SYNTHESIS OF SINGLE CRYSTAL SILICON NANOWIRES FROM SILICON NANO AND MICROPARTICLES

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One dimensional structures with nanometer diameter exhibit novel properties which differ from those of bulk materials [1]. Indeed, Si_3N_4 nanowires are used as a composite material due to their outstanding mechanical properties, e.g. high melting point and low density [2,3]. Moreover, Si_3N_4 is a common material in microelectronics and optoelectronics. For such reason, it is generally accepted that Si_3N_4 single crystal nanowires have a great potential in the development of electronic and optic nanodevices [4]. Consequently, several approaches have been implemented for the synthesis of Si_3N_4 nanowires, such as carbothermal reduction and nitridation of a mixture containing silicon oxide [5-7], combustion synthesis [8,9], carbon-nanotube-confined chemical reaction [10,11], catalyst reaction of silicon with nitrogen [12-14], catalystless reaction of silicon with nitrogen [15,16], reaction of Silicon oxide with ammonia [17], chemical vapor deposition [18], reaction of liquid silicon with nitrogen [19] and oxide-assisted growth [20]. Despite the large amount of literature on Si_3N_4 nanowires production, the synthesis of high purity Si_3N_4 single crystal in a controlled, reliable, simple and efficient manner is still challenging.

Owing to Si_3N_4 high melting point, a common feature of practically all synthesis routes is the crystal growth by reacting silicon with nitrogen. In addition, sustained solid state reaction is not allowed since solid silicon and Si_3N_4 are barriers for nitrogen and silicon diffusion respectively [21]. Accordingly, most of synthesis routes are based on vapor-solid (VS) and vapor-solid-liquid (VLS) mechanisms. Reaction in vapor/liquid phase results in the formation of α/β-Si_3N_4 phase respectively [21]. To achieve the VLS route, metal catalysts are added to lower the silicon melting temperature [22]. Both mechanisms involve volatization and nitridation of silicon. This means that two conditions should be fulfilled: no protective layer can exist and any competing reaction with nitridation must be minimized. The first condition involves removing any native silica layer from silicon particles and that the process must be kept at temperatures reasonably below the melting temperature to avoid the formation of a liquid silicon layer that can be easily transformed in a solid Si_3N_4 layer. The second condition entails a very low oxygen partial pressure and high temperatures (around 10^{-19} atm at 1350ºC [21,23]) to avoid silicon oxidation. In addition, carbothermal reduction method introduces another competing reaction resulting in the formation of SiC establishing an upper limit for temperature [6]. As a consequence, the majority of the approaches demand setting up a complex gas purity control, long reaction times (currently between 5 to 10 hours) and quite low production yield. Adding some catalyst can improve production yield to the cost of by-product formation and production contamination. However, in references [15,16,20] high production yield without catalyst or reductive gas is achieved for quite short reaction times. A common feature of these experiences was the lack of an oxygen and water filtering setup. In spite of that, Si_3N_4 nanowires are always covered by a silica shell. This surprising result can be explained in view of the competing process of active/passive oxidation [23,24]. Indeed, active oxidation is a source of SiO gas, which, in contact with nitrogen, results in the formation of α-Si_3N_4 nanowires. So the native silica layer is not a barrier but a source of SiO. Under these conditions, nitridation can take place at relatively high oxygen partial pressures. For example, active oxidation dominates at 1350ºC for an oxygen partial pressure lower than 5×10^{-3} atm.

In this work we propose a simple method consisting in heating silicon nano and microparticles in an alumina furnace under a continuous flow of nitrogen. No catalyst is used and the control parameters are oxygen partial pressure and temperature. The role of a silica layer to enhance the reaction kinetics and the oxygen partial pressure is studied. Thus, it will be stated that controlling the oxygen partial pressure, the formation of a silica shell is prevented (Fig 1). Moreover, the control over the oxygen partial pressure allows the production of Si_3N_4 nanowires in a temperature range from 1200 up to 1450ºC. Nanowire's length is around 5 to 25 µm, while their diameter ranges from 50 to 200 nm. The higher the temperature, the wider the nanowires are. Finally, under proper conditions a high production yield of Si_3N_4 single crystals is obtained.

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Figures:
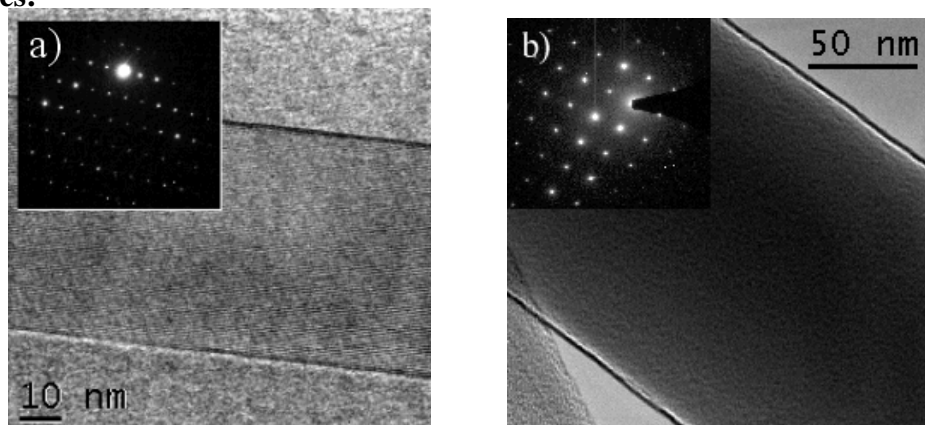
Figure 1. TEM micrographs of nanowires synthesized at 1400ºC for 1 hour from silicon nanoparticles at an oxygen partial pressure of 5 10^{-2} (a) and 2 10^{-3} atm (b). Insets are SAED (corresponding to monocrystalline α-Si_3N_4). EELS and SAED analyses show that figure 1.a is a α-Si_3N_4 single crystal covered by an amorphous silicon oxide shell.