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COMMUNICATIONS

EFFECTS OF HSQ E–BEAM RESIST PROCESSING ON THE FABRICATION OF ICP–RIE ETCHED TiO_2 NANOSTRUCTURES

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Patterning of metal oxide nanostructures with different shapes and well-defined size may play an important role in the improvement of MEMS systems, sensors and optical devices. We investigated the effects of HSQ e-beam resist processing on the fabrication of sputtered TiO_2 nanostructures. They were patterned using direct write e-beam lithography combined with ICP-RIE etching in CF_4/Ar plasma. Experimental results confirmed that the HSQ resist with a thickness of about 600 nm is suitable as a masking material for optimal etching process and allows patterning of the dots array in TiO_2 sputtered films with a thickness up 150 nm. TiO_2 arrays with a minimal dots diameter of 180 nm and spacing of 1000 nm were successfully developed.

K e y w o r d s: HSQ e-beam resist, ICP-RIE etching, TiO_2 dots array

1 INTRODUCTION

Titanium oxide (TiO_2), as a low-cost material, exhibits multifunctional properties which underpin many important energy-conversion applications, including photocatalytic environmental remediation, water splitting for hydrogen fuel, CO_2 reduction, self-cleaning coatings, electrochromic devices and sensors, and low-cost solar cells. It also has extraordinary properties such as high permittivity, wide band gap, high refractive index, brightness and high biocompatibility. In addition, TiO_2 has disinfecting properties making it suitable for applications such as medical devices, food preparation surfaces, air conditioning filters and sanitary ware surfaces. A lot of studies on TiO_2 nanostructures have been reported in the past decade [1–7].

In recent years, great expectations for MEMS systems, sensors and optical applications have been in novel nanostructures with a high aspect ratio, normally grown in a bottom-up approach. In spite of such benefits, also in this bottom-up approach many problems remain unsolved, such as poor repeatability due to a scarce control of the growth. The deposited nanostructures are mostly fabricated by the top-down method 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 a photoresist, dielectric or metal to achieve a high fidelity pattern transfer [8]. E-beam lithography is an ideal method for fabrication of nanostructures [9]. It is versatile and provides high resolution and precise control over the geometry of the nanostructures while it is able to guarantee fabrication reproducibility and precision to the nanometer scale. These nanofabrication approaches provide the possibilities for optimizing the shape, dimensions and spacing of the nanostructures. They have the advantage of being both tunable and reproducible. High surface-to-volume or high aspect ratio structures, such as arrays of nanodots, nanotips, nanotubes or nanochannels fabricated from functional materials, are currently attracting great attention [10, 11]. TiO_2 is one of the most fascinating materials in the modern era due to its chemical stability, biocompatibility, catalytic, optical and electrical properties [12–15]. For potential application in sensor technology it is vital to prepare TiO_2 nanostrutures with different shapes and well-defined size guaranteeing a continuous film [5, 7, 16]. In addition, these TiO_2 motives should cover the whole active area.

In this study, we analyzed the effects of HSQ e-beam resist processing on the fabrication of TiO_2 nanostructures. Sputtered TiO_2 thin films with 130 nm thickness were patterned using direct write e-beam lithography combined with dry etching in an inductively coupled plasma (ICP) system. The designed motives with dots diameter from 45 to 200 nm and spacing from 200 to 2000 nm were defined into HSQ negative resists at various thickness.

