

# Stability of ZnO nanofibers in processing liquid agents\*

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The aim of the research was to determine the impact of developers, removers and solvents on the stability of ZnO nanofibers. Surface imaging of nanofiber morphology was studied using Scanning Electron Microscope. From the obtained results a set of factors which have the least influence on the etching of ZnO nanofibers during device processing was selected. The dependence of the grains size on the fibers robustness in the liquid solutions was investigated. It was found that the nanofibers calcinated at higher temperatures were more stable. This was due to the grain size of the fiber as the fibers calcinated at higher temperatures revealed larger grain size. The studies have shown that smaller grains were dissolved much faster, leaving the porous core of the ZnO nanofiber.

Keywords: *nanofibers; zinc oxide; etching*

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## 1. Introduction

To increase the sensitivity and response time of sensor devices, the active area should have a high surface to volume ratio, which can be achieved using a porous material or low-dimensional structures. Electrospun metal-oxide nanofibers combine these two properties which makes them excellent candidates for sensing applications [1, 2].

The electrospinning technique is a relatively simple method for fabrication of the nanofibers with diameters ranging from several microns to tens of nanometers. Additionally, the electrospinning method is appropriate for creating long, straight and aligned nanofibers from a wide range of materials (polymers, metal oxides and their composites) and at the same time their positioning on the surface of the substrates [3, 4]. As-spun fibers undergo a calcination process in air atmosphere to remove organic phase of the sol-gel composite. As a result, highly porous structures consisting of

metal oxide nanoparticles are obtained. Moreover, the grain size and their distribution can be controlled by changing the thermal treatment conditions [5].

However, nanocrystalline structure of the electrospun nanofibers causes technological problems such as low mechanical strength and vulnerability to acid or alkaline environment. That complicates the use of standard semiconductor fabrication techniques, which limits the possibility of mass production of the devices based on metal-oxide nanofibers.

The mechanism of zinc oxide etching process in acid and alkaline solutions is well known. The tetrahedral coordination in wurtzite structure of ZnO gives surface polarity. The polarity is due to alternately arranged planes containing the two interpenetrating sublattices of corner-sharing tetrahedra with  $Zn^{2+}$  and  $O^{2-}$  ions, which induces positively charged Zn terminated (0001) and negatively charged O terminated (000-1) faces. The positively and negatively charged surface atoms with dangling bonds could be more easily attacked by ions of opposite charge such as hydroxide ( $OH^-$ ) and hydronium ( $H_3O^+$ ) [6]. Different types of defects

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could also accelerate the etching process due to less-ordered lattice and surface. For polycrystalline structure this effect is multiplied because the ions of etching agent can penetrate deep into the structure through the grain boundaries [7].

The aim of the research was to determine the impact of chemical agents, such as developers and removers used in the photolithography process, as well as alcohol used to wash and prepare the structures, on the stability of ZnO nanofibers in subsequent steps of technology. Surface imaging of nanofibers, to evaluate their morphology variation, was performed using Scanning Electron Microscope. As a result of this study a set of factors, which have the least influence on the etching of ZnO nanofibers, was defined.

## 2. Experiment

### 2.1. Preparation of ZnO nanofibers

The ZnO nanofibers were fabricated from sol-gel solutions of poly(vinyl alcohol) (PVA), acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) and deionized water. A droplet of such prepared solution was extended in accordance with the electric field lines toward the grounded collector on  $10 \times 10 \text{ mm}^2$  substrates cut from Si/SiO<sub>2</sub> wafer (300 nm thermally grown silicon dioxide (SiO<sub>2</sub>)), during the electrospinning process. The oxidation process of Si wafers was performed in dry O<sub>2</sub> at 1150 °C in a diffusion type furnace. Through the electrospinning the thin liquid jet creates a continuous composite network of fibers. Then, the as-spun fibers undergo calcination at 500 °C and at 700 °C in air atmosphere to remove organic phase of the composite. Details concerning the preparation and structural characterization of ZnO nanofibers were already published [8]. The obtained results showed that the fibers were made of pure ZnO material and had nanocrystalline wurtzite structure. The substrates, before nanofibers deposition, were subjected to washing in acetone.

