Actinic Damage of Y/Mo Multilayer Bragg-Optics by a Tabletop Plasma-driven Extreme Ultraviolet Laser

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ABSTRACT

Actinic irradiation (i.e. using ionizing light) of EUV pulses on a multilayer Bragg optics was investigated for characterizing the chemical effects. Photothermal effects are ruled out by the low repetition rate and low absolute energy of the EUV pulses. This would exclude the formation of melt-related particles, which have been however observed. Alternative explanations are discussed. The analysis concentrate on the structure and composition of the multilayer stack, with the aim of quantifying the kinetics.

Keywords: multilayer, extreme ultraviolet, EUV, X-ray Laser, damage, FFT

1. INTRODUCTION

Multilayer optics owes its functionality to specific compositional and structural characteristics. The choice of specific stoichiometries for the absorber and transmitter layer is between a *science* and an *art*. In fact, besides a robust theoretical understanding, trace-level contamination can drastically limit the performance. Therefore, the technical skill and quality of the fabrication infrastructure are as important as the design, based on theoretical arguments.

Further, the nano-structure of the system is crucial as low as at monolayer level. This demands precision of fabrication as well as durability under operating conditions. It has been shown previously that the surface quality of the substrate is "priming" the quality of the multilayer [1]. The adhesion of a bilayer on the substrate is not only a function of chemical but also physical characteristics. Often, manufacturers perform a "dry-run" deposition, and a second round of polishing, for the final full-stack deposition on a "chemically-tuned" substrate. The full-stack must be however thicker than the characteristic light penetration, also including proximity effects, in order to "bury" the two-round fabrication.

The interaction of extreme ultraviolet (EUV) with matter poses however serious challenges, because of a few specific issues. In a certain way, there is a "negative implantation" [2,3]. Roughly speaking one can identify two extreme processes upon laser—matter interaction, namely photophysical and photochemical ones. The latter gain in relevance in the case of EUV, as discussed below.

Photophysical processes imply macroscopic phenomena such as thermal and mechanical ones. In a heuristic picture, the former is related to temperature, while the latter is related to pressure. Temperature can increase as a consequence of collective collisions between the electrons and the matrix. Obviously, this effect scales with the repetition rate of the driving radiation pulses, which causes "*temporal incubation*" of the deposited energy. The increase of temperature is also more modest for a metallic material, due to enhanced delocalization.

Photochemical processes imply micro/nanoscale phenomena such as bond breaking or photo-oxidation. In a heuristic picture, the former is related to photoemission, while the latter is related ambient chemistry or charge transfer. Photoemission is clearly enhanced at *short* wavelength exposure (i.e. *high* photon energy), especially in the EUV, due to resonant cross-sections. At even shorter wavelengths, e.g. X-rays, the thick penetration distribute the photoionization

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process across a larger length-scale. The shallow penetration of EUV favors "*spatial incubation*", such that micro/nanoscale effects may coherently correlate and become macroscopically significant.

In the literature, the fact that EUV has energies amenable of single-photon ablation, was indicated as an argument for claiming threshold-free laser damage/ablation [4]. Results have shown a dramatic drop, approx. factor of 10, of the threshold, but still there is a threshold [5]. The effects of EUV can however become significant, even when the pulse is unfocused.

Fig. 1 shows a compilation of chemical bond energies, compared with the photon energies of popular laser systems. Ionization energies of elements go further as high as 24.6eV (He), which is not shown here. One concludes that radiation at EUV (10-100eV) can have dramatic effects while impinging on any material, efficiently inducing photoemission, electron transfer and chemical modification.

Figure 1. Compilation of energy of chemical bonds, showing the required minimum energy for bond breaking. Popular laser lines are indicated (red dots) to show the "*chemical limit*" they can achieve.

During a periodic shutdown of the in-house EUV laser system, it was decided to inspect the EUV optics in detail. Macroscopically a shading was observed, over a region of a few mm. Aim of this work was to generate preliminary data to understand the EUV-related processes causing the macroscopic modification, as well as the loss of reflectivity

2. EXPERIMENTAL

2.1 Samples

The multilayer optics have been described in Bleiner et al. [1]. Y/Mo multilayers were fabricated using an ultrahigh-vacuum DC magnetron sputtering deposition system. The base pressure in this cryogenic-pumped system was $2 \cdot 10^{-9}$ Torr before deposition. An ultrahigh-purity argon gas was used at a constant pressure of 2.0 mTorr during deposition. The operating powers for molybdenum and yttrium were regulated at 50 W. Substrates 1 cm by 1 cm in size were cut from a polished single-crystal Si[100] wafer.

2.2 Extreme Ultraviolet Source

Plasma-driven EUV laser [6,7] pulses were induced by means of a high-power pump laser of 2.7 J in 1.2 ps. EUV pulses of 2–3 μJ emerged across a plasma column as amplified spontaneous emission (ASE). Considering the high photon energies of 103 eV or $\lambda = 12$ nm, the interaction with any material can efficiently lead to secondary electrons and photoemission. The source and its working principle are described in detail elsewhere [6–12].

