Atmospheric plasma directed assembly for mask-less patterning

P. Dimitrakellis, V. Constantoudis, A. Smyrnakis, G. Kokkoris and E. Gogolides

Institute of Nanoscience and Nanotechnology, NCSR "Demokritos", Aghia Paraskevi 15341, Attiki, Greece

Abstract: We present a novel mask-less pattern formation method based on atmospheric plasma directed assembly (APDA) during AZ5214E resist etching in He/O_2 RF discharges. APDA leaded to the formation of periodic, sulphur containing, oxygen-plasma resistant residuals on the underlying substrate, with the O_2 content in gas feed determining their size and density. Anisotropic plasma etching in low pressure was applied to transfer the induced pattern on the underlying Si substrate fabricating quasi-ordered submicron Si pillars.

Keywords: atmospheric plasma directed assembly, nanofabrication, pattern formation

1. Introduction

Modern nanofabrication is implicated in numerous applications ranging from biosensors to photonics and electronics. Nanofabrication is based on definition of periodic nanostructures such as dots and pillars in high reliability and reproducibility. Pattern definition followed by plasma etching is undoubtedly the key top-down technology for micro- and nanofabrication [1]. The desired pattern is typically defined using several well established lithographic techniques [2,3], while anisotropic plasma etching is applied afterwards for pattern transfer and formation of high aspect ratio nanostructures [1]. As alternatives to conventional lithography methods, a plethora of self-assembly techniques have also been proposed for pattern definition, with the most popular being the block co-polymer directed assembly and the colloidal lithography [4,5]. "Plasma directed nano-assembly", a technique based on plasma-reactor wall interactions, can also be considered a promising approach for deposition of etching inhibitors that, when followed by anisotropic plasma etching, leads to the formation of nanodots and nanopillars [6].

Atmospheric pressure plasmas (APPs) are promising alternatives to low pressure plasmas due to their potential for cost-effective and large-area processing [7]. We have previously presented a dielectric barrier discharge (DBD) device with a showerhead electrode for polymer etching using He/O_2 discharges in ambient air conditions [8]. In our last work we noticed that during cleaning / ashing of AZ5214E dual-tone photoresist with RF atmospheric pressure plasma, etching resistant residues were remained on silicon substrate [9].

Herein we introduce atmospheric pressure plasma ashing of a sulfur containing (AZ5214E) photoresist as new plasma directed assembly technique for future application in large-area mask-less nanofabrication. The atmospheric plasma directed assembly (APDA) concept is presented in Figure 1.

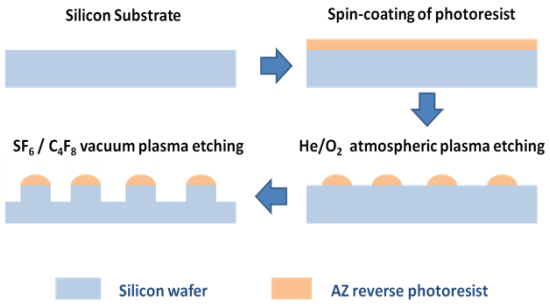


Fig. 1. Concept of atmospheric plasma directed assembly method for mask-less nanofabrication.

We study the evolution of plasma assembled nanostructures during atmospheric plasma etching in open-air conditions. Moreover, the utilization of advanced computational nanometrology tools enabled the characterization of the structures in terms of their size, density and periodicity. As a proof of concept we applied the novel plasma directed assembly method followed by anisotropic low pressure reactive ion etching in order to create high aspect ratio structures (pillars) on silicon.

2. Experimental section

The substrates used in this study were Silicon wafers coated with AZ5214E photoresist. The resist was further diluted in order to form films of less than 1μm thickness by spin-coating method. The prepared photoresist films were baked at 95°C for 15min. The atmospheric plasma etching experiments were performed in a showerhead-type dielectric barrier discharge source operating at RF 13.56 MHz. The design of the plasma source is described in detail elsewhere [8]. Helium and oxygen were used as process gases with the total gas flow rate being fixed at 5 slm and the O_2 fraction varying between 0% and 1% O_2. The electrode gap was fixed at 2 mm using spacers and the substrates were placed inside the gap. Successive 5s on / 15s off plasma pulses were applied to avoid overheating of the substrates and the processing time reported refers to the plasma on time.

