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## Study of quasi-1D SnO<sub>2</sub> nanowires

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**Summary.** — The descriptions of SnO<sub>2</sub> nanowires growth procedures are getting more and more frequent in the current literature. However, studies on the growth mechanisms are still lacking. In particular, no investigation has been reported on the growth process when the growth mechanisms are not based, as in the case of whiskers, on vapour-liquid-solid (VLS) transitions. In this paper, a new procedure is reported by the authors for growing SnO<sub>2</sub> nanowires, based on the presence of liquid-tin droplets on the substrate. The Sn vapour pressure developed by these droplets, which find themselves very close to the growing tip of the wire, gives rise to a sufficiently high supersaturation to enable the fast growth rate usually observed. The principal features and results of this new procedure, as well as possible growth mechanisms, are also discussed.

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PACS 81.10.Bk – Growth from vapor.

PACS 81.07.-b – Nanoscale materials and structures: fabrication and characterization.

### 1. – Introduction

New interesting results on the capability to synthesize semiconducting oxides like SnO<sub>2</sub>, ZnO, In<sub>2</sub>O<sub>3</sub> and others, in quasi-1D form (in literature these structures are often called “nanowires”, “nanobelts”, “nanoribbons”, etc...) by simple vapour transport techniques have recently been reported (*e.g.*, see the review by Wang in ref. [1]). They have stirred a great interest as to the potential applications in optics and microelectronics as well as the physico-chemical properties of their nanostructures.

A particular attention has been focused on the possible extension of these nanomaterials to the gas-sensor field. In fact, several semiconducting oxides have been successfully employed as “sensing” materials during the last years, mainly in the thick- and thin-film form. But a single-crystalline quasi-1D nanostructure (*i.e.* the nanowires) may substantially increase the “sensing” properties of metal-oxide (MOX) sensors, thanks to the increased surface/bulk ratio and the assumed larger time-stability. Preliminary tests of

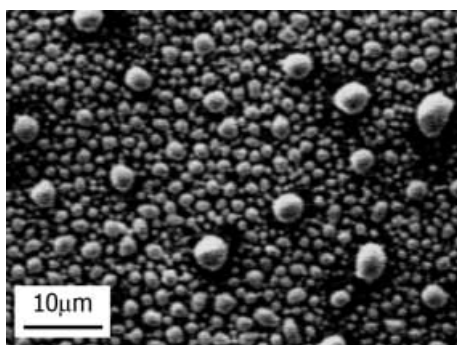


Fig. 1. – Metallic Sn micro-droplets condensed on the substrate during the first step of the growth. Their presence is fundamental for the nanowire growth.

SnO<sub>2</sub> nanowires-based sensor devices developed by this group confirmed a large increase of sensitivity, in comparison with the one of a traditional SnO<sub>2</sub> sensor [2].

Further investigation on the crystal growth mechanisms is needed if a good control of the nanowires growth process has to be achieved. In particular it is important to extend the technique to a reliable and large-scale growth on the desired substrates, or to different semiconducting oxides. Unfortunately this information is not available and only uncompleted and contradictory data can be retrieved from literature. Object of this paper is to report on a novel vapour-phase technique suitable for growing SnO<sub>2</sub> nanowires. Details on the growth procedure, as well as possible growth mechanisms, are also discussed especially in view of a future optimisation of the technique.

## 2. – SnO<sub>2</sub> nanowires growth and characterization

Tin oxide nanowires were grown in a home-made furnace, inside a quartz tube in which it is possible to have vacuum and flow different gasses. SnO powders (the source material) were located next to the substrates (Al<sub>2</sub>O<sub>3</sub>, Si, Si/SiO<sub>2</sub>, . . .) within an alumina boat, in the central part of the tube. The growth-system is then heated to 800–900 °C in an Ar flow. At high temperature SnO decomposes into liquid Sn and SnO<sub>2</sub> (*e.g.*, see ref. [3]) and Sn vapour can be carried on the substrates, where it condenses in micron-size droplets (fig. 1). The reaction with oxygen then promotes the crystallization of the SnO<sub>2</sub> nanowires. The mechanism of this crystal-growth will be discussed later in this paper.

