Etching of silicon surfaces using atmospheric plasma jets

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Abstract

Local plasma-assisted etching of crystalline silicon by fine focused plasma jets provides a method for high accuracy computer controlled surface waviness and figure error correction as well as free form processing and manufacturing. We investigate a radio-frequency powered atmospheric pressure He/N2/CF4 plasma jet for the local chemical etching of silicon using fluorine as reactive plasma gas component. This plasma jet tool has a typical tool function width of about 0.5 to 1.8 mm and a material removal rate up to 0.068 mm3 min−1. The relationship between etching rate and plasma jet parameters is discussed in detail regarding gas composition, working distance, scan velocity and RF power. Surface roughness after etching was characterized using atomic force microscopy and white light interferometry. A strong smoothing effect was observed for etching rough silicon surfaces like wet chemically-etched silicon wafer backsides. Using the dwell-time algorithm for a deterministic surface machining by superposition of the local removal function of the plasma tool we show a fast and efficient way for manufacturing complex silicon structures. In this article we present two examples of surface processing using small local plasma jets.

Keywords: plasma jet machining, plasma etching, surface roughness

1. Introduction

The manufacturing and deterministic surface waviness and figure error correction of complex surface shapes like aspheres or free-forms with small lateral dimensions of less than 20 mm are still challenging goals in ultra-high precision optics fabrication. The classical mechanical processes like grinding and polishing have their limitations with respect to geometric flexibility and achievable surface shape accuracy as well as production cost and time. In particular, for small lateral structures in the range of 1–5 mm with strong surface gradients, these methods reach their limits. As an alternative process for optical fabrication chemical vapour machining (CVM) was proposed more than 15 years ago. This dry etching process uses a localized plasma which is generated using a frequency of 150 MHz in a closed chamber filled with a mixture of inert and reactive gas components [1–4]. Further investigation in our group at the Leibniz Institute of Surface Modification on plasma-assisted chemical etching (PACE) led to the development of a local etching process dedicated for silicon-based materials like pure silicon, fused silica, SiC or ULE® by the interaction of a reactive plasma or radical jet with the substrate surface under rough vacuum conditions [5–9]. Later this etching process was transferred to atmospheric pressure. Plasma jet machining (PJM) is based on a chemically reactive plasma jet generated by a capacitive coupled microwave system. Atmospheric plasma jet machining with reactive gas components has great technological potential for ultra-precision modification and correction of optical surfaces [9, 10]. This process is comparable with the reactive atomic plasma technology (RAPT®) developed by RAPT Industries [11, 12] for the finishing of large optical surfaces of ULE® and fused silica. The material removal is generated by a chemical reaction of silicon or silicon-based compounds with free fluorine which is provided by dissociation of CF4, SF6, or NF3 admixed to inert plasma gases like argon or helium. PJM is applied for the deterministic generation or correction of the surface shape using the dwell-time method based on the targeted topography.
The tool function mature dwell time algorithms developed for plasma jet and ion beam processes are used to calculate the motion scheme and tool path over the work piece for optimum material removal. Recently, plasma sources capable of creating fine focused plasma jets with a tool FWHM of less than 1\,mm have been developed for effective surface machining with high lateral resolution. In this paper we present the main characteristics of such plasma jets with radio frequency (RF) excitation. Furthermore, examples of surface figure generation are shown. The capability of the plasma to smooth surface micro-roughness will be discussed.

