Preparation and applications of transition metal oxide nanofibres and nanolines

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ABSTRACT

In current paper we demonstrate the applicability of high viscous oligomeric alkoxide concentrates in fabrication of technologically interesting structures like nanometer diameter fibers (down to 200 nm), nanoneedles (tip radii 15-25 nm) and some micrometers wide linear surface structures. The approach is cost-effective and simple as it utilizes low-cost precursor materials (metal alkoxides) combined with low-tech processing (tape casting, fibers pulling, aging and baking).

Keywords: nanofibres, tape-casting, SPM tips, sol-gel, alkoxides

1 INTRODUCTION

During the last decade preparation of transition metal oxide nanofibres (wires), nanoribbons and related structures have attracted considerable attention. To produce materials for potential applications like gas and humidity sensors, optical sensors, filter materials etccheap chemical methods like solution-liquid-solid method, electrospinning, solvothermal method, vapor-liquid-solid template directed synthesis etc have been advised [1,2]. Still, some applications like nanometer diameter optical waveguides need fibres that have higher homogeneity than is achievable by these methods. Conventional taper-drawing technology enables to achieve the desired degree of homogeneity and fibers with diameters down to 20 nm can be made successfully, expressing ultra high smoothness, structural uniformity and perfectly circular cross-section [3]. However, the method has some drawbacks like very high processing temperature (2000K) and low refractive index of silica, which limit the possible technological applications. It is also demonstrated that SnO_2 high aspect ratio crystalline nanoribbons are suitable for optical waveguiding [4]. Furthermore, these methods leave a crucial issue – manipulation of the fibers – practically uncovered.

To overcome these limitations in producing ultra-high uniformity fibres we have developed a new method that utilizes oligomeric metal alkoxides as precursors. In our earlier works we have shown that high viscosity transition metal alkoxide concentrates can be used for making ultra-sharp needles [5] applicable as scanning tunneling and photon imaging microscopy probes [6], and also for making thin and narrow stripes on a substrate [7]. The method is similar to the well-know sol-gel process, where monomeric transition metal alkoxide is hydrolyzed and polymerized, followed by extraction of the solvent and water, and remaining highly viscous polymer concentrate:

Polymerization

$$\underbrace{M(OR)_4}_{\text{metal alkoxide}} + H_2O + \text{solvent} \rightarrow \quad (1)$$

$$\rightarrow (\text{-}\overset{OR}{\underset{OR}{M}}\text{-O-})_{n<10} + ROH + \text{solvent} \xrightarrow{\text{Solvent removal}} \underbrace{(\text{-}\overset{OR}{\underset{OR}{M}}\text{-O-})_{n<10}}_{\text{oligomeric concentrate}}$$

The material can be readily shaped to aforementioned nanometric structures at room temperature and then transformed to solid oxide state as a result of sufficient aging and baking.
In this paper we primarily refer to the possibility to prepare metal oxide nanofibres using highly viscous alkoxide concentrates. In addition we present our results on preparing oxide nanoneedles as possibilitie to prepare very sharp end fibres. Because of low-tech nature and low cost of the method, it may hold valuable impact on relevant technologies in the future.

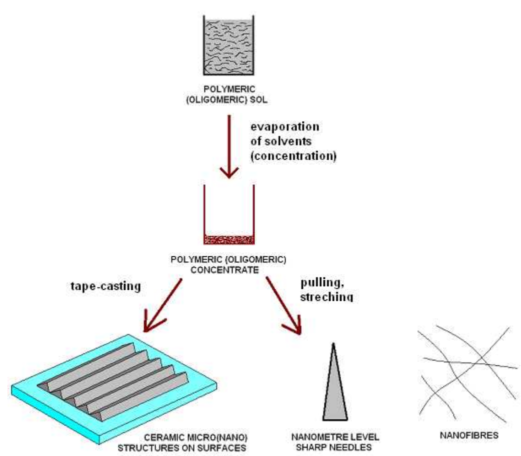

Figure 1. Schematic illustration of the different applications of high viscosity alkoxide concentrates.

2 FIBERS, NEEDELS AND MICROPATTERNS OF TRANSITION METAL OXIDES

Starting with neat liquid metal alkoxides (Ti, Sn, Si, Hf, Zr) the precursor material is made simply by addition of water in an appropriate solvent [5]. As a result, the alkoxide polymerizes (see eq. (1)) to the extent of up to ten monomers. The remaining alcohol and solvent are then extracted from the formed oligomeric mass, and the basic material for fabrication of nanostructures is obtained. The oligomeric concentrate is a highly viscous mass, which can only be stored in dry atmosphere. If introduced to humid air the material continues to polymerize via cross-linking the individual oligomer molecules near to the exposed surface, leading to very quick solidification of the surface. Eventually, the material becomes completely solid, but still containing some organics and water. These can be removed by heating the material to a sufficient temperature, depending on the type of the oxide and desired degree of crystallinity.