The Y/Mo-coating sample was exposed with a spot of approximately 1 mm at $<2^\circ$ off-normal incidence. The resulting fluence was approximately 0.5 mJ/cm^2 and the peak irradiance was 0.01 GW/cm^2 . Differently from literature works [13–15] done at free-electron lasers with ultrashort pulses, the irradiance in our work is presumably below the photophysical ablation threshold and represents a routine photon load on the x-ray optics. The laser was operated at 5 shots/hour, for several hundreds of shots over repeated irradiation runs during the daily source operation over years. EUV linewidths of $\Delta\lambda/\lambda < 10^{-4}$, i.e., 2 orders of magnitude smaller than the reflectivity bandwidth, make off-band load of no concern and permit deriving conclusions that are correlated to just the operative wavelength.

2.3 Data Acquisition and Processing

Figure 2. Image of the focused ion beam (FIB) milled lamella of the EUV optics, for Transmission Electron Microscopy. One notes a large spherical particle on top of the Mo/Y multilayer (whiter stripe) and the thick substrate.

Electron Microscopy

By means of focused ion beam (FIB) a 50-nm-thick lamella was milled [16] to obtain a cross section of the multilayer (Fig. 2), and related transmission electron microscopy (TEM) and scanning TEM (STEM) were carried out. Slices were cut in a dual-beam FIB/SEM (Zeiss NVision 40) with a gallium liquid metal ion source, a gas injection system and a micromanipulator. A layer of amorphous carbon was deposited on the surface to protect the thin film before digging two trenches from both sides. The extraction was a critical step in which the microscale lamella is transported on a mounting stem for the TEM. After the lift-out, the lamella was polished to ion transparency with currents down to 10 pA.

at 30 kV. The amorphization was diminished by low kilovolt showering for several seconds at 5 and 2 kV. Furthermore, the FIB preparation permitted to optimize the thickness and thus obtain high-resolution data on a transmission electron microscope (Tecnai F30 FEI, Eindhoven) equipped with a field emission gun being operated at 300 kV. The Tecnai F30 can be operated in TEM as well as in STEM mode and it is equipped with a silicon detector (EDAX) and a high-angle annular dark field (HAADF) detector for elemental-contrast imaging. It was used for bright-field TEM imaging, energy dispersive x-ray spectroscopy, as well as HAADF STEM imaging. One significant advantage of FIB preparation for electron microscopy is the fact that the optics are not fully destroyed, but only microprocessed locally on a small pit of approximately 25 by 25 μm .

FFT Analysis.

Considering a bilayer as a rectangular function, the *sec*-function (i.e. $f(x) = \sin(x)/x$) provides its frequency distribution, by means of a simple Fourier relation. Any increase of bilayer period would map in a sharper *sec*-function. Therefore, plotting the FFT of a measured multilayer, the width of the peak is inverse function of the *period of the bilayer*. Multi-periods would give FFT peaks with shoulders or even doublets. The FFT analysis can permit retrieving the phase of the bilayer, i.e. transverse loss of parallelism, by observing the position of the FFT peak. FFT peak amplitude provides additional information on the contrast of the stack. One should also understand that the FFT analysis is a powerful technique for a global quantification of the multilayer characteristics. Local characteristics are thus less relevant. In order to analyze the characteristics in different regions of depth, the FFT analysis was carried out across a region of the multilayer.

3. RESULTS

3.1 Structure of Multilayer Surface

A protective mask was mounted on the active surface of the Bragg optics, with a small opening corresponding the region to be used. The macroscopic inspection of the optics clearly indicated a different coloration in the region that was exposed to the EUV pulses. This darker shading could not be removed by contactless cleaning, such as air spraying, or by soft optics-compliant tissues. This would indicate a modification of the pristine material, rather than a deposition of veneering components.

A microscopic analysis has shown diffuse occurrence of laser-produced debris [17], which is a major inconvenience if one plan to use EUV for non-contact metrology applications [18-19]. The spherical shape of this debris would indicate a photophysical ablation mechanism. The origin of these particles is considered as due to two alternatives: (i) autochthonous, i.e. due to melt mobilization of the EUV irradiated surface; (ii) allochthonous, i.e. flying shrapnel from the plasma generation process during the high-power laser irradiation of the target, that may have reached the optics.

The former case seems unrealistic because of the remarkable size (i.e. where is the source pit?) and because of the need for high temperatures, which as discussed above should be ruled out. Unfortunately, it was not possible to analyze by means of electron beam Energy-Dispersive X-ray (EDX) emission [20], as the particle was not mechanically stable. The second hypothesis, although reasonable from the thermal consideration (2.7 joules do generate target debris), is surprising because the optics is located at 300 mm with a line-of-sight angle of 2° above the target surface, or 88° off-axis of the plasma expansion direction. Such large angle is expected not to give significant debris fall-out, still few rare events could be happening.

