Analysis of Factors Impacting Atmospheric Pressure Plasma Polishing

Ju-Fan Zhang[1,#], **Bo Wang**[1] and **Shen Dong**[1]

1 Center for Precision Engineering, Harbin Institute of Technology, 150001, Harbin, China
Corresponding Author / E-mail: zhangjufan@hotmail.com, TEL: +86-451-86412934, FAX: +86-451-86415244

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Atmospheric pressure plasma polishing (APPP) is a noncontact precision machining technology that uses low temperature plasma chemical reactions to perform atom-scale material removal. APPP is a complicated process, which is affected by many factors. Through a preliminary theoretical analysis and simulation, we confirmed that some of the key factors are the radio frequency (RF) power, the working distance, and the gas ratio. We studied the influence of the RF power and gas ratio on the removal rate using atomic emission spectroscopy, and determined the removal profiles in actual operation using a commercial form talysurf. The experimental results agreed closely with the theoretical simulations and confirmed the effect of the working distance. Finally, we determined the element compositions of the machined surfaces under different gas ratios using X-ray photoelectron spectroscopy to study the influence of the gas ratio in more detail. We achieved a surface roughness of Ra 0.6 nm on silicon wafers with a peak removal rate of approximately 32 mm^3/min.

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1. Introduction

The modern optics industry demands rigorous surface quality, presenting several formidable challenges for optics machining technology. In practical manufacturing systems, conventional mechanical technologies such as slicing, lapping, and polishing have played an important role.[1] Although they have sufficed for a long time, their removal rates are usually too low for many applications, especially for the hard brittle functional materials such as crystal, glass, and ceramic due to their special characteristics. In addition, these mechanical contact technologies always introduce defects on the final optical surfaces, which include plastic deformation, brittle fractures, dislocations, and microcracks. These defects in crystalline or amorphous substrates lower the damage threshold for high fluence use and increase the surface chemical sensitivity to corrosion. Therefore, the conventional contact machining technologies are not suitable for producing ideal physical properties in functional materials when the requirement for a perfect crystal structure exists.[2]

Considerable effort has gone toward solving these problems through the development of innovative methods that introduce completely new machining mechanisms and new devices. Among these, plasma-assisted surface processing technology has long been applied in a wide range of applications due to its unique advantages such as low cost, no waste, and excellent surface quality, which is difficult to obtain with conventional machining technologies. Many typical technologies are already based on plasma processes, including reactive ion etching, plasma-assisted chemical etching, and ion beam milling,[3,4] These earlier technologies all require vacuum systems that are difficult to support and limit the range of applications. Atmospheric pressure plasma machining has attracted worldwide attention and has become the dominant technology in the field since the 1990s because it does not require a vacuum system.[5]

Three institutes have conducted research into the development of atmospheric pressure plasma machining technology. Lawrence Livermore National Laboratory in the United States has developed reactive atom plasma technology, which uses an inductively coupled plasma (ICP) torch as the source.[6] Osaka University in Japan has developed the plasma chemical vaporization machining (PCVM) method, which uses various types of rotary electrodes to generate reactive plasma.[7-9] The Harbin Institute of Technology in China has developed the atmospheric pressure plasma polishing (APPP) method,[10] which removes atom-scale material through chemical reactions excited by plasma. APPP relies on a capacitance-coupled atmospheric pressure radio frequency (RF) plasma torch as the source.[11] This type of generator can reduce the difficulties in the machining caused by the high temperature of ICP and is more stable and repeatable than PCVM.

The APPP method is a complicated process affected by many factors. A preliminary process analysis showed that three of these key factors for stationary operations are the RF power, the working distance, and the gas ratio. Note that stationary operation means that both the workpiece and the plasma torch are fixed in the machining process with no motion relative to each other. The preliminary impacts were studied for further process optimization and system improvement. Atomic emission spectroscopy analysis revealed that the removal rate was proportional to the RF power within a certain range. We studied the spatial gas diffusion under different working distances using a theoretical simulation and then confirmed the results experimentally. The gas ratio has a significant influence on the element composition of the machined surface. Based on the analysis of results, initial optimal parameters were selected to achieve a 0.6-nm surface roughness average and a 32 mm^3/min removal rate.