The obtained samples have been then characterized by X-ray diffraction analysis, Scanning Electron Microscope (SEM) imaging, Transmission Electron Microscopy (TEM) investigations, Photoluminescence (PL) and Cathodoluminescence (CL) spectra measurements [4].

These measurements revealed that the nanowires are characterized by a rutile-like SnO<sub>2</sub> single-crystal structure. They generally show a “belt-like” morphology, with few tens of nanometers in thickness and hundreds of micrometers in length (fig. 2).

## 3. – Discussion

In spite of the presence of Sn droplets in the first step of the process, no evidence of a liquid phase could be found on the growing tip at the end of the growth. This

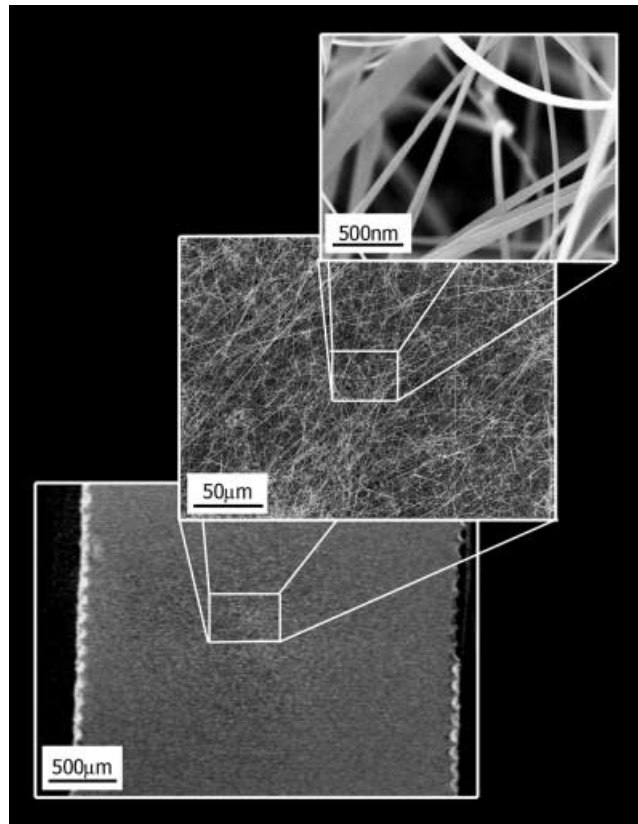


Fig. 2. – SEM images of the obtained samples of  $\text{SnO}_2$  nanowires grown on alumina substrate, at different magnification. The nanowires are homogeneously distributed on the substrate. Their morphology is mainly “belt-like”. The thinnest side is few tens of nanometers wide, while the length can reach hundreds of micrometers.

observation should exclude any whiskers-like VLS growth mechanism, though some other authors claimed to have evidence of this mechanism in their growth process [5-7]. Our observation is however in agreement with what reported in some recent papers [8-11], where VLS mechanisms were excluded.

An alternative explanation may be given by considering that the growth rate of the nanowires is rather high, as they can reach 50–500  $\mu\text{m}$  in length in a 30–60 minutes run. The nanowires often grow in a slightly bended or twisted shape, usually elongated for hundreds of micrometres in directions which are generally parallel to the substrate and close to it (usually the distance is smaller than 50  $\mu\text{m}$ ).

Now, simple considerations show that such high growth rates cannot be justified by the vapour transport of Sn (the limiting element in the reaction with oxygen) from source to substrate. Both diffusion and convection through the vapour phase are in fact not able to provide a sufficient amount of Sn to justify the crystallization flux necessary to explain the observed growth rate. In the case of diffusion of Sn through the carrier gas,

the flux can be estimated by

$$(1) \quad J_{\text{diff}} = -\left(D [p_{\text{Sn}(1)} - p_{\text{Sn}(2)}]\right)/RTd,$$

in which  $D$  is the binary diffusion coefficient of Sn in Ar,  $R$  is the gas constant,  $T$  the average temperature in the temperature profile between source and substrate a distant  $d$  far apart,  $p_{\text{Sn}(1)}$  and  $p_{\text{Sn}(2)}$  are the equilibrium partial pressures of Sn at source and substrate temperature, respectively. When  $D = 10^{-4} \text{ m}^2\text{s}^{-1}$ ,  $T = 1150 \text{ K}$ ,  $(p_{\text{Sn}(1)} - p_{\text{Sn}(2)}) = 10^{-4} \text{ mbar}$ ,  $d = 0.1 \text{ m}$ , one gets  $J_{\text{diff}} \approx 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$ .

