

Experimental Study of the Re-Emission During Thin Film Etching in the Outside the Electrodes Discharge Plasma

V. Podlipnov^{1,2}, V. Kolpakov²

¹ Image Processing Systems Institute of RAS – Branch of the FSRC “Crystallography and Photonics” RAS

E-mail: podlipnovvv@ya.ru

² Samara National Research University
Samara, Russia

Received: 28.11.2016

Abstract. The article presents the results of Cr-SiO₂ structure of the etching plasma high-voltage gas discharge in CF₄ + O₂ medium at a discharge current of 80 mA, voltage 1.2 kV and duration of the bombardment of the surface under study and 5-minutes. Detected sputtering deposition products within the windows in the mask in the chromium mode 1.2 kV, 80 mA. The deposited products formed a coating of vertically oriented pyramidal clusters. The images of scanning electron microscopy (SEM) are represented. Results of a study of the Raman spectra are presented. The results showed that the deposited film is a kind of compounds Cr₂NO_x.

Keywords: diffusion, ion-electron beam particles, annealing, pickling, reprecipitation, chromium, metal mask, chromium nitride, chromium oxide

INTRODUCTION

For a given topology semiconductor materials in microelectronics and micro-relief diffractive optical elements (DOE) plasma etching is widely used [1]. Previously, the authors in [2–4] has been shown to be promising application outside the electrodes high-voltage gas discharge plasma in the process of etching processes.

As the masking layer during the formation of micro-relief methods of plasma chemical etching wide application of metal masking thin films [5] In the process of etching the metal mask is irradiated with plasma. Interaction of reactive plasma components with masking layers, can affect the quality of the structures formed. It is also known that the products of plasma-chemical reactions may be deposited on the treated surfaces that may have a positive effect on the result of [6], and is negative. Previous authors effect was observed plasma chemical deposition reactions to products treated surfaces. However, a detailed study of plasma-chemical reactions occurring in the etching of silicon dioxide in outside the electrode plasma using chrome mask was carried out. In this connection, in this paper, experimental studies of plasma-chemical deposition processes, and research products of plasma chemical reactions, resulting in a film of non-volatile compounds, deposited on the substrate surface.

EXPERIMENTAL TECHNIQUE

As the initial substrate were chosen fused silica, diameter of 25 mm and a thickness of 3 mm. The thin chromium film on the substrate was deposited by magnetron sputtering to a thickness of 40–60 nm. Test pattern formed electron beam lithography using a scanning electron microscope (SEM) Carl Zeiss Supra 25, with device lithography Xenos Xedraw 2. This technique of lithography is described in [7]. On the surface of the chromium formed microrelief of the electron resist ERP-40. To create test structures for experimentation deposition products of plasma chemical reactions, have been formed rectangular windows measuring 30x70 mm. Chemical etching in a solution of cerium sulphate through the resistive layer, the window data has been transferred to the chromium layer. (Fig. 1).

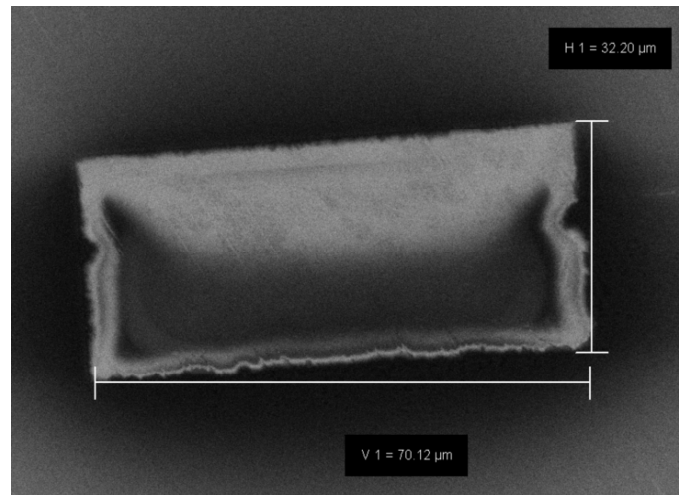


Figure 1. Chromium mask

Using this mask was carried out plasma etching of silicon dioxide on the outside of the electrode plasma modes: discharge current, I of = 50–80 mA, supply voltage $U = 1200$ V. As a generator electrode is used plasma source described in [8–9]. The experimental setup is shown in Fig. 2.

