DEVELOPING THE PROCESS FOR THROUGH-ETCHING OF SINGLE-CRYSTAL QUARTZ IN INDUCTIVELY COUPLED PLASMAS

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Abstract

The possibility of using the Taguchi method to create an optimized process for deep-through plasma-chemical etching of single-crystal quartz with a minimum number of experiments is considered. The technological parameters of the PCE process in CH_4/H_2 and SF_6/O_2 plasmas have been ranked according to the degree of significance of their influence on the etching rate. The influence nature of these parameters on the etching rate is analyzed.

Keywords: *dry etching, quartz, CF_4+H_2 plasma, SF_6+O_2 plasma, inductively coupled plasma, etching rate*

1. INTRODUCTION

Quartz and quartz glasses are widely applied as materials used in a variety of sensors, microelectronic and micromechanical devises, which are wildly using in medicine, telecommunication, optics, electronics and etc. [1-5]. Successful usage of quartz and quartz glass in high-tech industries (and prospects of its future application) are determined by the availability of their specific properties, and by the current level of high-precision technologies for their efficient processing, such as plasma-chemical etching (PCE). This method of processing became widespread in those industry areas where the quality and accuracy of the topography of the final product are strictly required.

Chemical reactions of the high-reactive or the high-energy particles of plasma with the surface of processing material are the base of PCE process. In particular, the chemical part of the etching process of SiO_2 in fluorine-based plasma can be described by the following reaction

$$4F^* + SiO_2 \rightarrow SiF_4\uparrow + O_2\uparrow, \qquad (1)$$

where plasma became a source of the fluorine radicals, which are formed from the molecules of the source gases (for example CF_4 or SF_6). Other plasma particles could also influence the etching process leading to the physical sputtering, activation or passivation of the etching surface.

The complexity of the PCE process and the requirements of the industry in high-performance, high-precision technologies have stimulated intensive research of this method of processing materials. However, the task of production productivity of PCE is still high-priority especially in the context of developing technology for high-speed deep etching (dozens of μm) of materials, in particular quartz single-crystals. It is obvious that the solution of this task can be provided with two ways:

1) Modernizing and improving of the processing chamber,
2) Optimization of the PCE process parameters.

We present the results of developing the quartz single-crystal deep etching process as achieved on the original equipment which is designed in the Institute of Metallurgy, Mechanical Engineering, and Transport of Peter the Great St. Petersburg Polytechnic University.

2. MATERIALS AND METHODS

2.1. Materials

Z-cut single-crystal quartz 76.2 mm diameter and 370 μm thickness substrates produced by Ostec-Integra Ltd (Moscow, Russia) were used as experimental samples. For mask,Cr-Ni film 7 μm with 3×10 mm windows was used.

2.2. Methods

The experiments were done on the original, specially-designed PCE system with inductivity coupled plasma (ICP) source (fig.1). The reaction zone consists of two chambers – discharge and reaction chambers. Plasma in discharge chamber was initialized by the applying of high-frequency (RF) power to the inductor with the specific shape (f = 13.56 MHz, W_{max} = 1000 W) through the resonant impedance matching device. RF plasma was diffusively propagated into the reaction chamber where flat, water-cooled, steel table (RF electrode) with substrate holder on it was located. The separate RF generator (f=13.56 MHz) was connected to the RF electrode in order to control the energy of the charged plasma particles by negative bias potential.