As the convective flux ( $J_{\text{drift}}$ ), a simple estimation leads to

$$(2) \quad J_{\text{drift}} = (v_{\text{drift}} p_{\text{Sn}})/(PV_{\text{m}})$$

in which  $v_{\text{drift}}$  is the drift velocity,  $V_{\text{m}}$  the molar volume of Ar (the carrier gas),  $p_{\text{Sn}}$  the average partial pressure of Sn and  $P$  the total pressure in the system. When  $V_{\text{m}} = 3.33 \text{ m}^3 \text{ mol}^{-1}$ ,  $p_{\text{Sn}} = 0.5 \times 10^{-4} \text{ mbar}$ , and  $v_{\text{drift}} = 0.05 \text{ m s}^{-1}$ , one obtains  $J_{\text{drift}} \approx 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$ .

One should notice that these values are estimated for the typical conditions of our growth system in which  $\Delta T = 100 \text{ K}$  (temperature drop between source and substrate when  $d = 0.1 \text{ m}$ ) and a flow of inert gas of about  $100 \text{ cm}^3 \text{ min}^{-1}$  at  $300 \text{ mbar}$ .

The obtained values may be compared with the Sn flux that is required to assure the mass balance ( $J_{\text{mb}}$ ) at the observed growth rate (at least  $0.1 \text{ mm/h}$ ):  $J_{\text{mb}} \approx 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ . It is easy to note that the value is much larger than the ones obtained in eqs. (1) and (2), meaning that the Sn transport from the source cannot steadily sustain the nanowires growth.

As previously mentioned, the nanowires usually grow near to the substrate surface, where the liquid-Sn droplets are located. In the experimental conditions that have been here reported, a particle mean free path  $\lambda \approx 10 \text{ }\mu\text{m}$  can be evaluated. So,  $\lambda$  is comparable with the distance between the Sn drop and the nanowire growing tip: the Sn vapour transport in this range is much larger, because the mean square velocity ( $u$ ) of a Sn particle is obviously larger than the average long-range transport velocity mediated by collisions. In this short range a new Sn flux ( $J_{\text{sr}}$ ) can be evaluated by

$$(3) \quad J_{\text{sr}} = 1/4 u n \approx 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1},$$

where  $u$  ( $\approx 4 \text{ m s}^{-1}$ ) is the mean square velocity and  $n$  ( $\approx 5 \times 10^{-7} \text{ mol m}^{-3}$ ) is the molar density derived in the ideal-gas approximation. This value is comparable with the required growth molar flux ( $J_{\text{mb}}$ ). So, if Sn evaporation kinetics from the droplets is high enough to support such transport, the liquid phase on the substrate has to be considered the effective feeding material for the nanowires growth and the mechanism may be considered as a “short-range vapour-solid” growth.

The above considerations underline the important role of the liquid-Sn droplets for the growth of nanowires. In fact, as experimentally evidenced, when the temperature gradient inside the furnace and the inert-gas flow are modified to prevent the condensation of the liquid phase on the substrate, leaving Sn vapours only coming from the source, the reaction with oxygen only gives rise to the formation of  $\text{SnO}_2$  nano-crystalline powders.

Another problem, which has deserved little attention so far, regards which are the growth mechanisms of these quasi-nanocrystalline structures and how they assemble in a supersaturated vapour phase.

Difficulties arise when attempting to explain the strong difference (usually amounting to more than three orders of magnitudes) between the fast-growth orientation parallel to the long size of the “wire” crystal and the other low-growth orientations.

As fast-growth rates are typical of atomically rough interfaces between the growing crystal and its nutrient phase (even at very small supersaturation) [12, 13], one has to postulate the existence of this type of interfaces in a crystal-vapour system such as ours. The difficulty is here that the atomistic models up to now developed [13-16] would only predict, for these systems, low roughness levels, *i.e.* atomically smooth interfaces, typically characterized by slow growth kinetics.