2. Plasma-assisted etching of silicon

Plasma-assisted etching of crystalline silicon has been performed using a radio frequency powered plasma jet source at 13.56\,MHz developed at the IOM. The source works in a normal atmospheric pressure environment using helium as a plasma carrier gas, tetrafluoromethane (CF\textsubscript{4}) as the reactive gas. Furthermore, a concentric nitrogen flow around the central plasma discharge is applied to minimize the possible influence of the surrounding atmosphere. The plasma jet source consists of a metallic coaxial conductor with an inner tube. The tube has an inner diameter of 1\,mm which forms the outlet for the He/C\textsubscript{4}F\textsubscript{4} plasma jet. RF power is supplied by an Advanced Energy CESAR 133 RF Power generator. Figure 1 shows the plasma jet in free burning and contact mode on a polished silicon wafer. In contact mode the plasma jet forms a plasma disc at the silicon wafer surface which determines the active etching region. The size of this disc depends on the distance between the substrate surface and the plasma jet outlet. Since the plasma jet has a maximal length of about 5.5\,mm at a helium flow rate of 1000\,sccm the contact area between surface and plasma is small at a working distance between nozzle and substrate surface of 5\,mm. This leads to narrow tool functions with half widths smaller than the inner tube diameter. The fine focused plasma jet creates a nearly Gaussian-shaped tool function with a full with half maximum (FWHM) of 0.5 to 1.8\,mm depending on the distance to the substrate surface. The material removal of silicon is based on the chemical reaction of silicon surface atoms and free fluorine radicals in the plasma jet active region forming volatile SiF\textsubscript{4} [13]. Free fluorine is provided by the dissociation of CF\textsubscript{4} admixed to the He plasma carrier gas. This reaction is enhanced by the local increase of the surface temperature in the contact zone and additional heating of the sample.

We investigated the relationship between the material removal rate and plasma jet parameters by installing the plasma source onto a standard CNC machine with an installed gas treatment system for filtering the fluorine components. Figure 2 shows the material removal rate in dependence on the plasma parameters: RF power $P$, working distance between silicon surface and inner tube nozzle $Z$, CF\textsubscript{4} gas flow and relative scan velocity $v$ of the plasma jet with respect to the substrate surface. For all of the experiments the central He carrier gas flow and the N\textsubscript{2} peripheral gas flow was kept constant at 1000\,sccm and 1500\,sccm, respectively. These are the optimal parameters to create a stable plasma jet for the plasma source under investigation. In order to avoid material re-deposition on silicon wafer during the etching process, the samples were heated up to 150°C by a conventional hot plate. At room temperature C- and F-containing reaction products are observed as cloudy deposits on the surface that affect the etching process by masking the surface and consequently the surface roughness. The parameter dependencies (RF power, surface distance, CF\textsubscript{4} gas flow, scan velocity) have been investigated using a raster path motion scheme with a line feed distance of 100\,$\mu$m and a plasma etched area of $10 \times 10$\,mm\textsuperscript{2}. The depth of these generated areas was measured with high accuracy using an interferometer (total...
Figure 2. Material removal rate dependence on RF power, surface distance, CF₄ gas flow and scan velocity. A maximum volume etching rate of 0.068 mm³ min⁻¹ was obtained using RF power of 80 W, CF₄ gas flow of 0.7 sccm, scan velocity of 1 mm s⁻¹ and a surface distance of 3.5 mm.

The silicon material removal rate depends almost linearly on the used RF power in the range of 60 to 80 W (see figure 2(a)). This behaviour displaces the greater plasma volume with higher RF power supply which leads to an increase of the generated plasma disc at the surface and a wider FWHM of the tools function at a constant surface distance. In addition, more CF₄ molecules can dissociate at higher plasma power. Since the plasma source is not equipped with a water cooling system RF power larger than 80 W leads to strong heating of the source components which is undesirable due to source deterioration. The material removal rate dependence on the distance between the plasma source outlet and silicon surface is shown in figure 2(b). The active region (plasma disc shown in figure 1(c)) strongly depends on this distance as the removal rate is high for small distances and low for large distances. This is also reflected in the plasma tool FWHM which is in the range of 1.8 mm for Z = 3.5 mm and 0.52 mm for a surface distance of 5 mm. The gas composition ratio of CF₄ to He is in the range of 1 : 1000 to 1 : 10 000 while the helium gas flow is held constant at 1000 sccm. The material removal rate displayed in figure 2(c) shows an almost linear increase in the range of 0.1 to 0.8 sccm CF₄. A further increase of CF₄ flow rate leads to a saturation of the removal rate at 0.054 mm³ min⁻¹. For the selected parameters (surface distance 3.5 mm, RF power 80 W) the maximum amount of reactive fluoride which can etch the silicon surface is reached with a CF₄ gas flow of 0.8 sccm. This maximum may have several reasons: the material etching removal rate is limited by the dissociation rate of CF₄ molecules or the maximum amount of reactive fluoride in the active plasma/silicon surface region is reached. The effect of the scan velocity on the material removal rate (see figure 2(d)) is almost negligible. This indicates that the surface temperature (and therefore the etching rate) is not significantly influenced by the plasma jet heat flux onto the substrate surface. Nevertheless there is a slight increase in the removal rate for a faster scan velocity. The origin of this effect could not be clarified until now. Measurements using a thermal imaging camera revealed a shallow bell-shaped surface temperature distribution with a maximum that lies constantly 20–30 °C above the base level of approximately 150 °C reflecting the high thermal conductivity of silicon (see figures 3(a) and (b)). On other materials like fused silica and ULE® the surface reactions are enhanced by the local increase of the surface temperature in the contact zone induced by the plasma jet. Thus, the removal function is a convolution of the radial beam profile and the surface temperature distribution [14].

