.Q. Feng, Appl. Phys. Lett. 73 (1998) 3076.
[7] J.Q. Hu, Y. Jiang, X.M. Meng, C.S. Lee, S.T. Lee, Chem. Phys. Lett. 367 (2003) 339.
[8] P. Gangopadhyay, R. Kesavamoorthy, S. Bera, P. Magudapathy, K.G.M. Nair, B.K. Panigrahi, S.V. Narasimhan, Phys. Rev. Lett. 94 (2005) 047403.
[9] L.A. Peyser, A.E. Vinson, A.P. Bartko, R.M. Dickson, Science 291 (2001) 103.
[10] N. Vigneshwaran, R.P. Nachane, R.H. Balasubramanya, P.V. Varadarajan, Carbohyd. Res. 341 (2006) 2012.
[11] A. Hilger, N. Cüppers, M. Tenfelde, U. Kreibig, Eur. Phys. J. D 10 (2000) 115.
[12] A. Abdullah, S. Annapoorni, Pramana-J. Phys. 65 (2005) 815.