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Metal Oxide Nanowires for Sensing and Advanced Applications

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Quasi one-dimensional (1D) semiconductor nanocrystals represent the forefront of today's solid state physics and technology and serve as the fundamental building blocks of highly integrated nanowires electronics and chemical sensors[1]. Bottom-up techniques, achieving quasi 1D nanocrystals by self-assembly growth mechanisms, have great potentials in terms of crystalline perfection, cost and high productivity. One of the most promising self-assembly method is the so-called evaporation-condensation vapour-solid (VS) and metal catalyst assisted vapour-liquid-solid (VLS) mechanism[2].

At SENSOR Lab. (*http//:sensor.ing.unibs.it*), we synthesize and characterise quasi monodimensional single crystals of Zn, Sn and In oxide nanobelts by thermal evaporation of oxide powders under controlled conditions and study their electrical and optical properties, see Figure 1**Error! Reference source not found.**, as bundles, vertically grown and single nanowire transistors. Functional applications selected are: sensor arrays for chemical sensing[3], dye based solar cells, electron source for X ray emitters, single nanowire transistors for biosensing. Other applications under study and development are: innovative electrodes for electrochemical biosensing, innovative electrodes for Li batteries, thermoelectric.

Recent achievements on synthesis and characterisation of nano sensors and devices based on quasi monodimensional single crystals of Zn, Sn and In oxide nanobelts will be reviewed.

Nanowires preparation :

Metal oxide nano-crystals have been prepared according to the recently proposed evaporation-condensation process, with Vapour-Solid (VS) and Vapour-Liquid-Solid (VLS) growth mechanism. Such a deposition technique consists of thermally-driven evaporation of bulk metal oxides followed by condensation.

The materials studied were In oxide, Sn oxide and Zn oxide. The experimental set-up for the oxide deposition consists of an alumina furnace capable to achieve as high temperatures as 1600 °C, in order to activate decomposition of the oxide and to promote evaporation. The controlled pressure of the inert atmosphere and the gradient of temperature within the furnace allow condensation and nucleation of the nanostructures downstream the gas flow. These peculiar thermodynamic conditions promote formation of nanosized 1-D structures. The pressure, the temperature gradient and the carrier flux have to be strictly controlled in order to guarantee the reproducibility of the deposition process. Catalyzed and catalyst-free growth was exploited.

Noble metal catalysts such as In, Pd, Pt and Au were deposited by sputtering on the substrate. The ability to control the size and dispersion of the catalyser is fundamental since it allows in turn the control of the size and dispersion of nanowires. Au nanoparticles dispersed in a colloidal solution (BBInternational) were also employed, granting uniform in size particles.

Depending on the substrate, nanowires can grow either randomly oriented, in case of polycrystalline substrate, or along preferential direction. In case of a-sapphire substrate, good matching exists between substrate lattice (lattice constant a=0,476 nm) and In_2O_3 lattice (a=1.01 nm), inducing alignment to the direction normal to the substrate surface (Figure 1).

Figure 2 reports SEM images of ZnO nanowires grown using different catalysts on alumina polycrystalline substrates, the growth is randomly oriented, nanowires are homogeneously distributed over the entire substrate, the nanowires length is of several microns and width ranging from 30nm to 200nm depending on the growth conditions.

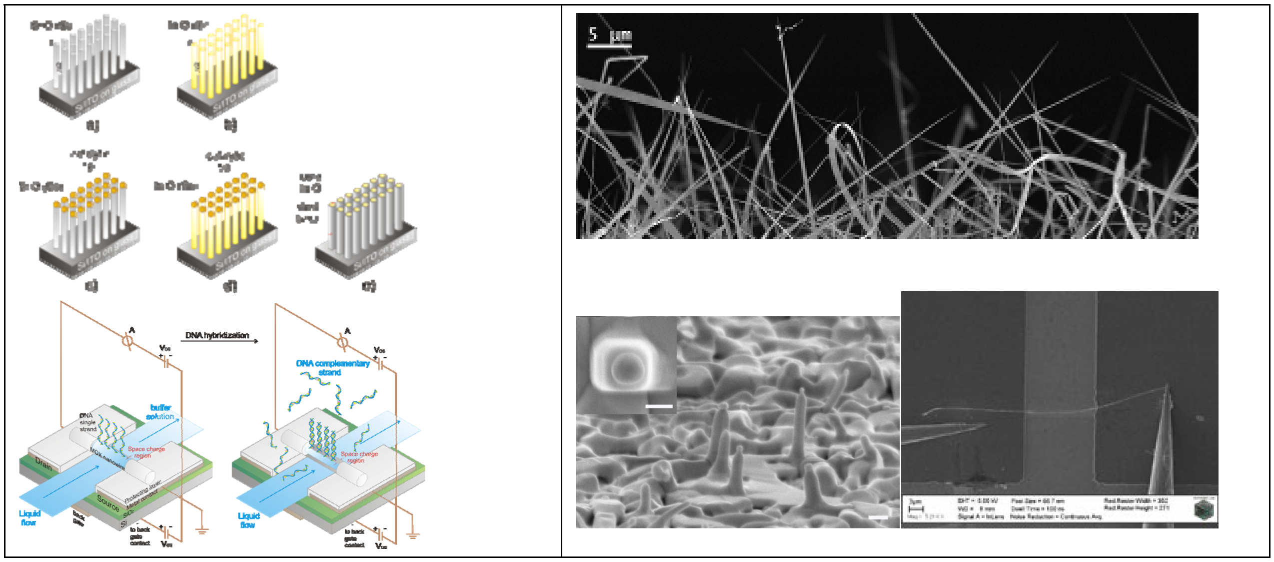

Figure (1) : Left up: Nanowire based structures aligned arrays of a) b), same structures via a growth catalyst c) and d), core-shell structure e). Left down: Single Nanowire Transistor for biosensing. Right up: SEM image of a bundle of nanowires. Right down: SEM image of In_2O_3 nanowires grown on sapphire incorporating the catalytic seed cluster (here Au) on top and of a single nanowire placed between two contacts by nanomanipulation.

