

# LOW-ENERGY ION-BEAM BOMBARDMENT FOR METAL OXIDE NANOWIRE SURFACE CLEANING AND MODIFICATION

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## Abstract

The paper presents results of study of the SnO<sub>2</sub> nanowire chemoresistor treatment by means of low-energy Ne<sup>+</sup> ion-beam bombardment. SnO<sub>2</sub> nanowires were obtained by means of vapor-solid method at the temperature 900°C. Ti/Au (20/500 nm) electrical contacts to individual nanowires were deposited via consequent PVD deposition through the shadow mask under high vacuum conditions.

Current versus voltage characteristics were measured in the range -10 to +10 volts both in high vacuum ( $P = 1 \times 10^{-6}$  Torr) and in the oxygen presence ( $1 \times 10^{-4}$  Torr).

Cleaning and modification of nanostructure surface *in situ* was performed through the series of Ne<sup>+</sup> bombardment cycles at the 275°C and Ne partial pressure  $P_{\text{Ne}} = 1 \times 10^{-6}$  Torr. Established experimentally optimal Ne<sup>+</sup> ion current has amounted to  $1.15 \times 10^{-4}$  A.

Electrical conductance and gas sensing performance changing due to the NW interaction with ion beam were used to control ion bombardment effect. It was established that conductivity is increased by two orders and superficially modified NW response to hydrogen with oxygen background is also higher.

## Introduction

One of the sensitive problems in the semiconductor device manufacturing is to provide high level of device surface cleaning for a best device performance. It is especially important in such fields as optoelectronics, chemical and biological sensorics, where any surface contaminants can seriously deteriorate device performance and even destroy it. This problem becomes more severe at the transition to the nanoscaled devices on the basis of nanowires (NW), nanobelts (NB), nanodots (ND), etc. The presence of not only micro particles but even separate atoms, group of atoms, molecules, or their radicals on the surface of given 1D and 0D structures can lead to a significant negative influence on device performance. In particular, H. Dai et al. have shown that molecules of H<sub>2</sub>O adsorbed on the carbon nanotubes (CNT) can cause the hysteresis effect in the characteristics of the CNT based field effect transistors [1].

Similar effect but for ZnO nanowire based transistors was described by P. Yang [2]. Another type of the negative effect described in [3] consists in the appearance of “parasitic” charging of surface and memory effect in SnO<sub>2</sub> NW due to environment influence. “Parasitic” charging, in particular, consists in the lateral spreading (with characteristic time constant in the order of 20-30 min) of the potential distribution under continuous bias and the retention of electric field after the bias is switched off.

To clean the nanodimensional structures surface from contaminants, thermal annealing technique [4], initiating thermal desorption of adsorbed gaseous particles can be used. How-

ever, some species, such as OH<sup>-</sup> groups, for example, remain on the surface up to 450-500°C [5] and not all devices can be treated at such temperatures (except for metal oxide based gas sensors). And even for the last ones the thermal treatment does not guarantee required cleanness. Another approach was demonstrated by Peidong Yang et al. [6] through UV photo stimulation of the adsorbed molecules desorption from nanoribbon surface and, as result, its gas sensing performance improvement.

In our paper, we report approach based on the utilization of ion irradiation of the metal oxide based nanowire gas sensor. Low energy ion beam (LEIB) technique (both focused and unfocused) has been already successfully used for patterning of the nanoscale structures [7], in application to MEMS technology [8], formation of the electrical contacts to NW [9], for the reduction of a nanostructure size [10], nanoparticles obtaining [11], and the formation of nanopores which could be ideal sink for adatoms [12].

In our case, the interaction of the low-energy (<10 keV) ion-beam with the surface of metal oxide NW gas sensor will allow us to clean the NW surface and considerably modify the surface structure, increasing the amount of surface defects, serving as adsorption centers for detectable gas measurands.

