Piezoelectric and opto-electrical properties of silver-doped ZnO nanorods synthesized by low temperature aqueous chemical method

Eiman Nour, A. Echresh, Xianjie Liu, Esteban Broitman, Magnus Willander and Omer Nour

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:
Eiman Nour, A. Echresh, Xianjie Liu, Esteban Broitman, Magnus Willander and Omer Nour, Piezoelectric and opto-electrical properties of silver-doped ZnO nanorods synthesized by low temperature aqueous chemical method, 2015, AIP Advances, (5), 7, 077163.
http://dx.doi.org/10.1063/1.4927510
Copyright: American Institute of Physics (AIP): Open Access Journals / AIP Publishing LLC
http://www.aip.org/

Postprint available at: Linköping University Electronic Press
http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-120876
Piezoelectric and opto-electrical properties of silver-doped ZnO nanorods synthesized by low temperature aqueous chemical method

E. S. Nour, A. Echresh, Xianjie Liu, E. Broitman, M. Willander, and O. Nur

Citation: AIP Advances 5, 077163 (2015); doi: 10.1063/1.4927510

View online: http://dx.doi.org/10.1063/1.4927510

View Table of Contents: http://scitation.aip.org/content/aip/journal/adva/5/7?ver=pdfcov

Published by the AIP Publishing

Articles you may be interested in

Tuning the emission of ZnO nanorods based light emitting diodes using Ag doping

Synthesis of highly efficient antibacterial agent Ag doped ZnO nanorods: Structural, Raman and optical properties
J. Appl. Phys. 115, 154308 (2014); 10.1063/1.4869736

Opto-electrical properties of Sb-doped p-type ZnO nanowires

Emission properties of Ag @ SiO 2 / ZnO nanorods' heterostructure

Tunable growth of ZnO nanorods synthesized in aqueous solutions at low temperatures
J. Vac. Sci. Technol. B 24, 288 (2006); 10.1116/1.2163889
Piezoelectric and opto-electrical properties of silver-doped ZnO nanorods synthesized by low temperature aqueous chemical method

E. S. Nour, A. Echresh, Xianjie Liu, E. Broitman, M. Willander, and O. Nur

Department of Science and Technology (ITN), Linköping University, Campus Norrkoping, SE-60 174 Norrkoping, Sweden
Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-58183 Linköping, Sweden

(Received 8 May 2015; accepted 16 July 2015; published online 23 July 2015)

In this paper, we have synthesized Zn$_{1-x}$Ag$_x$O (x = 0, 0.03, 0.06, and 0.09) nanorods (NRs) via the hydrothermal method at low temperature on silicon substrate. The characterization and comparison between the different Zn$_{1-x}$Ag$_x$O samples, indicated that an increasing Ag concentration from x = 0 to a maximum of x = 0.09; All samples show a preferred orientation of (002) direction with no observable change of morphology. As the quantity of the Ag dopant was changed, the transmittances, as well as the optical band gap were decreased. X-ray photoelectron spectroscopy data clearly indicate the presence of Ag in ZnO crystal lattice. A nanoindentation-based technique was used to measure the effective piezo-response of different concentrations of Ag for both direct and converse effects. The value of the piezoelectric coefficient ($d_{33}$) as well as the piezo potential generated from the ZnO NRs and Zn$_{1-x}$Ag$_x$O NRs was found to decrease with the increase of Ag fraction. The finding in this investigation reveals that Ag doped ZnO is not suitable for piezoelectric energy harvesting devices.

I. INTRODUCTION

The semiconductor zinc oxide (ZnO) has gained a lot of interest in the research community. ZnO is a group II–VI compound semiconductor with excellent thermal and chemical stability, has a relatively large excitonic binding energy (60 meV) and a direct wide band gap (3.37eV) at room temperature. In addition to its semiconducting properties, and due to the inherent crystal structure, ZnO also possesses strong piezoelectric properties.\(^1\) These characteristics make ZnO a material to be suitable for applications in electronic, optoelectronic, electrochemical, and electromechanical devices such as light-emitting diodes,\(^2\) photodetectors,\(^3\) photodiodes,\(^4\) gas sensors,\(^5\) solar cells,\(^6\) piezoelectric transducers\(^7\) and so on. Modification of ZnO properties by impurity incorporation is currently another important issue for possible different applications. Doping in ZnO with selective elements offers an effective method to adjust their electrical, optical, magnetic and piezoelectric properties, which is crucial for their practical applications.\(^8\) For ZnO, silver (Ag) is a good candidate for adjusting its optical properties. Ag ions can act as acceptors in ZnO, existing on substitutional Zn sites or in the interstitial form.\(^9,10\) In addition, in Ag doped ZnO, the location of the acceptor level remains contentious.\(^9,10\)

