COMMUNICATIONS

DEVELOPMENT AND FABRICATION OF TiO_2 TIP ARRAYS FOR GAS SENSING

Ivan HOTOVÝ * — Ivan KOSTIČ ** — Štefan HAŠČÍK * Vlastimil ŘEHÁČEK * — Jozef LIDAY * — Helmut SITTER ******

Titanium oxide thin films were deposited at room temperature by reactive magnetron sputtering in a mixture of oxygen and argon on oxidized silicon substrates. The optimal etching characteristics of TiO_2 films by reactive ion etching (RIE) and RIE with inductively coupled plasma source (ICP) were investigated. Patterning of TiO_2 tip arrays by electron beam lithography and dry etching were developed. Different spot sizes 200 and 500 nm in diameter and with spacing 500 and 1000 nm were investigated with regards to the minimal size and the pyramidal shape. Experimental results have shown that the exposure dose optimization wa a significant parameter for controlling the tip size and its shape. We successfully fabricated the pyramidal TiO_2 tip arrays over an 1×1 mm^2 area. The TiO_2 tip array can be expected to have an important application in gas microsensors.

K e y w o r d s: TiO_2 thin films, dc magnetron sputtering, reactive ion etching, electron beam lithography, tip array

1 INTRODUCTION

For semiconductor-type gas sensors based on metal oxides as SnO_2, TiO_2, ZnO, In_2O_3, Fe oxides, WO_3, Ga_2O_3 and perovskite-type oxides, the use of materials with a mean particle size well below 50 nm significantly improved the gas sensing properties [1–3]. A chemoresistive gas sensor generally consists of a thin film of semiconductor material, whose conductance is measured using a pair of miniature electrodes with dimensions much larger than the particle size [4–6]. Gas phase species can become adsorbed on the particles. Since the gas sensitivity is in this case a surface phenomenon, it is desirable to produce sensing films from the smallest possible particles.

In recent years, great expectations in gas-sensor field were in novel and fascinating quasi- one-dimensional structures (nanowires, nanobelts, nanotubes) that are single-crystalline nanostructures with a high aspect ratio, normally grown in a bottom-up approach. These intriguing characteristics make the structures potentially good candidates for chemoresistive gas sensors, reducing instabilities, suffering from their polycrystalline nature associated with grain coalescence and drift in electrical properties [7–9]. In spite of such benefits, also in this bottom-up approach many problems remain unsolved, such as poor repeatability due to a scarce control in the growth. There are also some difficulties in growing and difficulties in transferring the nanomaterial on the transducer platform and in making good electrical contacts to these nanostructures. Wang *et al* [5] considered grain size effects in particulate semiconductor gas sensors and concluded that gas sensitivity would increase sharply for particle diameters below about 35 nm. Studies on tin dioxide hydrogen sensors indicate that devices produced using 20 nm particles were around 10 times more sensitive than devices made from 25 to 45 nm particles. The top-down method is another way to achieve order patterns for different kinds of materials. The use of dry etching processes allows to tailor the vertical and horizontal etch rate of a film selectively masked by photoresist, dielectric or metal, to achieve high fidelity pattern transfer [10, 11].

In this study, patterning of titanium oxide tip array combining reactive ion etching and electron beam lithography was developed and investigated.

2 EXPERIMENTAL PROCEDURE

The polycrystalline TiO_2 films were deposited by dc reactive magnetron sputtering from an Ti target (4 in diameter, 99.99 % pure) in a mixture of oxygen and argon onto unheated oxidized Si substrates. A sputtering power of 600 W was used. Both argon inert flow and oxygen reactive flow were controlled by mass flow controllers. The relative partial pressure of oxygen, defined as $P = p(O_2)/p(O_2 + Ar)$, was 20 %. The total gas pressure was kept constant at 0.8 Pa and adjusted by a piezoceramic valve. X–ray diffraction confirms the formation of

* Institute of Electronics and Photonics, Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia, ivan.hotovy@stuba.sk;
** Institute of Informatics, Slovak Academy of Sciences, Dubravska cesta 9, 824 39 Bratislava, Slovakia,
*** Institute of Electrical Engineering, Slovak Academy of Sciences, Dubravská cesta 9, 845 07 Bratislava, Slovakia,
**** Institute of Semiconductor and Solid State Physics, Johannes Kepler University, Altenbergerstr. 69, A-4040 Linz, Austria