A high volume etching rate of 0.054 mm³ min⁻¹ was obtained using RF power of P = 80 W, CF₄ gas flow of 0.7 sccm, scan velocity of v = 1 mm s⁻¹ and a surface distance of Z = 3.5 mm. Under these conditions the etching process has an etching efficiency (silicon atoms etched by provided F atoms) of 15%. This value can be determined by calculating the number of fluorine atoms provided per minute and the number of silicon atoms per mm³. The material removal of silicon using fluorine chemistry is based on the formation of SiF₄(g) that ultimately desorbs from the silicon surface [13]. Therefore four fluorine atoms or one CF₄ molecule is needed to etch one silicon atom. With a density of 3.72 kg m⁻³ and a molar mass of 88.01 g mol⁻¹ the number of CF₄ molecules in 0.7 sccm can be calculated to 1.781 804 × 10¹⁵. The number of silicon atoms per mm³ can be calculated using the number of silicon atoms in a unit cell (8) and the lattice constant of
Figure 3. (a) temperature image of a silicon wafer heated to 150 °C and machined using a fine focused plasma jet, (b) temperature profile along the dotted line in figure (a).

Table 1. Plasma jet parameters for surface processing on silicon samples in section 2.2.

| Surface distance (mm) | RF power (W) | Tool function FWHM (mm) | Material removal rate (mm³ min⁻¹) |
|-----------------------|--------------|-------------------------|----------------------------------|
| setup 1 3.5           | 80           | 1.8                     | 0.054                            |
| setup 2 3.5           | 65           | 0.8                     | 0.0069                           |
| setup 3 5             | 80           | 0.52                    | 0.00122                          |

0.543 nm to 4.99678 × 10¹⁹. The theoretically maximum amount of silicon material etched by 0.7 sccm CF₄ per minute is therefore 0.356 59 mm³. The calculated etching efficiency of 15% uses the simplification that all CF₄ molecules dissociate in the plasma and are able to react with the silicon surface.

The parameter study has shown that with simple adjustments of power and working distance (see figures 2(a) and (b)) the characteristics of the tool function and the volume rate can be influenced. The tool function parameters given in table 1 have been chosen for surface processing on silicon samples. In section 2.2 of the article two examples of surface processing using small local plasma jets are presented.

2.1. Surface roughness

Surface micro-roughness after plasma jet etching was characterized using atomic force microscopy and white light interferometry. Due to the chemical removal of the silicon material the plasma jet machining works sub-surface damage free. That means no mechanical force takes effect on the sample surface. On polished and cleaned silicon wafers the micro-roughness after a 10 µm deep plasma etching was characterized using a MicroXAM white light interferometric surface profiler with 50× objective. The root mean square surface roughness S_q retained the initial value of 0.35 nm. However, Atomic force microscopy (AFM) measurements of 10 × 10 µm² reveal a homogeneous covering of the silicon surface with nanometre sized particles/structures changing the S_q initial value of 0.2 to 2.44 nm. The origin and composition of these particles has not yet been clarified so far. On the other hand the plasma jet process has the capability to smooth rough surfaces. We have investigated a stepwise removal of silicon material on mechanically ground and subsequently wet-chemically etched silicon wafer backsides on areas of 10 × 10 mm² using the following plasma parameters (see setup 1 in table 1): RF power of P = 80 W, CF₄ gas flow of 0.7 sccm, scan velocity of v = 1 mm s⁻¹ and a surface distance of Z = 3.5 mm. In figure 4(a) the stepwise removal is illustrated by surface profiles using a 2D profilometer system (nanofocus scan). The profiles have been taken on the initial surface and after removals of 3.1, 4.8, 8.2 µm. The plasma jet etching decreased the initial S_q value of 0.73 down to 0.2 µm. This smoothing effect was also observed on SiC [15]. The smoothing effect seems to be independent of the choice of plasma parameters (gas composition, working distance, scan velocity and RF power) and depends only on the etching depth. Further experiments need to be done to clarify the cause of this smoothing effect. Figure 4(b) summarizes the S_q values on plasma-etched ground/wet-etched silicon wafer backsides.

