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Branch-like NiO/ZnO heterostructures for VOC sensing

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ABSTRACT

We report for the first time on the synthesis of NiO/ZnO one-dimensional (1D) nanowire (NW) based heterostructures by applying a suitable methodology of transport and condensation. The synthesis involves, firstly the growth of NiO NWs on gold (Au) catalyzed alumina substrates using the vapor-liquid-solid (VLS) mechanism and then the formation of ZnO NWs directly on the NiO NWs using the vapor-solid (VS) mechanism. Sequential evaporation–condensation over Au-seeded alumina promotes the formation of NiO NWs, driven by the VLS growth mechanism. These NiO NWs act as backbones for the condensation of epitaxial ZnO nanostructures. The detailed morphological study of these heterostructures reveals that ZnO nanowires completely cover the whole NiO nanowires completely and growing out in the form of flat leaves from the NiO nanowire branches. The diameters of the NiO NWs have been found to vary from 15 nm to 60 nm. Selected area electron diffraction data (SAED) indicate an epitaxial growth of ZnO nanowires along (101)-planes on the strongly oriented NiO nanowires along (200) crystallographic planes. Finally, NiO NW and NiO/ZnO heterostructure based conductometric gas sensing devices have been fabricated and the comparison between their sensing performances have been compared. Interestingly, NiO/ZnO NWs heterostructure based sensing devices shows superior performance compared to NiO sensors toward volatile organic compounds (VOC).

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1. Introduction

Nowadays researchers are strongly focusing on the growth of different metal oxides in the form of nanostructures such as nanowires, nanorods etc. [1]. These materials have captured much attention due to their remarkable physical/chemical properties, thanks to their large surface to volume ratio and high degree of crystallinity [2]. In particular, one–dimensional (1D) metal oxides nanostructures have been attracting much interest in the field of gas sensors because they have exceptional electrical, chemical and physical properties [3]. N-type semiconductor metal oxide such as ZnO [4] have a wide band gap (3.22 eV), high chemical and thermal stability, are non-toxic, highly abundant in nature and can be grown easily into different morphologies. Due their wide band gap, electronic/optoelectronic devices based on ZnO show important features such as low electronic noise, ability to maintain high breakdown voltages and ability to run at high power [5,6].

On the other hand, in recent years p-type metal oxides have also been investigated in many applications like gas sensors, electrochemical capacitors etc. [7,8]. Among these, Nickel oxide (NiO) has a cubic rock salt structure and exhibits a wide band-gap ranging from 3.4 eV to 4.0 eV depending on the crystallinity and preparation method [9]. It has excellent chemical stability as well as good optical, electrical and magnetic properties. In the form of nanostructures, NiO can be used in different areas such as alkaline batteries [10], smart windows [11] and recently, it proved to be a promising functional material for applications in resistive-type gas sensors [12,13].

As a special branch of 1D nanostructures, heterostructured nanomaterials exhibit strong interactions between closely packed interfaces and their performances are considered superior and complex [14,15]. The fabrication of composite nanostructures based on a combination of p-type and n-type semiconducting metal oxides offers an important path to combine the different properties of the individual components into one single system [16]. In particular, there are many factors which can be attributed to the improvement of sensing performance by these heterostructured devices such as: charge carrier separation [17], band bending due

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to Fermi level equilibration [18,19], grain refinement [20], surface enhancement [21] and increased gas accessibility [22].

In these directions, Si et al. [23] prepared Fe_2O_3/ZnO heterostructured nanorods by a hydrolysis method for ethanol gas sensing. In 2003, Hiromichi Ohta et al. [24] reported the preparation of transparent NiO/ZnO composites. The authors successfully prepared transparent NiO/ZnO heterostructures with good rectifying properties by using pulsed laser deposition (PLD) and a solid-phase epitaxial growth technique. Moreover in the field of gas sensing, in 2013, Liu et al. [25] reported the growth of NiO/ZnO heterostructures by chemical bath deposition (CBD) for gas sensing and photocatalysis applications. Compared to all these methods, the vapor phase growth technique offers lower cost, simplicity and higher yield. For the growth of 1-D nanostructures two different mechanisms, namely, Vapor-liquid-solid (VLS) and Vapor-solid (VS) has been widely used. Both mechanisms shares advantages such as, no requirement of precursors, highly crystalline growth and direct growth on active substrates [26].

The VLS and VS growth mechanisms mainly differ in the way which the source material condensates on the substrates. In vapor-liquid-solid (VLS) growth, the nanowire growth involves three different phases: the vapor phase of the source material, the liquid catalyst droplet and the solid crystalline nanostructures. There, the catalyst forms nucleation sites for the growth of the nanowires [26]. In the VS (Vapor-solid) growth process instead, nanostructures the crystallization of the nanostructures take place by the direct condensation of the vapor phase without any involvement of the catalyst [27].

