Photolithographic Mask Fabrication Process Using Cr/Sapphire Carriers

Agnieszka ZAWADZKA, Joanna PRAZMOWSKA, Regina PASZKIEWICZ

Department of Microelectronics and Nanotechnology, Faculty of Microsystem Electronics and Photonics, Wroclaw University of Technology, Janiszewskiego 11/17, 50-372 Wroclaw, Poland

agnieszka.zawadzka@pwr.edu.pl, joanna.prazmowska@pwr.edu.pl, regina.paszkiewicz@pwr.edu.pl

DOI: 10.15598/aeee.v17i3.3357

Abstract. *Elaboration of the technology of novel photolithographic masks fabricated on sapphire substrates for UV and DUV application was described. The main technological steps of mask fabrication as Cr metallization deposition, selection of resist for lithography and Cr layer etching were developed and reported. The etching of Cr films was carried out through resist mask. Detailed study of Cr layer etching process was performed using different solutions such as $KMnO_4$, HCl and ceric ammonium nitrate-based solutions to obtain good-quality structures with the smallest possible undercut of Cr layer and smooth edge. The mask fabrication process was validated by fabrication of test structures of microelectronic device using photolithography technique.*

Keywords

Chromium etching, photolithography mask fabrication, sapphire substrate.

1. Introduction

Due to the development of microelectronics, study on microfabrication technology becomes more relevant. One of the most popular methods of manufacturing in microscale is photolithography. It is a technique that enables implementation of small structures on semiconductor surface for electronic applications. It requires UV or DUV illumination and a mask to transfer designed pattern. The quality of the pattern determines the quality of manufactured elements, therefore the mask fabrication technology has to be optimized either mask materials have to be appropriate [1]. As illumination absorbing layer, the chromium is commonly used, because of its good adhesion, chemical and thermal stability and mechanical strength. Moreover, it is suitable for wet etch mask processes [2].

For a carrier material, the optical transmission is the most essential feature and for this reason, only carriers transparent within demanded range of wavelengths are used. Thus, and also on account of appropriate mechanical properties, silica substrates or different types of glass are commonly applied as mask substrates [3].

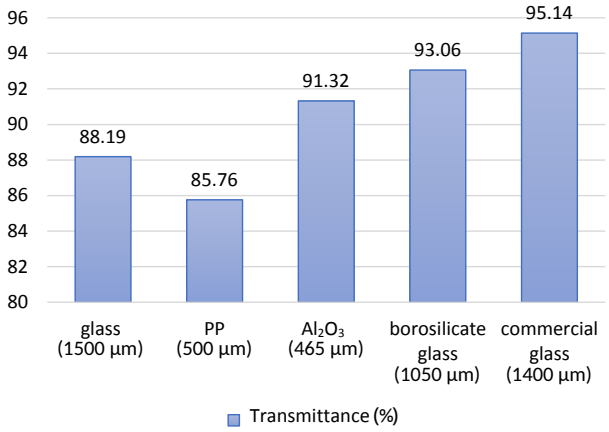


Fig. 1: The optical transmittance for different materials used as photomask substrates for 405 nm wavelength.

With progress in microelectronics technology forced by devices evaluation, the studies on physical phenomena are crucial for further development. It requires an elaboration of dedicated test structures, which are evolving along with research advancement. Thus, flexible and relatively fast method of photomasks fabrication for small series of samples, is demanded. In the work, application of Al_2O_3 2" substrates as photolithography mask carriers was proposed. The sapphire optical transmission, for the wavelengths range used in photolithography (380–450 nm) is acceptable (Fig. 1) [4]. Moreover, beyond its high hardness and

mechanical and chemical resistance, this material is also easily available.

Furthermore, sapphire substrates manufacturing costs are continuously reduced [5]. Compared to quartz and float glass, the transmittance of sapphire is not much lower and corresponding for mask applications.

In the work, the subsequent mask fabrication steps were briefly presented. As a result of elaborated technology, the structures with correctly recreated pattern shape with sharp edges and proper layers morphology were successfully obtained.

2. Experimental Details

The photolithography mask manufacturing process was studied dedicated to the microelectronic structures fabrication. The technology flow of photolithography mask is presented in Fig. 2.

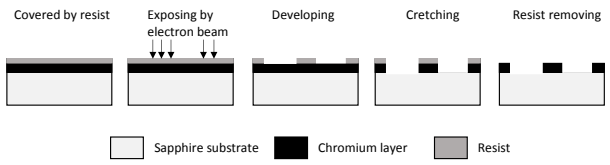


Fig. 2: Mask fabrication steps.

As test samples, the 18×18 mm^2 sapphire substrates were applied, however, in further research, the technology was successfully transferred to 2-inch substrates.

