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Vertical growth of titanium dioxide nanorods on nebulizer fluorine doped tin oxide deposited on silicon microarrays

A. Ghasemi Kordlar, J. Koohsorkhi*

Advanced Micro and Nano Devices Lab., Faculty of New Sciences and Technologies, University of Tehran, Tehran, Iran

ABSTRACT: In this paper, fluorine doped tin oxide layers are created as electrodes and seeds for the growth of titanium dioxide nanorods by spray pyrolysis coating based on silicon microarrays. The coating of this layer on the fluorine-contaminated tin oxide layer is of great importance for the fabrication of nanogenerators based on barium titanate. In this paper, two methods nebulizer and hydrothermal have been used. The effect of coating temperature as well as nebulizer volume on the surface resistance of the layers has been investigated by four-point probe device. Also, the samples were subjected to identical hydrothermal conditions for the growth of nanorods and the morphology of nanostructures grown on fabricated layers by scanning electron microscope has been investigated. The adhesion of the layers is also very important in this area and has been studied as one of the important parameters in the hydrothermal process. The results show that with this method, nanorods have grown on the side walls of the micro-machining structure, which can increase the quality of devices based on these structures. In this paper, low surface authorities up to 11 Ω / cm2 were achieved using the nebulizer method.

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1- Introduction

Titanium dioxide NanoRods (TiO_2NRs) are grown in various methods such as anodic oxidation [1], hydrothermal [2] and template [3], etc. Among these methods, hydrothermal is a simple, controllable, and cost-effective method to create nanorods. Several parameters affect the growth of Titanium dioxide nanotubes by hydrothermal method, including substrate, temperature, duration and also the acidity of the growth solution [2,4]. In 2010, Kumar et al. examined the growth of TiO_2 NRs on various substrates, including glass, Silicon / SiO_2, Fluorine doped Tin Oxide (FTO), and Indium doped Tin Oxide (ITO). They concluded that the orientation and formation of nanorods are highly dependent on the morphology of substrate. Because the structure of Fluorine doped Tin Oxide is tetragonal like that of titanium oxide, and the constant lattice difference between Fluorine doped Tin Oxide and rutile Titanium oxide is about 2%. This small difference leads to the regular, vertical and directional growth of nanorods on the Fluorine doped Tin Oxide layer [4]. The transparent and conductive layers of Fluorine doped Tin Oxide are n-type semiconductors with a bandgap energy and have unique properties and there are various deposition methods for Fluorine doped Tin Oxide such as the spin-coating [5], Magnetron sputtering [6] and spray pyrolysis [7]. The spray pyrolysis method is a simple and cost-effective method that has the advantages to create the uniform layer and possibility of growth rate on wide surfaces, working in atmospheric environment.

In this paper, spray pyrolysis Fluorine doped Tin Oxide layers are deposited on silicon microarrays for regular and vertical growth of Titanium dioxide nanorods, using the hydrothermal process.

2- Methodology

The fabrication process is shown in Fig. 1, which consists of 3 main steps. Step 1: creation of silicon microarrays, Step 2: creation of Fluorine doped Tin Oxide layers on the samples by spray pyrolysis method and Step 3: Placing the samples in the hydrothermal process for the growth of Titanium dioxide nanorods.

The deposition solution was prepared by dissolving 2 g of $SnCl_4.5H_2O$ in 5 ml of methanol and on the other hand, fluorine doping solution was prepared by dissolving 0.4 g of NH_4F in 5 ml of deionized water and then both solutions were mixed. After preparation of the solution, using the Beaur IH apparatus, which has undergone fundamental changes here, the substrates were nebulized under temperatures (350-450 oC) in different volumes, and then the samples for the growth of titanium dioxide nanorods were placed in an autoclave with a capacity of 50 ml containing 7.5 ml of deionized water, 7.5 ml of solution (HCl 37%) and 0.25 ml of titanium chloride at a temperature of 170oC for 3 h [2].