In general, the physical properties of ZnO are closely connected with the deposition method, deposition parameters, annealing treatments and doping. Due to these factors, the doping has been widely used to adjust the structural, electrical and optical properties of ZnO thin films.\(^10\) Ag doped

---

\(^{8}\)Corresponding author E-mail: eiman.satti.osman@liu.se
ZnO thin films have drawn considerable attention in many studies, e.g. as reported in Refs. 11–16. In these studies Ag doped ZnO thin films showed increase in the resistivity, in addition to enhancement of the UV emission, and reduction of the optical band gap. In general all these Ag doped ZnO thin film experiments were concentrated on the electrical or opto-electrical properties, but to our best knowledge, no study has been published on measuring the piezoelectric effect of Ag doped ZnO. Based on the surface roughness and the electrical resistivity, S-H Nam et al claimed that Ag doped ZnO thin films deposited by radio frequency magnetron sputtering are not appropriate for piezoelectric devices because the films have poor crystallinity and low resistivity; interestingly, they did not measured the piezoelectric properties of their films. Moreover, the published papers on Ag doped ZnO nanostructures are so far very limited. Among the many possible ZnO nanostructures, well-aligned nanorods (NRs) have attracted increased interest for many applications. Un-doped well aligned ZnO NRs have been grown on many substrates using both physical as well as chemical methods. Recently, aqueous chemical growth (ACG) methods used to synthesize metal oxide nanostructures have become very popular among researchers. This is due to the simplicity of the method, the low synthesis temperature (<100°C) which enables the use of soft substrates, like plastic, papers etc., Although this ACG method is a low temperature approach (<100°C) it has proven effective in controlling the morphology, structure and properties by varying the different growth conditions such as temperature, growth time, precursor concentration, and preparation conditions. It will be of great interest to investigate and control the incorporation of different impurities in ZnO nanostructures using the low temperature chemical methods.

In the present work, we report on the structural, optoelectronic and piezoelectric properties of Zn$_{1-x}$Ag$_x$O (x = 0, 0.03, 0.06 and 0.09) NRs synthesized using the low temperature ACG approach. The structural properties were investigated using scanning electron microscopy (SEM) and powder x-ray diffraction (XRD). The chemical state of Ag in the Zn$_{1-x}$Ag$_x$O was investigated by an X-ray photoelectron spectroscopy (XPS). The influence of the Ag doping on the optical properties of the different samples was investigated using UV-VIS spectrometer. Finally, the piezoelectric properties were investigated using direct and inverse nano-indentation measurements.

II. EXPERIMENTAL PROCEDURE

At first, silicon substrate coated with silver was cleaned by sonication in acetone, deionized water, and isopropanol, respectively. Then, the substrate preparation technique developed by Green et al was used to improve the quality of the grown nanorods. For the growth of the Zn$_{1-x}$Ag$_x$O NRs (x = 0, 0.03, 0.06 and 0.09), an equimolar concentration (0.075 M) of hexamethylenetetramine (HMT), and a mixture of zinc nitrate hexahydrate and silver nitrate solutions were prepared and mixed together. The different Ag concentrations were obtained by mixing different volume ratios of the zinc nitrate hexahydrate and silver nitrate. Next, the prepared solution was poured in a beaker and the pre-treated substrates were immersed in the solution with the growth side facing downward. After that, the beaker was sealed and heated in a laboratory oven at 90°C for 6 hours. Then, the growth beaker was allowed to cool down to room temperature. Finally, after the growth process, the samples were rinsed with deionized water and dried with flowing nitrogen in order to remove the residual salts.

A Schottky contact on the Zn$_{1-x}$Ag$_x$O NRs grown on silicon substrate (x = 0, 0.03, 0.06 and 0.09), was achieved using gold (Au) contact on top of the nanorods. The crystal structure of the pure and Ag-doped ZnO NRs arrays grown hydrothermally were investigated by Powder x-ray diffraction (XRD) Philips PW 1729 diffractometer equipped with Cu-Kα radiation (λ = 1.5418 Å). The surface morphology and physical parameters were measured using Field-emission scanning electron microscopy (FE-SEM) Gemini LEO 1550. The influence of the Ag doping on the optical properties of the different samples was investigated using a PerkinElmer Lambda 800/900 spectrometer part no. BV900ND0. The direct and converse piezoelectric properties tests were performed by a nanoindentation technique using a Hysitron IT- 950- Trid Gender at room temperature, as described in details in Refs. 27 and 28.
III. RESULTS AND DISCUSSION