2. Simulation and Analysis

APPP is a complicated method that is affected by many factors due to its chemical nature and the characteristics of the process. The amount of surface removed in a given time depends on the number of reactive radicals generated, i.e., the density of the reactive atoms. The key factor that determines this density is the RF power. Generally speaking, as the RF power increases, the density also increases until the reaction gas is sufficiently excited.

The gas path will confine the diffusion of the reactive atoms. We first simulated the process using commercial finite element analysis software (Fluent 6.1; Fluent Inc., Lebanon, NH, USA) with several simplifications and assumptions. The state inside the plasma torch is irrelevant to this process; what is more important is the condition in which the gas and reactive atoms flow from the torch and diffuse outward. Because of the rotational symmetry of the gas path, the two-dimensional cross section in Fig. 1 can be used for the purposes of illustration, and the results can be extended to three-dimensional space.

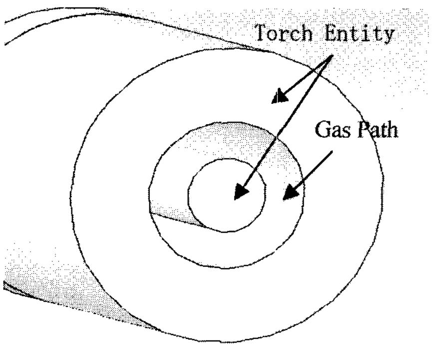


Fig. 1 Schematic diagram showing the rotational symmetrical structure of the torch outlet

If the plasma torch is placed close to the workpiece surface at a distance of less than 1 mm, the gas tends to diffuse outside, and few reactive radicals reach the central area. This is especially true at lower gas fluxes and speeds as shown in Fig. 2. Therefore, no obvious removal profile should occur in the center under such parameters; instead, the regular removal shape should be a spatial annular groove.

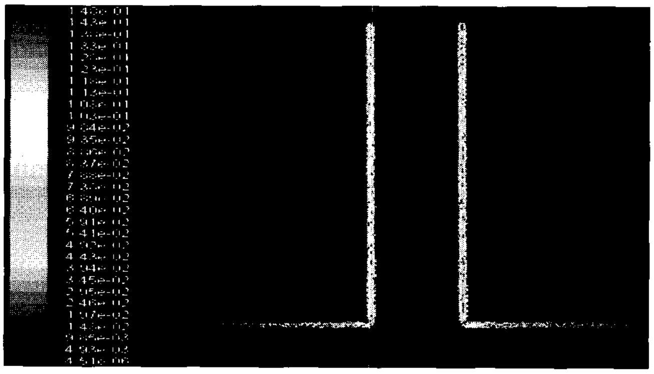


Fig. 2 Diffusion of the gas flow under a small working distance simulated by the finite element analysis method

If the working distance and gas flux increase, more gas containing more reactive radicals should diffuse into the central area due to local amplification, as shown in Fig. 3. The central area A is a turbulence region because both the gas paths D and E supply gas to this area in opposite directions. Simply because of this dual supply, the density of the radical atoms is maintained at approximately double amount from two paths individually, while the outside areas B and C are only supplied by one path. Thus, the removal rate in the center should be the highest, and decrease gradually toward the outside. This means that the practical removal shape should be a single large pit with the depth decreasing away from the center.

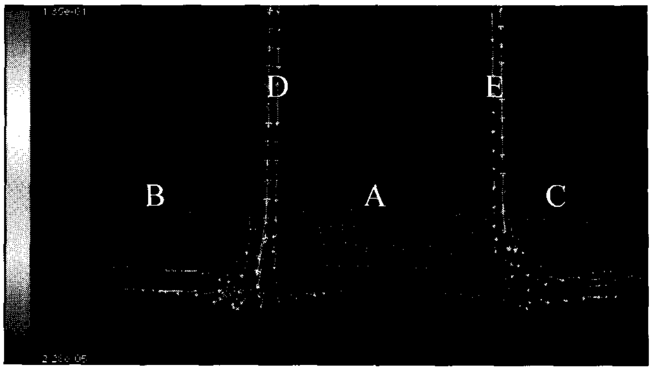


Fig. 3 Local amplification of the gas diffusion under a larger working distance simulated by the finite element analysis method

The third key process parameter is the gas ratio, the amount of reaction gas relative to the total amount. This determines the potential capability of the gas to generate reactive atoms. According to the plasma excitation mechanism, an optimal gas ratio should exist, outside of which the densities of the reactive atoms are both less than their maximums. Generally speaking, the gas ratio should be fixed before the operation and kept constant during the machining process. The composition of the working gas will certainly influence the atom composition in the plasma and the element composition on the machined surface.

