

# Chapter 23

## Surface Modification for Novel Nanosensors Creation

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**Abstract** A new method of sensor surfaces treatment has been proposed. The main feature of the developed approach is the creation of a large specific surface on silicon substrate and  $\text{TiO}_2$  nanotube arrays that are formed in surface trenches. A modified surface allows fabricating various types of sensors.

**Keywords**  $\text{TiO}_2$  nanotube arrays • Anisotropic wet etching • Focused ion beam etching

### 23.1 Introduction

Metal oxide materials, such as  $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{WO}_3$  having different catalytic metal additives deposited on their surface and characterized by different microstructures are used as sensing elements [1]. These gas sensors have been extensively studied [2]. The main problem in utilization of the indicated materials remains their poor selectivity due to high cross-sensitivity to various gases and humidity [3].

The important direction of novel sensor systems development is the fabrication of sensor arrays. One single sensor in many cases cannot give the necessary information to determine the chemical composition of the substances, for example, for a high-temperature or harsh environment. Within recent years the nose sensor arrays have been developed for high-temperature environments. They are fabricated using microelectromechanical systems (MEMS) based technology [4].

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The individual sensors are different devices (resistors, diodes, and electrochemical cells respectively) and have different responses to particular gases in the environment.

At present, sensor arrays are used in the chemical industry to control the work of power plants, to detect automotive exhausts, to test the environmental protection. A promising way of increasing the selectivity and sensitivity of gas sensors is to treat the signals from a number of different gas sensors with pattern recognition methods.

The achievements in the field of nanoscience and nanotechnology have led to new possibilities in the creation of sensor arrays. Novel nanomaterials, due to their size, larger surface to volume ratio, and the properties that differ significantly from their bulk counterparts, promise better performance than micro- and macro-sensors. The perspective nanomaterials include carbon nanotubes (CNTs) [5], inorganic nanowires of high-temperature oxides, semiconducting elements or compounds, and quantum dots. Wide possibilities in the field of bioanalysis are open due to the development of track electronics [6].

CNTs have attracted much attention for physical, chemical, and bio-sensors due to their unique physical, electrical properties. In the previous research [7], a sensor array consisting of carbon nanotubes is described as a sensing material and an interdigitated electrode as a transducer. The ability of carbon nanotubes and their derivatives to operate as gas and glucose sensors has been recently demonstrated [6].

The track-based sensors are a new generation of nanosensors that attract a great interest as multifunctional devices. Their main features are the following:

- Track-based devices (TBD) can be fabricated both as gas sensors and as biosensors [7];
- In fact, TBD are sensor arrays and have all their advantages;
- New effective mechanisms of sensor signal formation can be realized in TBD.

In this paper we propose methods for fabrication of silicon surfaces with complex architecture and arrays of  $\text{TiO}_2$  nanotubes suitable for creation of nanosensors of a wide range of applications.

## **23.2 Fabrication of New Sensor Surfaces and Their Applications**

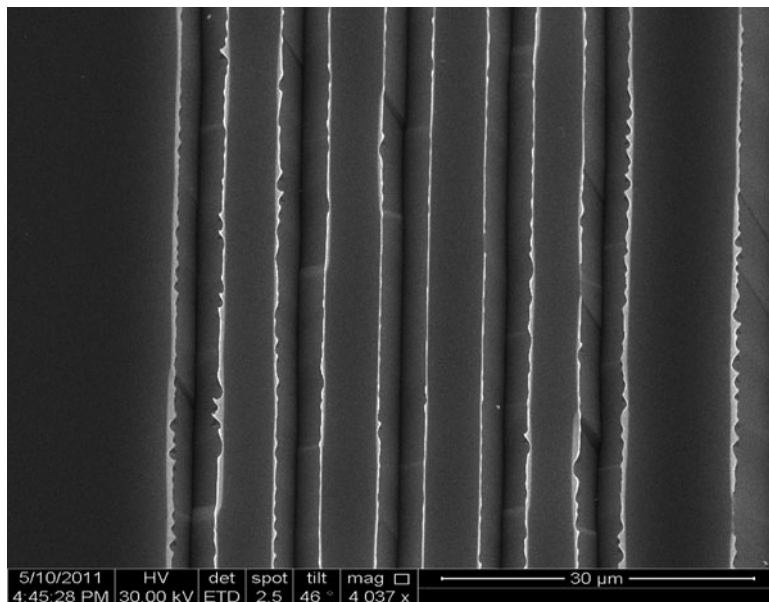
### **23.2.1 *Anisotropic Wet Etching (AWE)***

The anodized layer of 100 nm thick on Si surface was used as a mask for a patterning and a wet etching. Narrow strips in  $\text{SiO}_2$  layer were opened and the Si substrate was etched through these windows.