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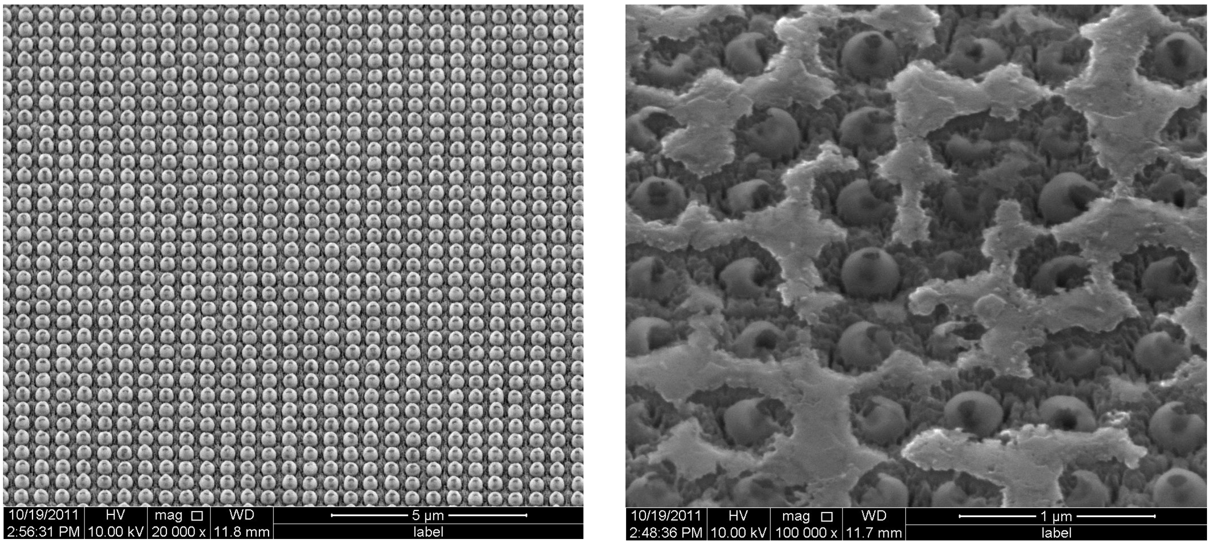

Fig. 1. SEM images of tip array with 200 nm diameter/ spacing 500 nm TiO_2 tip array etched by RIE for 20 min at the exposure dose $2600\,\mu C/cm^2$ (a) and $1300\,\mu C/cm^2$ (b)

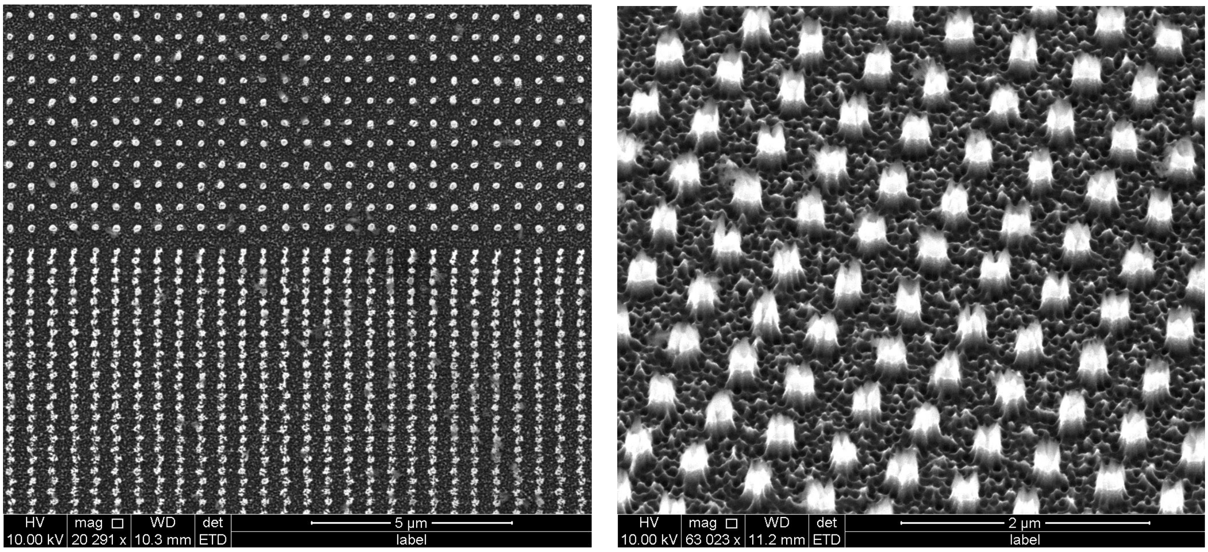

Fig. 2. SEM images of tip array with 200 nm diameter/ spacing 500 nm TiO_2 tip array etched by RIE/ICP for 5 min at the exposure dose $3000\,\mu C/cm^2$. The large view (a) and the detail tilted 45° (b)

polycrystalline anatase under these conditions. The film thickness was about 120 nm as measured by Talystep.

