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Nanochannels' fabrication using Kirkendall effect

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ABSTRACT

Evidences of nanochannel formation based on Kirkendall effect have been previously reported for oxide nanowires covered with a thin alumina shell layer. Here we will investigate the nanochannel formation on an in situ pulsed laser deposition (PLD) fabricated structure of iron oxide shell layer over ZnO and MgO nanowire core and will compare with the alumina shell layer results. In all (four) cases a chemical reaction takes place on the interface producing a spinel buffer layer. Nanochannel formation process could be understood based on material diffusion coefficients through the spinel buffer layer but shell layer crystal structure seems to play a significant role.

1. Introduction

Progresses in nanotechnology include devices' miniaturisation down to micrometers and even to nanometer scale while recent advance of the nanobiotechnology [1,2] increases the interest in nanopipes and nanofluidic channels as tools for DNA molecules' manipulation and investigation. Top-down technologies such as e-beam lithography [2,3], focused ion beam [4] or transmission electron microscopy (TEM) techniques [5] were continuously developed to fabricate nanostructures down to several nanometers. However, for nanopipes of sizes below several nanometers, bottom-up approach seems to be a much more promising option from both a technological and an economical point of view. In our case, the bottom-up approach is based on the asymmetric diffusion process in some material interfaces, also known as the Kirkendall effect. Thus, due to the fact that the materials are not going to diffuse symmetrically into one another, we obtain an effective material movement and void spaces remain behind. By controlling this movement we can control structure geometry and in our case, inside the cylindrical structure of the nanowire, a nanochannel formation. Using this technique nanochannel fabrication inside ZnO nanowires covered with an Al_2O_3 shell layer has been reported, even if some undiffused areas remained at the bottom of the structures [6]. Attempts have been made for MgO core wires with Al_2O_3 shell layer [7] but a wet etching had to be used to remove the remaining MgO core and, even so, some parts of the channels were still not continuous. The aim of the present study is to investigate the nanochannel formation for a Fe_2O_{3-X} shell layer using both ZnO and MgO core wires and to compare the results and diffusion process with the Al_2O_3 shell layer case.

2. Experiment

MgO and ZnO nanowires were grown by vapor–liquid–solid (VLS) method using laser ablation technique. We used a Lamda Physics ArF pulsed excimer laser for ablation of MgO and ZnO targets and we grew nanowires on MgO and alumina substrates in an oxygen atmosphere. We used Au as liquid catalyst. More details about growth techniques have been given elsewhere [8]. Furthermore, we covered these structures with a 5–50 nm thick shell layer using in situ PLD method. By changing the target ablation and deposition conditions we optimized shell layer morphology and crystal structure and properties, case by case [9].

The next step was to warm up the samples at various temperatures and time intervals in order to observe the diffusion process and nanochannels' formation based on the differences in the diffusion process known as the Kirkendall effect. We investigated temperatures up to 1500 °C and heating intervals up to 48 h. The morphology results were investigated by SEM (EFSEM JEOL JSM-6330FT) and TEM (HRTEM JEOL JEM-3000F). For a better inside

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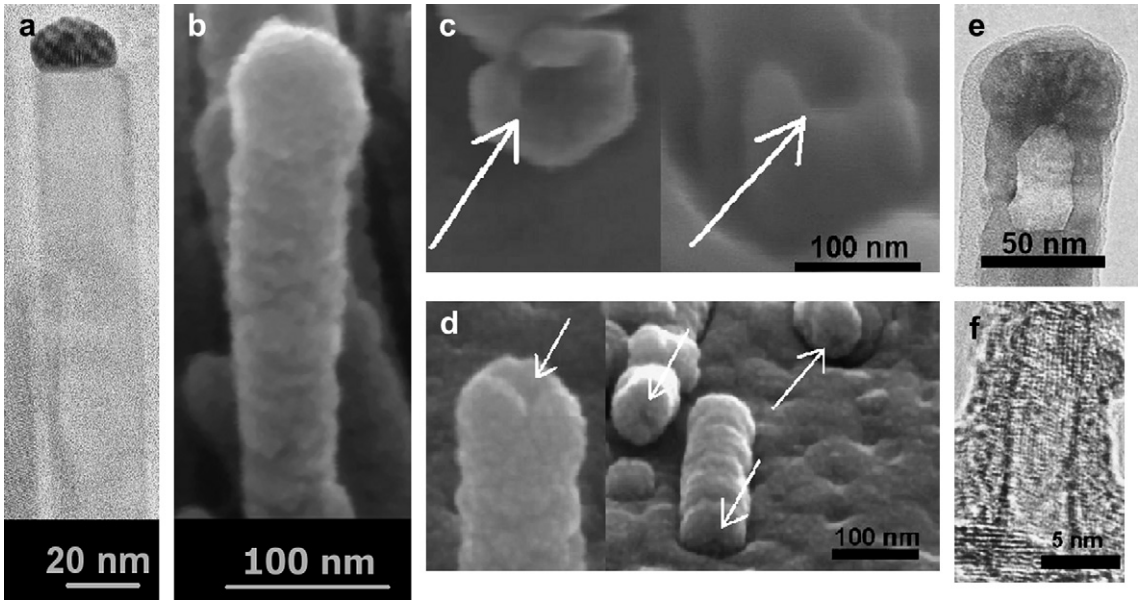