*Corresponding author's email: *koohsorkhi@ut.ac.ir

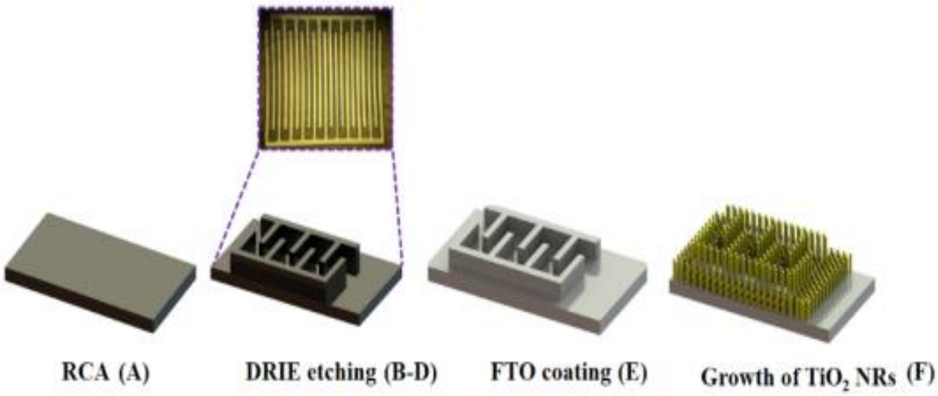

Fig. 1. Graphical schematic of the manufacturing process of FTO / TiO2 NRs and the real etched sample

3- Discussion and Results

3- 1- Investigation of electrical conductivity

Table 1 shows the sheet of the Fluorine doped Tin Oxide layer. According to Table 1, the best case is for the sample deposited at a temperature of 450 oC. In the following, the sheet resistance of the samples was examined under different nebulizer volumes. According to Table 2, it was observed that with increasing nebulizer volume, the sheet resistance of the layers decreases, which is because with increasing nebulizer volume, larger particle sizes and their distances is reduced, which in fact facilitates the transport of load carriers, thus reducing the sheet resistance.

Table 1.Sheet resistance versus temperature deposition samples in 1 ml Nebulizers

Temperature deposition	Sheet resistance
300 °C	389 kΩ/cm^2
350 °C	134 kΩ/cm^2
400 °C	34 kΩ/cm^2
450 °C	800 Ω/cm^2

Table 2. Sheet resistance and mean particle size of samples in terms of nebulizer volume under the coating temperature 450 oC

Nebulizer volume (ml)	Sheet resistance	Particle size (nm)
1	800 Ω/cm^2	148
1.5	98 Ω/cm^2	385
2	14 Ω/cm^2	473
2.5	11 Ω/cm^2	632

3- 2- Synthesis of titanium dioxide nanorods

Finally, the adhesion of the layers was examined under a temperature between 300 to 450 oC. To this point, the samples were subjected to the same conditions in a hydrothermal process, and we concluded that the samples that were nebulized at a temperature of 450 oC have good adhesion, and finally the sample Nebulizers under a volume of 1 to 3 ml at the optimum temperature were placed in hydrothermal to investigate the formation of nanorods.

Fig. 3 shows electron microscope images after hydrothermal process of a sample based on silicon microarrays coated with Fluorine doped Tin Oxide. The growth of nanorods has also grown successfully in the depths and walls of silicon microarrays, which characterizes the formation of Fluorine doped Tin Oxide layer in the depth and walls of silicon microarrays.

4- Conclusions

In this research, Fluorine doped Tin Oxide layers were created by spray pyrolysis on the substrates and it was found that with increasing the deposition temperature, the sheet resistance of the samples decreases and reaches its minimum value below 450 oC. The layers created for the growth of Titanium dioxide nanorods were subjected to the same hydrothermal process conditions. The samples that are fabricated in the hydrothermal layer at a coating temperature of less than 450 oC, do not have good adhesion. Layers created at temperatures below 450 oC were not hydrothermally isolated or did not have good adhesion after the growth of the sample, but at 450 °C temperatures successful growth and good adhesion were observed. In the next step, the coated layers with different nebulizer volumes were examined and the optimum condition was 2 ml. After obtaining the conditions, the Fluorine doped Tin Oxide layers were layered on the sample with silicon microarrays after the growth synthesis of nanorods. It has been done successfully on the walls and the reason is that the Fluorine doped Tin Oxide layer has also been applied on the walls.