### 2.2. Liquid environments

To determine the impact of chemical agents such as developers, removers and solvents on the

stability of ZnO nanofibers in subsequent steps of technological process, the samples were immersed in selected solutions for a specified period of time. The temperature of the solutions was stabilized at 21 °C. In case of the developers such temperature was set in order to properly reproduce the photoresist pattern. To improve the effect of remover, it is normally used at elevated temperature (60 – 80 °C), but this is not necessary to achieve the required result. Furthermore, the elevated temperature accelerates the etching process which makes it less controllable. Therefore the influence of temperature on etching process has not been studied.

From the removers group, Microposit 1112A, SVC (TM)-14, Microposit 1165 and from the cleaning solvents group, isopropyl alcohol, acetone and deionized (DI) water were selected. Detailed information on each substance, including the manufacturer, the application method and the pH value, are summarized in Table 1. Developer Microposit 351 was diluted in DI water in the ratio of 1:5, to increase the resolution in photolithography process, according to the producer's suggestion.

### 2.3. Characterization

For imaging the samples, a Field Emission Scanning Electron Microscope (Hitachi SU6600) was used. After immersion in the solutions, the samples were washed in DI water and dried on a hot-plate at 90 °C for 1 min. To prevent contamination, the samples were kept in the SEM chamber under high vacuum for 12 h. Scans were collected each time from the same fibers but not in the same location to prevent inclusion of artifacts due to the electron beam impinging on the fiber.

## 3. Results and discussion

ZnO fibers were deposited on the Si/SiO<sub>2</sub> substrates to determine the behavior of such a system in the potential application. This design can be useful in case of sensor devices (especially biosensors) in the configuration of MOS-FET with a highly doped Si wafer acting as a bottom gate electrode. The rarely dispatched electrospun nanofibers did not create a dense fiber network (called nonwovens) and after calcination they

Table 1. Details of the substances used in the experiment including the producer, the pH value and the application (in the case of developers and removers).

Developers	Removers	Solvents
Microposit 351 Developer (Rohm&Haas, pH ~ 13) photoresist: SPR700, S1813, SP15,	Microposit 1165 Remover (Rohm&Haas, pH ~ 8), photoresist: SPR700, LOL2000, LOR 5B, S1813,	Isopropyl alcohol (MicroChemicals, VLSI)
Microposit MF-321 Developer (Rohm&Haas, pH ~ 13), photoresist: LOL2000	1112A Remover (Rohm&Haas, pH ~ 12), photoresist: SPR700, LOL2000, LOR 5B, S1813,	Acetone (MicroChemicals, VLSI)
ma-D 331 (Micro Resist Technology GmbH, LOR 5B, pH ~12), photoresist: LOR 5B,	SVC (TM)-14 (Rohm&Haas, pH ~8), photoresist: SPR700, LOL2000, LOR 5B, S1813,	Deionized water (18.2 MΩcm)

revealed a flat nanocrystalline single fiber structure. ZnO nanofibers in such form showed relatively good adhesion to the substrate.

The topological stability of the nanofibers in a technological liquid environment was studied by immersion of the prepared samples in developers, removers and solvents. The results of the observations are presented in Fig. 1 and Fig. 2. To avoid contamination, the SEM observations were carried out each time at different location of the same fiber. Such procedure was the result of our earlier observation that a thin layer of carbon, deposited during the contamination, caused efficient passivation of fibers, which completely protected them against the influence of solutions.

In Fig. 1, the high magnification SEM images of the ZnO nanofibers calcinated at 500 and 700 °C, before and after immersion in different developers and removers for a time period up to 2 min are presented. These times are sufficient to perform the photolithography processes for the production of device structures. In the group of developers, ZnO nanofibers showed the highest vulnerability to etching under the influence of MF-321 Developer (Fig. 1 c), and the greatest resistance to Microposit 351 Developer (Fig. 1 a). Each developer is a relatively strong alkaline solution with pH value about 13. Greater resistance of fibers to the Microposit 351 Developer could be caused by dilution of this developer in DI water in the ratio 1:5. In the group of removers, ZnO nanofibers showed

