BaTiO₃ Based Nanostructures for Humidity Sensing Applications [†]

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Abstract: Our contribution focuses on humidity gas-sensing device formation of metal oxide materials such as BaTiO₃ nanorods and TiO₂-BaTiO₃ nanotubes. Processing of humidity sensors based on BaTiO₃ nanostructured materials, that can operate under severe environmental conditions is of great relevance due to their small size and small weight. As a result, these sensors possess high stability, fast response times and reproducibility. Furthermore, gas sensor properties are not only interesting in terms of device applications, but also pave the way to study in deep ionic and electronic conduction mechanisms in individual nano-based devices.

Keywords: metal oxide nanostructures; BaTiO₃ nanorods; TiO₂-BaTiO₃ nanotubes; electron microscopy; humidity sensors

1. Introduction

Complex metal oxide nanomaterials with perovskite structure in the form of ATiO₃ have unique properties with potential device functionalities. This is why much attention is being paid to integrate them in scalable circuit architectures [1,2]. Among them, BaTiO₃ possesses a variety of attractive characteristics, such as ferroelectricity, piezoelectricity and even semiconductor behaviour, when it is in a reduced state or when doped with aliovalent dopants. Therefore, BaTiO₃ is considered as a versatile functional material suitable for a wide range of technological applications [3–7].

Working into the direction of nanodevices based on this material, one-dimensional BaTiO₃ nanostructures with high surface-to-volume ratio in the form of nanorods and/or nanotubes were studied in the past; showing promising applications as building-blocks of, for instance, energy-harvester systems and sensors [5–8]. Nevertheless, the complete control of their synthesis and device integration still remains as a challenging issue. In this work, we report on the synthesis and structural characterization of BaTiO₃ nanorods and vertically aligned TiO₂-BaTiO₃ nanotubes. Following the prototyping of functional devices based on BaTiO₃ nanostructures and the assessment of their electrical performances.

2. Materials and Methods

Two electrochemical processing principles were used for the formation of nanostructures. Namely, sol-gel electrophoretic deposition technique was used for synthesis of BaTiO₃ nanorods [9] and electrochemical anodization technique followed by hydrothermal treatment was used for synthesis of TiO₂-BaTiO₃ nanotubes [7]. In the first case the stoichiometric BaTiO₃ sol was deposited

into the commercially available anodic alumina template (AAO) with the pore diameter of approximately 200 nm. For the electrophoretic deposition the potential of 30 V was applied between the AAO/Al working electrode and platinum counter electrode. After the deposition samples were annealed at 700 °C for 1 h with subsequent AAO template removal in 6M NaOH solution. In the second case, the anodic oxidation on Ti foil was conducted in order to obtain TiO₂ nanotubes followed by hydrothermal treatment in Ba(OH)₂ water solution to obtain TiO₂-BaTiO₃ nanotubes. Again, after synthesis steps the samples were annealed at 700 °C for 1 h to obtain crystalline material and to remove hydroxyl ions.

The crystal structure of resulting BaTiO₃ based nanostructures was determined using X-ray powder diffraction and Raman spectroscopy. The morphology, crystallinity and chemical composition were characterized by electron microscopy techniques (scanning and transmission electron microscopy).

To study electrical properties, devices were fabricated by focused ion beam (FIB) nanolithography techniques [8,10] or by sputtering [7]. In the case of integration of individual BaTiO₃ nanorod into the device, the BaTiO₃ nanorods were deposited onto the pre-patterned micro electrodes (Ti/Ni/Au micro electrodes on SiO₂/Si substrate) and four Pt-contacts were deposited between single BaTiO₃ nanorod and electrodes by FIB nanolithography. On the other hand, vertically aligned TiO₂-BaTiO₃ nanotubes, were integrated by simple sputtering of Pt contact on the top of tubes and as second contact Ti foil (which is the substrate for anodization of titania) was used. Finally, the integration of BaTiO₃ based nanostructures into simple and complex circuit devices allowed measurements of their electrical properties and responses under different environmental conditions.

3. Results and Discussion

BaTiO₃ nanorods were collected after sol-gel electrophoretic deposition into AAO template and subsequent annealing and template removal. The obtained BaTiO₃ nanorods had diameters ranging from 150 to 200 nm, with an average length of 10–25 µm. The BaTiO₃ nanorods were always polycrystalline and composed of well-crystallized nanosized BaTiO₃ grains with a pseudo-cubic structure and grain sizes ranging from 20 to 50 nm (Figure 1a). A high-temperature hexagonal BaTiO₃ polymorph, that was observed as intergrowth of more or less ordered sequences of (111) twins with the perovskite matrix, was present as a minor phase (Figure 1b). Its formation was most probably triggered by reduction of Ti⁴⁺ to Ti³⁺ as a consequence of the local reducing environment, due to the decomposition of the organic precursors during the annealing process.