A. Surface morphology and structure characterization

The x-ray diffraction pattern of pure ZnO NRs and different concentration of Ag doped ZnO NRs obtained at 6 hours growth durations are shown in Figure 1(a). All the x-ray diffraction spectra

![Graph 1(a)](image)

FIG. 1. (a) XRD patterns all the Zn$_{1-x}$Ag$_x$O NRs grown on silicon substrate (x value is as indicated). (b) The XRD patterns of the (002) diffraction peaks. (c) The FWHM and the 002 peak intensity as a function of doping concentration.
FIG. 2. SEM image of all the silver doped Zn$_{1-x}$Ag$_x$O NRs grown on silicon substrate (x value is as indicated).

were measured using the same acquisition parameters and hence are comparable. Three diffraction peaks are well consistent with the hexagonal phase of diffraction peaks of ZnO, and in agreement with the JCPDS Card No. 36-1451 file. In addition to the (111) Ag diffraction peak (from the substrate), the x-ray diffraction spectra of the different Zn$_{1-x}$Ag$_x$O NRs (x = 0, 0.03, 0.06 and 0.09), samples show diffraction peaks corresponding to the ZnO (002), (100) and (101) planes. The (002) reflection peak is intense and sharper in nature, as compared to other peaks, indicating a preferential c-axis growth orientation all the NRs. Nevertheless its intensity is decreasing with increasing the Ag concentration. Increasing the concentration of Ag leads to decrease the crystal quality of the ZnO NRs, in agreement with previous results reported by Xu et al.\textsuperscript{10} Figure 1(b) shows the XRD patterns of the (002) diffraction peaks for all samples. In this Figure there is also a clear slight shift of the angular position of the (002) peak. This shift indicates that the Ag ions replaced the Zn sites in the ZnO NRs crystal matrix. Additionally and because the radius of Ag$^{2+}$ ion (1.22 Å) is greater than that of Zn$^{2+}$ ion (0.72 Å), the increase of the number of Ag$^{2+}$ ion in the Zn ions lattice sites contraction the lattice parameter.\textsuperscript{13} The values of full width half maximum (FWHM) and (002) intensity for the different Zn$_{1-x}$Ag$_x$O NRs (x = 0, 0.03, 0.06 and 0.09) samples are shown in Figure 1(c). It can also be seen that FWHM is increased by the increasing the Ag dopant concentration. The FWHM change with the Ag incorporation demonstrates that the crystallinity of the NRs decreases with increasing the Ag concentration, indicating that large amount of Ag atoms may inhibit the c-axis preferential growth of the ZnO NRs.\textsuperscript{15}

SEM images of the different Zn$_{1-x}$Ag$_x$O NRs (x = 0, 0.03, 0.06 and 0.09) are shown in Figure 2. It is clear that all the NRs grown samples have a hexagonal structure with uniform, well aligned c-axis oriented nature. The average diameter is between 100-150 nm and the approximate length is 1 µm. As can be seen from these SEM images, the addition of the Ag does not affect the morphology: neither the size nor the spatial distributions of the NRs have been altered by the presence of the Ag in the ZnO matrix.

B. Electronic structure characterization

X-ray photoelectron spectroscopy was used to investigate the charge state and chemical composition of Ag in the Zn$_{1-x}$Ag$_x$O NRs (x = 0, 0.03, 0.06 and 0.09). Figure 3 shows the XPS spectra of the Ag 3d peaks (Ag3d$_{5/2}$ and Ag3d$_{3/2}$) for the pure ZnO (pink), Zn$_{0.97}$Ag$_{0.03}$O (red), Zn$_{0.94}$Ag$_{0.06}$O (blue) and Zn$_{0.91}$Ag$_{0.09}$O NRs (black). For the three doped samples, the XPS signal from Ag 3d
FIG. 3. XPS spectrum of Ag 3d peaks for the Zn$_{1-x}$Ag$_x$O NRs grown on silicon substrate (x value is as indicated). All XPS peaks were normalized. The dashed line indicates the change of the Ag peak position with doping.