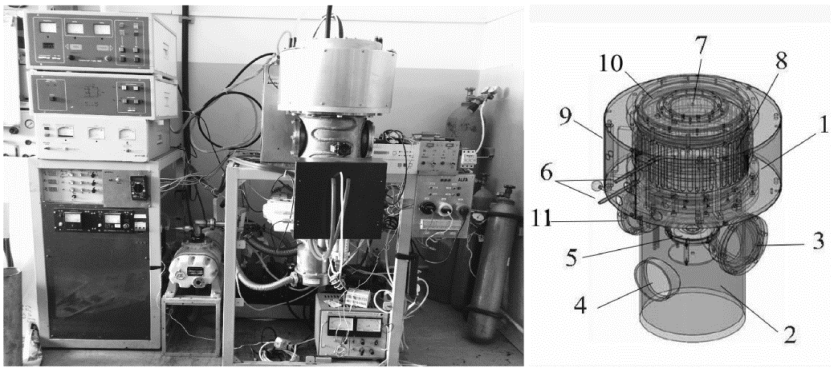


Fig. 1. General view of the PCE system and its 3D CAD drawing. 1 – discharge chamber; 2 – reaction chamber; 3 – samples loading flange; 4 – pumping connetion flange; 5 – sample holder; 6 – water-cooling ICP inductor; 7 – gas mixture inlet channel; 8 – faraday screen; 9 – inductor electromagnet screen; 10 – removable cap; 11 – window.

CF_4/H_2 or SF_6/O_2 gas mixtures were used for the etching process. The flow to the discharge chamber of process gases was regulated by mass flow controller (MFC) called RRG-10 (Eltochpribor Ltd) with a gas flow measuring error ±0.25%. Pressure in the reaction zone was measured with Baratrone pressure sensor (MKS Instruments, error ±0.001%), its values are independent from the composition of the gas mixture. Vacuum pumping system was based on three pumps: rotor pump (2NVR-5DM), buster pump (ZJC-50) and turbomolecular pump (Edwards STP-301C) and it allowed to support stable pressure in the chambers from 0.3 to 10 Pa.

The variable parameters in the experiments with the CF_4/H_2 gas mixture were: RF power (W), pressure in the chamber (P), bias voltage on the substrate holder (U_b) and H_2 flow (Q_{H_2}). The flow of the CF_4 was stable 15.15 sccm. Etching time was 30 minutes in each experiment.

In the case of developing the etching process of the quartz single-crystals in SF_6/O_2 gas mixture, the variable parameters were: U_b, W, (Q_{H_2}) and the distence between the surface of the sample holder and the lowest edge of the discharge chamber (h). In this experimental series the parametres of the pressure (0.7 Pa) and Q_{SF_6}(10.15 sccm) were fixed in every experiment. The etching time was the same as in the experiments with the CF_4/H_2 and was equal 30 min.

In both cases, before the etching process was started, the surface of the quartz substrates was processed in the argon plasma for 10 minutes to be cleaned from irrelevant contamination (Q_{Ar}= 21.75 ml/min, P = 0.7 Pa, W = 750 W and $|U_b|$ = 25 V).

The etching rate was calculated from the measurement results of the etching depth as determined from micrographs. Micrographs were taken with Zeiss Supra 55VP Field Emission Scanning Electron Microscope with an error ± 4 nm.

In the case of real technological processes with many technological parameters, the simple search for the optimal technological parameter combination can require a large number of experiments, hence this search is resource-consuming. To find the optimum technological parameters (in terms of etching rate) the Taguchi method [6] of the experiment optimization was used to plan the experimental matrices. This method allows to minimize the numbers of experiments in optimization tasks and to find the parameter that has the most influence on the research process (etching rate).

The peculiarity of the Taguchi experimental planning is the development of a plan in the form of a balanced orthogonal matrix, the size of which is determined by the number of parameters and the number of levels (possible values) of these parameters. The planning matrix is designed in such a way that all of its columns should be orthogonal coupled i.e. there are all combinations of researched parameters levels in every couple of columns and there are equal numbers of them.

In the experimental series of quartz single-crystal etching with the CF_4/H_2 gas mixture, the variable technological parameters were fixed on two levels (Table 1) and the Taguchi planned experimental matrix was designed (Table 2).

In the case of etching in the SF_6/O_2 gas mixture, the number of parameters was also equal to four, however the parameters were fixed on three levels (Table 3). The plan for etching in SF_6/O_2 gas mixture is presented in Table 4.

