Fabrication of heterostructured M@M´Ox Nanorods by low temperature PECVD

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Abstract

In this communication we report on the fabrication of two different heterostructured core@shell 1D materials by low temperature (135 ^{o}C) plasma enhanced chemical deposition: Ag@TiO$_2$ and Ag-NPs@ZnO nanorods (NRs). The controlled formation of these heterostructures on processable substrates such as Si wafers, fused silica and ITO is demonstrated. The NRs are studied by SEM, HAADF-STEM, TEM, XRD and in situ XPS in order to fully describe their microstructure and inner structure, eventually proposing a growth mechanism. The first type of nanostructures consists on a silver wire surrounded by a TiO$_2$ shell that grows following the volcano-like mechanism. The Ag-NPs@ZnO nanostructures are formed by supported ZnO nanorods decorated with Ag nanoparticles (NPs). The 3D reconstruction by HAADF-STEM electron tomography reveals that the Ag NPs are distributed along the hollow interior of highly porous ZnO NRs. The aligned Ag-NPs@ZnO-NRs grow by a combination of different factors including geometrical distribution of precursor, plasma sheath and differences in the silver/silver oxide densities. Tuning the deposition angle, Ag-NPs@ZnO-NRs depicting different tilting angles can be homogeneously grown allowing the formation of zig-zag nanostructures. The as prepared surfaces are superhydrophobic with water contact angles higher than 150º. These surfaces turn into superhydrophilic with water contact angles lower than 10º after irradiation under UV light. In the case of the AgNPs@ZnO NRs such modification can be also provoked by irradiation with VIS light. The evolution rate of the wetting angle and its dependence on the light characteristics are related with the nanostructure and the presence of silver embedded within the NRs.

Introduction

The growing interest in nanostructured and porous thin films and in supported 1D nanostructures such as nanowires (NWs), nanofibres (NFs), nanoribbons, nanorods (NRs), etc, has fostered the development of new procedures of surface and thin film tailored fabrication. Wet chemical and electrochemical routes [13], vapour phase condensation methods (e.g. vapour–liquid–solid (VLS) methods) [2], solution-phase methods [3], template-directed synthesis [4] or physical vapour deposition approaches [5] are currently used for the synthesis of these types of nanostructured materials.

Plasma deposition and, in general, plasma processing have also been successfully used for the surface nanostructuring of materials, either by etching [6] or, to a much lesser extent, by plasma-

[1] Yang P, Yan R and Fardy M 2010 Nano Lett. 10 1529

[2] Barth S, Hernandez-Ramirez F, Holmes J D and Romano-Rodriguez A 2010 Prog. Mater. Sci. 55 563

[3] Macak J M, Tsuchiya H, Ghicov A and Schmuki P 2005 Electrochem. Commun. 7 1133

[4] Wacaser B A, Dick K A, Johansson J, Borgstrom M T, Deppert K and Samuelson L 2009 Adv. Mater. 21 153

[5] Peng P, Milliron D J, Hughes S M, Johnson J C and Alivisatos A P 2005 Nano Lett. 5 1809

[6] Gogolides E, Constantoudis V, Kokkoris G, Kontziampasis D, Tsougeni K, Boulousis G, Vlachopoulou and Tserepi A 2011 J. Phys. D: Appl. Phys. 44 174021

[7] Borras A, Groening O, Koeble J and Groening P 2009 Adv. Mater. 21 4816

[8] Mieszawska A J, Jalilian R, Sumanasekera G U and Zamborini F P 2007 Small 3 722

[9] Rao C N R and Govindaraj A 2009 Adv. Mater. 21 4208

enhanced chemical vapour deposition (PECVD) of 1D nanostructures such as carbon nanotubes, oxide nanofibres (NFs) or nanorods [7, 8]. The main advantage of PECVD techniques in comparison with thermal CVD or other liquid-phase or chemical methods is that it operates at low temperatures and does not produce any substantial amount of waste materials.