Samples were cleaned chemically in 2-propanole and acetone (near boiling point), rinsed in DI water and dried in N_2 flow. Chromium layers of various thicknesses were evaporated in ultra-high vacuum system using electron beam. Then samples were coated with resist layer. Either applying metal and resist layer requires prior chemical cleaning of the samples to remove contaminations from surface and provide well adhesion of layer. The adhesion of materials is extremely important issue and ensures the ability of proper propagation of UV wave and mask durability [6]. Thus, additionally, morphology of Cr layers was investigated using AFM as well as adhesion was examined by blue-tape test [7].

For test purposes, positive (AZ 1813, PMMA/MA) and negative (AR-N 7520) resists were used to examine the resistance for Cr etching solution. The next stage of mask fabrication was the exposition process with parameters optimized earlier. The development process using the dedicated solutions was conducted after exposition to open the windows in resist layer.

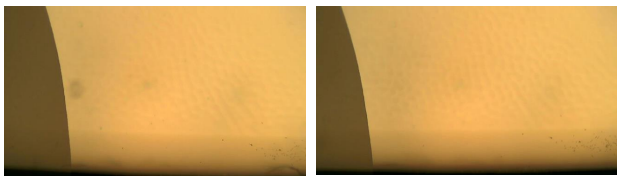
At so prepared samples, the wet etching process was executed. The compatibility of applied solutions and resists was checked to provide the accuracy of etching process. The influence of immersion in etchants on the polymer morphology, the occurrence of undercuts in resist layer and the precision of etching. Cr layers were etched in series of different etchants. The hydrochloric acid and DI water at various concentration 3:1, 1:4, 1:10, also with the addition of iron chloride, as well with glycerine was used. The temperature and composition of the etchant influenced the time of etching. For high concentrations and temperature, the etching proceeded even a 2 s, which was promising due to speed of mask fabrication, although very difficult to control, hence the optimization of etching solutions concentrations and process temperature had to be conducted. With glycerine and water 1:1, the time of etching structure was 5 min 10 s and was dependent on density of pattern. Additionally, the etching process was executed with the potassium permanganate with sodium hydroxide and hydrogen oxide and ceric ammonium nitrate with perchloric acid. The last one was examined in terms of the different etching time.

After etching process, the residual resist was removed by the dedicated reagents.

Samples were examined between subsequent steps of fabrication with optical microscope and Scanning Electron Microscope (SEM).

3. Results

To adhesion assessment, the blue tape test has been used. The tape applied to the chromium layer and then pulled off, determined and proved the required connection strength between the evaporated layer and substrate material. The results are presented in Fig. 3.

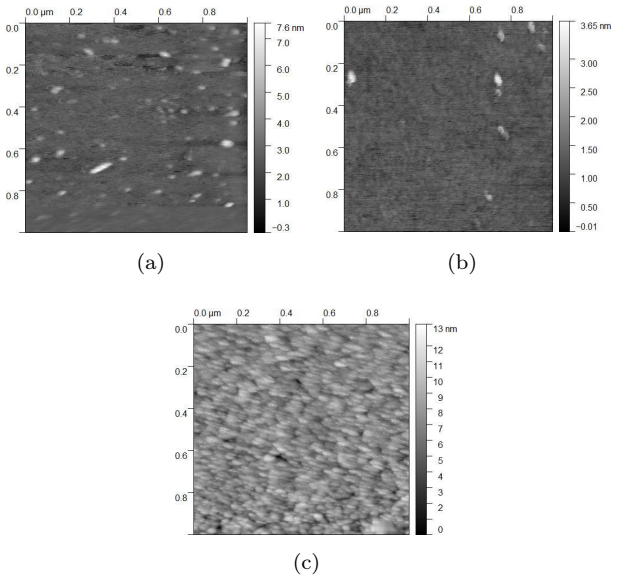


(a) Before. (b) After.

Fig. 3: Optical comparison of chromium structure before and after the blue tape test, magnification 20×.

Concerning the optical aspects, the morphology of Al_2O_3 will play an important role in wave propagation during resist layer irradiation. Thus, influence of wet etching solutions on the morphology of sapphire surface was examined before Cr evaporation and after Cr complete etching. There were no etching phenomena observed on the surface of sapphire (Fig. 4) and morphology parameters remained nearly the same what

permitted for excluding the influence of wet chemical etching of Cr layers on Al_2O_3 surface. Furthermore, morphology of Cr layers was investigated using AFM before etching to examine its homogeneity and undemanded voids.



(a) (b)

(c)

Fig. 4: Morphology of sapphire substrate before (a) and after Cr etching (b), and evaporated chromium layer on Al_2O_3 (c).