Table 1. Variable parameters and their levels (CF_4/H_2 plasma)

Parameter	**Levels**	
	1	2
Q_{H_2}, **ml/min**	2.5	5.0
***P*, Pa**	1.5	4.5
***W*, W**	550	750
$\|U_b\|$, **V**	40	70

Table 2. The plan of experiments designed with the Taguchi method (CH_4/H_2 plasma)

No.	Q_{H_2}	***P***	***W***	U_b	**<V_{etch}>, nm/min**
I	1	1	1	1	148±13
II	1	1	1	2	218±15
III	1	2	2	1	44±6
IV	1	2	2	2	112±7
V	2	1	2	1	225±9
VI	2	1	2	2	302±4
VII	2	2	1	1	30±2
VIII	2	2	1	2	43±3

Table 3. Variable parameters and their levels (SF_6/O_2 plasma)

Parameter	Level		
	1	2	3
***W*, W**	550	650	750
$\lvert U_b \rvert$, V	50	100	150
Q_{O_2}, ml/min	1.6	3.4	5.4
***h*, cm**	5	10	15

Table 4. The plan of experiments designed with the Taguchi method (SF_6/O_2 plasma)

No.	Q_{O_2}	*h*	*W*	U_b	$<V_{etch}>$, nm/min
I	1	3	1	1	114±15
II	2	2	1	2	237±4
III	3	1	1	3	367±17
IV	2	1	2	1	235±8
V	3	3	2	2	268±13
VI	1	2	2	3	403±15
VII	3	2	3	1	172±8
VIII	1	1	3	2	408±11
IX	2	3	3	3	366±10

In order to reduce statistical error of the etching rate, verify reproducibility and increase result reliability, each experiment was run three times. Therefore, etching rate was calculated as an average for the corresponding three measurements. The ranking of the technological parameters were carried out with the help of Minitab 17 software according to the principle of the greatest influence on the etching rate of single-crystal quartz.

3. RESULTS

3.1. CF_4/H_2 plasma

Average etching rates of Z-cut quartz single-crystals in the CF_4/H_2 gas mixture were determined for each combination of technological parameters as presented in Table 2. On figure 2, several photos of etching profile are presented. It is necessary to mention that microphotographs were taken under a 45° angle. Hence, to establish the real etching depth each result was divided on $\sqrt{2}/2$.

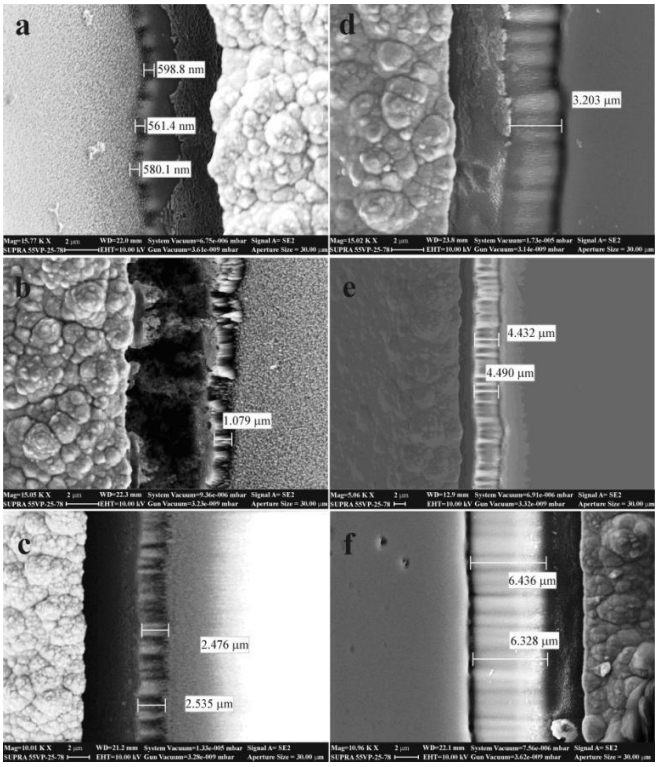


Fig. 2. Micrographs of the etched windows in Z-cut single-crystal quartz (CF_4/H_2). a – VII, b – III, c – IV, d – I, e – V, f – VI. (The photos were pictured at an angle of 45 ° to the plane of the etching window)

From Table 2, it follows that the highest etching rates were achieved in experiments with a low pressure (P = 1.5 Pa). Besides, the etching in low pressures has a positive effect to the quality of the etching surfaces (roughness). The ranking result of the process parameters (P, U_b, W, иQ_{H_2}) by their influence to the etching rate is presented on the figure 3a. According to the experimental data, results form the following order: $P > U_b > W > Q_{H_2}$.