3.2 Structure of Multilayer Bulk

As shown before [1], the multilayer was found to be structured with three blocks. The deep region and the shallow region have poorer periodicity and parallelism (for different causes discussed in ref. [1]), while an intermediate region showed better quality. The periodicity was defined as "longitudinal coherence" in ref. 1, while the parallelism as "transverse coherence". This descriptive approach permits to utilize established mathematical expressions, to quantify the structure quality. It should be said that the deviation between poorer and better quality regions is minimal in absolute terms, as

shown below (**Fig. 3**). Therefore, it is important to introduce quantification tools for comparing and understanding the processes. In terms of optical performance, such small deviations have substantial effects, e.g. loss of reflectivity.

Figure 3. A) Transmission Electron Microscopy of the Bragg-Optics, highlighting the absorber/transmitter layer contrast profile as a function of depth; B) Fourier Transform analysis of the multilayer after EUV irradiation. See text for details.

The FFT study highlighted region-wise the structure degradation. **Fig. 3** compares the FFT of the full multilayer stack (black line) to that of the various zones. The *shallow* zone is the one mostly exposed to the effects of the EUV pulses. The region's peaks matching those of the full stack are identified and labeled from the center to the right, showing only one correspondence (peak "a1"). The reader can in fact note that the purple line follows the black line only in correspondence of a1 (147 nm^{-1}).

In **Fig. 3** (*bulk* zone), there are more correspondences between the region (blue line) and the full stack's FFTs. This indicates that: (i) a1 did not shift much with respect to b1 (154 nm^{-1}), and it is a global feature; (ii) the higher frequencies (b2, b3, bx) appear in this deeper region: It is presumable that upon laser-interaction these higher frequencies (steep interfaces) were destroyed in the *shallow* zone. One can argue if b2 ($N=2$) and b3 ($N=3$) are harmonics of the fundamental b1 ($N=1$), i.e. spatial frequency $k = 154 \times N$.

In **Fig. 3** (*substrate* zone) there are two correspondences between the full stack and the zone, and both such peaks c1 and c2 are not found in the other zones. The reader should pay attention not to confuse the position of a1 and that of c1, which in the full stack appear as a doublet. The observed new peaks c1 and c2 represent shifts toward slightly higher frequency, which may indicate a slight enhancement of the low-scale roughness. This could be supported by the asymmetry of the peaks, especially c2, and the occurrence of a pattern modulation for $k > 330 \text{ nm}^{-1}$, which is substituted by pronounced b3 peaks in the *bulk* zone.

3.3 Chemical Analysis

As mentioned in the introduction, chemical effects are facilitated by EUV, since the generation of secondary electrons. Chemical analysis by EDX provide rapid information on the elemental composition. Our sample are relatively simple

from the chemical point of view, and thus an element menu including Y and Mo should be sufficient. However O was also included, to investigate processes of modification.

Figure 4. Elemental composition of the multilayer as obtained by EDX analysis. See text for details.

Fig. 3 shows elemental analysis results for the four target elements. One observed the structured offset periodicity of Mo and Y. The O signal is concentrated in the surface, and negligible elsewhere. Furthermore, it is very correlated with the Y signal, indicating the formation of yttrium oxide compounds. The analysis is only semi-quantitative and cannot give hints of the compound stoichiometry and surface activation. The latter is an indicator of the kinetics and is subject of ongoing work. It is interesting to observe, that the yttrium oxide is restricted to a surface pocket, indicating a chemical and structural modification. The fact that the oxidized region is not seen in the bulk at depth, suggests two observations: (i) need of oxygen, which may be source during vacuum venting, by introducing O_2 or H_2O ; (ii) enhancement of surface activation in the region of highest EUV intensity (which obviously decreases depthwise). It is questionable whether strategies with nitrogen venting, may trigger alternative N-containing compounds. This is subject of ongoing work.

4. DISCUSSION

EUV pulses can trigger electron transfer and with that chemical activity. The availability of third components, e.g. oxygen at the surface, dirt, water, etc. triggers formation of chemisorbed species (e.g. Y_2O_3), with reduction of the optical contrast between absorber (e.g. Mo) and transmitter (e.g. Y) layer. The photoemission produces ionized Y that can actively bind with oxygen. The interaction between adsorbate and surface creates strong bonds that optically alter the material, both in the visible (coloration and dark shading) and in the EUV (loss of reflectivity). As shown previously [1], the effect causes a drastic loss of reflectivity of approx. 0.1% per EUV shot. Thus the surface acts as a interface for the a photo-driven heterogeneous catalysis in the solid-gas (low pressure) interface. At low pressure the activity can be enhanced by means of mass-limited rates, which is subject of future work.

5. CONCLUSIONS

EUV pulses from a plasma-laser were exposed to a Mo/Y multilayer optics. It was observed a macroscopic darkening that could be supported by microscopic analysis. It was thus found that under the action of EUV pulses, the surface is not chemically stable within approx. 10 nm, i.e. the first bilayers. The bulk layers are instead chemically pristine but not structurally stable within a depth of 250 nm, i.e. approx. 40 bilayers. A preliminary model was discussed.

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