Probably, the most typical example of plasma synthesis of 1D nanostructures is the formation of deposited carbon nanotubes (CNTs) [9, 10]. In this case, the formation of nanostructures does not occur at low temperatures and metal particles acting as seeds are needed to catalyze the nanotube growth by favoring the preferential arrangement and diffusion of the carbon species arriving at the surface from the plasma phase. Previously, we have shown that supported core@shell Ag@TiO_2 NFs form at low temperatures when titanium oxide is deposited by PECVD on silver metal foil previously treated with oxygen plasma [11, 12].

The outstanding properties of Ag/ZnO heterostructures have prompted us to fully develop a robust methodology for their fabrication on processable substrates, as well as to propose a model accounting for their growth by plasma deposition

Experimental

Silver deposited on fused silica and silicon wafers have been used as substrates. The silver was deposited by DC sputtering from a metal wire in Ar atmosphere, controlling the equivalent layer thickness (ELT).

These silver-covered substrates were placed in a plasma deposition chamber. The sample holder was heated by irradiation with quartz lamps up to a maximum temperature of 405 K. The plasma reactor used for deposition of ZnO consisted of a stainless steel chamber supplied with a microwave plasma source (SLAN, from Plasma Consult, GmbH, Germany) in a remote configuration. Details about this reactor can be found elsewhere [13]. For the deposition of ZnO, the reactor was supplied with oxygen (5 x 10^{-3} mbar) and excited with a microwave power of 400 W. Diethylzinc (ZnEt2), used as the precursor of zinc, was dosed directly into the deposition chamber from a stainless steel bottle that was heated at 308 K. Substrates and precursor dispenser were separated by a distance of 5 cm, much larger than the mean free path of the gas particles at the working pressure during our experiments. The plasma source fed with oxygen was located above the dispenser tube, while the pumping system was located at the bottom, thus defining a preferential top-down direction for the gas species in the chamber. As we will show below, this configuration is critical in the formation of tilted nanostructures.

Results

Characteristic SEM and STEM images of the Ag-NPs@ZnO nanorods are gathered in Figure 1.There it is show that the layer consists of a continuous set of separated and vertically aligned NRs supported on the silicon substrate, with typical surface densities of the order of 10^9 NRs cm^2 (Fig. 1b). A statistical analysis of the images renders a mean diameter of 40 nm and a height of 900 nm for the NRs, i.e., an aspect ratio of 20. Both the diameter and length of the NRs are controlled by the experimental parameters, particularly the deposition time. The number of NRs is determined by both the distribution of silver particles on the substrate and the precursor arrival rate to the surface.

The internal microstructure of the nanorods was determined by HAADF-STEM electron tomography [14].

[10] Sharma S C and Tewari A 2011 Phys. Plasmas 18 063503
[11] Borras A, Barranco A, Yubero F and Gonzalez-Elipe A R 2006 Nanotechnology 17 3518
[12] Borras A, Barranco A, Espinos J P, Cotrino J, Holgado J P and Gonzalez-Elipe A R 2007 Plasma Proc. Polym. 4 515
[13] Barranco A, Cotrino J, Yubero F, Espinos J P, Clerc C and Gonzalez-Elipe A R 2001 Thin Solid Films 401 150
[14] Macias-Montero M, Borras A, Saghi Z, Romero-Gomez P, Sanchez-Valencia J R, Gonzalez J C, Barranco A, Midgley P, Cotrino J and Gonzalez-Elipe A R 2012 J. Mater. Chem. 22 134
[15] Gonzalez-Garcia L, Gonzalez-Valls I, Lira-Cantu M and Barranco A 2011 Energy Environ. Sci. 4 3426
[16] X. Feng, L. Feng, M. Jin, J. Zhai, L. Jiang and D. Zhu, J. Am. Chem. Soc., 2004, 126, 62.