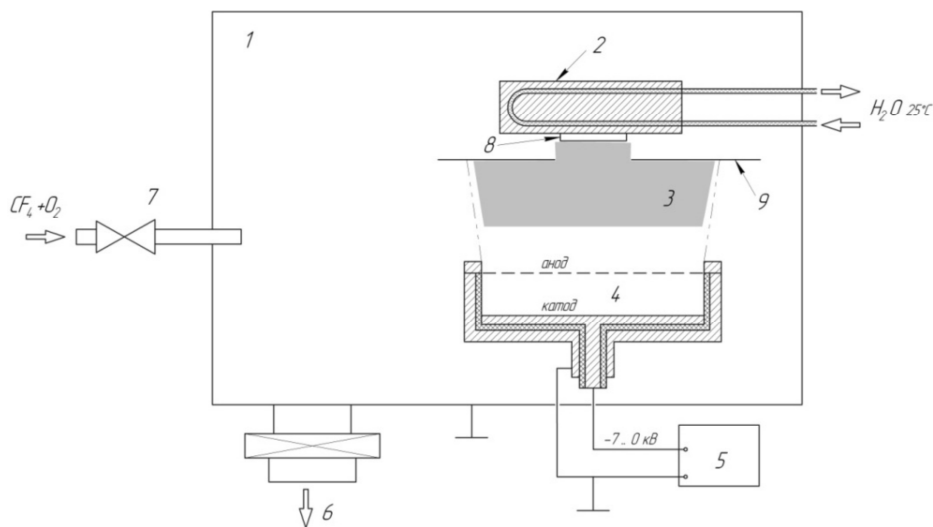


Figure 2. The experimental setup for the etching of microstructures: 1 – vacuum chamber; 2 – water-cooled substrate holder; 3 – the region of formation of low-temperature plasma; 4 – wide-source is an electrode of the plasma; 5 – high-voltage power supply; 6 – redundant system pump; 7 – inlet system of working gas; 8 – substrate; 9 – screen.

Samples (position 8 in Fig. 2) were placed in a vacuum chamber 1, and a water-cooled substrate holder fixed in 2, the temperature in the etching process is maintained in the range 23–26 °C. The vacuum chamber was evacuated to a pressure source 10^{-4} – 10^{-2} torr. The operation was performed 20–25 Pa inclusion of the plasma source 4, forming stream 3. To eliminate excessive heating of the substrate holder used the screen 9 from the window dimensions 35×35 mm. Large window sizes allowed to eliminate the edge effects and to obtain in the substrate plasma stream with a uniform particle distribution over its cross section is not less than 98 %. In the experiment using the plasma source anode mesh has a diameter of 110 mm, cell size of 1.8 mm, non-uniform flow field in the etching better than 2 %.

In operation, the mode used: $I = 80$ mA current, accelerating voltage $U = 1.2$ kV, duration of the bombardment of the sample surface 5 minutes.

The surface of the test sample was subjected to bombardment of negative plasma particles with an energy of 1.2–2 keV, 80 mA and a duration of 5 minutes. The composition of a mixture of $\text{CF}_4 + \text{O}_2$ in a ratio of 50 as the working gas: 1.