3.2. SF_6/O_2 plasma

Average etching rates of quartz single-crystals in the SF_6/O_2 gas mixture are presented in Table 4. It can be seen that the etching of quartz in a sulfur hexafluoride-based plasma allows higher etching rates, compared to etching in a CF_4/H_2 mixture (408 nm/min (SF_6/O_2) versus 302 nm/min (CF_4/H_2)). Besides that, comparing the microphotographs (Fig. 2 and 4) it can be argued that etching in SF_6/O_2 gas mixture provides better quality of the etching profile than in the CF_4/H_2 gas mixture. Researched technological parameters form the following series: $U_b > h > W > Q_{O_2}$ (Fig. 3a).

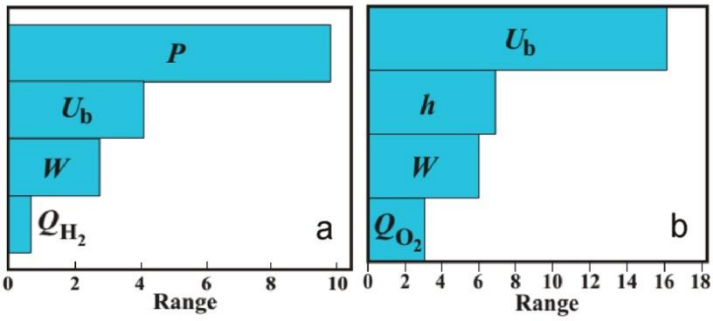


Fig. 3. Histograms describing the distribution of the technological parameters as regards their influence on the etching rate of single-crystal quartz (a - CF_4/H_2 plasma, b - SF_6/O_2 plasma).

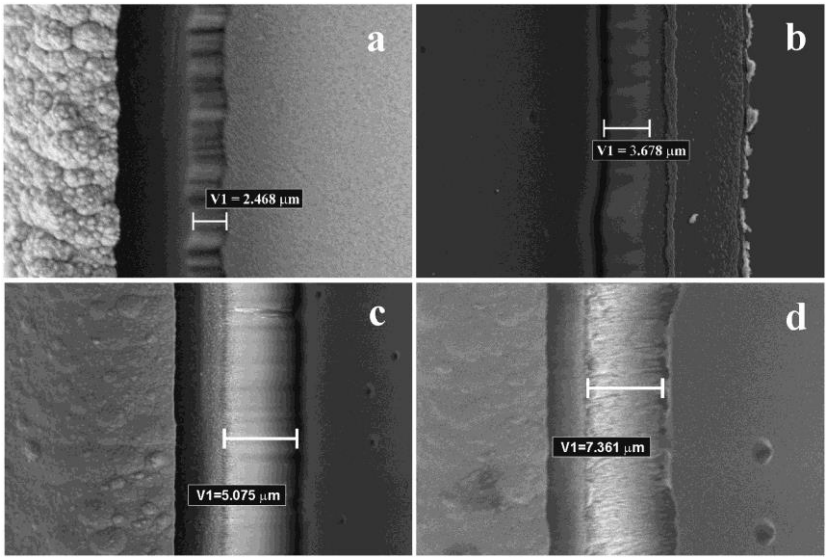


Fig. 4. Examples of the micrographs of the etched windows in the SF_6/O_2 gas mixture. Pictures a, b, c and d are matching the experiments I, VII, IV и III respectively. (The photos were pictured at an angle of 45° to the plane of the etching window)

3.3. Deep-through etching of single-crystal quartz (z-cut).

Deep-through etching experiment of a single-crystal quartz wafer 370 µm thickness was done in the SF_6/O_2 gas mixture because it provides higher etching rate when compared to CF_4 / H_2 etching process profile quality. Based on the previous experiments the best process parameters combination was used in this experiment: P = 0.75 Pa, W = 750 W, $|U_b|$ = 200 V, h = 5 cm иQ_{O_2} = 3.4 sccm (25% from the total gases flow). According to the electron microscopy results (Fig. 5) it was established that the etching rate was equal to 402 nm/min with the selectivity of quartz etching with respect to the mask material 120. The etched window inclination angle of the side wall was 101.3°.