No other key factors, for example, the traveling speed, have major impacts on the machining process since all the analyses here are for stationary operations.

3. Experiments

All experiments were performed under normal atmospheric pressure at room temperature.

Spectrograms at different moments can be displayed on the screen and collected immediately using a commercial micro fiber-spectrometer (AvaSpec-2048; Avantes Inc., Eerbeek, The Netherlands). A subsequent analysis using atomic emission spectroscopy reveals the categories and relative densities of major atoms in the plasma zone.[12,13] The helium plasma spectrograms for 200, 300, 400, 500, and 600 W were collected to study the general impact of a variation in RF power. We found reactive plasma spectrograms also useful for demonstrating the effective generation of reactive radical atoms. The densities of reactive atoms for different RF powers from 300 to 600 W in 50 W intervals were graphed to illustrate the dependency.

Then we conducted practical operations under different machining distances based on the previous theoretical simulations to confirm the analysis results. For this experiment, we set the RF power to 600 W and the gas ratio to 0.85%. We used commercial single crystal silicon (Si) wafers as the sample, and measured the removal profiles with a commercial form talysurf (PGI 1240; Taylor Hobson Ltd., Leichester, UK).

Finally, we recorded the spectroscopic characteristics for several typical gas ratios less than 3% to study the influence of the CF_4 percentage. We selected two representative gas ratios (0.2% and 0.85%) for which we determined the element composition on the machined surfaces using X-ray photoelectron spectroscopy (XPS; PHI 5700 ESCA system; Physical Electronics, Chanhassen, MN, USA).

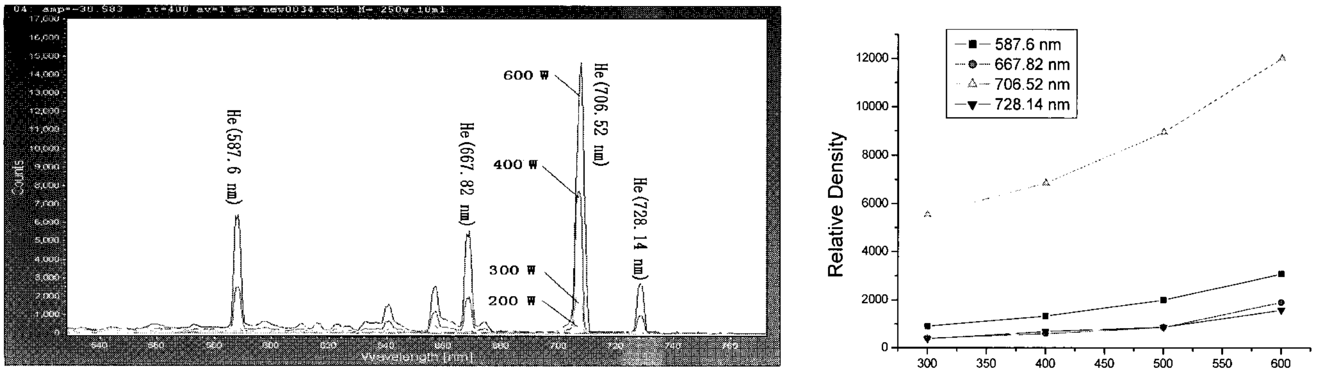


Fig. 4 Helium plasma spectrogram and the relationship of the densities to RF power