Control properties of thin films before and after plasma treatment was carried out using Ntegra Spectra Solaris NT-MDT in Raman spectroscopy mode using a laser with a wavelength of 532 nm, 10 mW. CCD is cooled to -50 °C Peltier temperature to reduce thermal noise when recording spectra. The accuracy of the range of $\pm 2 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

Exploring the plasma etching, it was found that the deposition of plasma chemical etching products within the rectangular windows, the view of which is shown in Fig. 3.

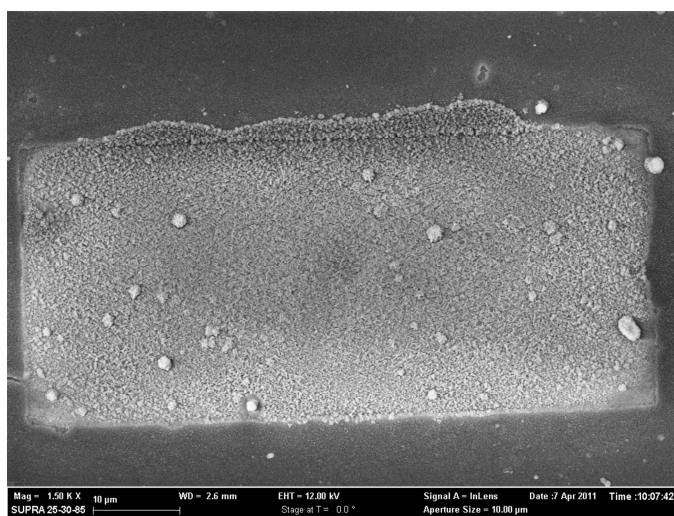


Figure 3. Deposition of etching products in the windows on the surface of the mask of silicon dioxide

Precipitated structure is a densely packed pyramidal crystallites whose shape is shown in Fig. 3. Furthermore, in the image (Fig. 3) can be seen on the long sides of the rectangle is “creeping” masking over chromium in the corners of the rectangle crystallite growth significantly smaller crystallite orientation that characterizes the process of growth in the center of the window towards the edges of the chrome. This configuration of the crystallite growth may be explained by the peculiarities of the distribution of the electric field generated as a result of treatment. The open surface of the quartz inside the open window is charged, and the metal film is removed effectively accumulating surface electric charge in the etching process. Negative surface charge in this case pushes or significantly reduces the kinetic energy of the plas-

ma of electronegative component. Thus, the physical sputtering mechanism in this area is greatly reduced, without hindering the deposition of neutral particles and positive plasma between the electrodes at a voltage of 1.2 kV plasma source. This assumption is consistent with the phenomena occurring in the process of electron beam processing, as described in [10].

Raman spectrum is shown in Fig. 4, c. On this spectrum can be identified characteristic broad band maxima correspond to the values of the wave number 152, 225, 278, 343, 619 cm^{-1} . A substantial width of the spectral bands of the spectrum indicates a high degree of structure, amorphous and non-uniformity of the film, due to the implementation of the deposition on a substrate fixed on a water-cooled substrate holder.