the highest vulnerability to etching under the influence of 1112A Remover (Fig. 1 e), and the greatest resistance to Microposit 1165 Remover (Fig. 1 d). In 1112A Remover, the samples were immersed for a time period up to 1 min only. The fibers, even in such a short time, were subject to substantial damage. In the group of solvents, ZnO nanofibers were affected due to the temporary impact of DI water (Fig. 2 c). In pure water, some of H<sub>2</sub>O molecules are dissociated into OH<sup>-</sup> and H<sup>+</sup> ions which enable the etching process. Organic solvents had no significant influence on the morphology of the nanofibers (Fig. 2 a, b).

In all cases, the nanofibers calcinated at higher temperatures, 700 °C, were more stable. This was due to larger grain size of the fibers processed at the higher temperatures. The studies have shown that smaller grains were dissolving much faster, leaving the porous core of the fiber (Fig. 1 – nanofibers calcinated at 500 °C). The size dependence of ZnO nanoparticles on the etching efficiency and significant increase in susceptibility with decreasing grain size have been reported [9]. Fig. 2 c shows the topography of the nanofibers before and after immersion in deionized water at different time intervals. With increasing detention time of the samples in DI water, the smaller grains of ZnO were etched away causing the exposure of larger grains. In Fig. 3, the normal distributions of grain diameters for the nanofibers calcinated at 500 °C and at 700 °C, before and after their immersion in DI water for dif-