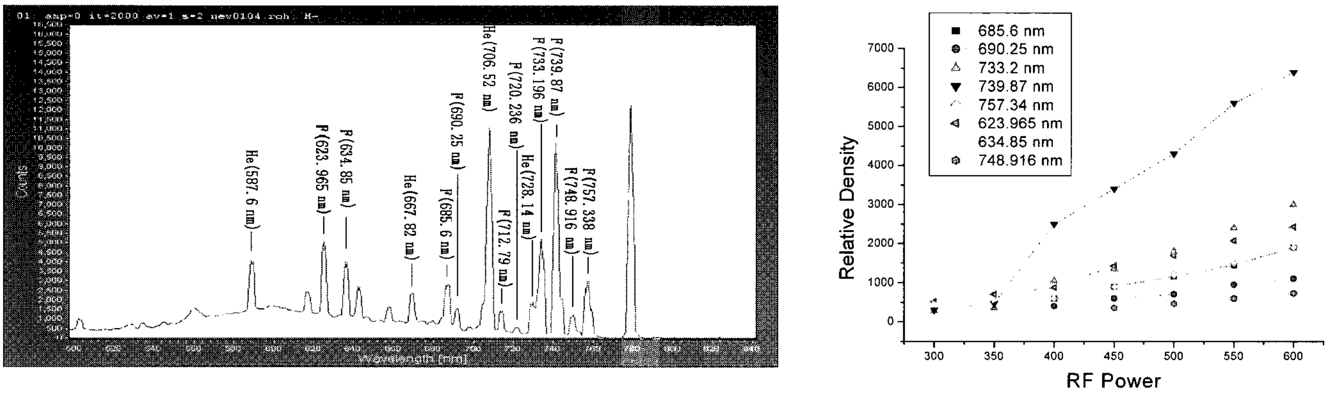


Fig. 5 Reactive plasma spectrogram and the relationship of the densities to RF power

4. Results and Discussion

4.1 RF Power

For RF power up to 200 W, a visible plasma flame appeared near the outlet of the torch. The discharge was stable and the phenomenon was quite evident. As we increased the RF power, the flame became brighter while the density of the plasma increased, as shown in Fig. 4. Then a trace of CF_4 gas was put into the plasma torch, and this made the atom composition of the plasma zone change remarkably. Reactive radical fluorine atoms appeared, as shown in Fig. 5. This figure shows ten obvious new spectral lines in the spectrogram, which indicate fluorine atoms at different excited states, including two most intelligent lines: 685.6 nm and 690.25 nm.[14] The densities of the radical fluorine atoms also increased as the RF power increased, but to different degrees as Fig. 5 shows. However, until the reaction gas was sufficiently excited, the density did not increase, even when more RF power was applied, because no more gas was present to be excited further. Thus in general, an increase in RF power results in an increased removal rate, within a certain range.

4.2 Working Distance

The images produced by the form talysurf show the two-dimensional cross-sectional view of the actual removal profiles after machining. Figure 6 presents the profile for a relatively small working distance. The sectional contour appears as two pits formed on the surface. Given the rotational symmetrical characteristics of the removal shape, it agrees well with our predictions of a spatial annular groove. Figure 7 shows the result for a larger working distance. This contour indicates that the material in the center was removed fastest, which is what the simulation model predicted. In both cases, the maximum removal depths can be measured from the images, and so the removal rates in depth or volume can be calculated. If a traveling speed were added to the process and the system produced a reciprocating motion between the torch and the workpiece, one removal profile would overlap the next, and the condition would be much more complex. In our investigation, we simply focused on how the gas diffusion influenced the removal profile. Figures 6 and 7 show that some fluctuation still existed in the removal profile. This means that the polishing process is not stable enough for large area machining. We initially concluded that the instability was mainly due to the weak fluctuation of the gas flow, and we proposed a modification of the torch structure to resolve this issue.