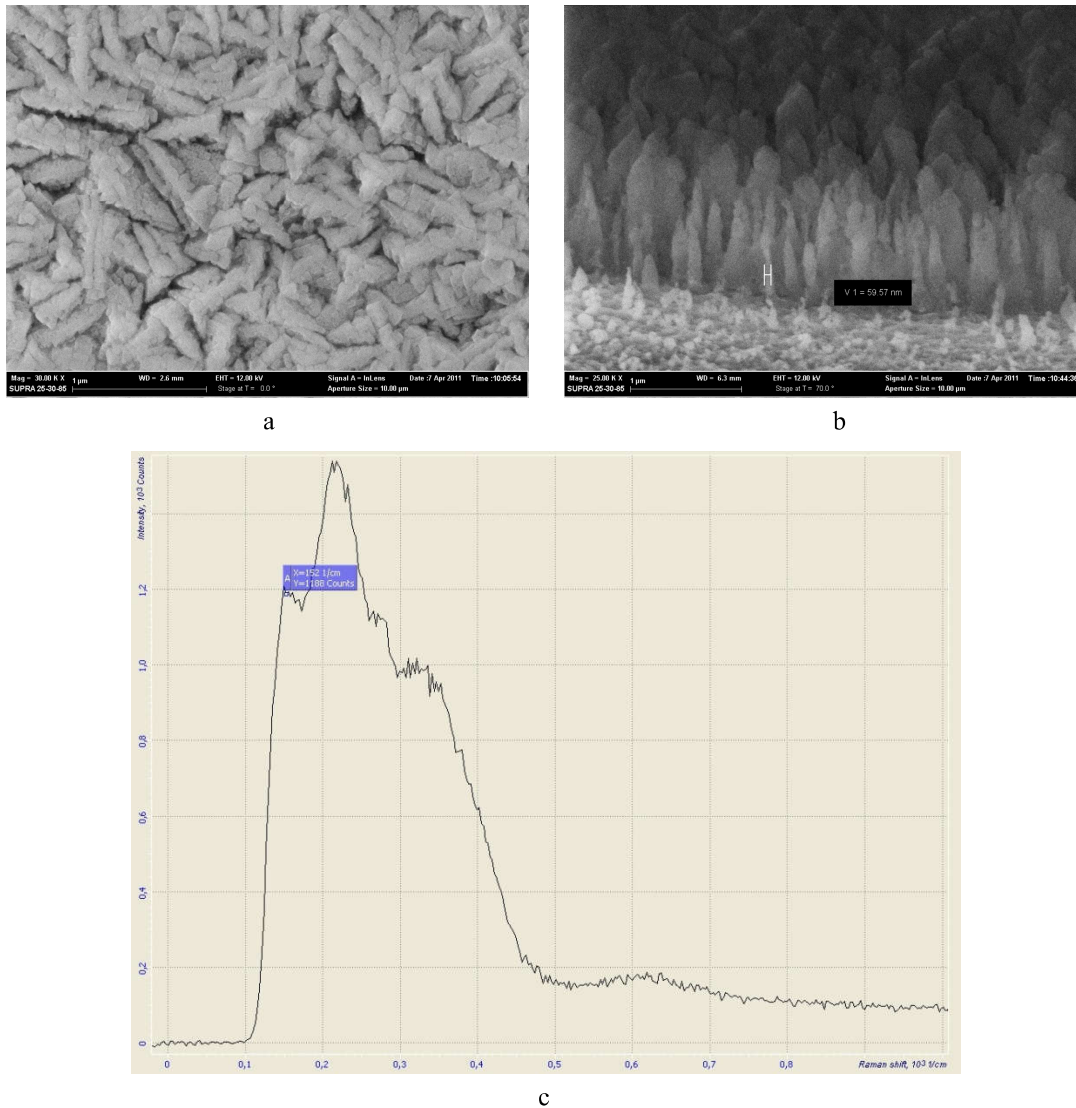


Figure 4. The product crystallites deposited on the surface of silica reactions:
a – a top view, b – side view, c – Raman spectra of the deposited structure

A broad band with a maximum of 152 cm^{-1} is correlated with the corresponding peak in the spectrum of metallic chromium, the measured Raman spectrum is shown in Fig. 4.c. The wide bands with maxima 225, 278 cm^{-1} indicate the presence of compounds in the test Cr_2N film [11].

Maxima wide strips 619, 343 cm^{-1} correspond Cr_2O_3 weak maxima 615 and 350 cm^{-1} [12].

The form and nature of the location of spectral peaks as a whole allows us to say that the basis of the composition of the film lie kristallitovosazhdaemoy connection type Cr_2N , with minor amounts of nanocrystallites Cr_2O_3 [11]. Forming on the surface of larger globular structures (Fig. 3), it is also characteristic hexagonal Cr_2N chromium nitride lattice.