2 EXPERIMENTAL PROCEDURES

Silicon wafers covered with thermally oxidized SiO_2 were used in this study as the substrates. The TiO_2 films were deposited by dc reactive magnetron sputtering from a Ti target in a mixture of oxygen and argon at room temperature with a constant thickness of approximately

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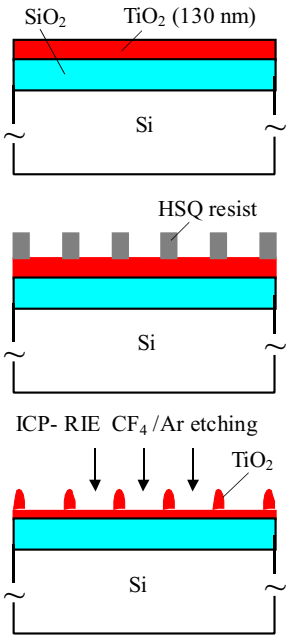

Fig. 1. Schematic illustration of fabrication procedure

130 nm. The relative partial pressure of oxygen in the reactive mixture was 20 %. The total gas pressure was kept constant at 0.8 Pa and adjusted by a piezoceramic valve. In order to stabilize the TiO_2 film properties, all films were annealed in a furnace at 500 °C in nitrogen for 1 hour. X-ray diffraction confirmed the formation of polycrystalline anatase phase under these conditions [17].

The nanostructures were defined by direct write e-beam lithography using negative e-beam resists. E-beam exposures were performed using the scanning electron microscope (SEM) Inspect F50 (*FEI*) equipped with a control system for nanolithography (*Elphy Quantum, Raith*) with a Gaussian beam. Negative e-beam resists HSQ XR-1541 and HSQ FOX25 (*Dow Corning*) with a thicknesses of 150 and 600 nm were spin coated on a TiO_2 thin film. Subsequently the resist was baked on a hot plate at 95 °C for 5 min. The energy of the electron beam was 30 keV and the beam current was 26 pA. After exposure, the resist was baked on a hot plate at 95 °C for 2 min, developed in tetra-methyl-ammonium hydroxide (TMAH) Microposit MF-322 developer at 22 °C for 60 s. After hard bake at 350 °C for 5 min, a mask for ICP RIE etching of TiO_2 was used. Nanostructure arrays were prepared with spacings from 200 and to 2000 nm.

Dry etching through HSQ resist nanomasks was performed in a Vacutec 310/320 reactor utilizing a planar inductively coupled plasma (ICP) source. TiO_2 thin films were etched in CF_4/Ar plasma. In each case, Ar was added to enhance the stability of discharge and to facilitate ignition of the plasma at the low operating pressures employed. The etching process conditions were performed at 130 W for ICP power, 0.6 Pa for process pressure, 20 °C for substrate temperature and the total flow rates was 14 sccm. In addition, the applied RF chuck power at 150 W was fixed in order to stabilize the ion flux and energy during TiO_2 etching. Figure 1 shows a schematic illustration of the fabrication procedure. The fabricated TiO_2 nanostructures were observed in a field emission scanning electron microscope (FE SEM) Inspect F50 (*FEI*).

3 EXPERIMENTAL RESULTS AND DISCUSSION

In our previous work [18] was shown that direct write e-beam lithographic process and plasma etching allow successful simple fabrication of the TiO_2 nanostructures. The shape and size of resist pillars change in dependence on the resist thickness, distance between the resist pillars, exposure dose, patterned thin film material and its thickness, substrate type and electron energy. The difference between the diameters of the designed motives and their real values on the top of the resist pillars is negligible. However, the measured diameters at the bottom of the resist pillars are changing significantly. This is due to backscattered electrons from the substrate which are significant in comparison with forward scattered electrons. This is well-known as the proximity effect. Therefore, we have investigated the influence of HSQ resist thickness and the distance between the resist pillars on their shape and size exposed on a TiO_2 surface. The energy of the electron beam 30 keV provided optimal resolution and conditions for well-defined size and shape of the exposed features.

Convenient application of the negative HSQ resist is the patterning of various nanostuctures while its thickness is varied usually in the range of 50-150 nm. Our first attempt was to use a 150 nm thin HSQ XR-1541 negative resist for TiO_2 etching. We have investigated the dependence of the pillar diameters on the exposure dose for various spacings. It was found that the resist pillar diameter was increasing slowly with the exposure dose, so it was possible to control the pillars diameter for various spacings using the exposure dose. Figure 2 demonstrates the arrays of the resist pillars with spacings 500, 1000 and 2000 nm in the 150 nm thin negative resist HSQ XR-1541 on a 130 nm TiO_2 surface after e-beam exposure. One can see that all patterned features are well-defined though slightly tapered in height direction due to the mentioned electron scattering in the resist.