The samples were etched in RIE and RIE/ICP modes in CF_4-based plasma in a Vacutec 310/320. The RIE plasma was generated by a radio frequency field at 13.56 MHz supplied via an Al electrode (ϕ 300 mm) whose temperature was stabilized at 20 °C. Some samples were etched in the same reactor utilizing an ICP source operating at 2.4 MHz and separate rf (13.56 MHz) biasing of the sample electrode. Before introducing of CF_4 the chamber was evacuated to a background pressure $< 5 \times 10^{-2}$ Pa. The gases were admitted into the reactor chamber through electronic flow controllers at a typical flow rate of 30 sccm for RIE and 10 sccm for RIE/ICP, respectively. In the case of RIE/ICP mode, Ar (10 sccm) was added to enhance stability of discharge. The etch depths were measured by Talystep.

The structures of tip arrays were defined by direct write e-beam lithography with 30 keV electron energy and a 300 nm thin negative resist SU-8 as a masking layer. Resist SU-8 2000 (Microchem) is a high contrast, epoxy based negative photoresist designed for micromachining and other microelectronic applications. It is sensitive to electron irradiation as well. Two types of patterns were prepared, spots 200 nm in diameter with a spacing of 500 nm and spots 500 nm in diameter with the spacing of 1000 nm. The over tip arrays area was $1 \times 1\,mm^2$. The influence of the exposure dose in the range of $5003500\,\mu C/cm^2$ at a beam current of 15 pA on

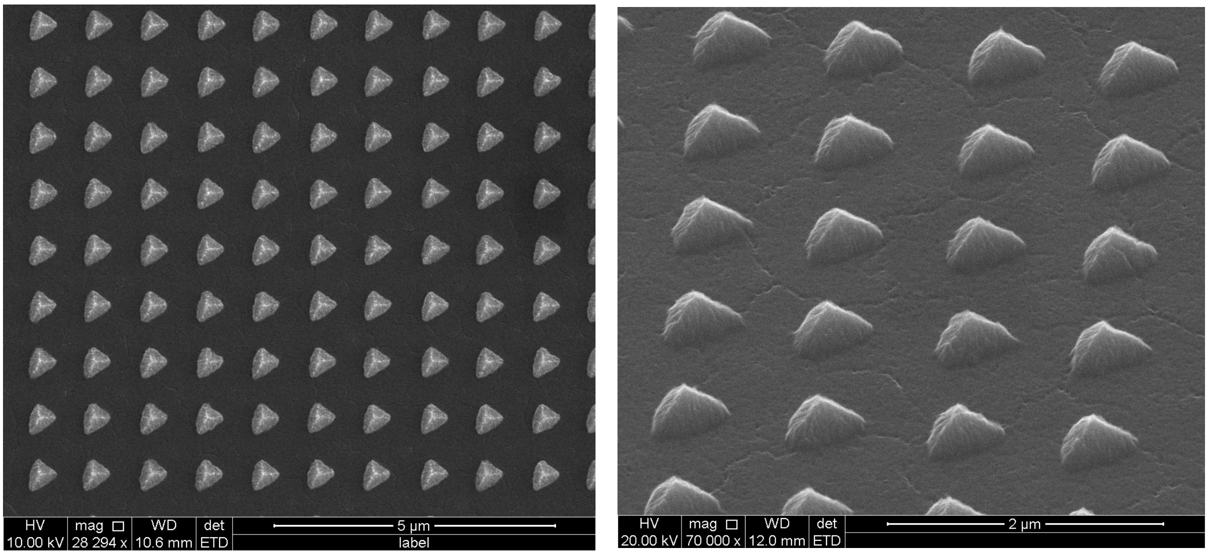

Fig. 3. SEM images of tip array with 500 nm diameter/ spacing 1000 nm TiO_2 tip array etched by RIE/ICP for 2.5 min at the exposure dose $900\,\mu C/cm^2$. The large view (a.) and the detail tilted 45° (b)

the TiO_2 tip features was investigated. The fabricated tip array structures were observed in a field emission scanning electron microscope Inspect S50 (FEI).

3 EXPERIMENTAL RESULTS

The first run of experiments was conducted to search for the optimal etching rate through photoresist pattern by conventional optical lithography. These etching experiments were performed at 5 Pa for RIE and 0.6 Pa in the case of RIE/ICP. The samples were etched for different times in each run. It was found the optimal etch rate was about 5 nm/min for RIE and about 35 nm/min for RIE/ICP.

Patterned tip array prepared by e-beam lithography and RIE are shown in Fig. 1. Detail of the TiO_2 tip array with 200 nm diameter and 500 nm spacing etched by RIE for 20 min is shown in Fig. 1a. The optimal exposure dose was $2600\,\mu C/cm^2$. In the case of a half exposure dose ($1300\,\mu C/cm^2$) (Fig. 1b) we can see degradation of the motives due to the insufficient resist protection to etch 120 nm TiO_2 at this dose value. This means that the thickness of the negative resist is smaller than the optimal one. In this figure note the resist rest of redeposition after RIE etching situated among the tips.