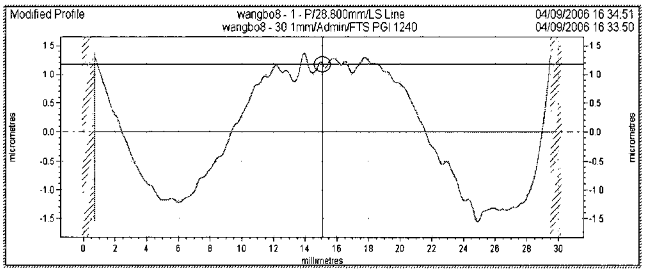


Fig. 6 Practical removal profile (cross-sectional view) for a small working distance

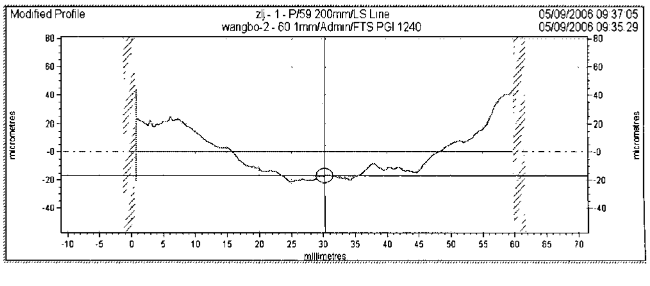


Fig. 7 Practical removal profile (cross-sectional view) for a large working distance

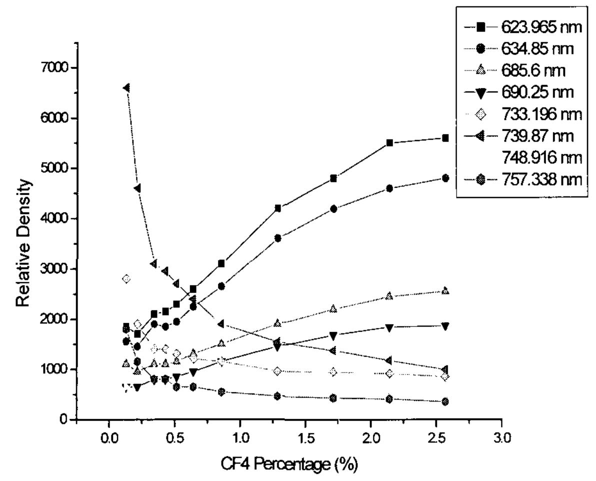
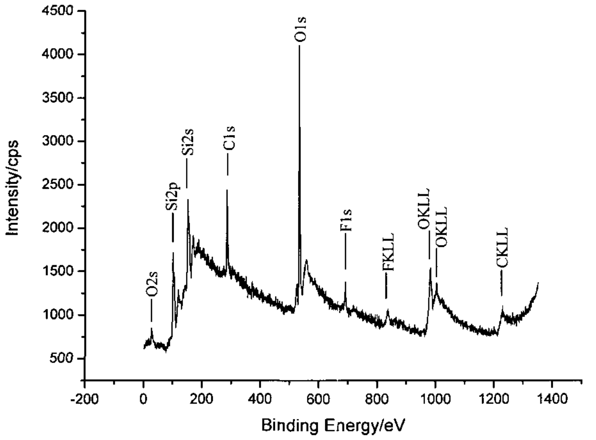
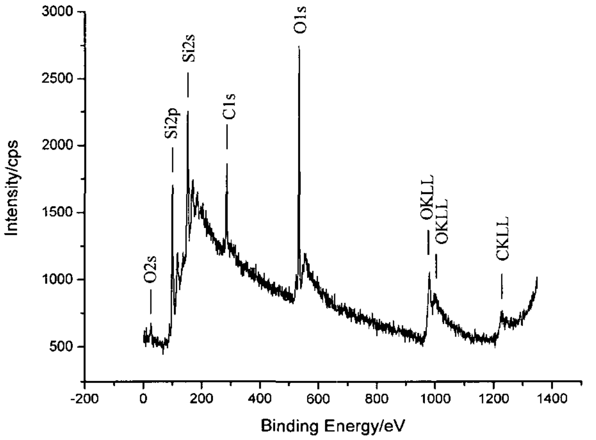


Fig. 8 Densities of different radical F atoms as functions of CF_4 percentage



(a) Composition of the surface machined under a 0.85 gas ratio



(b) Composition of the surface machined under a 0.20 gas ratio

Fig. 9 Element compositions of the surfaces machined under different gas ratios, determined by XPS

