INDUCTIVELY COUPLED PLASMA ETCHING OF BULK MOLYBDENUM

*J. Hu, Y. Zhang, S. Chen, S. He, N. Li and J. Chen**
National Key Laboratory of Science and Technology on Micro/Nano Fabrication,
Institute of Microelectronics, Peking University, Beijing, China

ABSTRACT

Molybdenum is a promising material for bulk MEMS applications for its high melting point, radiation resistance, high strength and conductivity. This paper reports on the development of wafer level bulk molybdenum ICP etching. Various etching chemistry are explored. The influence of process parameters (coil power/ICP power, platen power/RIE power and gas flow rate) on the etching rate, selectivity to SU-8 mask and etching profile anisotropy are investigated. With an optimized recipe, an etching rate of 2.63μm/min has been achieved with a profile of 70˚ and samples are employed as electrodes in micro Electrical Discharge Machining (μEDM).

INTRODUCTION

Single crystal silicon has been widely used for bulk MEMS, however, the intrinsic properties of silicon may somehow limit the device performance. Recent developments of fabrication technologies have allowed for applications of alternative bulk structure materials, such as metals and polymers. Polymers, including fibers, plastics and elastomers, have been used in sensors, actuators and biochips with the advantages of low cost, elasticity and biocompatibility [1]. Bulk titanium has demonstrated its potential in biomedical high-g devices for its excellent biocompatibility and fracture toughness [2].

Molybdenum is a very promising material for bulk MEMS applications. It has a high melting point of 2610°C and retains its strength at high temperatures, which is superior in many high-temperature applications, such as micro electrodes, emitter tips, heating elements and rocket engine nozzles. Molybdenum film has been employed as gate and schottky diode for its excellent electricity characteristics. Bulk molybdenum is also a good candidate for manufacturing micro-relays and micro-probes for its conductive properties and relative chemical inertia. The electronic structure of molybdenum makes it the main source for X-ray targets and also for shielding from high-energy radiations, which is necessary for anti-radiation devices used in aerospace and other radiant environments [3].

There have been reports on dry etching of deposited thin film molybdenum with fluorine/chlorine/bromine based etchants by reactive ion etching [4]. However, the etching rate and aspect ratio are too low to satisfy the requirements of bulk micromachining. Inductively coupled plasma (ICP) etching has proved its potential in achieving high etching rate and anisotropy by high density plasma and ion bombardment which can be controlled independently [5], its applications have extended from silicon to polymer, glass, GaAs, GaN and titanium, however the ICP etching of molybdenum has not yet been presented.

This paper reports on the development of bulk molybdenum ICP etching process. Various gas combinations are evaluated for etching ability. Effects of O_2 flow rate, RIE power and Cl_2/N_2 addition on etching rate, selectivity and anisotropy are studied. With the optimized process, an etching rate of 2.63μm/min has been achieved with a profile of 70°. Samples are also employed as electrodes with low wear ratio in micro Electrical Discharge Machining (μEDM).

EXPERIMENTAL

Substrate Preparation

The 4 inch one-side polished 500μm thick pure molybdenum wafers are used for this set of experiments. Figure 1 shows a bulk molybdenum wafer, which is fully compatible with most of the semiconductor facilities. The impurities are listed in Table 1.

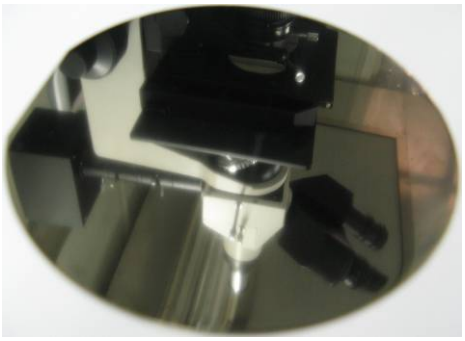

Figure 1: 4inch one side polished bulk molybdenum wafer.