We reported in [19] optimal etching characteristics of sputtered TiO_2 thin films in an ICP system as well as the etch selectivity for HSQ resist over TiO which was about 3. Recorded value of the selectivity is not sufficient for using resist thickness of 150 nm and it does not allow repeatable results. Therefore, we decided to investigate the proximity effect in a thicker resist film. We selected HSQ resist FOX-25 with a thickness of 600 nm. The proximity effect in this case is remarkable. Diameter measurements on the top of the resist pillars for various spacings were done yielding diameters/spacings 60/120,

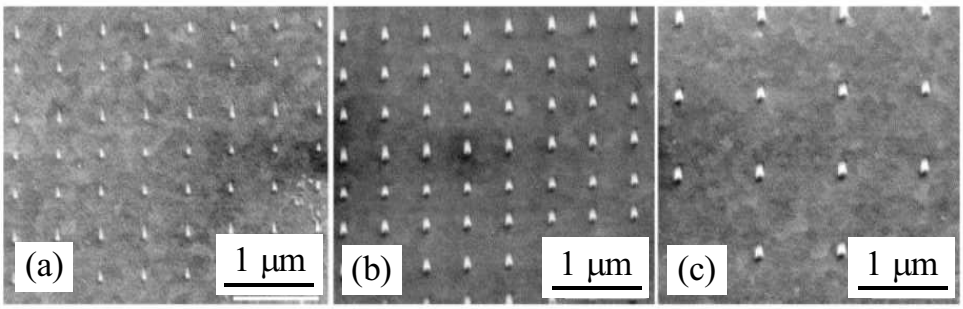

Fig. 2. Details of arrays in negative resist HSQ XR-1541 with a thickness of 150 nm on 130 nm TiO_2 thin film. Pillar diameters and spacings were (a) — 45/500 nm, (b) — 80/1000 nm, and (c) — 85/2000 nm. Exposure doses were 0.18 pC, 0.50 pC and 0.82 pC.

