Cleaning of Organic Contamination from EUV Optics Surfaces Using Hydrogen-based Plasmas

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The efficiency of optics used in extreme ultraviolet (EUV) range suffers from reflectivity degradation due to oxidation and carbon contamination of mirror surfaces. Therefore, an efficient cleaning procedure should be ascertained in order to facilitate applications of EUV lithography tools. Carbon contamination removal from the mirror surface has been reported in Hydrogen plasmas, and laser-induced Hydrogen plasmas in EUV tools. Here, we performed measurements in a helicon-type RF plasma reactor with hydrogen pressures similar to the ones used in laser-induced plasmas in EUV tools. The method of optical actinometry was used to determine hydrogen atom concentration and the degree of dissociation. The results are compared to those obtained by pressure-rise measurements. Preliminary results of plasma etching of thin organic films (PMMA) were also obtained to assess the cleaning efficiency.

Introduction

Extreme UV (EUV) lithography, which uses a wavelength of 13.5 nm, seems to be a promising solution for the optical lithography processes in the future, to improve attainable resolution and meet demands of shrinking feature sizes of transistors in silicon-based integrated circuit technologies [1]. The main difference between EUV lithography systems and conventional ones (using 248/193 nm radiation) is the use of reflective optical elements, such as grazing incidence and multilayer coated mirrors, since strong absorption of EUV radiation by all materials prevents the use of refractive optical components. On the other hand, normal incidence reflectivity at EUV wavelengths is only 10^{-4} – 10^{-3} which means that, in order to enhance the reflectivity, many layers have to be added up in phase. One of the solutions is multilayer coated mirrors, comprising a stack of materials with alternating high and low refractive index [2]. Moreover, it must be possible to apply these materials in thin smooth layers with low roughness, without intermixing or mutual reaction between them. One such combination is molybdenum-silicon, providing a reflectivity of 68% at 13.5 nm [3,4]. A special, capping layer is added on top of the multilayer stack to prevent reflectivity loss due to oxidation of the top silicon layer when exposed to air. Ruthenium is used as material for the capping layer [5], due to high resistance to oxidation, limitation of oxygen diffusion into the underlying silicon layer and high EUV reflectivity. A typical structure of a multilayer mirror is shown in Fig. 1 a).

***Table 1**. EUV-induced effects on optical surfaces [2].*

	Hydrocarbons	*Silicone*	*Oxygen (water)*
Process	*Carbon-based film deposition*	*Si-oxide-based film deposition*	*Surface oxidation*
Estimation of reflectivity loss per film thickness	*1% per 1nm*	*1% per 0.7nm*	*1% per 0.3nm*
Reversibility of the process	*Reversible*	*irreversible*	*Irreversible*

While under EUV exposure, the efficiency of EUV optics can be subject to recoverable and non-recoverable reflectivity losses [2]. Some of the effects of EUV-induced reflectivity losses are summarized in Table 1. One of the important mechanisms that can potentially threaten the mirror lifetime is carbon contamination growth on the mirror surface, which is probably the result of EUV radiation-induced dissociation of hydrocarbon molecules adsorbed on the surface [7]. The layer, which will continue to grow as long as hydrocarbon molecules and EUV radiation are supplied, drastically decreases the reflectivity of the mirrors, as shown in Fig. 1 b) [6]. Nevertheless, the removal of carbon layer without any damaging of the mirror surface restores the reflectivity of the mirror.