Table 1: Impurities of bulk molybdenum wafer.

Ingredient	Al	Ca	Fe	Mg	O	Ni	Si	C	N
$1*10^{-4}$ (wt.)	0.2	0.2	1	0.2	0.8	0.5	1	1	0.3

Fabrication Process

Negative photoresist KMPR SU-8 3050 is used as soft mask for its relative high chemical resistance. SU-8 film with thickness from 10 to 100μm and improved adhesion to substrate can be achieved. Figure 2 shows the etching process, SU-8 film of approximate 60μm is patterned as etching mask followed by ICP deep etching. After that, the SU-8 mask is selectively stripped by remover with ultrasonic agitation, then the etching profiles are measured for detailed analysis.

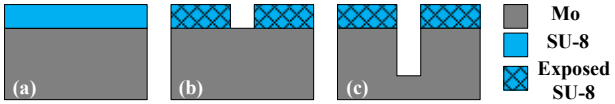

Figure 2: Process flow.
(a)Coating of SU-8; (b)Lithography; (c)ICP etching.

The ICP etching process is carried out in Trion Technology Minilock III ICP etcher. During the process, ICP power that generates high density plasma is set 800W for a high radical and ion density. To achieve a better anisotropy, a low chamber pressure of 23mTorr is applied,

which reduces ion scattering and enhances vertical bombardment. Moreover, low substrate temperature of -20°C is used to make the etching products less volatile, which can deposit on etched surface and serve as sidewall passivation. Etching gas chemistry determines the etching rate directly and significantly. CF_4, Cl_2 and SF_6 are attempted as etching precursor respectively, and then various $O_2/N_2/Cl_2$ gas flows are added to promote the etching and optimize the etching profile. RIE power is swung between 300W and 150W during the process.

Etching depth is measured by stylus profilometry at five random locations across the wafer and averaged for etching rate calculation. Samples are cut by laser and observed in high resolution scanning electron microscope (SEM) for profile analysis. Average surface roughness is measured with white light interferometry. Etching rate and selectivity data are plotted revealing the first-order trend of varied process parameter, and then the optimized bulk molybdenum etching recipes are determined.

RESULTS AND DISCUSSION

Etching Gas Chemistry

Bulk molybdenum etching rate with different gas chemistry are listed in Table 2 with the etching related ions and radicals. ICP etching process is a physically assisted chemical etching process, during which substrate surface is subjected to an incident flux of electrons, neutrals, ions and radicals. Molybdenum etching relies more heavily on radical induced chemical process, while SU-8 etching depends more upon physical etching. Compared with Cl_2, fluorine based chemistry has higher radical density and stronger ion bombardment, while SF_6 shows good etching capability with an etching rate much higher than that of CF_4.

Table 2: Gas chemistry (ICP power 800W, RIE power 300W, chamber pressure 23mTorr and substrate temperature -20°C).

Chemistry	CF_4	Cl_2	SF_6	CF_4/O_2	Cl_2/O_2	SF_6/O_2
Flow rate (sccm)	60	43	53	60/10	43/10	53/10
Mo rate (μm/min)	0.112	0.224	1.180	0.154	0.266	1.340
SU-8 rate (μm/min)	0.837	0.187	1.690	0.975	0.258	2.140
Ions	CF_x^+ x:1-4	Cl_x^+ x:1-2	SF_x^+ x:1-6	CF_x^+ x:1-4 O_y^+ y:1-2	Cl_x^+ x:1-2 O_y^+ y:1-2	SF_x^+ x:1-6 O_y^+ y:1-2
Radical	F	Cl	F	F	Cl	F

As listed in Table 2, 10sccm O_2 addition results in a higher etching rate, however, the combination of O_2/Cl_2 are still far lower than that of pure SF_6. O_2 enhances the etching rate by suppressing reaction of SF_x^+-F and inducing more F radicals. The dissociation or ionization of O_2 provides additional ions that help promote ion bombardment. A less volatile product $MoOF_4$ with boiling point of 186°C is also generated with O_2 addition, which promotes sidewall passivation, and an improved anisotropy is consequently expected.

