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Plasma Sheath Effects for the Formation of Supported 1D Nanostructures by Plasma Deposition

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The enormous effort carried out during the last decade in the controlled synthesis of 1D nanostructures has culminated in their outstanding performance in fields such as nanosensors, catalysis, photovoltaic, miniaturization of devices, microfluidic, lasers, etc. Within the different types of inorganic 1D nanostructures those formed by wide band gap oxide, specifically TiO_2 nanorods and nanofibers, are of especial interest because of their applications in solar cells and photocatalysis. Recently, we have developed an unprecedented methodology for the growth of core@shell Ag@TiO_2 at low temperature by a plasma deposition procedure.[1-3] These nanofibers are formed by a nanometer-size single-crystal silver thread surrounded by a TiO_2 shell. The experimental procedure provides the formation of a high density of Ag@TiO_2 nanofibers on silver substrates at temperatures ~ 130 ºC by remote plasma enhanced chemical vapor deposition of metal organic Ti precursor (Ti-tetraisopropoxide, TTIP) in an O_2 MW plasma. The growth mechanism leading to the formation of these nanofibres, that we have named volcano-type (see Figure), is a complex combination of factors being the most important: i) modification of the silver substrates by plasma oxidation, ii) release of the mechanical stress of the silver oxide substrates through the formation of 1D nanostructures, iii) reduction of the silver oxide in presence of partially fragmented TTIP precursor and deposition of the TiO_2 shell, iv) preferential growth of TiO_2 on metal nanoparticles driven by inhomogeneities of the plasma sheath and v) formation of 1D nanostructures directed by the focalization of the electric field lines in the plasma sheath. Although the determination of the factors that contribute to the growth of Ag@TiO_2 has been published previously,[2] the main objective of this communication is to present a thorough analysis of the role played by the inhomogeneities of the plasma sheath and focalization of the electric field in the formation such nanofibers. With this aim we have carried out a thorough characterization by optical emission spectroscopy (OES) and Langmuir probe of the plasmas used for deposition and studied the morphological modifications undergone by the silver at silver/Si substrates when exposed to O_2 plasma and/or subjected to heating treatments to form controlled-size silver nanoparticles. A preliminary theoretical study of the modifications of the electric field in the plasma sheath region because of the presence of metal nanoparticles supports the great importance of directionality effects in modifying the trajectory of particles and, therefore, in the formation of the nanofibers.

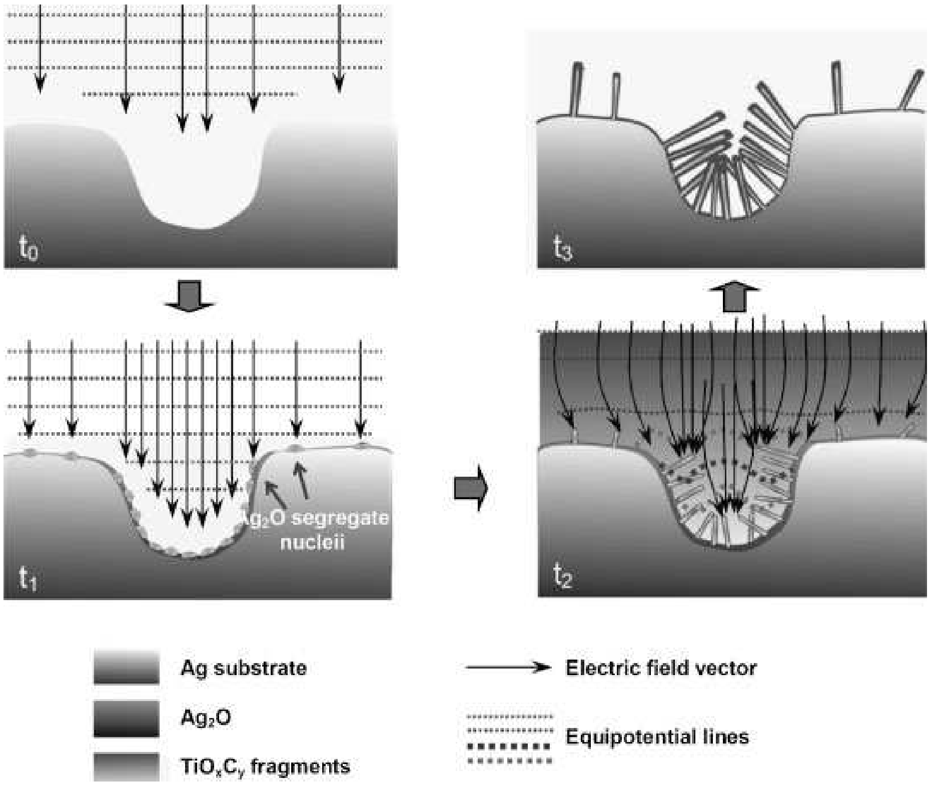

Fig. 1: Representation of the different stages of the 'volcano'-type mechanism of formation of the Ag@TiO_2 nanocomposite fibers and the possible effect of the inhomogeneities of the electrical field of the plasma sheath in their formation.

Reference

[1] A. Borras, A. Barranco, F. Yubero, A. R. González-Elipe 2006 *Nanotechnology* **17** 3518.
[2] A. Borras, A. Barranco, J. P. Espinos, J. Cotrino, J. P. Holgado, A. R. González-Elipe 2007 *Plasma Process. Polym.* **4** 515.
[3] A. Borras, A. Barranco, A. R. González-Elipe 2008 *Langmuir* **24** 8021.