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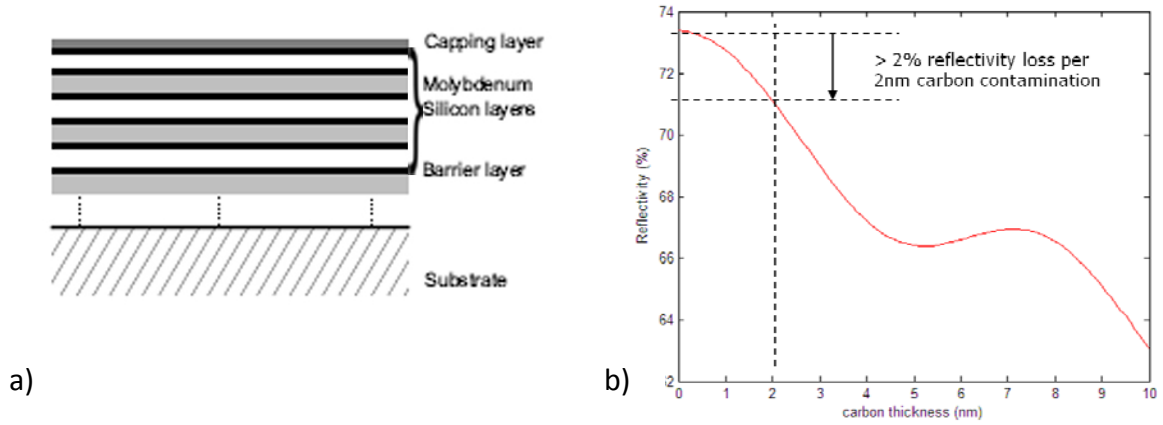

Fig.1 a) Typical structure of Mo-Si multilayer mirror with Ru capping. b) Optical simulation of EUV mirror reflectivity loss with the thickness of carbon layer deposited [6].

So far, oxygen discharges have been used for cleaning optical components involved with X-ray radiation. However, the effectiveness of oxygen cleaning is questionable for EUV optics since there is a threat of oxidation of the multilayer mirrors. Silicon-oxide is a strong EUV radiation absorber and cannot be removed from the optic surfaces, while maintaining critical optical properties [8]. Recently, several investigators have studied removal of carbon layers in hydrogen RF plasmas [1,8,9], and also as an in-situ contamination removal method using atomic hydrogen [10]. Removal of the carbon layer from the surface has been reported with a minimal change of surface properties and with H atoms playing an important role in the removal [8]. Hence, hydrogen-based plasmas appear to be a promising solution for effective removal of carbon contamination from EUV optics. We aim to explore hydrogen-based plasma conditions that will provide us with high cleaning rates and minimal increase of surface roughness. In this report, preliminary results of measurements in low pressure hydrogen plasmas are presented, aiming in determining the Hydrogen atom densities. We obtained the extent of hydrogen dissociation and processed an organic film (PMMA) in order to test etching/removal rates in the plasma.

Experimental details

Low pressure RF plasma (13.56 MHz) was created in a 95% H_2 / 5% Ar gas mixture in a helicon-type plasma reactor (Micromachining Etching Tool, MET, Adixen-Alcatel). The reactor chamber consists of two parts: the upper plasma generation (source) part comprising a quartz tube surrounded by one-turn coil-antenna, which is positioned on top of a diffusion region with a sample holder. The power was applied to the antenna while the aluminum sample holder was grounded. For the plasma characterization measurements, a blank sample holder was used. Emission from the diffusion region was guided through an optical fiber to the Spectra-Pro 500 spectrometer from Acton Research Corporation equipped with a CCD camera. To investigate etching properties, silicon wafers spin-coated with organic film were processed and measured using Woollam M2000 optical multiwavelength ellipsometer before and after etching.

Results and Discussion

In Fig. 2 a) the dependence of line peak intensities on power forwarded to plasma is shown. The maximum intensities are presented for Halpha (656.3 nm), Hbeta (486.1 nm) and Ar line (750.4 nm). The data show rise of line intensity with power.