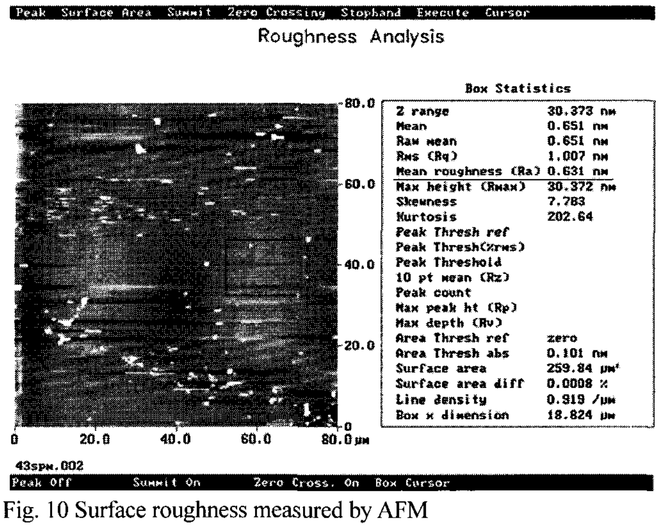
4.3 Gas Ratio

The gas ratio plays a major role in the machining process although the reaction gas involved is usually only a trace amount. Figure 5 shows that various kinds of radical fluorine atoms are excited in the plasma. The results of atomic emission spectroscopy analysis in Fig. 8 show the densities of different radical atoms as functions of the gas ratio. This figure clearly shows that the densities of some atoms decrease when the CF_4 percentage rises and some obviously increase, but also that some remain almost constant, especially beyond 0.85%. The region can be divided into two sections below and above the 0.85% mark. We conducted experiments in both sections, and the results indicate insignificant differences in the removal rate and surface roughness. However, the element compositions in the machining regions under different ratios exhibit very obvious differences. Figure 9 shows the XPS analysis results for two representative gas ratios of 0.85% and 0.20%. Si, F, O, and C atoms clearly occur on the machined surface. Some of the O and C are from the air, deposited on the surface when the surface contacted the outside environment. The rest are from the recipe gases involved in the chemical reaction. The O and C are unwanted by-products of the process that should be eliminated. The Si and F are the main elements involved in the reaction and combine in different ways.

In theory, some F atoms will bond with the Si atoms on the surface by chemical adsorption.[15-17] So, since no F was found on the surface for the 0.20% ratio, we initially concluded that the chemical reaction did not tend to occur because few reactive atoms were excited under such a low gas ratio. For the 0.85% ratio, the observed F constituted evidence for the occurrence of the anticipated main reaction. The unnecessary elements and contamination can be removed by chemical cleaning.

4.4 Initial Process Optimization

Based on the analysis above, the initial process parameters were set as follows: RF power = 600 W, gas ratio = 0.85%, and working distance = 2 mm. After 10 min of machining, the maximum removal depth was about 40 μm as shown in Fig. 7. From the symmetrical three-dimensional shape, we were able to calculate the approximate removal rate as being 32 mm^3/min. The surface roughness of the machined region was also measured by a commercial atomic force microscope (AFM; Dimension 3100; Digital Instruments Inc., Newport Beach, CA, USA).[18] The result indicated that the roughness average in the local area was about 0.6 nm as shown in Fig. 10, more than 1 nm higher after machining. The surface quality was still not sufficiently uniform for a large area, which indicates a need for further improvement in the process.



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Box Statistics
Z range                  30.373 nm
Mean                     0.651 nm
Raw mean                 0.651 nm
Rms (Rq)                 1.007 nm
Mean roughness (Ra)      0.631 nm
Max height (Rmax)        30.372 nm
Skewness                 7.783
Kurtosis                 202.64
Peak Thresh ref
Peak Thresh(%rms)
Peak Threshold
10 pt mean (Rz)
Peak count
Max peak ht (Rp)
Max depth (Rv)
Area Thresh ref          zero
Area Thresh abs          0.101 nm
Surface area             259.84 μm²
Surface area diff        0.0008 %
Line density             0.919 /μm
Box x dimension          18.824 μm
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Fig. 10 Surface roughness measured by AFM

5. Conclusions

Our initial process analysis confirmed that three key factors had impacts on stationary operations: the RF power, the working distance, and the gas ratio. We established preliminary impact relationships, and these results were fundamental for further process optimization and system modification. Through technological improvements, we achieved an average roughness on Si wafers of 0.6 nm and a removal rate of about 30 mm^3/min. Thus, the APPP method has the potential to produce optical components with high quality ultrasmooth surfaces.