 A characteristic example of the internal microstructure of these NRs can be seen in figure 1(d) where it is appreciated a hollow structure with porous walls and an approximately 15 nm wide channel extending all along its length. It is also apparent that in the interior of this channel there are partially percolated silver nanoparticles of different sizes and shapes. Owing to this internal microstructure, we will consider these nanostructures as hollow nanorods rather than as compact nanofibres as was the case in our previous works on Ag@TiO$_2$ structures [11, 12]. GAXRD analysis of these NRs revealed that they consist of a crystalline wurtzite ZnO phase. Further HRTEM characterizations have demonstrated the preferential orientation of the ZnO along the (002) direction [14].
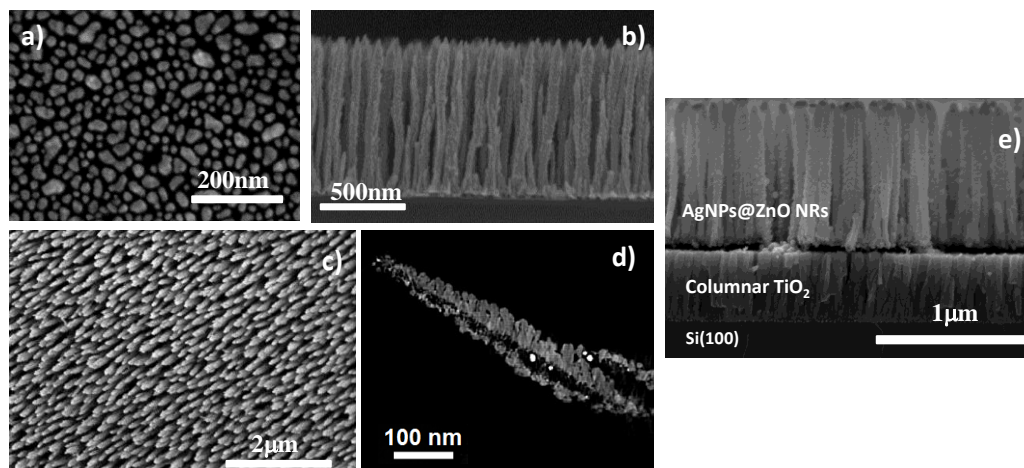
Figure 1. (a) SEM image of the silver oxide NPs developed after heating in O$_2$ at 135 ℃. (b) Cross-section and (c) norma SEM views at two different amplification scales of the Ag-NPs@ZnO nanorods obtained after deposition of ZnO at 135 ℃. (d) Vertical orthoslice through one of the formed Ag-NPs@ZnO nanorods after 3D reconstruction by HAADF-STEM. Bright spots along the inner channel of the rod correspond to the silver nanoparticles. (e) Cross-section SEM micrograph of the Ag-NPs@ZnO NRs grown on plasma made columnar TiO$_2$ previously coated with a silver layer.

This methodology is compatible with the fabrication of two-oxide heterostructured systems. Figure 1(e) shows an example of the formation of Ag-NPs@ZnO NRs on TiO$_2$ nanocolumns previously decorated with a silver coating. The method provides the formation of a high density and homogeneous NR layer similar to those presented in Figure 1(b-c) on the top of the mesoporous TiO$_2$ film. The fabrication of this type of heterostructured multilayers might be of special interest in applications such as microfluidics and nanosensing.

Formation of tilted nanocolumnar structures is a common feature of oxide thin films prepared by physical evaporation at glancing angle (GLAD) [15[3]]. This method is a line-of-sight procedure where shadowing is the main factor controlling the formation of the tilted nanocolumns. To control the orientation of the zinc oxide NRs with respect to the substrate, we have carried out a series of experiments by modifying the deposition geometry. Figure 2 shows three different cross-section micrographs corresponding to samples grown onto horizontal or 60° oriented substrates as indicated in the schemes. At first glance it is apparent that the deposition geometry is crucial for the orientation of the NRs and that, by its adjustment, it is possible to obtain zigzag or even more complex structures. Zigzag structures were obtained by performing a first deposition with the substrate at 60° and a second deposition with the substrate in a symmetrically mirrored orientation.

Previous works have demonstrated that ZnO-NR surfaces become superhydrophilic (i.e. WCA < 10°) under UV irradiation because the surface of this material becomes photon activated and the water may then smoothly spread over the whole internal surface of the wire structure [16]. A similar behavior is depicted by the system Ag-NPs@ZnO-NRs where the conversion from a

[17] V. Rico, C. Lopez, A. Borras, J. P. Espinos and A. R. Gonzalez-Elipe, Sol. Energy Mater. Sol. Cells, 2006, 90, 2944.