The etching profiles are shown in Figure 3. Volatile MoF_6 with a boiling point of 37°C tends to deposit at the low substrate temperature of -20°C. In addition to O_2, Cl radical induces a nonvolatile $MoCl_5$ with a high boiling point of 268°C, which also helps achieve a vertical profile. Figure 3a shows the sidewall profile, Figure 3b shows the detail of the etched bottom.

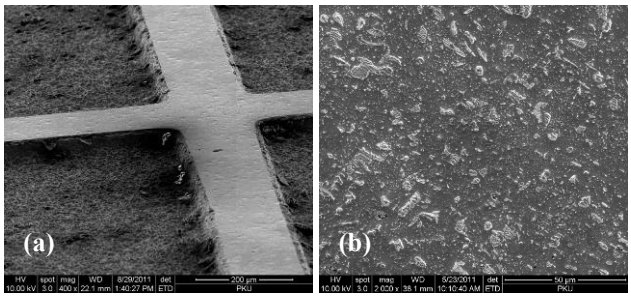

Figure 3: SEM of bulk molybdenum etching profile. (a)Sidewall profile; (b)Bottom surfaces.

Etching Rate

SF_6 and O_2 combination is proved to be a good candidate for bulk molybdenum ICP etching and is further optimized. Figure 4 shows the relationship between molybdenum etching rate and O_2 flow rate. A maximum flow rate 53sccm of SF_6 is constantly employed in each experiment run. Molybdenum etching rate is enhanced significantly by increasing O_2 flow rate. The etching rate increases from roughly 1.18 to 2.26μm/min as O_2 flow rate is increased from 0 to 80sccm at the RIE power of 300W, the same trend is observed for the RIE power of 150W. Higher O_2 flow results in a high F radical density and enhanced ion bombardment.

Increased RIE power from 150W to 300W also contributes to the etching reaction, because RIE power dominates the incident ion energy on the substrate surface, more energetic ion bombardment assists in removing residuals to promote chemical reaction on bare molybdenum surface. However, the etching rate increasing is not significant.

Cl_2 addition slightly increases the etching rate to 2.63μm/min, while N_2 addition tends to decrease the etching rate. Cl_2 promotes the etching by introducing reactive Cl radicals, while the inert N_2 addition dilutes radicals on the etching surface.

Etching Selectivity of Molybdenum to SU-8

The influence of O_2 flow rate on the etching rate of SU-8, which indicates mask selectivity, is shown in Figure 5. Both increasing O_2 flow rate and RIE power enhances the SU-8 etching, which results in a low selectivity. However, the SU-8 etching is mainly determined by ion bombardment that is dominated by RIE power. Selectivity is decreased from roughly 0.7 to 0.47 as O_2 is increased from 0 to 80sccm at the RIE power of 300W and from roughly 1.5 to 1.41 as O_2 is increased from 80 to 98sccm at the RIE power of 150W. A 10sccm Cl_2 addition at RIE power 150W further decreases selectivity to 0.88, while 10sccm N_2 addition at RIE power 300W drops the selectivity to 0.44.

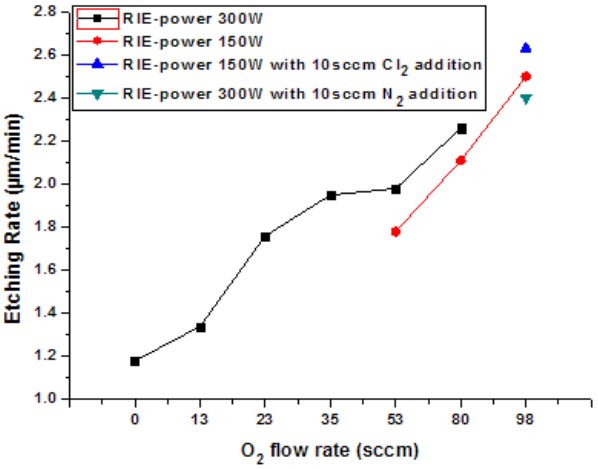

Figure 4: Etching rate vs. O_2 flow rate. (ICP power 800W, SF_6 flow rate 53sccm, chamber pressure 23mTorr, substrate temperature -20°C)