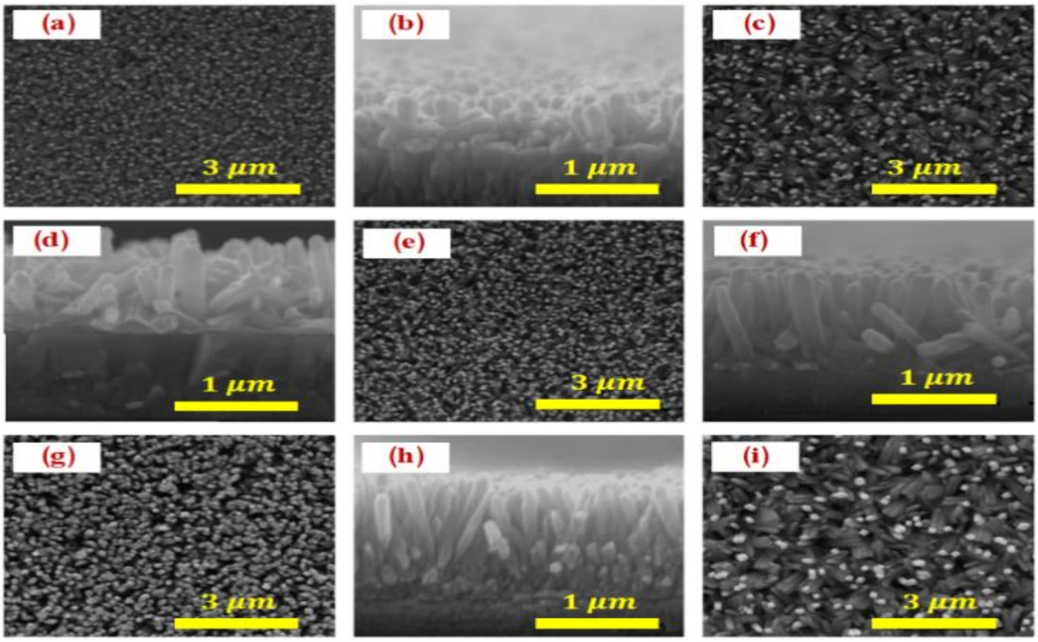

Fig. 2: SEM images of the growth of TiO2 NRs on silicon substrates coated with FTO layers in different volumes Nebulizer (a): 1 ml (b): Cross-sectional image (a). (c): 1.5 ml (d): Image of cross-sectional view (c). (e): 2 ml (f) Image of cross-sectional view (e). (g): 2.5 ml (h): Image of cross-sectional view (g). (i): 3 ml

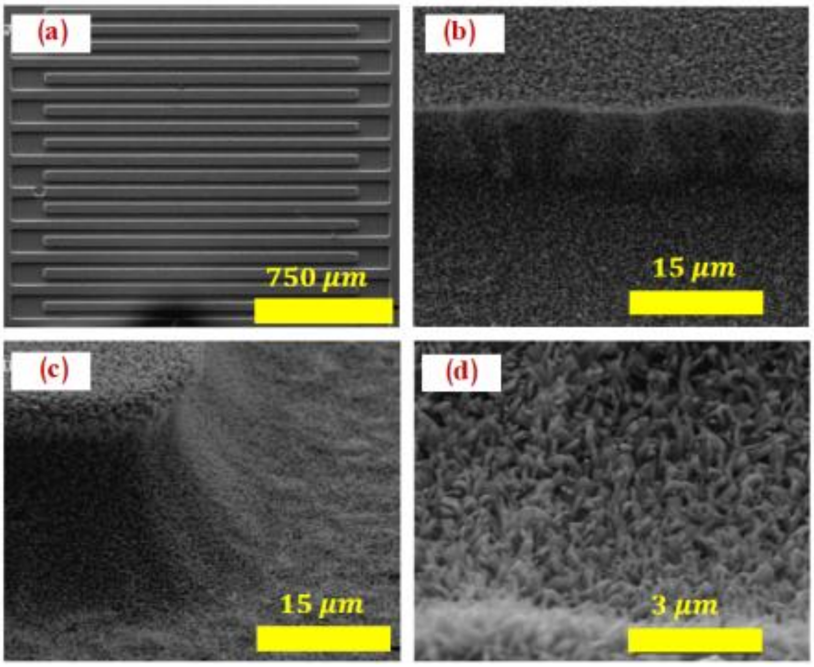

Fig. 3: SEM images of TiO2 nanowires on micromachined silicon substrate

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