As often reported (*e.g.*, see [17]), a way out is here relying on VLS growth mechanisms. The presence of a tiny liquid layer on the growing tip of the filamentary crystal would act, from the atomistic viewpoint, as an almost ideally rough interface, thus favouring a very fast growth. Unfortunately, no experimental evidence exists in our case, of the formation of such liquid phase.

A further way for explaining the observed fast-grow rates might very likely be in relation with possible modifications of the strength field at the growing interface due to the rearrangements of the unsaturated bonds. As pointed out after revisiting the earlier atomistic models [18], surface reconstructions should favour an increase in surface roughness in the presence of catalyst impurities and/or marked off-stoichiometry in compound crystals.

Research work is presently under way, along these lines, in our laboratory.

#### 4. – Conclusions

A new technique for growing  $\text{SnO}_2$  nanowires has been developed and studied in details. It is shown that the formation of liquid-tin droplets appears to be crucial for an efficient growth process, since the Sn liquid phase acts as a feeding material for the growth. The short distance between the Sn droplets and the growing tip of the nanowire enables a fast vapour Sn transport, which allows to achieve the needed high supersaturation and to keep it for the entire growth process.

By optimisation of this procedure it was possible to extend the nanowires deposition area from a few square millimetres to about some square centimetres, by improving in the same time the deposition homogeneity and quality.

Finally, since a further optimisation of the growth technique requires a deeper understanding of the growth mechanisms, possible approaches to the atomistic growth models have been briefly discussed, especially in view of future research work along these lines.

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#### REFERENCES

- [1] WANG Z. L., *Materials Today*, **7** (2004) 26.
- [2] COMINI E., FAGLIA G., SBERVEGLIERI G., CALESTANI D., ZANOTTI L. and ZHA M., in press on *Sensors and Actuators B*.

- [3] AURBACH D., NIMBERGER A., MARKOVSKY B., LEVI E., SOMINSKI E. and GEDANKEN A., *Chem. Mater.*, **14** (2002) 4155.
- [4] CALESTANI D., LAZZARINI L., SALVIATI G. and ZHA M., in press on *Crystal Res. Technol.*
- [5] DANG H. Y., WANG J. and FAN S. S., *Nanotechnology*, **14** (2003) 738.
- [6] CHEN Y., CUI X., ZHANG K., PAN D., ZHANG S., WANG B. and HOU J. G., *Chem. Phys. Lett.*, **369** (2003) 16.
- [7] JIAN J. K., CHEN X. L., WANG W. J., DAI L. and XU Y. P., *Appl. Phys. A*, **76** (2003) 291.
- [8] PAN Z. W., DAI Z. R. and WANG Z. L., *Science*, **291** (2001) 1947.
- [9] DAI L., CHEN X. L., JIAN J. K., HE M., ZHOU T. and HU B. Q., *Appl. Phys. A*, **75** (2002) 687.
- [10] HU J. Q., MA X. L., SHANG N. G., XIE Z. Y., WONG N. B., LEE C. S. and LEE S. T., *J. Phys. Chem.*, **106** (2002) 3823.
- [11] ZHANG J., JIANG F. and ZHANG L., *J. Phys. D*, **36** (2003) L21.
- [12] ROSENBERGER F., in *Interfacial Aspects of Phase Transformations, Crystal Growth Kinetics*, edited by MUTAFTSHIEF B. (Reidel, Rotterdam) 1982, pp. 315-464.
- [13] MUTAFTSCHIEF B., in *The Atomistic Nature of Crystal Growth* (Springer, Berlin) 2001, chapt. 16.
- [14] BURTON W. K., CABRERA N. and FRANK F. C., *Philos. Trans. R. Soc. London, Ser. A*, **243** (1951) 299.
- [15] BENNEMA P. and GILMER G. H., in *Crystal Growth: an Introduction, Kinetics of Crystal Growth*, edited by HARTMAN P. (North Holland, Amsterdam) 1973, pp. 263-327.
- [16] JACKSON K. A., *J. Crystal Growth*, **5** (1969) 13.
- [17] GIVARGIZOV E. I., in *Current Topic Mat. Sci., Growth of Whiskers by the VLS mechanism*, edited by KALDIS E., Vol. **1** (North Holland, Amsterdam) 1978.
- [18] CHEN G. S., MING N. B. and ROSENBERGER F., *J. Chem. Phys.*, **84** (1986) 2365.