ACKNOWLEDGEMENT

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REFERENCES

1. Li, B. G., Xiong, C. Y. and Li, C. G., "Machining Technology of Super Smooth Surface," Manufacturing Technology & Machine Tools, No. 6, pp. 60-66, 2006.
2. Alagumurthi, N., Palaniradja, K. and Soundararajan, V., "Cylindrical Grinding – A Review on Surface Integrity," International Journal of Precision Engineering and Manufacturing, Vol. 8, No. 3, pp. 24-44, 2007.
3. Zhang, H., Wang, W. and Pang, Y. Y., "Ultra-precision Machining Technology of Optical Surfaces," Optical Instruments, Vol. 25, No. 3, pp. 47-51, 2003.
4. Zhao, G. X., Li, Y. and Zheng, Y. N., "Discussion on the Principle of Ion Beam Removal Machining," EDM and Mould, Vol. 1, pp. 26-28, 2001.
5. Detrick, M. S., Washington, G. N. and Subramaniam, V. V., "Control of Polishing of Diamond Films Using Microactuation and an Atmospheric Pressure Plasma," IEEE/ASME Transactions on Mechatronics, Vol. 8, No. 1, p. 45, 2003.
6. Carr, J. W., "Atmospheric Pressure Plasma Processing for Damage-free Optics and Surfaces," Engineering Research Development and Technology, Vol. 3, pp. 3-1-3-9, 1999.
7. Mori, Y., Yamamura, K. and Endo, K., "Creations of Perfect Surfaces," Journal of Crystal Growth, Vol. 275, pp. 39-50, 2005.
8. Mori, Y., Yamauchi, K., Yamamura, K. and Sano, Y., "Development of Plasma Chemical Vaporization Machining," Review of Scientific Instruments, Vol. 71, No. 12, pp. 4627-4632, 2000.
9. Yamamura, K., Kato, K., Sano, Y., Shibahara, M., Endo, K. and Mori, Y., "High-Spatial-Resolution Machining Utilizing Atmospheric Pressure Plasma: Machining Characteristics of Silicon," Japanese Journal of Applied Physics, Vol. 45, No. 10, pp. 8281-8285, 2006.
10. Wang, B., Zhao, Q. L., Wang, L. P. and Dong, S., "Application of Atmospheric Pressure Plasma in the Ultrasmooth Polishing of SiC Optics," Materials Science Forum, Vol. 532-533, pp. 504-507, 2006.
11. Zhang, J. F., Wang, B. and Dong, S., "The Design of an Atmospheric Pressure Plasma Torch Used for Polishing Ultra-Smooth Surfaces," Key Engineering Materials, Vol. 364-366, pp. 340-345, 2008.
12. Dean, J. A., "Analytical Chemistry Handbook," Science Press, p. 7.1, 2003.
13. Ke, Y. K. and Dong, H. R, "Analytical Chemistry Manual (III): Spectral Analysis," Journal of Crystal Growth, Vol. 275, pp. 39-50, 2005.
14. Information on http://physics.nist.gov.
15. Jeong, H. C., Choi, G. M. and Kim, D. J., "The Precision of Lead Frame Etching Characteristics Using Monte-Carlo Simulations," International Journal of Precision Engineering and Manufacturing, Vol. 8, No. 1, pp. 73-78, 2007.
16. Carter, L. E. and Carter, E. A., "F2 Reaction Dynamics with Defective Si (100): Defect-insensitive Surface Chemistry," Surface Science, Vol. 323, pp. 39-50, 1995.
17. Shibahara, M. and Katsuki, M., "Molecular Dynamics Study of the Effects of Adsorbed Molecules on Reaction Probability and Energy Transfer," Combustion and Flame, Vol. 144, pp. 17-23, 2006.
18. Asai, T., Motoki, T., Gao, W., Ju, B. F. and Kiyono, S., "An AFM-based Edge Profile Measuring Instrument for Diamond Cutting Tools," International Journal of Precision Engineering and Manufacturing, Vol. 8, No. 2, pp. 54-58, 2007.