A time-multiplexed pulsed-gas low pressure plasma process, alternating an SF_6 gas etching step and a C_4F_8 gas passivation step, was applied for pattern transfer to silicon. Etching was performed in a high-density helicon coupled plasma reactor (Micromachining Etching Tool from Alcatel-Adixen), typically working in the inductive mode. The conditions used were: frequency 13.56 MHz, temperature 20°C, power 1800 W, bias voltage -70 V, pressure 5 Pa, 171 sccm SF_6 flow for 2s step and 110 sccm C_4F_8 flow for 1s step.

Plasma treated surfaces were observed using a JEOL JSM-7401F FEG Scanning Electron Microscope and a FEI Quanta Inspect Scanning Electron Microscope. The top-down SEM images were analyzed to quantify the residues size and periodicity using nanoTOPO^{TM} software.

3. Results

The experimental procedure as depicted in Fig. 1 starts with coating AZ5214E dual-tone photoresist on a silicon wafer and proceeds with atmospheric plasma etching in He/O_2 DBD discharges. In this step, self-organized, non-etchable, nanostructures are formed on the silicon surface.

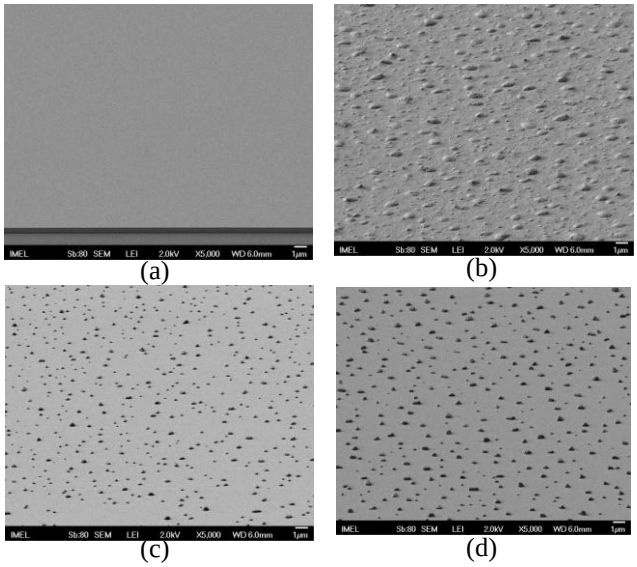


Fig. 2. SEM images (70°tilt-angle) during AZ etching of Si surfaces using 0.6% O_2 in He atmospheric pressure plasma in open-air condition: (a) untreated sample (t = 0 min), (b) t = 4 min, (c) t = 6 min and (d) t = 8 min.

Figure 2 presents the SEM images of untreated and atmospheric plasma treated surfaces (tilt-angle 70°). All samples were treated using 0.6% O_2 in He. The untreated AZ5214E coating is completely smooth and without any defects on its surface (Fig. 2a). After 4 min plasma etching a rough surface is created and micrometer-sized structures tend to self-organize (Fig. 2b). The surface texturing continues till etching is completed; we obtained identical surface images both after 6 and 8 min treatment, showing that the film has been completely etched after 6 min treatment (Fig. 2c and 2d). Plasma does not affect the photoresist material any further and periodic, etching resistant residues are distributed on silicon.

