Silicon Nanowire Forests for biosensing applications

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Nanomaterials, such as metallic or oxide nanoparticles, carbon nanotubes, graphene, and semiconductor nanowires, are emerging as new platform of highly performing sensors for label-free detection of biological species. High surface-to-volume ratios, comparable dimensions between sensing structures and target molecules, and surface tailorability make these materials excellent transducers (either electrical or optical), enabling to effectively and selectively detect different analytes also down to single molecule. Among all these nanomaterials, silicon nanowires (SiNWs) play a strategic role for the realization of the next sensor generation, because of their unique electrical properties, rapid response and full compatibility with the well-established silicon technology. Recently, ultrasensitive SiNW sensors based on field-effect transistors (FETs) have been demonstrated for the detection of ions [1], small molecules [2], proteins [3], DNA [4] and viruses [5]. The SiNW-FET consists of single or few SiNWs, prepared as single-crystal and doped structures, which are connected to source and drain electrodes by forming the active channel whose conductivity changes in response to variations in the electric field or potential at the surface caused by a molecular recognition. For effective devices, electrically addressable array of NW FETs should be developed. This requires a fine control of the fabricated structure and the use of sophisticated and complex technological processes, such as nanolithography techniques or the growth of these nanostructures on support substrates and their successive removing and positioning onto devices within ordered array. The drawbacks are the high cost and low throughput capability, scalability, reliability and reproducibility of the sensing devices. In this work, we propose to overcome all these limitations by investigating the biosensing potential of very dense, disordered and randomly oriented ensemble, i.e. forest, of SiNWs. These materials can be deposited by using very cheap and scalable techniques, such as Plasma Enhanced Vapor Deposition (PECVD), at low temperature (below 350°C) allowing the use of flexible substrates, such as polyimide films, metallic electrodes, steel foils and glasses as substrates. They are characterized by unique morphological and optical properties, very attractive for biosensing application. Indeed, they form a macroporous framework easily to functionalize and accessible by analyte molecules. In addition, NW forests provide strong light trapping effects due to multiple scattering events from each NW that the light undergoes passing through them. In this work, we show the potential of these properties in biosensing and the versatility of the NW forests in the sensor design. For this purpose, we fabricated electrochemical and plasmonic biosensors starting from SiNWs grown by PECVD. In particular, a forest of 1-2 μm long SiNWs, covered by an evaporated Au layer, formed the working electrode of the integrated electrochemical biosensor, shown in Figure 1; it was functionalized with biotin as binding receptor for avidin. Impedance measurements showed that NW forest can efficiently detect the avidin as evident in Figure 2. The plasmonic biosensor consisted of SiO_2 NWs, long tens of micron, obtained via thermal oxidation of Si NWs. The SiO_2 NWs were successively decorated with Au or Ag nanoparticles by dewetting evaporated metal films on the NWs (Figure 3). The potential as plasmonic sensor was demonstrated by monitoring their behavior as refractive-index sensors (Figure 4) [6], and after immobilization of BSA (Bovine Serum Albumin) by detecting the binding with Anti-BSA antibodies. In both the cases,very low detection limits were achieved.

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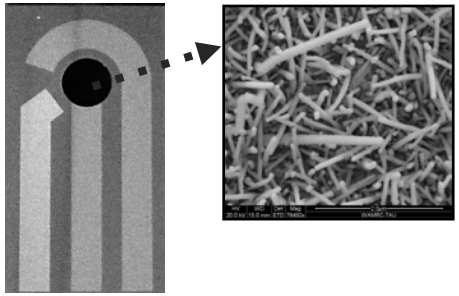

Figure 1. Electrochemical sensor with Au covered SiNWs as working electrode, a counter electrode made of gold and a reference electrode made of Ag

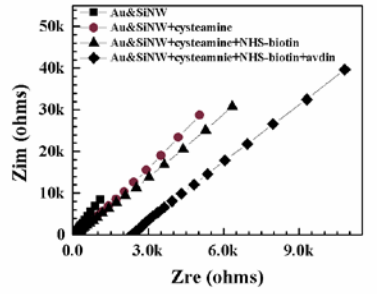

Figure 2. Nyquist plot of the electrochemical SiNW based sensor following modification with Cysteamine, Cysteamine+NHS-Biotin, and Cysteamine+NHS-Biotin+Avidin (1μM).

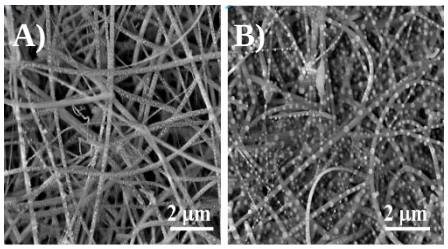

Figure 3. SEM images of SiO_2 NWs with Au NPs A) and Ag NPs B). Both samples were obtained with a metal coverage of 12 nm and an annealing temperature of 900 °C.

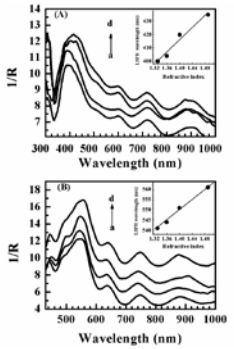

Figure 4. Inverse of the reflectivity (1/R) spectra of Ag-NP/SiO_2NWs A) and Au-NP/ SiO_2NWs B) immersed in solvents with different refractive indices (RIs) as follows:(a) methanol (n = 1.329), (b) acetone (n = 1.359), (c) tetrahydrofuran(n = 1.394), and (d) toluene (n = 1.496). In the insets there are the dependencies of the plasmonic wavelengths on the RIs.