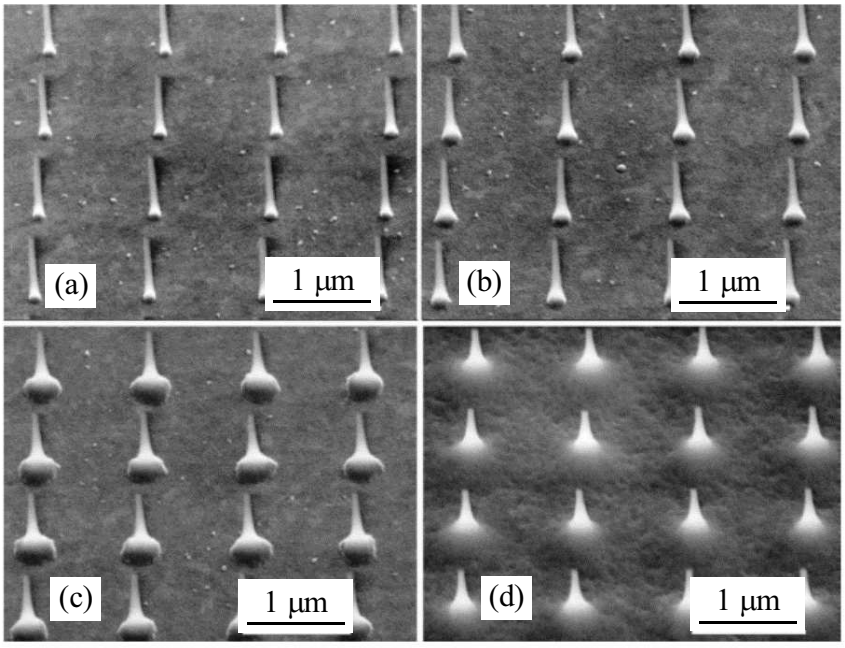

Fig. 3. Dependence of the resist pillar diameters on the exposure dose for the spacing of 1000 nm. The masking layer was a 600 nm thin HSQ resist. Diameters on the top/ at the bottom of resist pillars were: (a) — 50/105 nm, (b) — 50/195 nm, (c) — 50/375 nm, (d) — 50/500 nm. Exposure doses were 0.052 pC, 0.059 pC, 0.078 pC and 0.12 pC, dot time was 0.25 ms, beam current 26.7 pA, and electron energy 30 keV.

55/140, 75/160, 50/200, 60/250 and 70/500 nm, respectively. The smallest diameter on the top of the resist pillars exposed in 600 nm thin resist film was 35 nm. It is comparable to the diameter exposed and measured in the 150 nm thin resist film (45/500 nm). But significantly another is the situation at the bottom of the resist pillars. The dependence of the resist pillar diameters on the exposure dose for spacing 1000 nm is shown in Fig. 3. While the diameter on the top of resist pillar is nearly equal to 50 nm, at the bottom it is increased from 105, 195, 375 nm up to 500 nm when the exposure doses is increased from 0.0052, 0.059, 0.078 up to 0.12 pC. One can state that the shape and the size of the resist pillars depend mainly on the exposure dose.

If it is required continuous nanostructures which exhibit the electrical conductivity then the etching time is crucial factor for fabrication of TiO_2 nanostructures with precisely controlled geometries at optimal etching parameters [20]. For the next etch experiments we selected the resist pillar structures with a diameter of 180 nm at the bottom and a spacing of 1000 nm. Figure 4 compares the etch times of 30, 60, 90 and 120 s and one can see that HSQ resist mask with 600 nm thickness is almost not attacked by etching. TiO_2 fabricated dots arrays are well-defined. One can see that the resist mask remained on the top of TiO_2 after etching for all examined times and confirmed good etch selectivity for optimal etching process. Only after the last investigated etch time of 120 s, the TiO_2 film was over-etched. However, TiO_2 dots covered by the resist mask are still preserved (Fig. 4(d)).

Figure 5 shows the HSQ resist pillars with a diameter of 180 nm and spacings of 1000 nm fabricated in a 130 nm sputtered TiO_2 film after etching. Figure 5(b) reveals the smallest etched TiO_2 dots array with a spacing of 1000 nm after resist striping in diluted HF acid. In this case of the fabrication using SEM with a control system for nanolithography we were able to pattern the overall area of $1 \times 1\,\mathrm{mm}^2$.