### Experimental details

The material chosen for this study is SnO<sub>2</sub> arguably the most studied and best understood material in use for Me-Ox-based sensors. The SnO<sub>2</sub> NW were synthesized via traditional vapor–solid growth mechanism [13] in the Lindberg/Blue Scientific tube furnace at the temperature  $T = 900^{\circ}\text{C}$  from the powder precursor. Briefly, Argon (99.998%), used as carrier gas, was fed into the quartz tube through a solenoid valve activated by a computer-controlled power supply, allowing the argon gas flow to be shut off and turned on in a programmable sequence [14].

X-ray diffraction (XRD) and Scanning Electron Microscopy were used to characterize the structure, composition, and shape of the SnO<sub>2</sub> NW.

Consecutive Ti/Au (20/500 nm) PVD deposition through the shadow mask in high vacuum was used to produce electrical contacts to individual NWs.

Current versus voltage characteristics were measured in the range -10 to +10 volts both in high vacuum ( $P = 1 \times 10^{-6}$  Torr) and in the oxygen presence ( $1 \times 10^{-4}$  Torr). The reported electrical measurements were performed on the samples in a two-point configuration at the temperature 548 K to speed up the adsorption/desorption kinetics at surface of developed chemoresistor.

For NW surface cleaning and modification there was used sputter ion gun phi model 04-191 (Physical Electronic Industries, USA). We used in our experiments Ne<sup>+</sup> ions with energy 3 keV. For the ion current optimization the preliminarily study of the current magnitude dependence on Ne pressure in chamber was carried out. It was established that Ne partial pressure  $P_{\text{Ne}} = 1.15 \times 10^{-5}$  Torr is optimal for the obtaining of maximal ion current  $I_{\text{Ne}} = 2.3 \times 10^{-4}$  A. This optimized  $I_{\text{Ne}}$  was used in all experiments on surface cleaning and modification. Density of ion flux impinging NW surface at the 80 degree with respect to surface was estimated as  $2.84 \times 10^{-11}$  A. Nanostructure temperature in the process of ion bombardment was kept at  $T = 275^{\circ}\text{C}$ . Duration of the NW exposure to LEIB has amounted to 30 min in the first two experiments, 60 min at the third bombardment and 90 min for the last one. For the control of the ion beam influence on the NW there were used I-V measurements and gas sensing performance control before and after each exposure.

## Results and discussion

The width of the XRD reflections of as-grown  $\text{SnO}_2$  NW (Fig. 1) indicates them to be highly crystalline. Few major reflections are observed in the  $25-60^\circ$   $2\theta$  range, which are assignable to the (110), (101), (200), (111), (210), (211), and (220) crystal planes, characteristic of tetragonal (rutile)  $\text{SnO}_2$ . Length of NW is  $5\ \mu\text{m}$  and the diameter is approximately 200 nm.

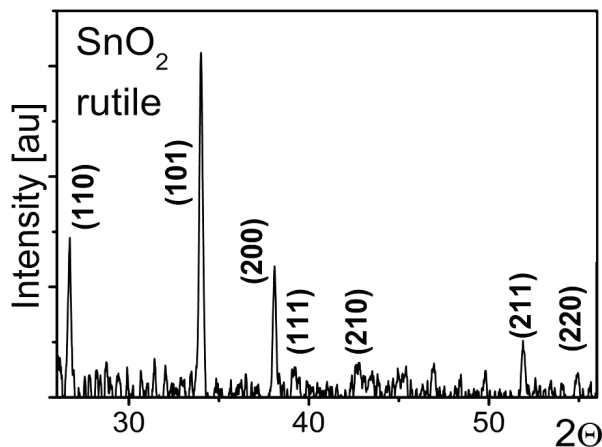


Fig. 1. XRD spectra of as-grown  $\text{SnO}_2$  NW.

