Modification of green synthesized ZnO nanorods for actuation application

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Abstract

Zinc oxide (ZnO) nanostructures as amazing piezoelectric materials have been recently extensively investigated in order to harvest energy. ZnO nanorods with hexagonal wurtzite structure oriented along c-axis were grown on the glass substrate by combining the facile sol–gel and chemical bath deposition techniques. Zinc acetate dihydrate as a Zn²⁺ source, ethanol and acetone as solvents were used in the sol preparation without using any organic stabilizer additive. ZnO sol’s structure was characterized by FTIR spectroscopy. Particles forming the sol were analyzed to be zinc (hydroxo and/or oxo) acetate, according to the characterization results. The influence of the binary solvent system on the stability and optical properties of the particles as well as morphological properties of ZnO grains were studied. The positive effect of an optimum percentage of acetone in the precursor sol which reduced the zinc (hydroxo and/or oxo) acetate dissolution and ensured the particles stabilization could subsequently be understood. Dense ZnO grains with high aspect ratio on the seed layer which led to vertically aligned ZnO nanorods were obtained using the sol with 1:1 ratio of EtOH and acetone. To increase the piezoresponse of the nanorods, their crystal structure needed to be modified. Therefore, they were subjected to oxygen plasma in order to reduce oxygen vacancies and repair the crystal structure (defects) of the as-grown n-type ZnO nanorods. Photoluminescence analysis was used to analyze the crystal before and after the plasma treatment. Piezoresponse Force Microscopy (PFM) has also been employed to evaluate the reverse piezoelectric response of the nanorods as an actuator before and after plasma treatment. The magnitude and phase RMS value increase of 27% and 143% was observed after plasma treatment.

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1. Introduction

Recently fabrication of nanostructure semiconductors by efficient, low temperature and cost effective approaches has been favored. ZnO nanomaterials are attractive nanosystems with outstanding optical, piezoelectric, chemical and biochemical properties suited for a wide range of novel applications [1,2]. Functional ZnO nanorods among other nanostructures with extensive applications in high performance nanosensors [3], solar cells [4], field emission devices [5], piezoelectric nanogenerators [6–8], ultraviolet detectors [9], and blue-light emitting diodes (LEDs) [10] have been synthesized by various techniques. Its piezoelectric applications to harvest energy have so far been, no doubt, of concern. The advantage of using ZnO nanorods for energy harvesting is their ability to build up a piezoelectric potential field inside itself [11].

Among the methods of synthesis described in literature such as wet chemical routes [12–15], chemical vapor deposition (CVD) [16] and pulsed laser deposition (PLD) [17], wet chemical methods known as chemical bath deposition (CBD) has attracted more attentions due to its simple, catalyst free, cheap and low temperature particularities [18]. Whereas other techniques usually require high temperature, catalysts, high experimental costs and complicated equipment [11]. In order to achieve well-aligned ZnO nanorods, it is important to apply the deposition on an appropriate seed layer since researches have reported that ZnO nanorods grow epitaxially
from the columnar grains of a seed layer [17–19]. There are two most commonly routes used to obtain a ZnO seed layer; sol–gel method and radio frequency (RF) sputtering process [21]. The latter is employed to gain high quality seed layer, nevertheless it can’t be performed without requisite conditions such as low pressure [20]. These requirements limit the usage of this technique. In contrast, sol–gel as a versatile, low temperature, low cost and very simple method can be easily coupled with dip-, drop- or spin-coating techniques to provide a dense ZnO seed layer. The variety of preparation conditions such as zinc acetate dihydrate (ZAD) as the zinc precursor, the solvent, the stabilizer and the substrate used in the sol–gel method makes it difficult to conclude on the important factors leading to highly oriented ZnO grains [22]. However, the role of solvent on the morphological properties of ZnO seed layer is undeniable. There are many studies reporting EtOH as solvent for synthesis of ZnO seed layers [21–23] while there are just a few reports on acetone usage as a solvent due to insolubility of zinc precursor in it [24]. Besides, in almost all of the studies on precursor sol, an additive (monoethanolamine, diethanolamine or triethanolamine) is used to stabilize ZnO particles. This is inconsistent with the concept named as "atom economy" in green chemistry philosophy [25]. Using acetone as a co-solvent in the sol–gel process for the seed layer preparation has not been extensively explored. Therefore, the present study has focused on optimizing the formation conditions of a sol free of amino additives by using acetone as a co-solvent which subsequently leads to optimized nanorods. PFM, as a novel standpoint to evaluate actuation [26], is applied here to evaluate the converse piezoelectric properties of the nanorods which accords to displacements of the ZnO surface by the interaction between the local electric field and this surface known as reverse piezoresponse. The next mission is to obtain an improved actuating response from simply achieved ZnO nanorods. In order to modify the converse piezoelectricity, we have treated the nanostructures with oxygen plasma to reduce the oxygen defects and increase the actuation response.