[18] W. Lu, S. Gao and J. Wang, J. Phys. Chem. C, 2008, 112, 16792 13 D. Lin, H. Wu, R. Zhang and W. Pan, Chem. Mater., 2009, 21, 3479

[20] R. Georgekutty, M. K. Seery and S. C. Pillai, J. Phys. Chem. C, 2008, 112, 13563.

[21] M. K. Seery, R. george, P. Floris and S. C. pillai, J. Photochem. Photobiol., A, 2007, 189, 258.

superhydrophobic to superhydrophilic state under UV illumination is completed after 8 min of irradiation. In agreement with ref. [16] and [17] the surface recovered its superhydrophobic character after keeping the samples in the dark. A similar superhydrophobic– superhydrophilic conversion was found when this surface was irradiated with visible light. The WCA decreases under the visible illumination until reaching a superhydrophilic state. Visible light activation of ZnO can be surprising since this material is a band gap semiconductor which requires UV photons (E = 3.2 eV) for excitation. However it is already established that the deposition of noble metals on semiconductors promotes an enhancement in their photocatalytic activity by indirect influence on the interfacial charge transfer process [18-21].
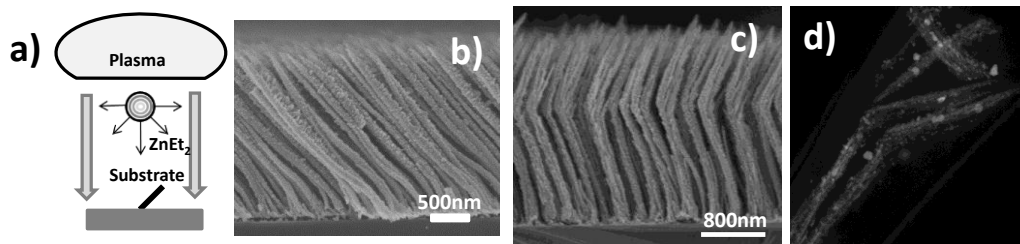
Figure 2. (a) Schematic showing the geometry of the ZnO deposition; (b) cross-section micrographs of Ag@ZnO NRs prepared by placing the substrates at the position and angle with respect to the sample holder indicated by the schematic in (a). The zigzag microstructure in (c) is obtained by first placing the substrates first in the position in (a) and then symmetrically. (d) HAADF-STEM micrograph of the zigzag NRs in (c) showing the distribution of silver nanoparticles along the microstructure.

Discussion

The scheme in Figure 3 shows a pictorial description of the nanorod formation under our experimental conditions. According to it (step i), some nuclei of the oxidized silver layer act as nucleation points of the NRs. Once these NR nuclei precursors have been formed, mobilization of silver or silver oxide in the interior of the NRs contributes to have a silver core within a NR which grows preferentially in length (step ii). The preferential linear growth of the NRs must be related with the presence of some small silver/silver oxide particles at the NR tip where, simultaneously, they react with the $ZnEt_2$ precursor and favor the confinement of the electrical field lines of the plasma sheath. As a result, sharp NR tips are produced and the hollow structure is preserved below the silver NP at the tip. After this initial nucleation, silver continues moving through the interior of the growing NRs until most silver has been removed from the substrate layer to decorate the ZnO phase (steps iii and iv). At this stage, the growth mechanism is no longer controlled by the silver located at the tip and different ZnO nanostructures can then be obtained.
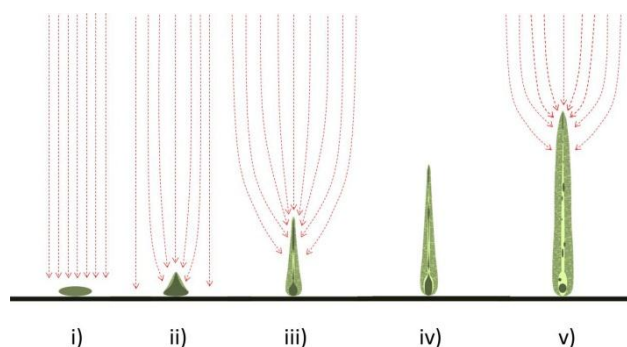
Figure 3. Model of the growth mechanism proposed for the formation of the Ag-NPs@ZnO NR. Grey features correspond to silver or silver oxide clusters, green to the ZnO and blue arrows to the electric field lines.