2.2. Plasma jet machining

Local plasma-assisted etching provides a method for high accuracy computer-controlled surface waviness and figure error correction as well as free form processing using a deterministic material removal based on a dwell time algorithm. The traditional processing techniques for optical systems are limited by the size of the tools used for grinding and polishing. For surface structures with small features or large slopes the machining tools have to be small enough to represent the surface structures. The two examples given below were carried out on polished silicon substrates with (1 0 0) orientation on a 3 axis CNC machine. Due to the plasma tool FWHM of less than 1 mm and Gaussian profile
the machining of free-form surface shapes is possible. To demonstrate the efficiency of the process, an input topography was generated using a mathematical surface description in terms of Zernike polynomials \((Z3: 0.5, Z8: -0.15, Z10 -0.25, Z18 -0.5, Z24 -0.25)\) exhibiting a peak-to-valley PV value of 1 \(\mu\)m (see figure 5(a)). Although this particular surface form has no practical relevance in optics, it shows the potential of plasma jet technology for free-form generation. Figure 5 shows the plasma jet machining summary using a reduced RF power of 65 W with a tool function of 0.8 mm and a material removal rate of 0.0069 mm\(^3\) min\(^{-1}\) (see setup 2 in table 1). In figure 5(a) the calculated input topography is visualized. The velocity profile determined by deconvolution algorithms is shown in figure 5(b). After a plasma machining process of 7 min the generated surface profile was measured by interferometry. A final residual error of 90 nm PV (simulated theoretical residual error 51 nm PV) indicates a slight over-etching at the substrate edge (see figure 5(c)).

Plasma jet machining can also be used for deterministic generation of analogous structures with fixed periods in the millimetre range and amplitudes of some nanometres. The second example is a sinusoidal surface structure with a peak-to-valley value of 100 nm and a sine period of 1 mm. The total machining time for this 10 \(\times\) 10 mm\(^2\) area was 17 min. For this fine structure process a higher surface distance \((Z = 5 \text{ mm})\) and therefore a smaller tool function of 0.52 mm FWHM was used. This leads to a material removal rate of 0.001 22 mm\(^3\) min\(^{-1}\) and depth removal rate of 66.7 nm s\(^{-1}\) (see setup 3 in table 1). Figure 6 shows an interferometric measurement of the generated surface with an extracted surface profile. Such structures can be used as a calibration standard for optical systems to determine the optical resolution and the lateral scale.

3. Conclusion

In this paper we present detailed investigations of local plasma-assisted etching of crystalline silicon with a fine focused plasma jet for ultra-precision waviness and figure error correction. This technology provides a powerful tool
for efficient manufacturing especially of non-standard optical elements. The plasma jet machining is a contactless, non-abrasive technology. Hence, no mechanical defects are generated on the surface. The process is based on a chemical removal mechanism of substrate material, therefore only silicon-based components like pure silicon, fused silica, SiC or ULE® can be machined using fluorine chemistry. Since there are almost no geometric restrictions for the contactless plasma jet tool machining there exist nearly no limitations for surface design and correction. Depending on the application the size (FWHM) of the tool function can be varied between 0.5 and 1.5 mm. Thus, this technology is capable to perform deterministic surface shape improvements in the sub-millimetre lateral spatial region.

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