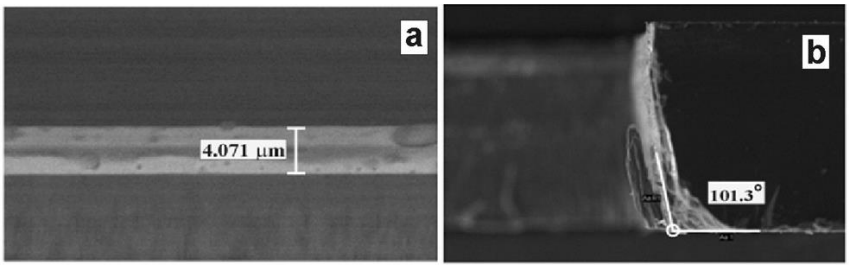


Fig. 5. Micrographs of the residual layer of the Ni-Cr mask (a) and the etched window sidewall (b).

4. DISCUSSION

4.1. Pressure

As seen from figure 3a the pressure in the reaction camera is the most significant technological parameter to the etching rate of the PCE process. As previously known, the dissociation rate of the gas molecules in gas discharges (and hence the rate of chemically active particles (CAP) generation in the plasma) is determined by the number of collisions between electrons and molecules and can be described by the following equation [7]:

$$G = \sqrt{\frac{8}{\pi m_e}} n_r n_e \frac{C_r (kT_e)^{3/2}}{\bar{\lambda}_e} \left(2 + \frac{E_d}{kT_e}\right) exp\left(-\frac{E_d}{kT_e}\right) \qquad (2).$$

In this equation: m_e is the electron mass, n_r and n_e are the concentration of gas and electron molecules, respectively, C_r is the constant depending on the type of gas, T_e is the temperature of the electron gas, $\bar{\lambda}_e$ is the mean free path of electrons in the gas, and E_d is dissociation energy of the gas molecules. In the low-pressure range when $kT_e >> E_d$, the ratio E_d/kT_e is tending to zero and consequently:

$$exp\left(-\frac{E_d}{kT_e}\right) \approx 1.$$

With reduction in pressure, the gas molecule (n_r) and electron (n_e) concentrations also decrease. The free-path length ($\bar{\lambda}_e$) increases more than T_e increasing. As a result, there is a decrease of dissociation rate (CAP generation) which provides the deceleration of the etching rate. On the other side, when the pressure is high, when $kT_e \sim E_d$, further pressure increase will lead to the moment when multiplication factor $\exp(-E_d/kT_e)$ will tend to zero. As a result the etching speed will decrease because of the decreasing of the gas molecules dissociation rate and the CAP generation. This means that the function $V_{rp}(P)$ must have an extremum (maximum), displacement from which in the direction of pressure decreasing or increasing will lead only to decreasing of the CAP concentration and as result to the decreasing of the etching rate. The fact that in experimental series with the CF_4/H_2 the highest etching rate was reached in low-pressure range shows us that we worked in relatively high pressures. Clearly, these arguments are fully valid for the experiment with the SF_6/O_2 gas mixture because the type of gas mixture is a multiplier C_r in the equation (2). Thus, the influence of pressure in the reaction chamber on the etching rate is due to a strong dependence of the discharge CAP concentration on the pressure.

4.2. Bias voltage

From the tables 2 and 4, we can see that the highest values of the etching rate were reached when the bias voltage on the sample holder was high. Without ion bombing, the fluorine atoms are reacting slowly with SiO_2 but the presence of ion impact significantly accelerates the etching process of quartz [8, 9]. By increasing the substrate holder negative potential the ion energy rises and also the direction of their movement to the negatively charged electrode improves (increasing of the positive ion flow density). Thus, in cases when the bias value is high, the increased etching rate related to two facts; reaction activation between SiO_2 and fluorine radicals and sputtering of the substrate as consequence of ion bombing.