The resistivity of applied resists to the exposition to etching solutions was checked to provide proper quality of shadowing Cr layers without any thinnings and voids.

Studies indicated avoiding of alkali containing solutions, even in small concentrations, due to the development of resist layer which could lead to deformation of the patterns shape (overdevelopment), development of patterns edge, loss of edge sharpness, and, in the worst case, removal of resist layers.

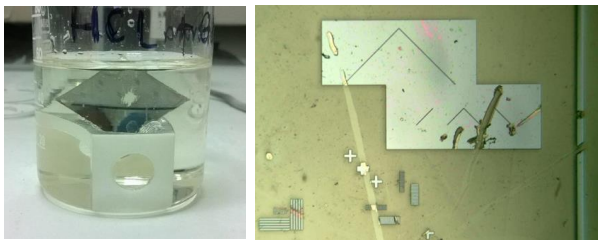
The time of etching depends strongly on the solution temperature and composition homogeneity. Even small changes of solution temperature as 2 °C resulted in acceleration of etching process by 10 %. Thus, all operations were carried out at room temperature.

The mask fabrication tests were performed for different etching solutions (Tab. 1). The etch rate, except for the temperature, was influenced by the pattern density. Bare Cr layers without any pattern on the surface reached the rate of 0.79 nm·s^{-1} while layers with pattern of 0.91 nm·s^{-1}, and very dense pattern of 1.21 nm·s^{-1} (for the same etching solution).

Tab. 1: Etch rates of Cr layers with pattern in various solutions.

Solution	Concentration	Etch rate (nm·s^{-1})
HCl:H_2O (DI)	3:1	55.00
HCl:H_2O (DI)	1:4	5.00
HCl:H_2O (DI)	1:10	3.21
HCl:$C_3H_8O_3$	1:1	9.08
DI:ACA:HNO_3	100 ml:18 g:10 ml	0.79
$KMnO_4$:NaOH:H_2O	5 g:7.5 g:30 ml	1.21

The occurrence of native chromium oxide on metal layer was an impediment to initiate etching with HCl dilution and it demanded to provide current flow between liquid and chromium. For this purpose, the aluminum wire was used and the samples surface was rubbed by it because soft contact did not manage to begin the etching process (Fig. 5(a)). The initiation was uneven at sample surface and depended on the contact point, hence it was necessary to maintain the uniformity of rubbing at surface which led to damage of the Cr layer (Fig. 5(b)). The same results were observed for the HCl and glycerine solution. Thus, the HCl based solutions should be avoided.

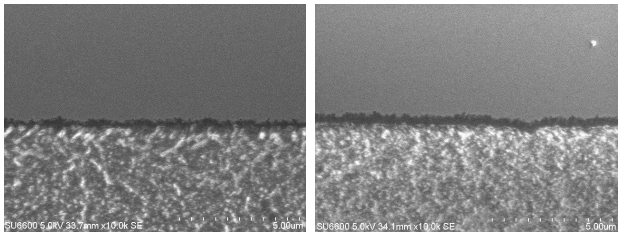


(a) (b)

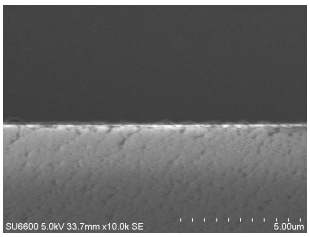
Fig. 5: The initiation of etching process by rubbing with aluminium wire (a) and damages on structures (b).

Immersion of test sample in $KMnO_4$:NaOH:H_2O (5 g:7.5 g:30 ml) caused removal of both, the resist and metal after 1 min. This lack of resistance of the resist to the solution excluded its further examination. The studies were also performed for etching solution widely described in literature, i.e. $2NH_4NO_3.Ce(NO_3)3.4H_2O$:$HNO_3$:$H_2O$ (5 ml:18 g:100 ml).

SEM observations enabled to examine the edge sharpness for different etching solutions. Chromium etching with HCl:$C_3H_8O_3$ solution, where the etch rate was relatively high, revealed the dissolution reaction no uniform inside the structures leading to high roughness of edges (Fig. 6(a)). The path width corresponded to the designed value, although the shape of the pattern exhibited some falsities as e.g. roundings at the ends of rectangular patterns. Such rapid reaction rate made the etching control difficult. And additionally, thin chromium residuals remained on the surface of sapphire. Similar defects were observed for HCl:H_2O

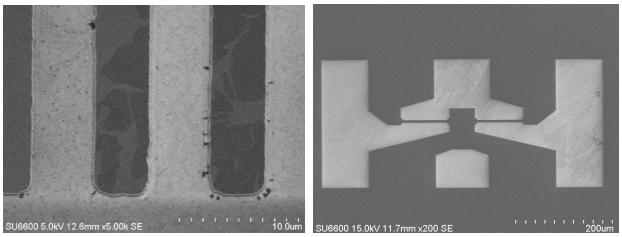


(a) (b)

