Optical and electrical properties of $p$-type Ag-doped ZnO nanostructures

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Abstract

$\text{Zn}_1-x\text{Ag}_x\text{O}$ nanoparticles (NPs) ($x=0$, 0.02, 0.04, and 0.06) were synthesized by a sol–gel method. The synthesized undoped ZnO and $\text{Zn}_1-x\text{Ag}_x\text{O}$-NPs were characterized by X-ray diffraction analysis (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and UV–visible spectroscopy. The XRD patterns indicated that undoped and Ag-doped ZnO crystallize in a hexagonal wurtzite structure. The TEM images showed ZnO NPs with nearly spherical shapes, with particle size distributed over the nanometer range. Evidence of dopant incorporation is demonstrated in the XPS measurements of the Ag-doped ZnO NPs. The Raman measurements indicated that the undoped and Ag-doped ZnO-NPs had a high crystalline quality. From the result of UV–vis, the band-gap values of prepared undoped and Ag-doped ZnO were found to decrease with an increase in Ag concentration. The obtained undoped and Ag-doped ZnO nanoparticles were used as a source material to grow undoped and Ag-doped ZnO nanowires on $n$-type Si substrates, using a thermal evaporation set-up. Two probe method results indicated that the Ag-doped ZnO nanowires exhibit $p$-type properties.

Keywords: C. Electrical properties; C. Optical properties; Ag-doped ZnO nanoparticles; $p$-type ZnO

1. Introduction

Zinc oxide can be used in many applications, including transparent conductive coatings [1], electrodes for dye-sensitized solar cells [2], gas sensors [3], and field emission materials [4]. Apart from the technological significance of ZnO nanostructures, their quasi-one-dimensional structure, with diameters in the range of tens of nanometers to hundreds of nanometers, makes them interesting from a scientific point of view. In this size range, they are expected to possess interesting physical properties, and pronounced coupling quite different from their bulk counterpart [5]. In order to obtain better crystallization quality and optical, electrical, and ferromagnetic properties, researchers carried out doping in ZnO. Recently, we have also studied the effect of anionic and cationic dopants on optical and electrical properties of $n$-type ZnO nanomaterials [6,7]. However, the key challenge that needs to be overcome for the realization of the most ZnO-based applications is the fabrication of $p$-type material. $p$-type ZnO may be achieved by the substitution of group-IA elements (Li, Na, and K) [8–10] and group-IB elements (Cu and Ag) [11,12] on the Zn-site, and group-VA elements (N, P, As, and Sb) on the O-site [13–15], respectively. Although significant progress has been made recently, full control over the materials’ conductivity type is still to be obtained, and hence a comprehensive investigation of the fundamental properties of acceptors in ZnO is needed. Recently, we studied the effect of the group-I elements on structural and optical properties of ZnO nanostructures. However, although substitutional group IA elements make shallow acceptors, it has been found that they tend to occupy the interstitial sites in ZnO, where they behave as donors and impede $p$-type [16]. Thus, group-IB elements have been proposed as the best possible candidates for $p$-type ZnO doping. Owing to the $p$-type ZnO nanostructures’ importance and their application in different fields, several investigations have been made to find the best method for their formation. The provided methods are transition vapor evaporation, hydrothermal, polymerization, deposition, thermal solubility and sol–gel.

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We believe that the sol–gel method is the best method to obtain uniform distribution of dopant materials in semiconductors. In addition, the thermal evaporation method is one of the best methods to obtain high crystalline quality of the nanostructures, as a result of using high temperature. Therefore, in this work, we combine these two methods to achieve high crystalline quality and stable p-type ZnO nanowires. According to these reasons, in this research paper, the obtained Ag-doped ZnO nanoparticles, which were grown by a sol–gel method, have been used to grow Ag-doped ZnO nanowires using the thermal evaporation method. The nanowires were grown on an n-type Si(111) substrate. The electrical measurements showed that the Ag-doped ZnO nanowires have p-type properties.

2. Experimental

To begin the synthesis of Ag-doped ZnO NPs, analytical grade zinc nitrate hexahydrate Zn(NO$_3$)$_2$·6H$_2$O, gold nitrate Ag(NO$_3$)$_3$, gelatin (type B from bovine skin) and distilled water were used as starting materials. All the materials used were purchased from Sigma-Aldrich. The precursors were measured as Zn$_{1-x}$Ag$_x$O ($x=0, 0.02, 0.04,$ and 0.06) to obtain final products. First, a gelatin solution was prepared by adding gelatin (3.65 g) to distilled water at 60 °C. After that, the compound solutions were stirred and heated at 80 °C for 5 h, at a heating rate of 2 °C/min. The metal nitrates were dissolved separately in a minimal amount of distilled water at room temperature, and then added to the gelatin solution. After that, the compound solutions were stirred and heated at 80 °C until gels were obtained. The gels were calcined at 550 °C for 5 h, at a heating rate of 2 °C/min. The resulting powders were characterized by several tools to check their quality.