4.3. The distance between the surface of the sample holder and the lowest edge of the discharge chamber

This parameter is almost never reviewed in PCE optimization works. Nevertheless, our data show that the varying of the holder position has an equal influence (and even slightly larger) as it does the applied RF power on the etching rate (Fig. 3b). The strong dependence of the etching rate on the h value is apparently associated with the existence of CAP concentration gradient in the direction from the discharge chamber to the substrate holder. As the distance decreases between the etching surface and the discharge area the amount of CAP which can reach the material surface increases and this provides the increasing of the etching rate.

4.4. HF power

The dissociation rate of gas molecules in plasma is determined by the number of collisions between gas molecules and electrons, the energy of which must be higher than threshold for molecule dissociation. However, these collisions with high-energy electrons do not always result in molecule dissociation because this process has a probabilistic character. It is obvious that if in the discharge volume there are more electrons with the necessary energy, the greater the probability of dissociation.

Since the energy of the electrons in the plasma is directly determined by the RF power, then its increasing promotes the molecules dissociation with CAP generation and this means the increase of the etching rate.

4.5. The adding effect of H_2 and O_2.

Adding of the hydrogen and oxygen to the base-etching gases (CF_4 and SF_6 in our case) are affecting to the number of CAP in discharge and thus on the etching rate. Research of the chemical composition of CF_4/H_2 plasma as a function of H_2 concentration in the gas mixture was done by Knizikevicius et al [10]. It was shown that by increasing hydrogen concentration, the amount of F and CF_3 radicals gradually decrease but the CF_2 radicals increase rapidly and reach their maximum at 30% of H_2 in gas mixture. As well as fluorine radicals in the case of ion bombing, the $CF_2$and theCF_3radicalsinteract with the SiO_2formingvolatile compounds

$$2SiO_2 + 2CF_3 \rightarrow SiF_2 + SiF_4 + 2CO_2 \quad (3),$$

$$SiO_2 + 2CF_2 \rightarrow SiF_4 + 2CO \quad (4),$$

That is why the contribution of the chemical component to the etching rate is determined not only by the concentration of fluorine atoms in the plasma, but the total concentration of all radicals that can react with SiO_2 and form the volatile compounds. Maximum concentration of the F, CF_2, CF_3radicals accumulates in the range of 20-30% of H_2 and after this number, it starts to decrease. Hence, the etching rate depends on the concentration of H_2 at which the concentration of active radicals is at its greatest. These findings are in accordance with previous assumptions [11, 12]

Similar theoretical research [13] of the chemical composition and SiO_2 etching rate of adding O_2 to the gas mixture in plasma based on the sulfur hexafluoride showed that when the concentration of oxygen raises up to 20-30% the number of F atoms concentration rapidly increases. At 30-50% of O_2 in the gas mixture, the amount of fluorine atoms decrease slowly and after that region the number falls. The increment in the fluorine atoms concentration is compensated by the SF_6decrease in the mixture. The etching rate dependence from the oxygen concentration has a qualitatively similar character [13]. Therefore, the etching rate in SF_6/O_2 plasma is determined by the concentration of F atoms in the discharge.

5. CONCLUSIONS

With use of the Taguchi method the technological parameters optimization of the single-crystal quartz PCE in CF_4/H_2 and SF_6/O_2 plasmas and low RF power was done. Based on the collected data the deep-through etching of a 370 μm thickness quartz wafer in SF_6/O_2 gas mixture was done. The etching rate of the process was 402 nm/min and the selectivity of quartz etching with respect to the mask material, equal to 120.

A number of technological parameters of the process have been ranked according to the degree of significance of their influence to the etching rate. By this criterion these parameters form the following decreasing series: $P > U_b > h > W > Q$. Pressure and RF power affect the stable gas molecule dissociation rate and consequently on CAP generation. The amount of negative bias determines the ion bombing of the etching surface which provides the CAP heterogeneous reaction with substrate materials and physical sputtering of the wafer. The etching rate dependence on the distance between the substrate holder and the plasma generation region is most likely due to a change in the CAP delivery condition to the etching surface, and the adding of additional gases (H_2 and O_2) in the mixture allows controlling the chemical composition of the plasma.

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