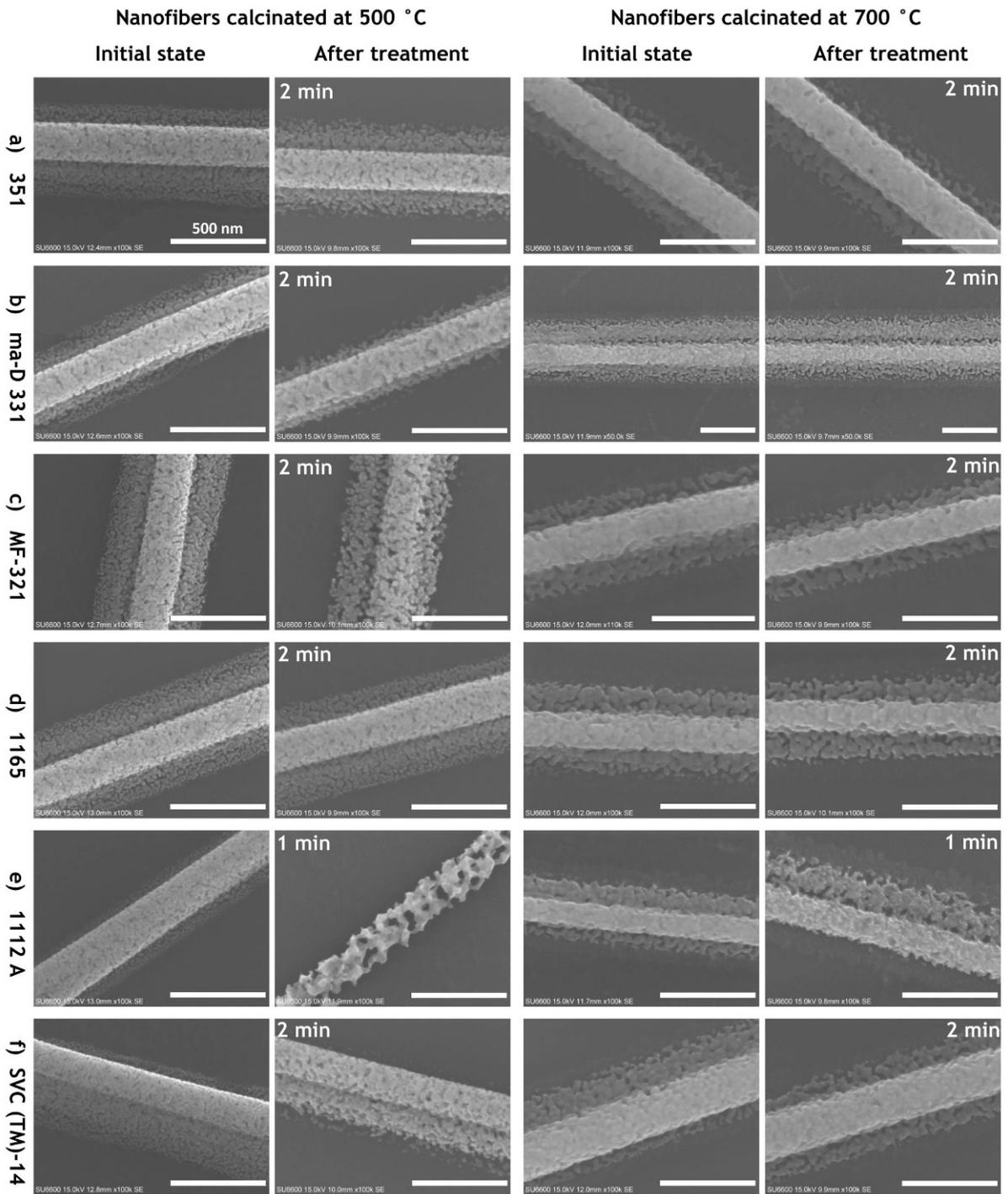


Fig. 1. SEM images at high magnification of the ZnO nanofibers calcinated at 500 °C and 700 °C, before and after immersion in different solutions, a) Microposit 351 Developer, b) Microposit MF-321 Developer, c) ma-D 331 Developer, d) Microposit 1165 Remover, e) 1112A Remover, f) SVC (TM)-14 Remover.

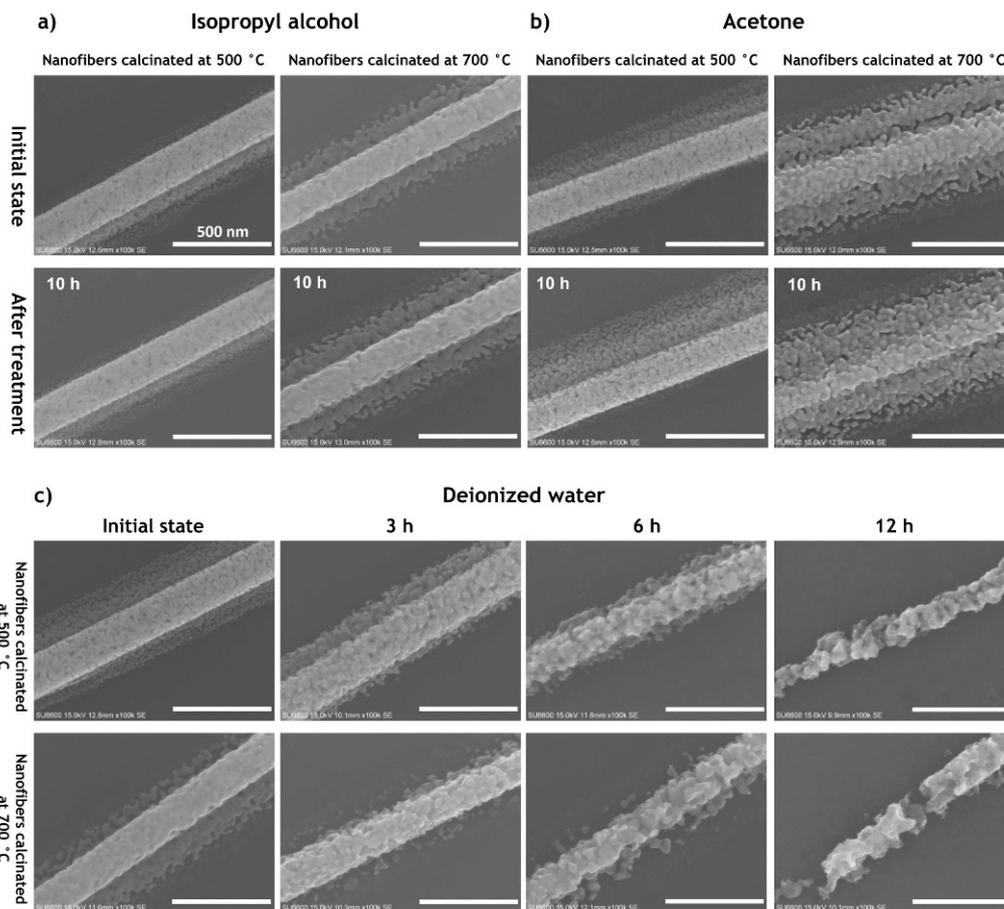


Fig. 2. SEM images at high magnification of the ZnO nanofibers calcinated at 500 °C and 700 °C, before and after immersion in different solvents, a) isopropyl alcohol, b) acetone, c) DI water.