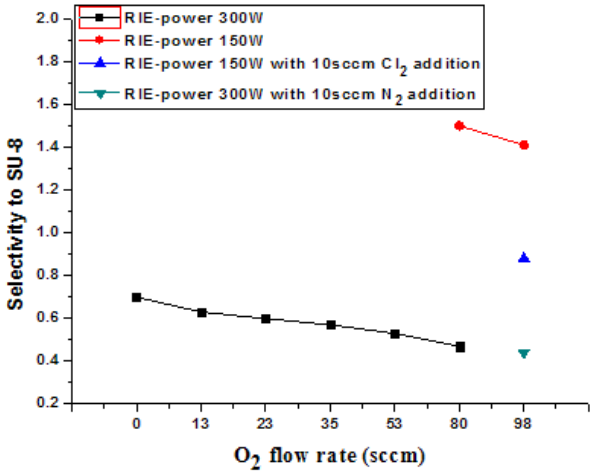

Figure 5: Selectivity to SU-8 vs. O_2 flow rate. (ICP power 800W, SF_6 flow rate 53sccm, chamber pressure 23mTorr, substrate temperature -20°C)

Etching profile anisotropy

Figure 6 shows the etching profile anisotropy with different process parameters. As shown in Figure 6a, etching with pure SF_6 tends to be isotropic with severe undercut on the top surface. As shown in Figure 6b, O_2 addition promotes anisotropy a lot by introducing less volatile products as sidewall protection and the undercut is eliminated. Higher O_2 flow rate generates a further improved anisotropy, as proved in Figure 6c. RIE power controls the ion flux directionality, strong ion flux scattering on the sidewall at low RIE power ruins the anisotropy, as shown in Figure 6d the RIE power drops from 300W to 150W. Figure 6e reveals that a 10sccm Cl_2 addition can achieve a more vertical profile by introducing more nonvolatile products for sidewall protection. A promotion of anisotropy can also be observed in Figure 6f, where 10sccm N_2 additional is added at the RIE power of 300W. Increasing O_2 flow rate and RIE power helps generate a vertical profile and N_2/Cl_2 can also be added to enhance the etching anisotropy.

Optimized ICP Etching Process

To summarize, SF_6 gas chemistry and O_2 addition determine the etching rate, while RIE power influences the selectivity. Cl_2 addition can further improve the etching performance. Using a higher O_2 flow rate with Cl_2 addition at a relatively lower RIE power, an etching depth of 35μm has been achieved, as shown in Figure 7. The optimized etching parameters of various gaseous combinations are listed in Table 3.