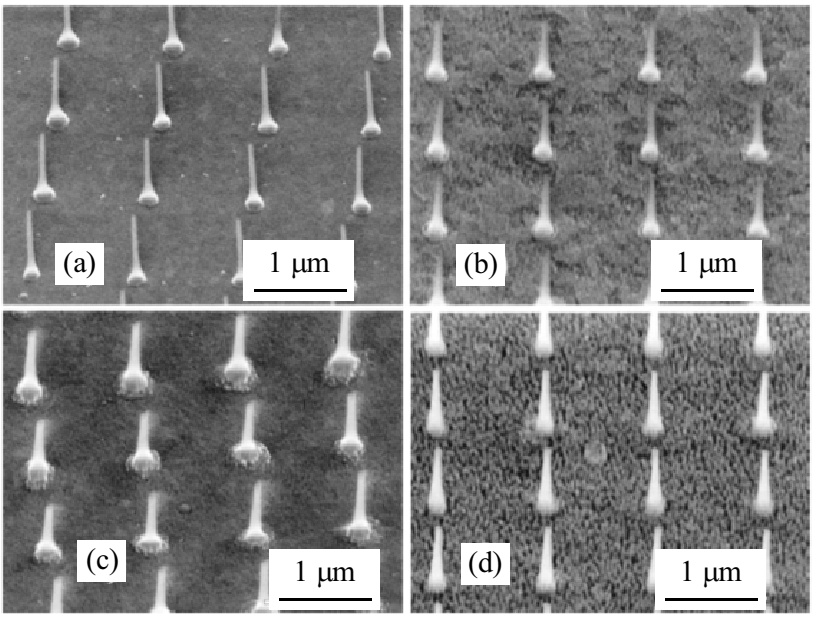

Fig. 4. The influence of the etching time on the array of resist pillars with spacing 1000 nm. Etched TiO_2 dots are seen at the bottom under the resist pillars. Etching times were (a) — 30 s, (b) — 60 s, (c) — 90 s and (d) — 120 s. The masking layer was a 600 nm thin HSQ resist.

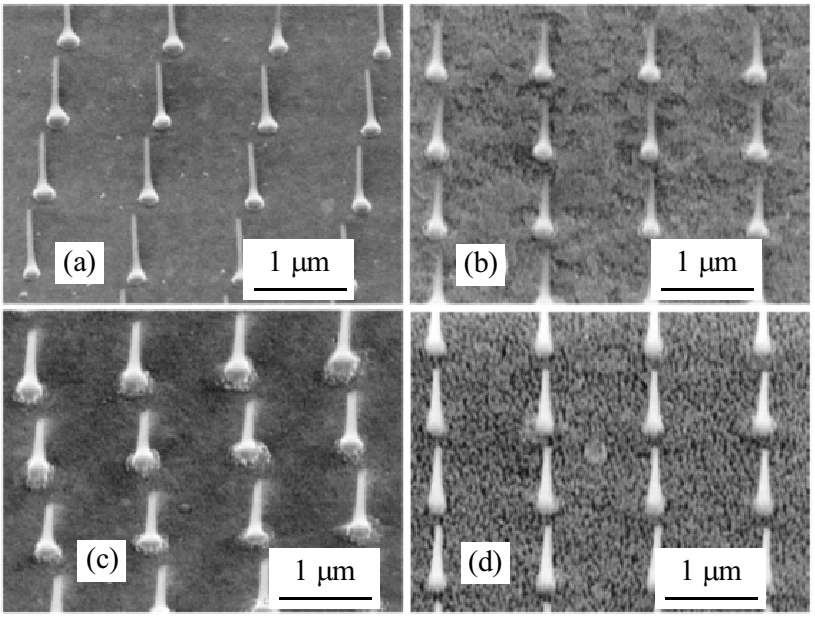

Fig. 5. (a) — Array of resist pillars on 130 nm TiO_2 thin film after ICP-RIE etching, and (b) — fabricated array of 180 nm TiO_2 dots in diameter with spacing 1000 nm after resist stripping. The masking layer was 600 nm thin HSQ resist. Etching time was 30 s.

4 CONCLUSIONS

The effects of HSQ e-beam resist processing on the fabrication of TiO_2 dots array were investigated. We have studied the influence of HSQ resist thickness and the distance between the resist pillars on their shape and size exposed on a TiO_2 surface. It was found that the shape and the size of the HSQ resist pillars depend mainly on the exposure dose. Experimental results confirmed that the HSQ resist with a thickness of about 600 nm is suitable as a masking material for optimal etching process and allows patterning of the dots array in TiO_2 sputtered films with a thickness up 150 nm. TiO_2 dots arrays on the overall area of $1 \times 1\,\mathrm{mm}^2$ with a minimal diameter of 180 nm and spacing 1000 nm were successfully fabricated by ICP-RIE etching in CF_4/Ar plasma. We assume that the TiO_2 nanostructures may play an important role in MEMS systems, sensors and optical devices.

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