Fibers and needles are both made by pulling the concentrate jet in air [5]. Here, the outcome depends on the viscosity of the concentrate, pulling speed and humidity of the surrounding atmosphere [5]. By carefully optimizing the parameters nanometrically sharp needles (Figure 2) and ultra-narrow fibers (Figure 3) can be drawn. As transition metal oxides are typically transparent and can be readily made conductive via addition of appropriate dopants the structures may have many practical applications, e.g. probes for simultaneous STM and photon imaging [6] and others.

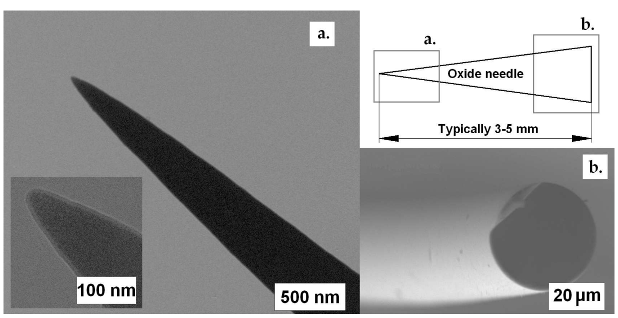

Figure 2. Nanometrically sharp oxide needles (SnO_2).

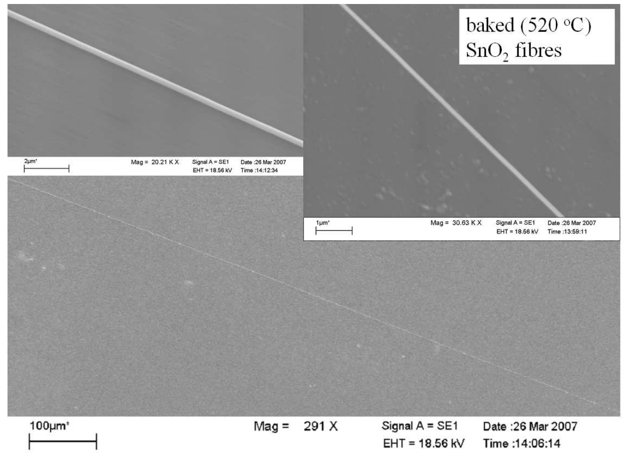

Figure 3. Oxide nanofibers (SnO_2) after 2h baking at 520 °C. The fibers can be drawn up to some cm-s in length.

Nanopatterning is performed by tape casting the precursor to a substrate using an appropriate blade. We prepared the structured blade from a cleaved silicon monocrystal using conventional wet etching technique [7]. The surface typically does not require any special treatment and ordinary glass can readily be applied. Figure 4 shows an example of obtained structures.

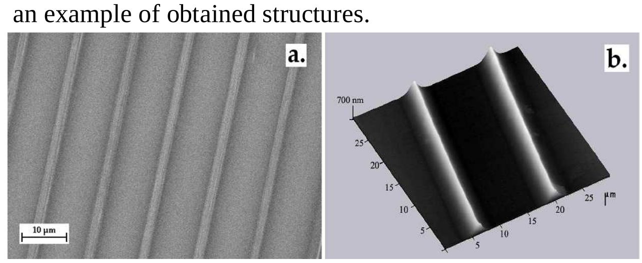

Figure 4. A fragment of a tape casted microstructured film prepared using a blade with triangular cross-section grooves.

The cross-section as can be seen in Figure 4 is determined by the shape of the grooves on the blade, volume loss during aging and baking and flow properties of the precursor. There is no fundamental limit on the lengths of the structures and tens of square centimeters of patterned areas have already been demonstrated in practice. Furthermore, the lines can intentionally be made nonlinear and even applied to uneven substrates.

The described structures can be doped with appropriate dopants in order to modify the useful properties of the material such as conductivity, hardness, fluorescence and others. We have also demonstrated that the structures can be doped by carbon nanotubes in order to prepare transparent CNT/oxide electrodes [8].

3 CONCLUSIONS

Transition metal alkoxide concentrates are promising materials for fabrication of nanometric fibers, needles and micropatterns because of low cost and simplicity of production. The method is focusing more on the lower resolution and flexible production of micro- and nanostructures and is thus complimentary to the conventional lithographic methods. Transition metal oxide nanostructures have useful practical applications in nano-optics, -electronics and -optoelectronics, since optically transparent and conductive materials can be fabricated.

ACKNOWLEDGEMENTS

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