The obtained nanoparticles were used to grow ZnO nanowires by the thermal evaporation method in a tube furnace. First, n-type Si(111) substrates were cleaned ultrasonically, using ethanol and deionized water. Then they were etched lightly with an HF (43%) and deionized water mixture (1:10) for about 10 min, to remove the native oxide layer. The undoped and Ag-doped ZnO nanoparticles (Zn$_{1-x}$Ag$_x$O, $x=0.06$) were used as the source materials. In fact, a mixture of the Ag-doped ZnO nanoparticles and commercial graphite powder at a 1:1 weight ratio was used as the precursor material to grow the Ag-doped ZnO nanowires. The precursor material was placed at the closed end of a small quartz tube, and the Si (111) substrate was placed above the precursor materials. The small tube was then inserted into a vacuum chamber, so that the closed end was placed at the center of the furnace. The precursor materials and the Si substrate were heated to 1000 °C. High purity N$_2$ gas was fed into the furnace at one end, at about 100 sccm, while another end was connected to a rotary pump. The growth process was allowed to proceed for 1 h. A vacuum of 250 Torr was maintained inside the tube furnace during the deposition of the nanostructures. The undoped ZnO nanowires were also grown on a Si substrate under the same conditions.

The morphology and crystal structure of the products were investigated using transmission electron microscopy (TEM; LEO 906 E) and X-ray diffraction (XRD; Philips PW3040/60), respectively. Elemental analyses of the products were undertaken using X-ray photoelectron spectroscopy (XPS; VG-Microtech ESCA-2000). The XPS spectra were recorded using Mg-K$_\alpha$ radiation (1256.6 eV). UV–visible spectroscopy (Perkin-Elmer spectrometer) was applied for considering the optical properties. Raman measurements (Jobin Yvon Horiba HR 800 UV) were carried out to study the crystallinity of the obtained products. An Ar ion laser with an emission wavelength of 514.5 nm was used for the Raman measurements. The morphology of the nanowires was studied using a scanning electron microscope (SEM, Quanta 200F). A two probes method was used to measure the $I$–$V$ characteristic of the p-type ZnO nanowires/n-type Si substrate hetero-junction.

3. Results and discussion

Fig. 1 shows the XRD patterns of the undoped and Ag-doped ZnO NPs. The XRD patterns indicate that apart from ZnO and Ag, no other reaction phases are present. All the samples were crystalline and were of hexagonal wurtzite phase (JCPDS card no. 36-1451). However, the Ag-doped samples indicate some additional diffraction peaks associated with the face-centered-cubic (fcc) phase of metallic Ag (JCPDS card no. 04-0783). The appearance of Ag peaks in the diffraction patterns clearly indicates the formation of crystalline silver clusters in the nanoparticles [17]. A decrease in the peak position value is generally observed when a doping element with a larger ionic radius than Zn$^{2+}$ is replaced at the substitution sites of the ZnO crystal lattice. Ag$^+$ ion (1.22 Å) has a higher ionic size than a Zn$^{2+}$ ion (0.74 Å), probably substituting Zn$^{2+}$ ions, and the appearance of Ag peaks in the diffraction patterns clearly indicates the formation of crystalline silver clusters in the nanoparticles. Therefore, the increment in the XRD peak position in this case suggests that the Ag ion has occupied the interstitial sites of ZnO, which is consistent with the reported data by Ahn et al. [18]. This is possible, since Ag acts as an amphoteric dopant, having a tendency to occupy both substitutional Zn and interstitial sites. However, it has been predicated theoretically that the incorporation of Ag$^+$ ions at the interstitial sites is a difficult proposition owing to their high formation energy, ~3 eV [19]. Moreover, the large size difference between Zn$^{2+}$ and Ag$^+$ ions limits the solubility of Ag in ZnO lattice [18].
However, a high-temperature growth process may solve this problem.

The crystalline sizes of the ZnO-NPs were determined by means of an X-ray line-broadening method, using the Scherrer equation:

$$D = \frac{k\lambda}{\beta_{hkl}\cos\theta}$$

where $D$ is the crystalline size in nanometers, $\lambda$ is the wavelength of the radiation (1.54056 Å for Cu Kα radiation), $k$ is a constant equal to 0.94, $\beta_{hkl}$ is the peak width at half-maximum intensity, and $\theta$ is the peak position. The (1 0 1) plane was chosen to calculate the crystalline size (either plane can be used for this purpose). The crystalline size of the Zn$_{1-x}$Ag$_x$O-NPs ($x=0$, 0.02, 0.04, and 0.06) is found to be 17 ± 2, 18 ± 2, 21 ± 2 and 26 ± 2 nm, respectively.