Figure 1. (a) Bright-field TEM image of a uniformly shaped and polycrystalline BaTiO₃ nanorod. The inset in the upper right corner shows a higher-magnification bright-field TEM image of polycrystalline BaTiO₃ nanorod with grain sizes in the range from 20 to 50 nm. (b) HRTEM image of slabs of hexagonal BaTiO₃ polymorph intergrown with cubic BaTiO₃ as seen in the (1 – 10) zone axis. The inset presents the SAED corresponding to the hexagonal polymorph.

The vertically aligned TiO₂-BaTiO₃ nanotubes were obtained after anodic oxidation and subsequent hydrothermal treatment. The anatase TiO₂ nanotubes were during hydrothermal treatment partially transformed to TiO₂-BaTiO₃ nanotubes. As a consequence, vertically aligned, polycrystalline heterostructures were formed (Figure 2). The crystal structure was observed to be

pseudo-cubic. The diameter and length of $\text{TiO}_2\text{-BaTiO}_3$ nanotubes was similar to pure BaTiO_3 nanorods.

Figure 2. SEM images of a vertically aligned and uniformly shaped $\text{TiO}_2\text{-BaTiO}_3$ nanotubes. (a) Side view and (b) top view of $\text{TiO}_2\text{-BaTiO}_3$ nanotubes.

For the electrical characterization the prototype devices were formed by integration of individual BaTiO_3 nanorod using FIB nanolithography (Figure 3a) or integration of vertically aligned $\text{TiO}_2\text{-BaTiO}_3$ nanotubes into simple circuit architecture, as explained in section 2. In first case, four-probe electrical measurements performed on individual BaTiO_3 nanorods revealed the resistivity values between 10 and 100 $\text{ohm}\cdot\text{cm}$, which corresponds to typical values for oxygen-deficient BaTiO_3 .

The feasibility of prototyping functional devices based on individual BaTiO_3 nanorods was successfully evaluated; some of them were tested at room temperature as proof-of-concept humidity sensors, showing reproducible and scalable responses towards different moisture concentrations (Figure 3b), good long-term stability and fast response times. A sharp reduction of R was found in water-rich atmosphere due to the contribution of the dominant charge carrier (H^+) that is present in high moisture environments. According to the literature [11], ionic conduction mechanisms rules the water sensing mechanisms in ceramics materials like BaTiO_3 , after a two-stage interaction mechanism of water molecules with the ceramic surface that involves chemisorption and physisorption. While the first stage leads to the ionization of water vapour into hydroxyl groups (OH^-) and protons (H^+), the second one forms a bulk-liquid water layer on the top of the BaTiO_3 nanowires and chemisorbed species, with the key contribution of hydronium ions to the ionic conduction of the device. As regards stability, the sequence shown in Figure 3b was repeated on a weekly basis during a whole month displaying minor variations of the signal. The baseline resistance values of the sensors drifted less than 15% and the sensor response (relative variation of the resistance in presence of gases) was less than 5%, in the worst cases. Therefore, these sensor properties are not only interesting in terms of device applications, but also pave the way to study in deep ionic and electronic conduction mechanisms in individual nanorod-based devices.

Figure 3. (a) Detail of a BaTiO_3 nanorod contacted with FIB nanolithography in 4-probe configuration. The inset in the upper left corner shows low-magnification image of the same device. The platinum strips deposited with FIB are clearly shown. (b) Sensing response of individual BaTiO_3 nanorod towards pulses of 100, 50 and 25% of relative humidity (RH) measured at room temperature. Synthetic air was used herein as carrier gas. The inset shows I-V curves obtained in dry and humid (100% RH) air. A sharp and reversible modulation of the electrical response was observed.

Since integration and measurements of single BaTiO₃ nanorods presents a complex and time consuming component, two terminal resistivity sensor based on TiO₂-BaTiO₃ nanotubes was introduced and tested. The resistivity measurements at wide range of relative humidity (RH) were performed and compared to results collected on individual BaTiO₃ nanorods. The samples were tested at the RH from 15% to 95% at room temperature.

4. Conclusions

In summary, individual BaTiO₃ nanorods and vertically aligned TiO₂-BaTiO₃ nanotubes were synthesized. By investigation with electron-microscopy techniques it was found that both types of nanostructures were dense and polycrystalline in nature with diameters from 100 to 250 nm and with lengths ranging from a few micrometres up to a few tens of micrometres. The polycrystalline nanorods were composed of well-crystallised nanosized grains with a cubic structure and with grain sizes ranging from 20 to 50 nm. For the electrical characterization the prototype devices were formed by integration of individual BaTiO₃ nanorod or vertically aligned TiO₂-BaTiO₃ nanotubes into simple circuit architecture. Two- and four-probe electrical DC measurements were performed. Furthermore, BaTiO₃ nanorods were tested as proof-of-concept humidity sensors showing a large and reversible response towards different water concentrations. Therefore, BaTiO₃ nanorod and TiO₂-BaTiO₃ nanotubes devices could be used as humidity sensors in the future.

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