2. Experimental details

2.1. Formation of ZnO seed layer by sol–gel process

In the present approach, ZnO seed layer was deposited on glass substrate by a sol–gel method. To compare the effect of different amounts of acetone as a co-solvent, 0.054 g ZAD was dissolved in five various 50 ml solutions as the details are shown in Table 1. All of the solutions were heated at 80 °C for 3 h to yield stable and whitish particles. The resultant solutions were then spin coated (3000 rpm/30 s) on cleaned glass substrates. The spin-coating procedure was applied five times on the substrates to ensure a uniform coverage of seed layer. The films were then annealed at 380 °C for 30 min in air to obtain ZnO films.

2.2. Growth of ZnO nanorods

The second step was growing the ZnO nanorods on the as-prepared ZnO seed layers by the CBD technique. In this process, equimolar solutions of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and hexamethylenetetramine (HMTA, C₆H₁₂N₄) both 0.012 M were dissolved in 100 ml ethanol and deionized water with 1:1 ratio. Then five substrates with ZnO films were submerged upside down in similar growth solutions. The solutions were heated at 78 °C for 3 h which was 12 °C less than what was reported in the literature [19]. The substrates were then removed and washed with deionized water to eliminate any residual salt and later dried in air at room temperature.

2.3. Modification of reverse piezoresponse of the ZnO nanorods

In order to evaluate the actuation properties of the nanorods, they were grown on the Au-coated glass substrates since a conductive surface is needed through piezoelectricity measuring. To check the effect of filling the O₂ surface vacancies, the as-grown nanorods were treated with oxygen plasma at room temperature for 15 min. Then the substrates were placed under a PFM instrument to evaluate the converse piezoelectricity of the nanorods.
ZnO nanorods were subjected to oxygen plasma (200 sccm O2 flow with 250 W plasma power for 30 min) and the mechanical displacement due to the applied electrical field before and after the plasma treatment were measured.

2.4. Characterization

Fourier transform infrared spectroscopy (FTIR, SHIMADZU 8400S) measurements were employed to identify the sol components. Atomic force microscopy (AFM, SOLVER NEXT NT-MDT) was used both for seed layer monitoring and evaluating the actuation properties of the ZnO nanorods in PFM mode. The morphology of aligned ZnO nanorods was observed by field emission scanning electron microscopy (FESEM, HITACHI S-4160). The crystal structure of ZnO nanorods was analyzed by X-ray diffraction (XRD, PANanalytical XPERT PRO using Cu Kα radiation (λ = 0.15418 nm)). Photoluminescence (PL, Cary Eclipse fluorescence spectrophotometer with a He–Cd laser of wavelength 325 nm) measurements were employed to identify the effect of plasma treatment on the ZnO crystal recombination sites.

3. Results and discussion

3.1. FTIR analysis

Herein, acetone is used as a co-solvent to increase the stability of particles in the sol. This can be explained by its disability in dissolving ZAD and its derivatives. Furthermore, acetate groups as anions of the precursor salt play an important role in stabilizing the ZnO particles [23]. In fact, acetone and acetate groups with their lone pair electrons on oxygen atoms can act as nucleophiles, surround the Zn ions, and increase the sol stability by steric hindrance. In order to study this phenomenon, different amounts of acetone were added to the fresh solutions of ZAD and EtOH to obtain precursor sols as it was shown in Table 1. Gelation was then occurred on the glass substrates during the spin-coating process while all the sols were stable in the whole procedure (Fig. 1).