Photoemission was substantially detected, for instance the peak of Ag 3d in the Zn$_{0.91}$Ag$_{0.09}$O NRs sample appears at around 368.12 eV and 374.17 eV for Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$, respectively. Therefore, these spectra clearly confirm the incorporation of Ag into the ZnO crystal lattice. The overall observed XPS spectrums of Zn$_{1-x}$Ag$_x$O NRs were in agreement with earlier reports.\textsuperscript{10,29–32} Besides the appearance of Ag in the doped film, there is a shift of Ag 3d peak upon the different doping levels. From Zn$_{0.97}$Ag$_{0.03}$O NRs to Zn$_{0.91}$Ag$_{0.09}$O NRs, the peak position of Ag3d$_{5/2}$ downshifts to the lower binding about 0.1 eV, as marked by the dashed line in Figure 3, where all the intensity were normalized to show the change of peak position. Such behaviors could indicate that there is more metallic properties of Ag in the higher doped sample than lower doped sample.

C. Performance of the device

1. Optical properties

The optical band gap of the Zn$_{1-x}$Ag$_x$O NRs (x = 0, 0.03, 0.06 and 0.09) samples was determined using Tauc method. From this method, the (\(\alpha h\nu\))^2 plot versus \(h\nu\) for ZnO is as shown in

FIG. 4. Plot of (\(\alpha h\nu\))^2 versus \(h\nu\) of the ZnO (black), Zn$_{0.97}$Ag$_{0.03}$O (red), Zn$_{0.94}$Ag$_{0.06}$O (orange) and Zn$_{0.91}$Ag$_{0.09}$O NRs (blue).
FIG. 5. (a) Schematic diagram of nanoindentation instrument used for measurement of direct piezopotential. (b) Generated piezoelectric potential as a function of applied load.

Figure 4, and according to the equation:\textsuperscript{18,33,34}

\[
(\alpha h\nu)^{1/r} = A(h\nu - E_g)^{1/2}
\]  

where \(\alpha\) is the optical absorption coefficient of the material, \(h\nu\) is the photon energy, \(A\) is a constant coefficient, \(E_g\) is the optical band gap, and the exponent \(r\) depends on the nature of the transition of the material. Band gap narrowing upon doping is a well-known general phenomenon in semiconductors, not just in ZnO. Shallow level donor impurities create energy levels in the band gap near the conduction band edge and shallow acceptor impurities create energy levels near the valence band edge. With increase in the amount of doping, the density of states of these dopants increase and form a continuum of states\textsuperscript{8,9} just like in the bands, and effectively the band gap decreases. In this work, the values of optical band gap for the Zn\(_{1-x}\)Ag\(_x\)O NRs (\(x = 0, 0.03, 0.06\) and 0.09) samples are shown in Figure 4, calculated by the extrapolation method. The values obtained were 3.30 eV (black curve), 3.26 eV (red curve), 3.22 eV (orange curve) and 3.17 eV (blue curve), for the different Zn\(_{1-x}\)Ag\(_x\)O NRs (\(x = 0, 0.03, 0.06\) and 0.09) samples, respectively. As it can be seen, the optical band gap decreased by increasing the amount of the Ag doping.
This might be an indication that the Ag has substituted the Zn in the lattice. This is consistent with
the observation from the x-ray results discussed above. So we can conclude that the optical band
gap of Ag doped ZnO nanostructures is strongly dependent on the lattice sites of Ag in the ZnO.
Additionally, the interaction of Ag states with the ZnO host states resulted in creating energy levels
in the band gap that leads to reduce the optical band gap.

2. Piezoelectric properties

a. Direct piezoelectric effect. A Schematic diagram of nanoindentation instrument used for
measurement of converse piezoelectric under the applied voltage shown in Figure 5(a). Figure 5(b)
shows the relation between the maximum applied force and the generated piezo potential at the point of maximum applied force for the four different samples. Among different reported results, A. Khan et al investigated ZnO nanowires (NWs) grown on conductive fabric. The generated output potential was up to 13 mV at 1000 µN applied load. M. Hussain et al obtained up to 3 mV at 400 µN applied load for ZnO NRs sample synthesized on FTO. Here from our samples, it’s observed that when the applied load was increased up to 160 µN, the resulting piezoelectric potential consistently increased for the four samples. In addition, while piezoelectric potential values of up to 7 mV were generated for pure ZnO NRs, output values of 2, 1.9 and 1.4 mV were generated from the Zn$_{0.97}$Ag$_{0.03}$O, Zn$_{0.94}$Ag$_{0.06}$O and Zn$_{0.91}$Ag$_{0.09}$O NRs, respectively. It is clear that the addition of Ag dopant decreases substantially the generated piezoelectric voltage. Missing points in the Figure for samples with Zn$_{0.94}$Ag$_{0.06}$O and Zn$_{0.91}$Ag$_{0.09}$O NRs were for points that did not generate voltage, probably due to a short circuit.

b. Converse piezoelectric effect. The converse piezoelectric effect is measured by applying a DC voltage in the range 0 to - 40 V while there is a relatively low applied force of 15 µN applied to the samples to allow the tip to be always in physical contact with the NRs; as shown in Figure 6(a).