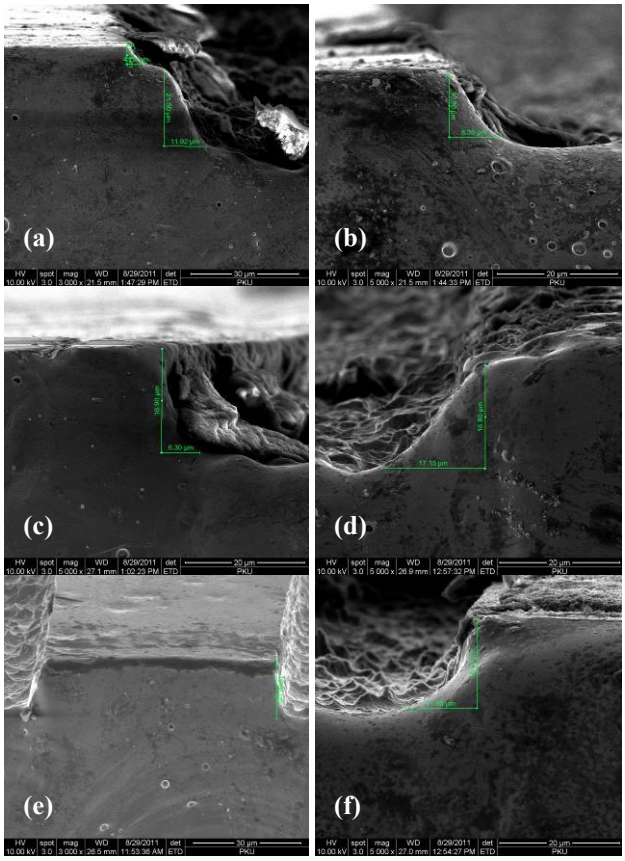

Figure 6: SEM of bulk molybdenum etching profile. (a) RIE power 300W, O_2 0sccm; (b)RIE power 300W, O_2 35sccm; (c)RIE power 300W, O_2 80sccm; (d)RIE power 150W, O_2 98sccm; (e)RIE power 150W, O_2 98sccm, Cl_2 10sccm; (f)RIE power 300W, O_2 98sccm, N_2 10sccm. (ICP power 800W, SF_6 flow rate 53sccm, chamber pressure 23mTorr, substrate temperature -20°C)

APPLICATIONS IN MICROEDM

Micro-EDM is a competitive microfabrication technology for making variable shaped three-dimensional metal structures with fine surface finishes [6]. The batch fabricated high aspect ratio electrodes are mainly based on LIGA process at present, the materials are limited to nickel or copper. Molybdenum for its high melting point and rigidity is a good candidate electrode material with low wear ratio and high duration. With the ICP etching process, batch fabricated high aspect ratio molybdenum electrodes with arbitrary patterns and steps could be manufactured rapidly and precisely. A preliminary attempt has been carried out on DX45NC electro sparking machine using a standard 1μs/3μs pulse width/interval. Figure 8a shows the SEM of a bulk molybdenum sample utilized as tool electrode for μEDM. The workpiece is 301 stainless steel, as shown in Figure 8b. A good uniformity in depth has been achieved with a low electrode wear ratio of 6%, which is suitable for long-time precise μEDM machining.

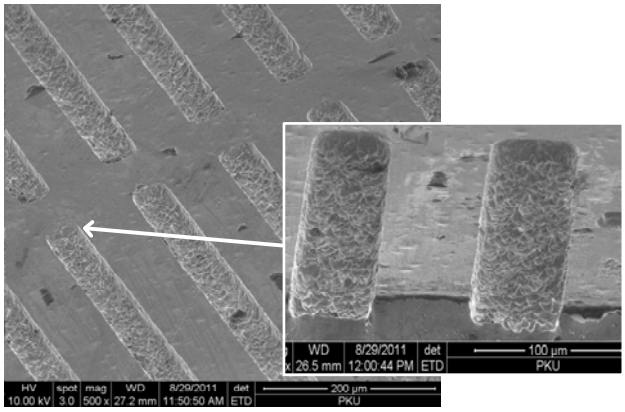

Figure 7: Microstructures fabricated on bulk molybdenum. (ICP power 800W, RIE power 150W, SF_6 53sccm, O_2 98sccm, Cl_2 10sccm, chamber pressure 23mTorr, substrate temperature -20°C, etching depth 35μm, profile angle 70°.)

Table 3: Optimized etching parameters (ICP power 800W, chamber pressure 23mTorr, substrate temperature -20°C).