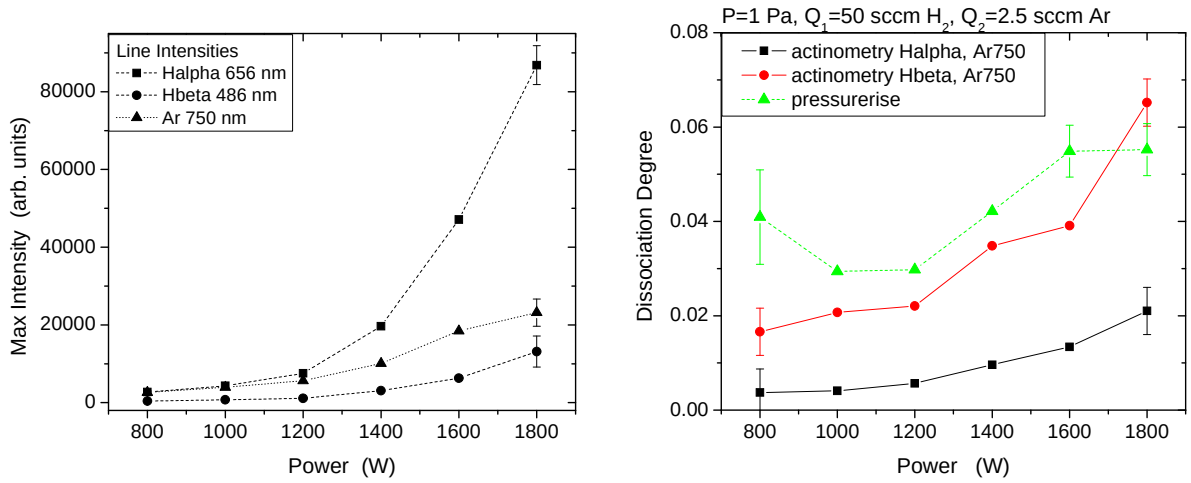

Fig. 2 *a) The dependence of peak line-intensity on power forwarded to plasma. Recordings done at p = 1 Pa and Q = 50sccm. b) Change of the dissociation degree of H_2 with power. H densities and dissociation degree were determined with actinometry measurements (shown with full lines calculated for Te = 3 eV), and pressure rise measurements (dashed line).*

Monitoring of the intensities of these lines and using optical actinometry allows the determination of H density and the dissociation degree in the plasma - an important parameter in hydrogen - containing low-temperature plasmas, when it comes to understanding the surface processes [10]. However, in order to employ this method properly, one should take into account all important kinetic processes in the plasma [11,12]. For the case of gas mixture of H_2 with Ar as actinometer gas, important processes and the data related are given in Table 2. Since the discharge pressure is below 100 Pa, the quenching can be neglected [13].

Table 2. *Processes in H_2/Ar low-pressure plasma with threshold energies and reference data.*

	Process		Eth	Ref.
1a	H atom excitation	H(n=1) + e -> H(n=3) + e	12.09	[14]
1b		H(n=1) + e -> H(n=4) + e	12.75	
2	H_2 dissociative excitation	H_2 + e -> H(n=3,4) + H(n=1) + e	16.90*	[14]
3	Ar direct excitation	Ar(3p) + e -> Ar(4p) + e	13.48	[15]
4a	Radiative de-excitation	H(n=3) -> H(n=2) + *hv (656nm)*	-	[16]
		H(n=4) -> H(n=2) + *hv (486nm)*		
4b		Ar(4p) -> Ar(4s) + *hv (750nm)*	-	[16]

*average from dissociative channels producing Hα and Hβ lines

By solving simple collision-radiative model involving reactions in Table 1, an actinometric formula consisting of a 'classical' actinometry term, describing direct electron excitation of hydrogen and argon levels, and a 'dissociative' term, describing the dissociative excitation channel in H_2, can be obtained.

In Fig. 2 b) dissociation degrees of H_2 for different powers are shown. Solid-line data is obtained from actinometry measurements, and dashed line results are from pressure-rise measurements: after ignition of the discharge, the rise in pressure can be attributed to the creation of H in the plasma, provided that the pumping speed (throttle valve position) is constant in the reactor.

Both methods predict similar increment of the dissociation extent with power. In case of actinometry data, difference between results obtained using Hα and Hβ hydrogen lines may come from the fact that the threshold energy for Hβ excitation is closer to the Ar line than Hα line threshold. As a consequence, electrons exciting monitored lines can have different energies i.e. come from different parts of electron energy distribution function. Thus, it is safer to use theHβ lines

since they are also close to the pressure-rise measurements. Both predict a small dissociation degree of H_2 and thus H densities below 10% of H_2.