RIE/ICP mode was also applied for patterning of tips and typical results are presented in Fig. 2 and Fig. 3. SEM images of the TiO_2 tip array with 200 nm diameter and spacing of 500 nm etched by RIE/ICP for 5 min are shown in Fig. 2. The optimal exposure dose was $3000\,\mu C/cm^2$. Figure 2a) below shows the critical spacing of 50 nm where the side walls of neighbourhood tips are in touch. Detail view of the tip shape is better seen in a SEM image from a tilted sample (Fig. 2b). It seems that the etching time of 5 min is too long for 120 nm TiO_2 and the silicon substrate has already been etched. Detail of the TiO_2 tip array with 500 nm diameter and spacing 1000 nm etched by RIE/ICP for 2.5 min is shown in Fig. 3. The optimal exposure dose was $900\,\mu C/cm^2$. This figure represents the optimal thickness of the masking resist for 120 nm TiO_2 film. The size of resist motives is transferred with precision smaller than 100 nm into the etched film (in Fig. 3a, sample is not tilted). Detailed examination of the tilted sample in SEM reveals the pyramidal shape of the tips (Fig. 3b). The shape of etched tips is pyramidal despite even though the masking resist motives were the circular columns. This can be due to isotropical etching of TiO_2 in CF_4 plasma. We can assume that the RIE/ICP etching mode generates a well-defined size, shape and feature arrangement, and a shorter time for patterning of the TiO_2 tip array in comparison with RIE. The surface of etching was very smooth. The feature height of TiO_2 tips can be controlled by the masking resist thickness and can be easily varied.

4 CONCLUSIONS

The process characteristics of TiO_2 tip arrays patterned using e-beam lithography and dry etching were studied. It was shown, that the tip size and shape were influenced by the exposure dose and etching parameters. Optimization of the pattering procedure for 200 nm diameter with 500 nm spacing of the tips was accomplished. Pyramidal TiO_2 tip arrays were successfully fabricated by RIE/ICP etching over the $1 \times 1\,mm^2$ area. We assume that the TiO_2 tip arrays may have important application in gas microsensors. Therefore, in the next work, large area TiO_2 tip arrays will be prepared and examined for gas sensing application.

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Ivan HOTOVÝ (Assoc Prof, DrSc) received his MSc in Electronics from the Slovak University of Technology in Bratislava in 1982 and his PhD in Electronics from the Slovak University of Technology in 1994. He is a scientific worker and lecturer at Department of Microelectronics, FEIT STU. His current research interests include the development of gas sensors, magnetron sputtering of metal oxide films and plasma etching of compound semiconductors.

Ivan KOSTIČ (Dipl-Phys, RNDr) received his Dipl-Phys degree in Physics from Moscow State University, USSR, in 1980. He joined the Laboratory of Electron-beam lithography of the Institute of Technical Cybernetics at the Slovak Academy of Sciences, Bratislava, where he was involved in the research and development of e-beam lithography. Currently he is the leader of the Department of E-beam lithography at the Institute of Informatics of the Slovak Academy of Sciences in Bratislava, where he continues his work on microlithography and microfabrication. His research interests are concentrated on Electron-beam lithography application to microelectronic devices, sensors, microsystems and nanofabrication. He is co-author of more than 60 publications recorded in Current Contents Connect database and more than 110 publications recorded in Web of Science with Conference Proceedings database.

Štefan HAŠČÍK was born in Žilina, Slovakia in 1956. He received his master degree in physical electronics from Comenius University in 1982. Since 1983, he has been working in the Institute of Electrical Engineering of Slovak Academy of Sciences, Bratislava. His research interests are in the field of plasma and reactive ion etching of materials for microelectronics. Since 1995, he is also the member of research team in the field of design and development of both III-V and III-N compound semiconductor based M(N)EMS devices.

Vlastimil ŘEHÁČEK received his MSc in Nuclear Chemistry from the Comenius University in Bratislava in 1982 and his PhD in Electronics from the Slovak University of Technology in 2005. He is a scientific worker in Department of Microelectronics, FEIT STU. His current research interests include the development of voltammetric sensors, gas sensors and photolithography.

Jozef LIDAY (Assoc Prof, PhD) graduated in solid state physics in 1968 and received his PhD in electronics and vacuum technology, both from STU, in 1985. His teaching and research activities include materials analysis, thin films and surface science.

Helmut SITTER (Assoc Prof, PhD) graduated in 1975 and received his PhD in technical physics in 1980, both from the University of Linz. His research and teaching activities include the technology and diagnostics of advanced semiconductor structures and devices.