Gas composition		SF_6	SF_6/O_2	$SF_6/O_2/N_2$	$SF_6/O_2/Cl_2$
Characte ristics	Rate (μm/min)	1.18	2.50	2.40	**2.63**
	Selectivity	0.70	**1.41**	0.44	0.88
	Average Area Roughness (Ra/μm)	2.36	**2.03**	2.67	3.21
	Profile Angle(°)	39	45	52	**70**
Differed Process Parameter	RIE power/W	300	150	300	150
	Flow rate/sccm	53	53/ 98	53/98/ 10	53/98/ 10

CONCLUSION

In this paper, bulk molybdenum ICP etching process is reported. Gas chemistry, O_2 flow rate, RIE power and Cl_2/N_2 addition are varied to determine their first-order effects on etching rate, selectivity and profile anisotropy. With a preliminary optimized bulk molybdenum ICP etching process, a high etching rate of 2.63μm/min has been achieved with a profile of 70°. Samples are employed as electrodes in μEDM with a very low wear ratio. Molybdenum DRIE will open up a new horizon to bulk micromachined MEMS.

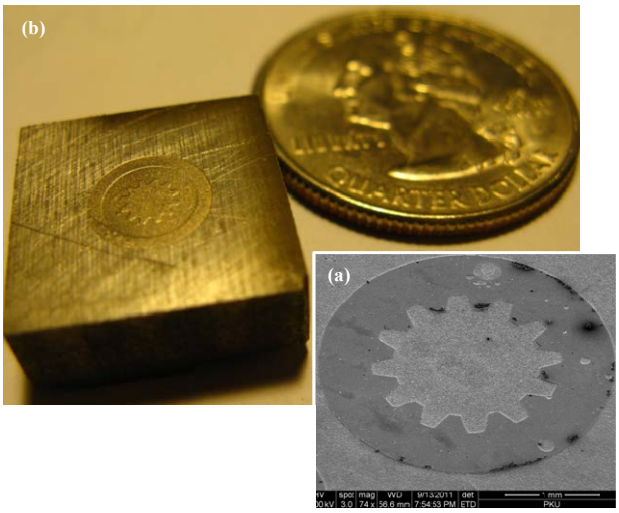

Figure 8: Bulk molybdenum electrode and workpiece by μEDM.

ACKNOWLEDGEMENTS

The authors would thank Mr. Xing of the Institute of Microelectronics of Chinese Academy of Sciences for SU-8 lithography, Mr. Yang of Tianjin University for white light interferometry measurement and Mr. Ning of Department of Electronics of Peking University for SEM photography.

REFERENCES

[1] B. Ma, J. Ren, J. Deng, W. Yuan, "Flexible Thermal Sensor Array on PI Film Substrate for Underwater Applications ", in *MEMS'10 Conference*, pp. 679-682.

[2] E. R. Parker, B. J. Thibeault, M. F. Aimi, M. P. Rao, N. C. MacDonald, "Inductively Coupled Plasma Etching of Bulk Titanium for MEMS Applications", *J ELECTROCHEM SOC*, vol. 152, pp. 675-683, 2005.

[3] R. B. Brown, M. L. Ger, T. Nguyen, "Characterization of Molybdenum Thin Films for Micromechanical Structures", in *MEMS'90 Conference*, pp. 77-81.

[4] D. Ha, H. Takeuchi, Y. K. Choi, T. J. King, "Molybdenum Gate Technology for Ultrathin-Body MOSFETs and FinFETs", *IEEE TED*, vol. 51, pp. 1989-1996, 2004.

[5] M. P. Rao, M. F. Aimi, E. R. Parker, N. C. MacDonald, "Single-Mask High Aspect Ratio, 3-D Micromachining of Bulk Titanium", in *MEMS'05 Conference*, pp. 64-67.

[6] S. Mahendran, R. Devarajan, T. Nagarajan, A. Majdi, "A Review of Micro-EDM", in *IMECS'10 Conference*

CONTACT

*J. Chen, tel: +86-10-6275-2536; jchen@ime.pku.edu.cn