The TEM images of the undoped and Ag-doped ZnO-NPs are shown in Fig. 2. Nearly spherical shapes with particle size distributed over the nanometer range can be seen. The particle size measurements from the TEM images indicate that the average particle sizes of the Zn$_{1-x}$Ag$_x$O-NPs ($x=0$, 0.02, 0.04, and 0.06) are obtained as 45 ± 2, 48 ± 2, 49 ± 2 and 51 ± 2 nm, respectively. It can be seen that the particle sizes of the NPs increase by increasing Ag content. The obtained results from the TEM are in good agreement with the XRD results.

The XPS analysis was used for further evaluation of their purity and the composition of the NPs and is depicted in Fig. 3. Fig. 3(a)–(c) shows the XPS spectra of the core level regions of Zn-2p, O-1s, and Ag-3d for the Zn$_{1-x}$Ag$_x$O-NPs ((a) $x=0.02$, (b) 0.04, and (c) 0.06). In all cases, the spin–orbit splitting of 23 eV for Zn-2p$_{3/2}$ and Zn-2p$_{1/2}$ confirm that the Zn atoms are in a completely oxidized state [20]. The peak which exhibited around 530–533 eV is attributed to the oxide-metal ions bands ions in the NPs, namely, O–Zn in the ZnO lattice. The Ag-3d binding energy region consists of an asymmetric peak that could be fitted with two doublets assigned tentatively to the Ag-3d$_{5/2}$ and 3d$_{3/2}$ core levels of two different species: (i) metallic Ag or Ag$_2$O and (ii) a Ag–Zn–O ternary compound. An assignment of the first doublet to metallic Ag would be in agreement with the literature. Interestingly, the XRD data indicated the formation of Ag clusters on their samples. In addition, from the XPS intensity (integrated area) ratios (Ag-3d/Zn-2p), Ag doping of ~2, 4, and 6 (at%) was determined.

Raman spectroscopy is an effective technique for estimating the crystallinity of materials. According to the group theory, single crystalline ZnO belongs to the C$\text{\Gamma}_{\text{4V}}$ space group having two formula units per primitive cell, and eight sets of optical phonon modes at the $\Gamma$ point of the Brillouin zone, classified as $A_1$ + $E_1$ + 2$E_2$ modes (Raman active), 2$B_1$ modes (Raman silent), and $A_1$ + $E_1$ modes (infrared active). The $E_1$ mode is a polar, and is split into transverse optical (TO) and longitudinal optical (LO) branches. The Raman spectra for the undoped and Ag-doped ZnO NPs are shown in Fig. 4. As shown in Fig. 4, the Raman spectra of all the NPs show a sharp, strong, and dominant peak at 437 cm$^{-1}$, corresponding to the $E_2$(high) mode of the Raman active mode, a characteristic peak for the wurtzite hexagonal phase of ZnO. The $E_1$(LO) mode at 583 cm$^{-1}$ is associated with impurities and formation of defects such as oxygen vacancies. Therefore, no visible $E_1$(LO) peak for the

Fig. 2. (a) TEM image of the undoped ZnO NPs; (b) TEM image of the Zn$_{0.98}$Ag$_{0.02}$O NPs; (c) TEM image of the Zn$_{0.96}$Ag$_{0.04}$O NPs; (d) TEM image of the Zn$_{0.94}$Ag$_{0.06}$O NPs.

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undoped and Ag-doped ZnO NPs indicates a higher crystalline quality and lower oxygen vacancy of the ZnO NPs. In addition, Fig. 4 shows peaks at 330 cm\(^{-1}\), assigned to the \(E_{2h}-E_{2l}\) (multi-phonon process) mode for all samples. It is well known that \(E_{2h}-E_{2l}\) can only be found when ZnO is a single crystal [21].