CONCLUSION

When the voltage to 1.2 kV in a metal mask windows is deposited reaction products. We studied the Raman spectra of the resultant structure, based on which it can be said that the main component of the crystallite deposited film is chromium nitride Cr_2NO_x .

ACKNOWLEDGMENT

The work was partially funded by Presidential grants for support of young Russian doctors of science (MD-5205.2016.9) and Russian Foundation of Basic Research Grants (project 16-07-00494 A).

REFERENCES

1. Donnelly, V. M., & Kornblit, A. (2013). Plasma etching: yesterday, today, and tomorrow. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 31(5), 050825. doi:10.1116/1.4819316
2. Kazanskiy, N. L., & Kolpakov, V. A. (2009). *Formirovanie opticheskogo mikrorel'efa vo vneelektroodnoy plazme vysokovol'nogo gazovogo razryada [Study of optical microrelief formation in the plasma generated high-voltage gas discharge outside the electrode]* (220 p.). Moscow, Russia: Radio i Svyaz (in Russian).
3. Kolpakov, V. A., & Podlipnov, V. V. (2015). Mechanism of interaction between a directed beam of negative particles from a gas-discharge plasma and the melted nickel surface. *Technical Physics*, 60(1), 53–56. doi:10.1134/S1063784215010168
4. Kazanskiy, N. L., Kolpakov, V. A., Krichevskiy, S. V., Ivliev, N. A., & Markushin, M. A. (2017). A gas-discharge plasma focuser source of the document. *Instruments and Experimental Techniques*, 60(5), 748–751. doi:10.1134/S0020441217040157
5. Cheng, C. C., & Scherer, A. (1995) Fabrication of photonic band - gap crystals. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*, 13(6), 2696–2700. doi:10.1116/1.588051
6. Laerme, F., Schilp, A., Funk, K., & Offenber, M. A. O. M. (1999). Bosch deep silicon etching: improving uniformity and etch rate for advanced MEMS applications. *Twelfth IEEE International Conference on Micro Electro Mechanical Systems (MEMS'99)*, Orlando, USA, 211–216. doi:10.1109/MEMSYS.1999.746812
7. Khonina, S. N., Nesterenko, D. V., Morozov, A. A., Skidanov, R. V., & Soifer, V. A. (2012). Narrowing of a light spot at diffraction of linearly-polarized beam on binary asymmetric axicons. *Optical Memory and Neural Networks*, 21(1), 17–26. doi:10.3103/S1060992X12010043
8. Kazanskiy, N. L., Kolpakov, V. A., & Podlipnov, V. V. (2014). Gas discharge devices generating the directed fluxes of off-electrode plasma. *Vacuum*, 101, 291–297. doi:10.1016/j.vacuum.2013.09.014
9. Kolpakov, V. A., Kolpakov, A. I., & Podlipnov, V. V. (2013). Formation of an out-of-electrode plasma in a high-voltage gas discharge. *Technical Physics*, 58(4), 505–510. doi:10.1134/S1063784213040130
10. Nikonorov, N. V., Sidorov, A. I., Tsekhomskii, V. A., Nashchekin, A. V., Usov, O. A., Podsvirov, O. A., & Poplevkin, S. V. (2009). Electron-beam modification of the near-surface layers of photosensitive glasses. *Technical Physics Letters*, 35(4), 309–311. doi:10.1134/S1063785009040063
11. Barata, A., Cunha, L., & Moura, C. (2001). Characterisation of chromium nitride films produced by PVD techniques. *Thin Solid Films*, 398–399, 501–506. doi:10.1016/S0040-6090(01)01498-5
12. Barshilia, H. C., & Rajam, K. S. (2004). Raman spectroscopy studies on the thermal stability of TiN, CrN, TiAlN coatings and nanolayered TiN/CrN, TiAlN/CrN multilayer coatings. *Journal of Materials Research*, 19(11), 3196–3205. doi:10.1557/JMR.2004.0444