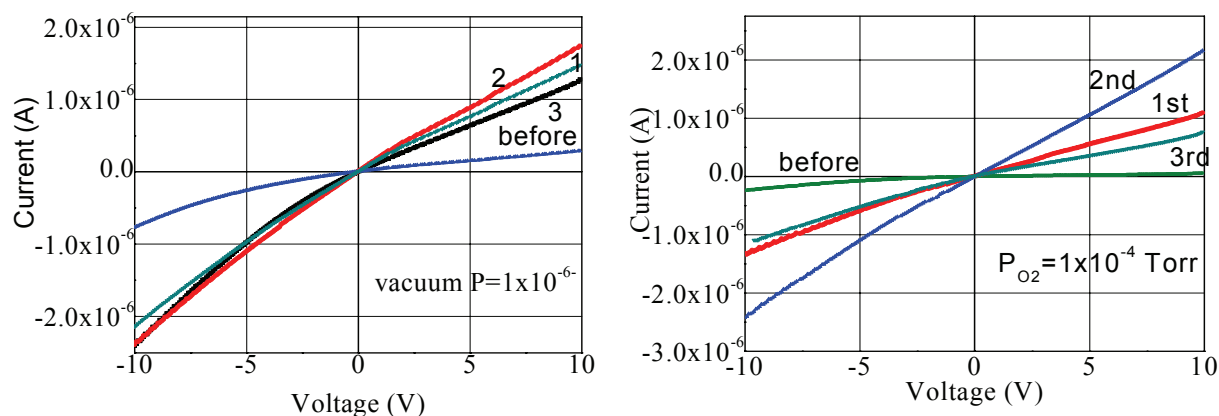


Fig. 2. I-V curves measured at  $T = 275^\circ\text{C}$  under vacuum conditions (a) and in the presence of oxygen (b) before and after three  $\text{Ne}^+$  bombardment cycles.

I-V curves measured at  $T = 275^\circ\text{C}$  under vacuum conditions ( $P = 1 \times 10^{-6}$  Torr) and in the presence of oxygen ( $1 \times 10^{-4}$  Torr) before and after exposure to  $\text{Ne}^+$  ion beam are presented in Fig. 2. Basic features of the obtained curves can be summarized as follows: (1) in all cases I-V are slightly asymmetrical; (2)  $\text{Ne}^+$  ion treatment does not change the observable asymmetry of the curves; (3) changes in current ratios before and after  $\text{Ne}^+$  ion flux exposure are more noticeable for I-V obtained in the presence of oxygen. In particular, under vacuum conditions the current ratio for  $U = +10$  V before and after exposure amounts to ca 6 times while in oxygen presence it reaches more than 35-fold increase after the second  $\text{Ne}^+$  ion bombardment cycle; (4) one more interesting feature consists in the I-V curve order changing for both vacuum and oxygen cases with the exposure dose growth. After third ion bombardment further current growth could be expected. However, we observe its decrease to the lower current. The possible reason for observed phenomenon will be discussed below.

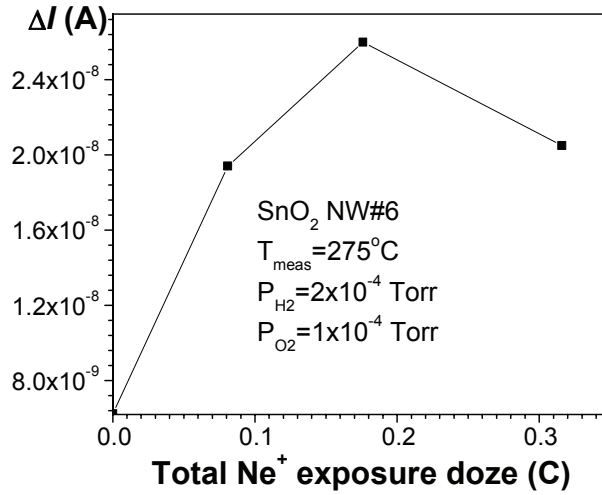


Fig. 3. Ion bombardment influence on SnO<sub>2</sub> NW structure response to hydrogen.