UV–vis absorption spectra of ZnO NPs at room temperature are shown in Fig. 5. The spectra reveal a characteristic absorption peak of ZnO, at wavelengths from 360 to 380 nm, for the samples made with different concentrations of silver and undoped ZnO, which can be assigned to the intrinsic band-gap absorption of ZnO, owing to the electron transitions from the valence band to the conduction band (\(O_2p\rightarrow Zn_3d\)) [22]. As shown in Fig. 5(a), the maximum peak in the absorbance spectrum does not correspond to the true optical band gap of the ZnO NPs. One of the best ways to obtain the band gap from absorbance spectra is to get the first derivative of the absorbance with respect to photon energy, and find the maximum in the derivative spectrum at the lower energy sides [23]. The derivatives of the absorbance of the ZnO NPs are shown in Fig. 5(b), which shows a band gap of 3.23, 3.22, 3.22, and 3.20 eV for the undoped, Ag(2%), Ag(4%), and Ag(6%)-doped ZnO NPs, respectively. Compared with the undoped ZnO NPs, the results of the doped ZnO NPs show an obvious red-shift in the UV emission. This red-shift in the UV emission could be a result of obtaining \(p\)-type ZnO NPs. A widening of the band gap is usually observed for ZnO doped with donors, while \(p\)-type ZnO has shown band-gap reduction if doped with acceptors. In fact, the UV peak of the optical measurements of the ZnO nanostructures, which have been doped by donor materials, exhibited a blue-shift in comparison to that observed for the undoped ZnO nanostructures [24–26]. Our previous experiments about dopants materials as donors also confirm these results [6, 7].

The undoped and Zn\(_{0.94}\)Ag\(_{0.06}\)O NPs were used to grow undoped and Ag-doped ZnO nanowires by the thermal evaporation method in a tube furnace. Fig. 6(a) and (b) shows

![Fig. 3. XPS spectra of the (a) Zn\(_{0.98}\)Ag\(_{0.02}\)O NPs; (b) Zn\(_{0.96}\)Ag\(_{0.04}\)O NPs; and (c) Zn\(_{0.94}\)Ag\(_{0.06}\)O NPs.](image1)

![Fig. 4. Raman spectra of the undoped and Ag-doped ZnO NPs.](image2)
SEM images of the undoped and Ag-doped ZnO nanowires, respectively. A hexagonal cross-section can be seen for the nanowires. Therefore, the orientation of nanowire growth is, preferentially, in the direction of the $c$-axis ($[0 0 0 1]$).

As observed in the SEM images, the nanowires are completely straight and tapered, with a tip diameter of $\sim 50 \pm 5$ nm and a base diameter of $\sim 150 \pm 5$ nm. This tapering could be a result of the Si substrate position that has been placed above the source material, in the center of the furnace. In fact, in the first step, most of the source material has evaporated, and then rate of evaporation decreased. This changing of the evaporation rate of the source materials resulted in tapered nanowires.

Fig. 6(c) and (d) shows the EDX spectra of the undoped and Ag-doped ZnO nanowires. EDX spectra of the (c) undoped and (d) Ag-doped ZnO nanowires.

Fig. 5. (a) UV–vis absorption spectra of the undoped and Ag-doped ZnO NPs; (b) derivative of the UV–vis absorption spectra of the undoped and Ag-doped ZnO NPs.

Fig. 6. SEM images of the (a) undoped; and (b) Ag-doped ZnO nanowires. EDX spectra of the (c) undoped and (d) Ag-doped ZnO nanowires.

Fig. 7 shows the XRD patterns of the nanowires in the range $2\theta = 25-75^\circ$. All detectable peaks are from the ZnO wurtzite structure (JCPDF card no. 00-005-0664). There are no other peaks related to Ag, or other mixed compounds. The disappearance of the Ag peak from the XRD pattern of the Ag-doped ZnO nanowires, in comparison to the XRD pattern of the Ag-doped ZnO NPs, could be a result of using high temperature during the growth process of the nanowires.
In fact, no changing in the has been performed after 2 and 60 days of the perpetration of the

4. Conclusion

Zn$_{1-x}$Ag$_x$O ($x = 0, 0.02, 0.04$, and $0.06$) NPs were synthesized by a sol–gel method. The synthesized NPs were characterized successfully by the XRD, TEM, XPS, Raman, and UV–vis. The crystallite and particle size of the Zn$_{1-x}$Ag$_x$O nanoparticles were found to increase with an increase in Ag content, without changing the wurtzite hexagonal single-phase structure of ZnO. The XRD patterns of the NPs revealed that, apart from ZnO and Ag, no other reaction phases are present. The XPS spectrum of Zn 2p showed that the split value of binding energy could be the characteristic value of ZnO. The UV–vis results showed a decrease in the band gap for Ag-doped ZnO NPs. The obtained nanoparticles were used as the source materials to grow undoped and Ag-doped ZnO nanowires, using the thermal evaporation method. The SEM image of the nanowires showed that the undoped and Ag-doped ZnO nanowires were straight and tapered. The $I$–$V$ measurements demonstrated rectification properties for the Ag-doped ZnO nanowires that were grown on an $n$-type Si substrate. In addition, the $I$–$V$ measurements indicated stability for the $p$-type behavior of Ag-doped ZnO nanowires. It can be recommended that the obtained sample could be used as an optoelectronic device.

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