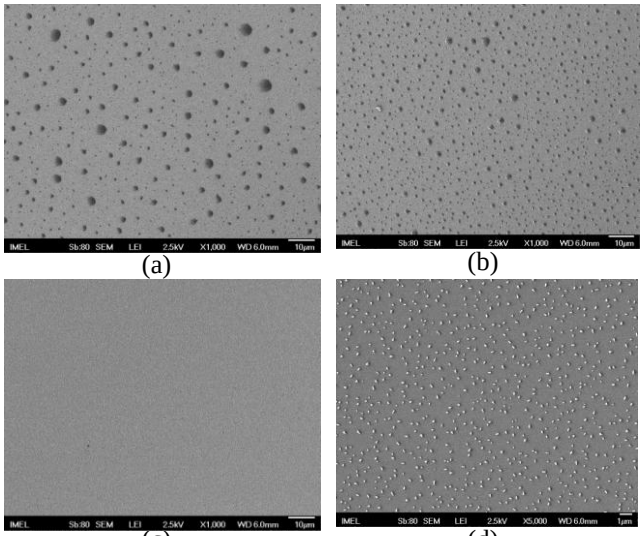


Fig. 3. SEM images (top down) of atmospheric plasma etched samples with decreasing % O_2 fraction in He gas feed and after etching is finalized: (a) 1% O_2 at t = 8 min, (b) 0.6% O_2 at t = 8 min, and (c, d) pure He feed (0% O_2) at t = 28 min at two different magnifications.

Next we investigated the effect of % O_2 fraction in He on the resulting topography of AZ5214E samples at the stage when etching is completed. Fig. 3a, 3b and 3c present SEM images (top-down) of atmospheric plasma treated samples using 1% O_2, 0.6% O_2 and pure He gas feed, respectively. Fig. 4d shows the latter at a higher magnification. For 0.6 and 1% we compare the surfaces after 8 min, contrary to pure He discharges where the etching rates are much lower and longer treatment is required for completing etching (28 min). Moreover, we select the top-down images in order to measure the size and distribution of plasma assembled micron and submicron structures. We observe that the increase of O_2 content from 0.6% (same as Fig. 2) to 1% results in less dense but larger structures formed on the surface giving rise to inhomogeneity of the size distribution (Fig. 3a and 3b). On the other hand, for 0% (pure He) the resulting surface topography is characterized by much smaller (nanoscale) structures (Fig. 3c and 3d).

A straightforward way to quantify the spatial order (periodicity) of nanostructure distribution is to calculate the 2D Fourier spectrum of the image. As the distribution of AZ5214E residues appears isotropic, we can squeeze the directional information and extract the radial averaging of 2D Fourier spectrum to emphasize the presence of periodicity. The square of the amplitude of

the 1D Fourier spectrum is the Power Spectral Density (PSD) shown in Fig. 4 in semi-logarithmic scales versus spatial frequency or wavenumber k for the three fractions of O_2 considered in our work. Firstly, one can easily notice the prominent peaks of PSD curves prevailing in all cases, which demonstrate the periodic uniform arrangement of AZ5214E structures. Furthermore, the inverse of the spatial frequencies of the peaks gives the period of the pattern, i.e. the mean distance between nearby residues. The lateral shift of the PSD curves towards lower frequencies reveals the sensitivity of the period on O_2 content. As shown in Fig.4, it goes from 7350nm at 1% O_2 content to 3840 at 0.6% and then to 500nm when no O_2 gas participates in the etching process. Correspondingly, the density increases from 0.035/μm^2 at 1% O_2 content to 1.8/μm^2 at 0% O_2 while at 0.6% takes on the intermediate value 0.092/μm^2.