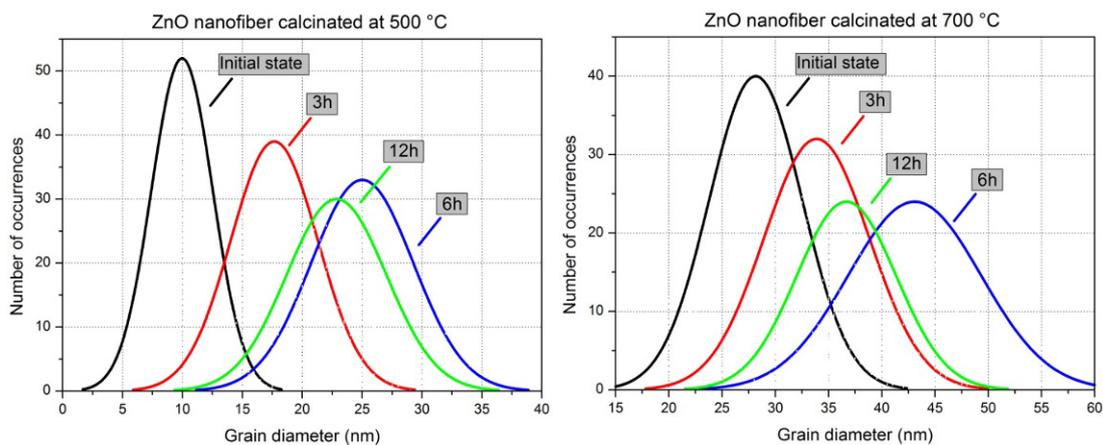


Fig. 3. Normal distributions of the grain size for nanofibers calcinated at 500 °C and at 700 °C and after immersion in deionized water for different time periods.

ferent periods of time are presented. The grain size was determined from SEM images. The average grain diameter was 10 nm for the fibers calcinated at 500 °C and 28 nm for the fibers calcinated at 700 °C. The grain size increased with increasing detention time of the samples in DI water, reaching a maximum value after 6 h and then decreased. Of course, one should be careful in calculating grain size from SEM scans because of low resolution of the images, typical of the system investigated (Si/SiO<sub>2</sub>/ZnO). Large grains could be formed as agglomerates of smaller grains. Such arrangement can be difficult to each in the solvents. Otherwise, we would have to deal with the phenomenon of grain size segregation, where their size decreases gradually, from the central axis of the fiber towards its perimeter.

#### 4. Conclusion

The aim of the research was to determine the impact of chemical agents such as developers and removers, used in the photolithography processes, as well as solvents used to wash and clean the structures on the stability of ZnO nanofibers. Surface imaging of nanofiber morphology was performed using Scanning Electron Microscope. From the obtained results a set of factors which have the least influence on the etching of ZnO nanofibers was selected. In the group of developers, ZnO nanofibers showed the highest vulnerability to etching in MF-321 Developer, and the greatest resistance to Microposit 351 Developer. In the group of removers, ZnO nanofibers showed the highest vulnerability to etching in 1112A Remover, and the greatest resistance to Microposit 1165 Remover. In the group of solvents, ZnO nanofibers were dissolved due to the temporary impact of deionized water. Organic solvents had no significant effect on the morphology of the nanofibers. In all cases, the

nanofibers calcinated at higher temperatures were more stable. This was due to a larger grain size of the fibers calcinated at higher temperatures. The studies have shown that smaller grains were dissolving much faster, leaving the porous core of the ZnO nanofiber.

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