All the five sols were exposed to quality analysis by FTIR spectroscopy to choose the best sol to carry out the further experiments. Fig. 2 shows the FTIR spectra of the five sols. The peaks around 3000–3500 cm⁻¹, 1400–1560 cm⁻¹ and 1000 cm⁻¹ are attributed to O–H stretching, symmetric and asymmetric vibrations of COO⁻ and the long chain band, respectively. These peaks are somewhat the same in all the spectra since there are some amounts of ethanol, acetone and acetate ions in each one of them. As it can be seen, the spectrum related to 100% of acetone in the sol, shows no salient peak apart from the peaks related to carbonyl group. ZAD as a precursor scarcely dissolves in acetone and that is why acetone is not largely used for sol preparation [23]. For the other sols, the peaks at low frequencies around 430 cm⁻¹ which is our main focus, is related to Zn–O bond stretching [27]. The shift from 443 cm⁻¹ which is reported in the literature to 430 cm⁻¹ is due to the solvent screening effect on the surface which implies that the binding between carboxylic groups and Zn²⁺ surface is not as strong as in dry powder [28]. Explicitly, sol C shows the most intense spitting peak at around 430 cm⁻¹ which proves the most probability of presence of the Zn–O particles. Hence, sol C with the largest amount of particles was chosen to use its precipitation to study the particles molecular structure. To gain the dry precipitation, sol C was aged for 72 h and cooled down to room temperature. The FTIR spectra of sol’s C precipitation and pure ZAD as a precursor salt for
comparison are displayed in Fig. 3. As it can be seen, the peaks around 1554 and 1452 cm$^{-1}$ are attributed to the symmetric and asymmetric vibrations of COO$^-$ for both pure ZAD and the intermediate [22,29]. The shift from 1670 to 1820 cm$^{-1}$ as a free carboxylic group to 1554 and 1452 cm$^{-1}$ is due to oxygen binding to Zn$^{2+}$ as chelate that weakens the vibration frequency [28]. Furthermore the splitting value of the left and right bonds in chelated carboxylic group ($\Delta \nu = 102$ cm$^{-1}$) is close to the one expected for bridging acetate ligand [29]. The sharp peak at low frequency around 443 cm$^{-1}$ which makes the precipitation highly distinguishable from pure ZAD is related to Zn–O bond stretching [22,23,26]. The O–H stretching is evidenced by broad peak in the range of 3000–3500 cm$^{-1}$ which is attributed to two water molecules in a pure ZAD structure. However, this amount of water is enough for ZAD hydrolysis to zinc (hydroxo and/or oxo) acetate. This is the result of acetate groups chelating to Zn$^{2+}$ and confirms the broad O–H stretching bond observed [27,29].

In fact, small zincoxoacetate oligomers Zn$_n$O(CH$_3$COO)$_6$ as more stable species than ZAD are formed by acetate chelation and thermal hydrolysis [22,28,30,31]. In the suggested structure by Qu et al., ZAD possesses a central Zn atom, which is surrounded by four O atoms in two acetate (CH$_3$COO$^-$) groups perpendicular to each other to form an approximate tetrahedral coordination. The Zn$_4$O(CH$_3$COO)$_6$ complex possesses a central O atom, which is surrounded by four Zn atoms in a perfect tetrahedral coordination. The six edges of the Zn$_4$ tetrahedron are bridged by acetate groups. Therefore, the zincoxoacetate complex contains two non-equivalent kinds of O atoms. One in the center is fourfold coordinated and the other O atoms in the acetate bridges are only twofold coordinated [32]. The two slightly different peaks in the range of 400–500 cm$^{-1}$ of the two O atoms might have overlapped, however, the clearly distinct peak in 443 cm$^{-1}$ for the precipitation is more likely to attribute to the bond stretching of Zn and the four coordinated O atoms since the two coordinated O atoms are observed in the ZAD structure as well. Fig. 4 which represents the process of ZnO formation from the sol’s components is therefore suggested by considering the FTIR spectra.