To test etching–removal of organic matter in hydrogen plasma, a sample with 500 nm thick polymethylmethacrylate (PMMA) organic film was placed inside the chamber. The thickness of every sample was measured before processing and after 3 minutes of etching using multiwavelength ellipsometry. The sample holder was grounded, i.e. there was no bias applied to the samples. This means that ions reached the substrate with energy of 10 - 20eV (plasma potential). In Fig. 3, results of etching rates at different source powers forwarded to plasma are shown. An increase in etching rate with power increase is observed as a consequence of higher densities of hydrogen atoms in plasma and possibly the larger ion fluxes. Etching rates are relatively high, suggesting that cleaning could be a fast processes.

Further research will focus on hydrogen plasma characterization: obtaining the densities and fluxes of ions, which are also important for material processing. We plan to use Ion Flux and Langmuir probes. Furthermore, the method of optical actinometry will be evaluated by using measurements of hydrogen atom densities with a catalytic probe. Investigation on organic layer removal will continue using samples with a thin carbon layer. Optical damage rates will also be investigated.

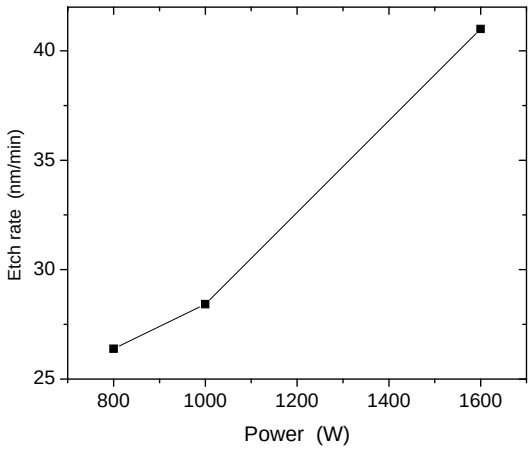

Fig. 3 *Dependence of etching rate of thin PMMA film on power forwarded to plasma. Etching conditions: p = 1 Pa of H_2 with Q = 50 sccm.*

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References

[1] S Wurm, C.W Gwyn, Microlithography, 2nd ed, CRC Press/Taylor & Francis Informa Group, FL (2007) Ch. 8
[2] Marc Hubertus Lorenz van der Velden, PhD, Technische Univ. Eindhoven, The Netherlands, 2008
[3] T. W. Barbee Jr., S. Mrowka, and M. C. Hettrick. Appl. Opt., 24, 883 (1985)
[4] B.L. Henke, E.M. Gullikson, and J.C. Davis, At. Data and Nucl. Data Tables, 54, 181 (1993)
[5] T.E. Madey, N.S. Faradzhev, B.V. Yakshinskiy, and N.V. Edwards, Appl. Surf. Sci., 253, 1691 (2006)
[6] B Mertens, *et al,* Microelectron. Eng., 73-74, 16 (2004)
[7] L.E Klebanoff, M.E Malinowski, W.M Clift, C Steinhaus, and P Grunow, J. Vac. Sci. Technol. A, 22, 425 (2004)
[8] S. Graham *et al*., J. Vac. Sci. Technol. B, **20**, 2393 (2002)
[9] I. Nishiyama *et al*., J. Vac. Sci. Technol. B **23**, 3129 (2005)
[10] S. Graham *et al*., Proc. of SPIE, **5037** (2003) p. 460
[11] A. Gicquel, M. Chenevier, Kh. Hassouni, A. Tserepi and M. J. Dubus, Appl. Phys. **83**, 7504 (1998).
[12] V. Schulz-von der Gathen and H. F. Doebele, Plasma Chem. Plasma Process. **16**, 461 (1996).
[13] M. J. Wouters, J. Khachan, I. S. Falconer and B. W. James, J. Phys. B: At. Mol. Opt. Phys. **32**, 2869 (1999).
[14] B. P. Lavrov B P and A. V. Pipa, Opt. Spectrosc. **92**, 647 (2002).
[15] M. Hayashi, National Institute For Fusion Science, Report No. NIFS-DATA-72 (2003).
[16] http://www.nist.gov/pml/data/asd.cfm (NIST)