Fig. 1. a) TEM image of ZnO nanowire, b) SEM image of ZnO/alumina structure as deposited, c) SEM image of cavity on top of a broken ZnO/alumina structure after annealing – top view and 60° tilted view, d) SEM image of top and bottom cavities of ZnO/Fe_2O_{3-X} after annealing, e) TEM view of the top of ZnO/alumina nanostructure after annealing and f) TEM view of a ZnO/Fe_2O_{3-X} structure after annealing.

channel investigation, nanostructures were in some cases braked using ultrasounds or ablated using Ar plasma.

3. Experimental results

ZnO nanowires (Fig. 1a), covered at room temperature with a 25 nm layer of alumina (Fig. 1b) and respectively iron oxide were annealed at 700 °C for 3 h. SEM images of topless and braked nanowires with alumina shell layer are presented in Fig. 1c. Considering the hole diameter, the ZnO core seems to completely diffuse into the alumina shell layer forming a 20 nm cavity visible from the top of any broken structure. In the case of the iron oxide shell layer, the same annealing conditions lead to a considerably smaller cavity diameter, as the one that could be observed in Fig. 1d. In the case of a 300 °C deposited shell layer and respectively a better shell layer crystal structure [9] spotted cavities are even smaller. Since we are starting from the same morphology of the core and shell layer, differences might come only from the Zn diffusion in alumina and iron oxide layers. Fig. 1e presents a TEM image of nanochannel formation on top of ZnO/alumina structures. It is interesting to mention that the channel does not form uniform along the wire but it starts from the top of the structure, as it has been previously observed as well [6], and does not have smooth boundaries. In our case the average channel length is less than

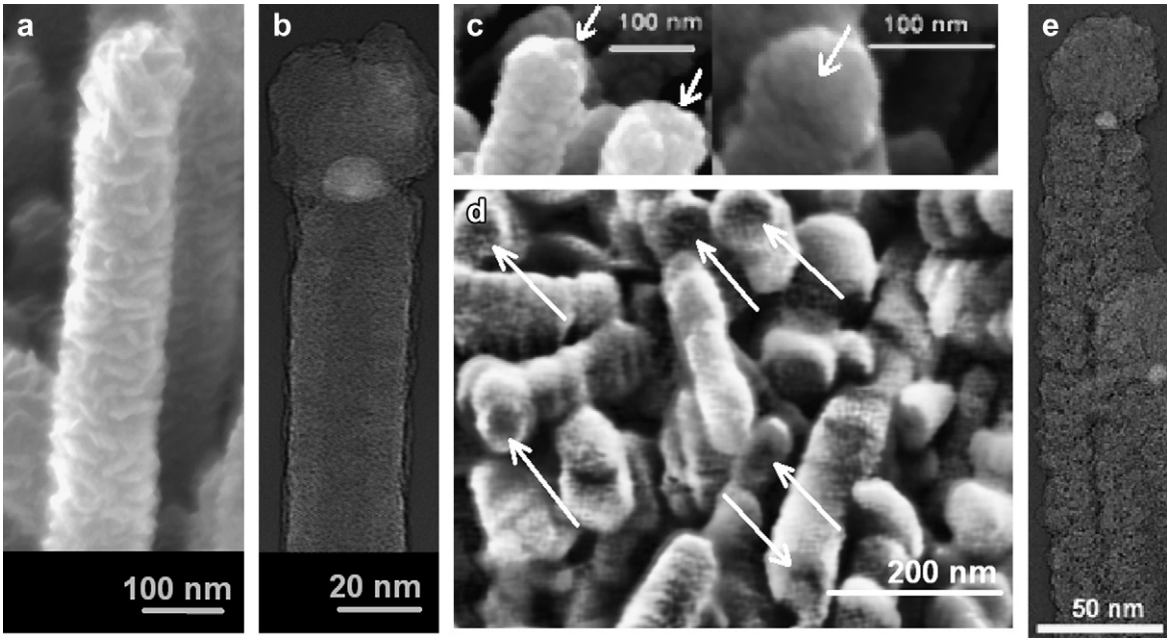

Fig. 2. a) SEM image of MgO/Al_2O_3 as deposited, b) TEM image of MgO/Fe_2O_{3-X} as deposited, c) SEM image of top cavities of MgO/Al_2O_3 structures after annealing – 60° tilted view and top view, d) SEM image of cavities' traces on MgO/Fe_2O_{3-X} structures after annealing and e) TEM image of nanochannel inside MgO/Al_2O_3 structures after annealing.