### 3.3. Morphological characterization of ZnO nanorods

The top view of FESEM images of ZnO nanorods obtained from the seed layers A–E grew in EtOH and water are shown in Fig. 6. As it was expected, the distinct nanorods with average length of 1.3 μm grown on seed layer C are predominantly aligned perpendicularly to the glass substrate. As the SEM images shows, there are some places on the samples A, B, D and E that no ZnO seed layer was formed and no ZnO nanorods were grown subsequently. Fig. 6 illustrates a wider view of the sample C to show the uniformity of the coating across the substrate. This shows that seed layer quality plays an important role in growth and alignment of the nanorods since each ZnO atom synthesized in the solution, grows reaction, but also helps to control the morphology and particle size of ZnO grains hence prepares the optimized seed layer for growing ZnO nanorods.

### 3.2. Surface morphology analysis

The AFM images (Fig. 5) illustrate ZnO grains after thermal annealing of 380 °C. Annealing in the air results in the final ZnO seed layer. Contact mode was used to identify the surface morphology of the seed layers. As it is displayed, compact, uniform and well-aligned ZnO grains have been achieved from sol C. Average length, diameter and aspect ratio of ZnO grains of the five samples are shown in Table 2. Sol C with 1:1 ratio of EtOH and acetone led to the highest aspect ratio of ZnO grains on the seed layer. Accordingly, it can be assumed that EtOH and acetone with 1:1 ratio as solvent not only does provide the medium for the
heterogeneously on a ZnO grain of the seed layer. In fact, ZnO atoms, synthesized in the solution by reacting Zn$^{2+}$ with HMTA, interact with the ZnO grains of the seed layer. HMTA plays a crucial role in producing the OH/C0 and at the same time chelating the Zn$^{2+}$ ions so that the Zn(OH)$_2$ precipitants are not formed. It is actually a weak and nonpolar base that not only does control the reaction kinetically but also hinders the growth of nonpolar surfaces of ZnO by coordinating to them [14].

The aspect ratio of ZnO nanorods is largely directed by the polarity and saturated vapor pressure of the solvent. High polarity solvent molecules have stronger interactions with polar surfaces of ZnO and thus hinder the precursor molecules from adsorbing on to the polar surfaces [11,33]. Replacement of pure H$_2$O by mixture of EtOH and H$_2$O not only decreases the polarity of solvent but also lowers the boiling point resulting in relatively low temperature required for ZnO nanorod growth [34].

### 3.4. Structural characterization of ZnO nanorods

The crystal structures of the nanorods grown on the seed layer C, was analyzed by the X-ray diffraction (XRD) (Fig. 7). It is readily seen that ZnO nanorods show strong peak corresponding to the ZnO (002) planes. This shows that the ZnO nanorods are preferentially oriented along the c-axis and they also have the hexagonal wurtzite structure according to ASTM card 36–1451.

### 3.5. Photoluminescence properties of ZnO nanorods

The PL spectra of the ZnO nanorods before (dashed-blue line spectrum) and after (solid-red line spectrum) the oxygen plasma treatment is shown in Fig. 8. Mainly, ZnO nanorods luminescence spectrum consists of an excitonic ultraviolet (UV) emission around 380 nm which is attributed to its well-known free excitonic emission from the wide band gap of ZnO nanostructures and the deep level arc-shaped emission which is mostly due to the transitions between available energy states (defect) on the surfaces which are located within the band gap. These surface energy states are mostly located from 500 nm to 650 nm due to the oxygen vacancies [35].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Length (nm)</th>
<th>Diameter (nm)</th>
<th>Aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>14</td>
<td>396</td>
<td>0.03</td>
</tr>
<tr>
<td>B</td>
<td>32</td>
<td>305.98</td>
<td>0.10</td>
</tr>
<tr>
<td>C</td>
<td>33.8</td>
<td>158.28</td>
<td>0.21</td>
</tr>
<tr>
<td>D</td>
<td>28</td>
<td>585.94</td>
<td>0.04</td>
</tr>
<tr>
<td>E</td>
<td>40</td>
<td>1500</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 2

Average length, diameter and aspect ratio of ZnO grains of the five samples.