Figure 3 presents results of Ne<sup>+</sup> bombardment influence on developed nanostructure response to hydrogen ( $P_{H_2} = 2 \times 10^{-4}$  Torr) with oxygen background on the level  $P_{O_2} = 1 \times 10^{-4}$  Torr. This influence was estimated as current alteration at the hydrogen leaking-into the chamber before and after each consecutive Ne<sup>+</sup> exposure:

$$\Delta I = (I_{after} - I_{before}). \quad (1)$$

Analyzing the results presented in Fig. 3 we can state that there is observed the situation similar to the described above; that is, third Ne<sup>+</sup> bombardment leads to the conductance drop after sharp growth of current response at the first exposure and less but continuing growth after the second cycle of Ne<sup>+</sup> bombardment.

Conductance increasing after the first and second ion bombardment procedures can be connected with a few different processes undergoing at the surface and in the subsurface region of NW:

(a) First of all, the question is the process of the cleaning of NW surface from different atoms, molecules, and some radical groups, such as OH<sup>-</sup>, which are present on the SnO<sub>2</sub> metal oxide surface. The complete removing of the mentioned species from the surface is usually required for annealing of the material at the temperature 450°C (723 K) and higher [5].

(b) Another phenomenon, responsible for the current (conductance) difference increase after the first two treatments is connected, in our opinion, with Ne<sup>+</sup> ion beam interaction directly with NW lattice and considerable lattice oxygen removal from surface and subsurface region of the NW. Similar situation was observed by Erickson for SnO<sub>2</sub> film [15]. In particular, XPS study performed in this work has shown that 2-kV Ar ion bombardment decreases the O/Sn ratio as much as 40%. The last one leads to the appearance of additional oxygen vacancies serving as donors in the SnO<sub>2</sub> NW.

(c) The process described in (b) is enhanced by the relatively high measurement temperature of the sample (275°C or 548 K), which also can contribute to the process of oxygen vacancy formation. As shown in work [15], the thermodesorption of lattice oxygen atoms from the surface of SnO<sub>2</sub> film is observed already at ~600 K. This should lead, as result, to the oxygen thermal diffusion from internal subsurface layers of NW to the surface. This process is accelerated by the permanent oxygen removing by impinged Ne<sup>+</sup> ions.

(d) We also should take into account that fact that local temperature of the NW is higher than 548 K due to heat transfer at the power transfer by the incident ions. In particular, at 3 kV and 23 μA (used in our case) the dissipated power will amount to 63 mWt, which is

more than enough to locally heat NW up and accelerate the oxygen diffusion from the bulk to the surface and its further desorption with simultaneous formation of oxygen vacancies. As a result, conductivity in SnO<sub>2</sub> NW is increased.

However, situation is changed after the next, third, ion bombardment procedure. For observed decline in the conductance after third (90 min) exposure to Ne<sup>+</sup> ion flux can be explained either by charge carrier mobility decrease due to the ion-beam induced disorder in subsurface region of nanowire or decrease of the nanowire size in general due to the sputtering. In both cases the effective cross-section of conductance channel in NW is decreased that leads to the drop of the NW response to hydrogen.

Changing of nanowire dimensions due to the ion beam is a real fact. Our fourth nanowire exposure to Ne<sup>+</sup> ions during 90 min has led to complete nanowire sputtering that was confirmed by the consequent SEM.

### **Conclusions**

The influence of the low energy Ne<sup>+</sup> bombardment on the state of the surface and electrical and gas sensing properties of SnO<sub>2</sub> nanowire is studied. It is found that optimal electrical and, as result, gas sensing properties can be achieved after a single 90-minutes-ion-bombardment cycle of surface cleaning and modification (30 min (1<sup>st</sup> cycle) + 60 min (2<sup>nd</sup> cycle)). The observed alterations in conductivity and response to hydrogen are considered from the position of formation of the additional oxygen vacancies in SnO<sub>2</sub> nanowire.

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