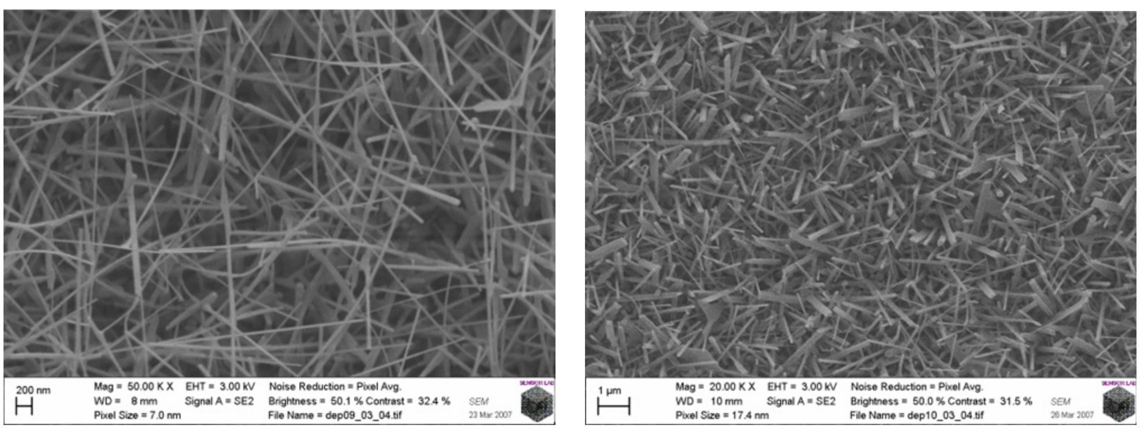

Figure (2) : Zinc oxide nanowires deposited with Pt (left) and Pd (right) catalyst at a deposition temperature of 320-340°C.

Sensor arrays for chemical sensing

Nanobelts of semiconducting oxide with a rectangular cross section in a ribbon-like morphology, are very promising for sensors due to the fact that the surface to volume ratio is very high, the oxide is single crystalline, the faces exposed to the gaseous environment are always the same and the size is likely to produce a complete depletion of carriers inside the belt, almost all of the adsorbed species are active in producing a surface depletion layer. A further reduction of belt size could envisage the development of quantum confined structures and nanodevices where single-electron charging effect and conductance quantization become important and can be exploited to develop mesoscopic chemical and biosensors.

The last decade has witnessed an increasing interest in the study and realization of Artificial Olfactory Systems, or Electronic Noses (EN), which can be useful in application domains like environmental monitoring and food processing control. ENs analyze gaseous mixtures for discriminating between different (but similar) mixtures and, in the case of simple mixtures, quantifying the constituents' concentration. The development of an instrument capable of recognizing odors is the ultimate applicative justification for the study of chemical sensors.

In the period 1997-2003, the SENSOR Lab developed successive versions of the Electronic Nose Pico-X (X=1,2). A collaboration with a medium size company, SACMI (Imola - Bologna), started in 2001 to engineer and commercialize the research findings coming out from the SENSOR Lab. In 2003 the first commercial EN, the SACMI EOS 835 olfactory system, an engineered version of the last Pico EN, was put on the market.

E-nose applications tackled inside the SENSOR Lab range from food quality control (e.g. optimization of coffee roasting process, detection of oil defects, screening of fungal contamination in mais), to environmental monitoring (e.g. quantification of malodors in landfill sites), to security (detection of TNT), to medical diagnostics (control of the state of wounds).

Dye Sensitized Solar Cell

Solar energy conversion efficiency of 11% has been reported for the Grätzel cells employing nanocrystalline TiO_2 films and Ru-based organic dye as sensitizer. However, the slow percolation of electrons through a random TiO_2 polycrystalline network and the high recombination rate on the surface of TiO_2 nanoparticles at high electron injection rate (under strong sunlight) and the slow hole-transporting through the liquid electrolyte are the main processes responsible for the relatively low efficiency of Grätzel cells. A new architecture based on array of modified nanowires offers an outstanding expectative: i) Films based on nanowires are more easily filled with the non-volatile hole conductors needed for improved device stability; ii) electron transport within a monocrystal nanowires must be much faster than transport through nanocrystalline networks; iii) surface fields in each nanowires should enforce charge separation and longer diffusion length.

Electron Field Emission

Development in cold cathode based devices brought with it a need for more compact and economically viable electron sources capable of delivering high and stable current density at a low applied field. Field emission from 1D nanostructures exhibits great promise in this direction compared to the conventional microfabricated emitters. Many applications in vacuum micro/nanoelectronics are foreseen.

Single Nanowire Transistor (SNT) based biosensors

The development of electrically addressable devices for label-free detection of DNA and of other biological macromolecules has the potential to impact on basic biological research as well as screening in food safety and medical bioterrorism applications. The main purpose of this activity is to develop a new and innovative technology based on a SNT for electrical label-free DNA detection with extreme sensitivity and good selectivity, providing a pathway to integrated, high-throughput, multiplexed DNA detection. The sensors are basically transistors that are 'switched' on or off (that is, between a high-current and a low-current state) not, as in normal transistors, by applying a voltage to one of their electrodes, but by the binding of a molecule to their surface.

Acknowledgements

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