In this work, we are presenting the fabrication and characterization of the epitaxial growth of NiO/ZnO heterostructures using VLS-VS growth mechanisms on alumina substrates. To the best of our knowledge, this is the first time that the vapor-phase technique has been employed to grow these nanowire-based NiO/ZnO heterostructures. The morphological, elemental analysis and crystalline properties of these heterostructures were investigated by using scanning electron microscopy (SEM), Energy Dispersive X-ray (EDX), grazing incident X-ray diffraction (GI-XRD) and Raman Spectroscopy. For the detailed investigation of the epitaxial growth, transmission electron microscopy (TEM) has been employed. Lastly, conductometric NiO/ZnO heterostructure-based sensing devices were prepared, and their performance towards specific chemical species were investigated.

2. Experimental

2.1. Substrate preparation

Alumina substrates (3 mm × 3 mm 99% purity, Kyocera, Japan) were ultrasonically cleaned in acetone for 15 min and dried with synthetic air. In this work, gold (Au) was used as a catalyst for the deposition of NiO nanowires. The deposition of an ultrathin layer of catalyst on the alumina substrates was performed using RF magnetron sputtering (Kenotec Sputtering system, Italy). The deposition of Au particles on alumina substrates was performed at 7SCCM Ar flow, for 5 s using an electrical power of 70 W at a pressure of 5×10^{-3} mbar. On the other hand, for the deposition of ZnO nanowires on NiO nanowires, no metal catalyst was used.

2.2. Growth of NiO nanowires

NiO nanowires were synthesized on Au-catalyzed alumina substrates using the VLS mechanism in an alumina tubular furnace (custom design based on a commercial Lenton furnace). NiO powder (Sigma-Aldrich 99% purity) was used as a source material. Alumina crucibles containing NiO powder and Au-catalyzed substrates were placed inside the tubular furnace. The powder was placed at higher temperature and heated up to the required temperature to induce evaporation. Substrates were placed in colder regions to promote the condensation of evaporated material. The pressure inside the alumina tube was kept at 1 mbar. The growth of NiO nanowires was carried out using an evaporation temperature of 1400 °C, while keeping the substrates at 930 °C. During the evaporation, the carrier gas flow (argon) was set at 100SCCM. [12] The deposition time was set for 15 min.

2.3. Growth of NiO/ZnO NW based heterostructures

To fabricate the NiO/ZnO heterostructures, ZnO nanowires were grown onto the NiO nanowires using the VS technique without any catalyst. To induce evaporation, ZnO source powder was heated to 1200 °C while substrates with NiO nanowires were placed at a lower substrate temperature of 380 °C. During the deposition process, the argon flow was set to 100SCCM and the pressure was kept at 10 mbar during the deposition time of 5 min.

2.4. Characterizations

The surface morphology of NiO nanowires and NiO/ZnO heterostructures has been examined using field emission SEM (Leo 1525 Gemini) operated at 3–5 kV. The elemental compositional analysis was examined with an EDX INCA microanalysis system (Oxford Instruments, UK). The EDX spectrum was recorded in the energy range extending from 0 to 10 keV.

The crystalline properties of NiO/ZnO heterostructures were investigated by the GI-XRD technique (Empyrean diffractometer, PANalytical, Netherlands). The GI-XRD analysis was performed in the glancing angle mode, with 1.5° incident angle using Cu-LFF (λ = 1.5406A°) operated at 40 kV and 40 mA in the diffraction angle range of 5–90°.

Raman spectra of NiO/ZnO heterostructures, NiO nanowires, ZnO nanowires and alumina substrate were measured using a HORIBA monochromator iHR320 configured at room temperature with a grating of 1800 g mm^{-1}, coupled to a Peltier-cooled Synapse CCD. A He-Cd laser (442 nm) was focused on the sample by a fiber coupled optical microscope (HORIBA) at 100× magnification. Spectra were recorded in the wavelength of 200–1500 cm^{-1} wavelength range.

A detailed microscopic structural investigation of NiO/ZnO heterostructures was carried out using a JEOL JEM ARM 200F analytical transmission electron microscope (TEM). The microscope was operated a 200 kV in TEM mode.

2.5. Gas sensor device fabrication

For the conductometric gas sensing measurements, a set of NiO/ZnO heterostructure devices was fabricated by DC magnetron sputtering. The complete fabrication process involves a number of steps as depicted in Fig. 1. The first step is the deposition of a 50 nm titanium tungsten alloy (TiW) adhesion layer (70W argon plasma, 300 °C, and pressure (5.3×10^{-3} mbar)) on one side of the NiO nanowire sample, followed by a 1 μm platinum contact using the same deposition conditions to form an electrical contact to the p-type NiO nanowires.

After the deposition of ZnO nanowires on top of the NiO nanowires, the same process of contact deposition was repeated on the other side of the sample (top of ZnO NWs) to form contacts to the n-type side of the NiO/ZnO heterostructures. On the backside of the alumina substrates a heating element was deposited, to study sensor's behavior at different working temperatures. Prepared devices were finally mounted on TO packages using electro-soldered gold wires.

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