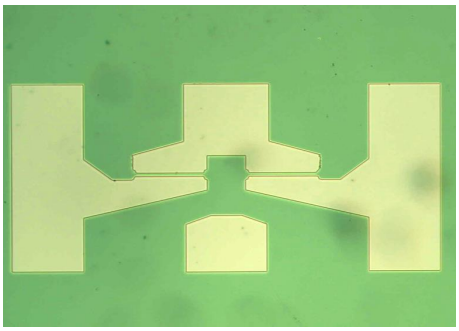


(c)

Fig. 6: SEM image of path sharpness (path width of 10 μm) at test structures etched using the HCl:$C_3H_8O_3$ solution (a), the HCl:H_2O (1:4) solution (b) and the ceric ammonium nitrate (c).



(a) (b)



(c)

Fig. 7: SEM image of path (width of 5 μm) at test structure etched using the solution with ceric ammonium nitrate (a), transistor shape at mask (b) and at silicon substrate after photolithography with fabricated mask (c).

(1:4) solution, where the etch rate was almost twice as high. On the transparent substrate the continuous thin layer of chromium was noticed (Fig. 6(b)). For ceric ammonium nitrate, the observations proved the good quality of elaborated structures, lack of contaminations and chromium residues on the sapphire substrate (Fig. 6(c)).

The etching with ceric ammonium nitrate provides the lack of damages in windows, smooth path edges and the correct shape representation.

To verify the technology, a mask with transistor structure was made and used for further photolithography process. The 2-inch mask was used. The silicon samples were covered with LOR and SPR resists and exposed (405 nm) with density of irradiation power equal to 14.4 mW·cm^{-2} (exposure time 6 s). The two-step development process was conducted with dedicated solutions and optimized time.

The quality of obtained pattern was appropriate for the purpose of microelectronic devices fabrication (Fig. 7(b) and Fig. 7(c)).

4. Conclusion

In the work, the photolithographic mask fabrication process on sapphire substrates has been presented. It was demonstrated the Al_2O_3 substrates have high and enough optical transparency to conform as photomask. Proper adhesion, no influence of etching solutions on sapphire surfaces morphology and etching process were examined. The non-compatibility of PMMA/MA and ARN 7520 resists with $KMnO_4$ with NaOH dilution was demonstrated. The high roughness of path edges and the chromium residuals on sapphire substrate was observed after etching with HCl and glycerine and HCl and H_2O. The shape falsities were noticed for solutions with high etch rate. The etching ceric ammonium nitrate solution was selected in terms of proper, uniform and relatively slow removal of the chromium layer without leaving any defects and assuring sharp edge without undercuts. The appropriate quality of pattern and proper path smoothness was obtained at samples after photolithography process with fabricated masks.

Acknowledgment

This work was co-financed by the National Centre for Research and Development grants TECHMASTRATEG No. 1/346922/4/NCBR/2017 and LIDER No. 027/533/L-5/13/NCBR/2014, the National Science Centre grant No. DEC-2015/19/B/ST7/02494, Wroclaw University of Technology statutory grants and by the Slovak-Polish International Cooperation Program. This work was accomplished thanks to the product indicators and result indicators achieved within the projects co-financed by the European Union within the European Regional Development Fund, through a grant from the Innovative Economy (POIG.01.01.02-00-008/08-05) and by the National Centre for Research

and Development through the Applied Research Program Grant No. 178782.

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About Authors

Agnieszka ZAWADZKA received her M.Sc. degree (2018) in Mechatronics in Faculty of Mechanical Engineering from Wroclaw University of Science and Technology. She is a Ph.D. student at Faculty of Microsystem Electronics, Wroclaw University of Science and Technology. Her current research is focused on technology of semiconductor devices e.g. development of lithography processes.

Joanna PRAZMOWSKA received M.Sc. degree (2005) and Ph.D. degree (2011) from Wroclaw University of Technology. Since then, she has been assistant professor in Division of Microelectronics and Nanotechnology, Wroclaw University of Science and Technology. Her current research is focused on lithography process development of electronic, optoelectronic devices and gas sensors.

Regina PASZKIEWICZ received her M.Sc. degree (1982) in Electrical Engineering from St. Petersburg Electrotechnical University, Russia and Ph.D. degree (1997) from the Wroclaw University of Technology, Poland. Now she is full professor at Wroclaw University of Science and Technology. Her research is focused on the technology of (Ga, Al, In)N semiconductors, microwave and the development of optoelectronic devices technological processes.