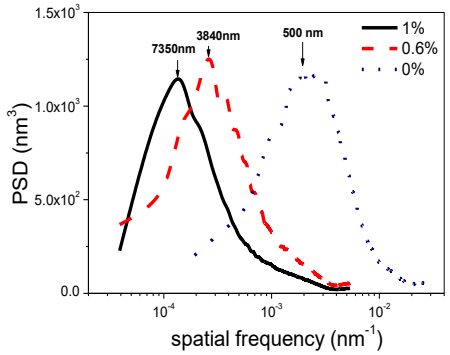
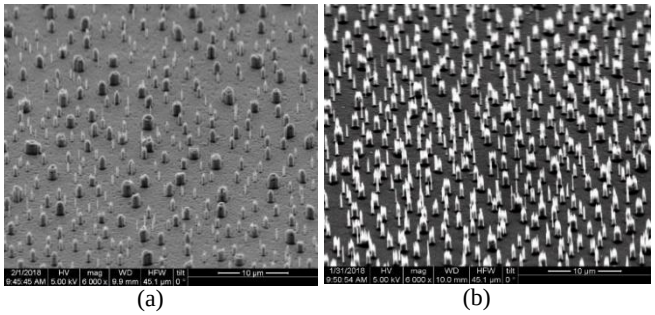


Fig. 4. Power Spectral Densities (PSD) in semi-logarithmic scales versus spatial frequency for the three contents of O_2. One can easily notice the prominent peaks demonstrating the well-defined periodicity of residues as well the dependence of their period on O_2 content.

The atmospheric plasma directed assembly can be applied to form a periodically arranged pattern, which can be used as an etching mask to transfer the pattern to the underlying layer. As a proof of concept we performed pattern transfer to Si substrates for the fabrication of Si micron and submicron pillars. Si etching was performed in a low-pressure plasma reactor using a pulsed-gas plasma process alternating SF_6 gas and C_4F_8 gas steps [10]. Fig. 5a and 5b show SEM images of the result of pattern transfer after 40s and 60s of silicon etching, respectively. The mask pattern was identical with that shown in Fig. 2d, and 3b. For the case of 40s the height of the resulting Si pillars is ~2μm. Some residues of the mask material can be seen on top of pillars meaning that the mask is not completely etched. In contrary, after 60s of Si etching the mask material is etched completely leading to the formation of hollows on the top of the pillars, the height of which varies from ~2.4 to 3.0 μm.



(a) (b)

Fig. 5. SEM images of silicon pillars fabricated by atmospheric pressure plasma directed assembly followed by low-pressure plasma etching in a pulsed-gas alternating plasma process for (a) 40s and (b) 60s.

4. Conclusions

We presented a mask-less pattern definition method via atmospheric plasma directed assembly (APDA) during AZ5214 photoresist ashing. We demonstrated control of the structure size and spacing by alternating the gas feed. Fourier Analysis enabled quantification of the periodicity, size and density of the plasma assembled structures. As a demonstrator we applied anisotropic plasma etching for pattern transfer to the Silicon substrate fabricating quasi-ordered micro and submicron pillars.

5. Acknowledgements

We acknowledge support of this work by the project MIS 5002772, implemented under the Action "Reinforcement of the Research and Innovation Infrastructure", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

6. References

[1] B. Wu, A. Kumar, S. Pamarthy, J. Appl. Phys. **108** 051101 (2010).
[2] S. Franssila, Optical Lithography, Introduction to Microfabrication, John Wiley & Sons Ltd, 103 (2010).
[3] R. H. Stulen, D. W. Sweeney, IEEE Journal of Quantum Electronics **35**(5) 694 (1999).
[4] I. W. Hamley, Nanotechnology **14** 16 (2003).
[5] J. C. Hulteen, P. Van Duyne, Journal of vacuum Science & Technology A **13**(3) 6 (1995).
[6] A. Smyrnakis, A. Zeniou, K. Awsiuk, V. Constantoudis, E. Gogolides E, 2018 Frontiers in Chemical Science and Engineering, (2019).
[7] L. Bárdos, H. Baránková, Thin Solid Films **518** 6705 (2010).
[8] P. Dimitrakellis, A. Zeniou, Y. Stratakos, E. Gogolides, Plasma Sources Sci. Technol. **25**(2), 025015 (2016).
[9] P. Dimitrakellis, E. Gogolides, Microelectronic Engineering **194** 109–15 (2018).
[10] A. Zeniou, K. Ellinas, A. Olziersky, E. Gogolides, Nanotechnology 25 035302 (2014).