In order to evaluate the performance of any piezoelectric material clamped to a substrate, the most important parameter to calculate is the effective piezoelectric coefficient $d_{33}^{\text{eff}}$. In the case of NRs, this coefficient is directly related to the change of the longitudinal elongation $\Delta l$ when the NRs are subject to a change of the applied voltage $\Delta V$ in their $c$ axis direction: $d_{33}^{\text{eff}} = \Delta l / \Delta V$.

The converse piezoelectric effect $d_{33}^{\text{eff}}$, of technological importance for the design of devices, can be related to the “true” piezoelectric coefficient $d_{33}$ of bulk material by the following relationship:

$$d_{33} = d_{33}^{\text{eff}} (s_{11} + s_{12})/(s_{11} + s_{12} + s_{13})$$

where $s_{11}$, $s_{12}$, and $s_{13}$ are the mechanical compliances of the piezoelectric NRs.

From the results are shown in Figure 6(b)-6(e) we can estimate the value of $d_{33}^{\text{eff}}$ to be $\sim$ 130 pm/V for the pure ZnO NRs sample. A piezoelectric coefficient value of 33.2 pmV$^{-1}$ from ZnO NWs grown on conductive fabric substrate was reported by A. Khan et al. Additionally, the value of the $d_{33}^{\text{eff}}$ for the Zn$_{0.97}$Ag$_{0.03}$O, Zn$_{0.94}$Ag$_{0.06}$O and Zn$_{0.91}$Ag$_{0.09}$O NRs were about 8.75, 6.25 and 4 pm/V, respectively. Figure 7 illustrate the substantial decrease of the piezoelectric response with the addition of Ag.

Because of the non-central symmetric feature in the ZnO wurtzite structure, the cations and anions are tetrahedrally coordinated and the centers of the positive ions and negative ions overlap with each other under strain-free conditions. When an external stress is applied, the centre of the cations and anions is displaced, and this produces a non-zero dipole moment. A constructive sum

![FIG. 7. Piezoelectric coefficient as a function of doping concentration.](image-url)
of these dipole moments results in a macroscopic potential, which is the origin of piezoelectricity.\textsuperscript{38} In some materials, like AlN, the doping with one foreign element can increase the piezoelectric response, as demonstrated in Sc-doped AlN thin films.\textsuperscript{28} On the other hand, in ZnO thin films, the crystalline quality decreased considerably with increasing Ag atom\%\textsuperscript{17}. By introducing a very small doping amount, the effect will be such that; this dopant addition distorts the unit cell of the ZnO crystal. If the doping level is further increased, there will be a high deformation of the crystalline structure, leading to loss of the symmetry and decreasing thereafter the piezo response. Our optical and structural results are consistent and similar to those reported in Ref. 17, nevertheless, we have not observed any change of morphology of Ag doped ZnO nanorods.

IV. CONCLUSION

In summary, silver (Ag) doped ZnO NRs have been successfully synthesized on silicon substrate. Structural characterization (x-ray and SEM) indicated that the morphology of the NRs was preserved while growing ZnO NRs samples up to 9\% atom fraction of Ag doping concentration. The increase of Ag concentration result in creating an energy donor levels in the band gap which leads to reduce the optical band gap. XPS data clearly shows the incorporation of Ag into the ZnO crystal lattice. The direct and converse piezoelectric properties of highly c-axis oriented ZnO and Ag doped ZnO NRs grown by low temperature ACG method on silicon substrate were measured and analyzed by the nanoindentation technique. The value of the piezoelectric coefficient $d_{33}^{eff}$ was found to decrease from 130 pm/V to 8.75 pm/V for the pure ZnO NRs and Zn$_{0.97}$Ag$_{0.03}$O, respectively. Upon further increase of the Ag fraction the piezoelectric coefficient has slightly decreased further. When the nanoindenter is used to measure the direct piezoelectric effect, the piezoelectric potential generated values from the pure sample of ZnO NRs and for the Zn$_{0.97}$Ag$_{0.03}$O were decreased from 7 mV to 2 mV, respectively. These results indicated that, even preserving the crystallinity and electrical resistivity of the Ag doped ZnO NRs, the material is not suitable for piezoelectric device applications.

ACKNOWLEDGMENT

- Partial financial support the Advanced Functional Materials (AFM), and CeNano grant both at Linköping University, Sweden, is highly appreciated.