The 100 nm  $\text{SiO}_2$  layer was etched using the composition  $\text{NH}_4\text{HF}_2:\text{NH}_4\text{F}:\text{H}_2\text{O}$  (3:4:12). The next etching of silicon was performed by solution of KOH and IPA



**Fig. 23.1** An anisotropic etching was realized and V-shape furrows (grooves) in substrate were obtained (a). This method has allowed us to create a large silicon specific surface (b) that can provide the desirable parameters of nanosensors



**Fig. 23.2** Si substrate with V-shape furrows along direction (111)

(isopropylalcohol) at 60°C (see Fig. 23.1). All etched trenches (in plane (111)) were smooth if the strips were exactly in (100) direction (Fig. 23.2). But we observed a rugged (terraced) topography of the surface relief when the strips had some inclinations to (100) direction (Fig. 23.3). In this case the further increase of silicon specific surface was obtained.

On the treated silicon substrate (by the described way), the Ti film of 0.5–1 μm thick was deposited and TiO<sub>2</sub> nanotubes were created. Precisely ordered vertically oriented TiO<sub>2</sub> nanotube arrays were fabricated by potentiostatic anodization of titanium (Fig. 23.4).

All in all, we have obtained a complex silicon surface architecture consisting TiO<sub>2</sub> nanotube arrays with important features: a large specific surface and structural configurations that can be used for novel nanosensors fabrication. Conductivity measurements have shown that the created structures consist of electron

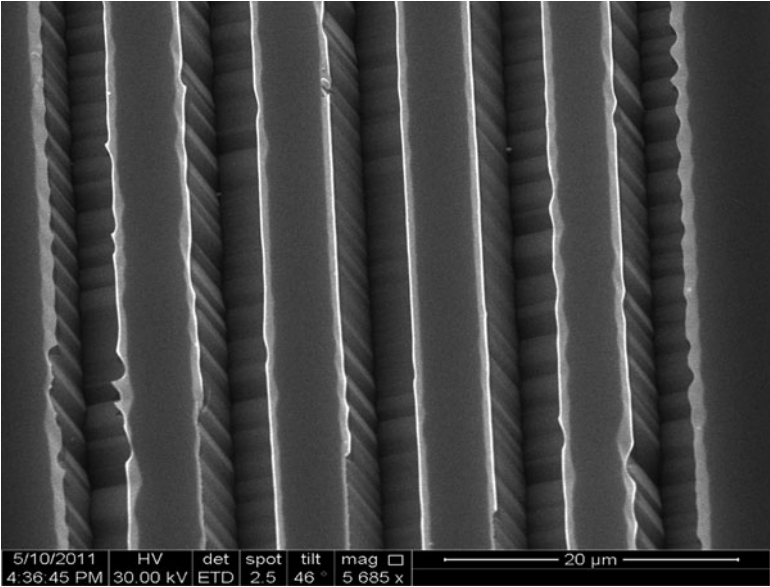


Fig. 23.3 Si substrate with V-shape furrows under small angle to (111) direction

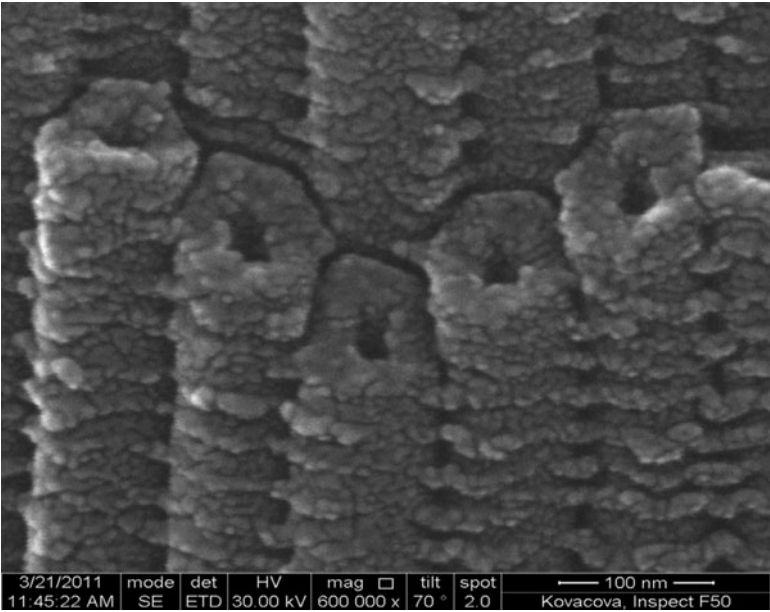


Fig. 23.4 Vertical TiO<sub>2</sub> nanotubes (Kovacova)

percolation pathways that determine the unknown earlier parameters of sensor devices.