Fig. 6. Top view FESEM image of the ZnO nanorods.
Both spectrums show an intense peak in 373 nm which attributes to the band gap direct recombination of the carriers. The exposure of the nanorods to oxygen plasma reduces these defects by filling the O₂ vacancies on the surfaces [36] in which in turn will improve the nanorod’s actuation response. As the solid-line spectrum shows the defects due to the oxygen vacancies are significantly diminished after plasma treatment. So, it can be concluded that the parameters used for plasma treatment were good enough to continue for reverse piezoresponse measurement.

3.6. Reverse piezoresponse evaluation of the nanorods

Piezoresponse Force Microscopy (PFM) with a Pt-coated tip was employed to measure the converse (reverse) piezoelectric response of the ZnO nanorods before and after the plasma treatment. The effect of oxygen plasma can be explained by the fact that ZnO nanorods are n-type due to the huge number of oxygen vacancies. These free electrons screen the positive piezoelectric charges and reduce the piezoelectric properties [37]. By exposing the nanorods to the oxygen plasma, oxygen atoms will fill the vacancies on the surface leading to an almost defect free ZnO structure which subsequently decreases the free electrons and enhances both the mechanical signal and electrical dipoles.

The ZnO unit cell has a Zn²⁺ cation situated inside a tetrahedral cage formed by O²⁻ anions. Under non-stress conditions, the positive and negative centers of mass coincide with each other in a way that there is no average dipole moment. When the crystal is subjected to a mechanical force, however, the positive and negative centers of mass become displaced with respect to each other, leading to an electrical dipole [11]. Therefore, when the material’s dimensions change as a result of an imposed mechanical force this will produce an electric field. This phenomenon is known as the piezoelectric effect. However, when an electric field is applied across a piezo-material, the dipoles will align themselves with the electric field, resulting in induced dipoles within the whole crystal structure. This alignment of dipoles (molecules) will cause the material to change its dimensions. This phenomenon is known as converse (reverse) piezoelectric. This occurs in PFM through subsequent analysis of displacements of the ZnO surface by the interaction between the local electric field and this surface. Changes in the ZnO geometry depend on the magnitude and mutual orientation of the electric field and the ZnO’s polarization vector. In this measurement, a bias voltage is applied to the Pt-coated tip. This induces a local electric field under the probe. As ZnO nanorods have different domain structure, applying similar local electric field to different areas of the surface yields different results. Therefore, in this experiment we can measure the magnitude of surface oscillations, the magnitude of the cantilever normal deflection and the oscillation phase for different domains. In the case of horizontally oriented domains, surface displacements will be lateral with respect to the surface rather than normal. In this measurement, the applied magnitude of normal oscillations of the cantilever is set to zero. However, due to friction between the tip and the ZnO surface according to the reverse piezoresponse of the nanorods, some displacement of the tip will occur and, also, its orientation to the surface will be changing. Therefore, piezoresponse force microscopy yields both surface topography images and distributions of amplitudes of lateral and normal oscillations.

In the present study, an electric field is applied vertically to the ZnO nanorods and the vertical dimension variations are measured as the outputs (Fig. 9). As it shows, the mechanical displacement is much more intense after the plasma treatment. The curves in this figure illustrate a considerable increase in the non-zero displacement counts. The dipole moment at each point of the array is also significantly increased after subjecting the nanorods to oxygen plasma according to (Fig. 10). In this figure, dipole moments of 180° and 0° refer to the normal dipoles to the surface in which dipoles in 180° have the ideal angle for reverse piezoelectricity. Thus, applying O₂ plasma does not only increase the magnitude of the oscillations but also increases the non-lateral dipoles. Information from PFM is summarized in Table 3 where AP and BP are referring to after plasma and before plasma, respectively. It is worth mentioning here that plasma treatment did not have a remarkable
This information makes it possible to study the domain structure of the transitional zinc (hydroxo and/or oxo) acetate complex. The binary solvent system provides an appropriate condition to form thin nanowire-layered basic zinc acetate/ZnO nanoparticle composite film. Cryst. Growth Des. 8 (2008) 283–290, http://dx.doi.org/10.1021/cg070461x.