### ***23.2.2 Focused Ion Beam (FIB) Etching***

FIB systems use a finely focused beam of gallium ions that can be operated either at low beam currents for imaging or at high beam currents for site specific sputtering or milling.

At low primary beam currents, very little material is sputtered. Modern FIB systems can achieve 4 nm imaging resolution. At higher primary currents, a great deal of material can be removed by sputtering, allowing precision milling of the specimen down to a submicron scale.

In our case, the furrows with rectangular profile were formed on silicon substrate by  $\text{Ga}^{+3}$  focused ion beam. Then  $\text{TiO}_2$  nanotubes were formed as in the case of AWE. The oxygenation led to increase of the volume and specific surface of  $\text{TiO}_2$  nanotubes.

### ***23.2.3 Applications of New Architecture of Silicon Surfaces***

Combination of the developed complex architecture of silicon surface with the created vertical  $\text{TiO}_2$  nanotube arrays on this surface allows fabricating original sensor systems. Preliminary results have shown that  $\text{TiO}_2$  nanotube arrays in the developed structures reveal electric characteristics similar to the observed in track-based devices but, at the same time, they have new important peculiarities. The obtained electronic structures have lead to the creation of gas sensors as well as biosensors of extremely high quality.

The  $\text{TiO}_2$  surfaces effectively adsorb inorganic molecules from the environmental pollution. Using titanium or other metals as electrodes and fabricating devices based on the new surface architecture we are able to fabricate sensors with unusually high sensitivity for detection of some reducing gases in the atmosphere in a wide temperature interval.

Most biological processes that occur in/or around a living cell are electrostatic or electrochemical in nature. Field-effect transistors that use single-walled carbon nanotubes can be used as sensitive probes for cell studies. The developed silicon surface configurations with  $\text{TiO}_2$  nanotubes give new opportunities to improve these devices.

## 23.3 Conclusion

The creation of new nanosensors depends mainly on the nanostructure of sensor surfaces and chemical properties of adsorption centers. New possibilities for nanosensors development are linked to the development of track electronics. The next important direction of novel nanosensors creation is the fabrication of sensor devices based on nanotube arrays. In this work we have proposed methods of silicon surface treatment that leads to a significant increase of the specific surface. Nanotube arrays are formed on this surface. The final surface architecture allows fabrication of different types of novel nanosensors.

## References

1. Neri G, Bonavita A, Micali G, Rizzo G, Callone E, Carturan G (2008) Resistive CO gas sensors based on  $\text{In}_2\text{O}_3$  and  $\text{InSnO}_x$  nanopowders synthesized via starch-aided sol-gel process for automotive applications. *Sens Actuator B* 132:224–233
2. Epifani M, Comini E, Arbiol J, Diaz R, Sergent N, Pagnier T, Siciliano P, Faglia G, Morante J (2008) Chemical synthesis of  $\text{In}_2\text{O}_3$  nanocrystals and their application in highly performing ozone-sensing devices. *Sens Actuator B* 130:483–487
3. Suche M, Katsarakis N, Christoulakis S, Nikolopoulou S, Kiriakidis G (2006) Low temperature indium oxide gas sensors. *Sens Actuator B* 118:135–141
4. Zampolli S, Elmi I, Mancarella F, Betti P, Dalcanale E, Cardinali GC, Severi M (2009) Real-time monitoring of sub-ppb concentrations of aromatic volatiles with a MEMS-enabled miniaturized gas-chromatograph. *Sens Actuator B* 322:141–147
5. Bellucci S, Chiaretti M, Cucina A, Carru GA, Chiaretti AI (2009) Multiwalled carbon nanotube buckypaper: toxicology and biological effects in vitro and in vivo. *Nanomedicine* 4(5):531–540
6. Lerner MB, Goldsmith BR, McMillon R et al (2011) Zirconia grafted carbon nanotubes based biosensor for M. Tuberculosis detection. *Appl Phys Lett* 99:43702
7. Fink D, Klinkovich I, Bukelman O, Marks RS, Kiv A, Fuks D, Fahrner WR, Alfonta L (2009) Glucose determination using a re-usable enzyme-modified ion track membrane. *Biosens Bioelectron* 24:2702–2706