Depth Profiling of Multilayer Mo/Si Nanostructures

A. Tolstoguzov[1,*], B. Ber[2,†], P. Chapon[3,‡], M.N. Drozdov[4,§]

[1] *Centre for Physics and Technological Research (CeFITec), Dept. de Física da Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal*
[2] *Ioffe Physical-Technical Institute, Polytechnicheskaya 26, 194021 Saint Petersburg, Russian Federation*
[3] *HORIBA Scientific, 91165 Longjumeau, France*
[4] *Institute for Physics of Microstructures of the Russian Academy of Science (IPM RAS), 603950 Nizhny Novgorod, Russian Federation*

A round-robin characterization is reported on the sputter depth profiling of [60×(3.0 nm Mo/ 0.3 nm B_4C/ 3.7 nm Si)] and [60 × (3.5 nm Mo/ 3.5 nm Si)] stacks deposited on Si (111). Two different commercial secondary ion mass spectrometers with time-of-flight and magnetic-sector analyzers and a pulsed radio frequency glow discharge optical emission spectrometer were used. The pros and cons of each instrumental approach are discussed.

Keywords: Sputter Depth Profiling, Glow Discharge Optical Emission Spectroscopy (GDOES), Mo/Si Interferential Mirror, Round-robin Characterization, Secondary Ion Mass Spectrometry (SIMS).

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1. INTRODUCTION

Sputter depth profiling is a powerful tool for compositional analysis of nanometer-thick multilayer structures. In recent years, evident progress has been made in this field, especially regarding secondary ion mass spectrometry (SIMS) and glow discharge optical emission spectroscopy (GDOES) [1].

The present work is a continuation and further development of our previous round-robin study [2]: we have analyzed Mo/Si and Mo/B_4C/Si stacks. From a practical point of view, Mo/Si interferential mirrors are of considerable interest for high resolution X-ray lithography. The introduction of B_4C layers suppresses interlayer diffusion, which worsens the reflectivity and thermal stability of mirrors.

Two commercial SIMS instruments – CAMECA IMS7f by Cameca SAS at Ioffe Physical-Technical Institute and TOF.SIMS-5 by ION-TOF at Institute for Physics of Microstructures, and a modified GD-Profiler 2 at Horiba Scientific were involved in our interlaboratory experiments. This study is driven by necessity to perform accurate and rapid analysis of nanometer-thick periodic multilayers in order to optimize and improve their production technology.

2. EXPERIMENTAL DETAILS

2.1 Multilayer samples

The investigated samples are commercially available multilayer interferential mirrors produced by magnetron sputtering at IPM RAS [3].

The samples are ca. 420 nm-thick nanostructures consisting of 60 layer period superlattices - Mo/B_4C/Si in the case of the PM596 sample and Mo/Si for the

PM615 sample (Fig. 1). In both cases, each period is 7.00 ± 0.05 nm thick. The dimensions of individual Mo and Si layers are estimated to be 3.0 ± 0.2 nm (Mo) and 3.7 ± 0.2 nm (Si) for the PM596, and 3.5 ± 0.1 nm (Mo) and 3.5 ± 0.1 nm (Si) for the PM615. The B_4C barrier layer is a single atomic layer with a nominal width of ca. 0.3 nm. This technological parameter is estimated via the deposition and shutting rates of the magnetron sputtering processing.
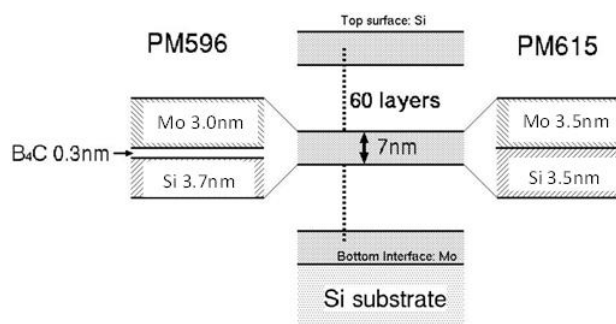
Fig. 1 – Schematic view of the structure of the sample under study

The starting layer put directly onto the substrate is Mo, and the top surface layer is Si. The B_4C layer is deposited onto the Si layer in every period of the sample PM596. The substrates are 0.4 mm-thick commercial Si (111) wafers with an average surface roughness of 0.3 nm.

2.2 Instruments

Pulsed radiofrequency (RF) mode is used to power the glow discharge optical emission spectrometer GD-

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* a.tolstoguzov@fct.unl.pt
† boris.ber@mail.ioffe.ru
‡ patrick.chapon@horiba.com
§ drm@ipm.sci-nnov.ru

Profiler 2 [4, 5]. In GDOES measurements, samples are etched by Ar^+ ions and accelerated neutrals with very low kinetic energies; the sputtered atoms are then excited by the plasma and de-excited via photons emission with characteristic wavelengths, enabling their elemental identification. In our experiments, the operating conditions were: argon pressure of 550 Pa, 17 W RF power, 5 kHz pulse frequency with 0.25 duty cycle. The sputtered area in GD is the largest in comparison to other techniques: here a disk of 4 mm in diameter, and the useful signals are collected from the whole sputter area.

Time-of-flight secondary ion mass spectrometer TOF.SIMS-5 works in the dual beam mode using 25 keV Bi^{3+} ions for analysis and 1 keV Cs^+ ions for sputtering. The angle of incidence was 45° for both ion beams. The sputter beam was scanned over an area of 250×250 µm^2, and the analyzed region was ca. 4% of the sputter area. Detailed description of the experimental conditions can be found in [6].

Magnetic-sector secondary ion mass spectrometer CAMECA IMS7f employs Cs^+ primary ions with an impact energy of 5.8 keV and an incidence angle of 32° relative to the surface normal (the accelerating and sample potentials were 7 keV and 1.2 keV, respectively) while the positive secondary ions are detected. The primary beam was scanned over a 250×250 µm^2 area, and the secondary ions were collected from a central region of 60 µm in diameter. The "energy window" of the spectrometer was fully opened (130 eV), and the mass resolution was $M/\Delta M$=400. The crater depths were measured by an AMBIOS XP-1 surface stylus profilometer by Ambios Technology.

Atomic force microscopy (AFM) was used to measure the initial surface roughness of the samples and the roughness at the bottom of the craters after sputter depth profiling. Different instruments were involved in this study: a Dimension 3100 by VEECO in tapping mode for the magnetic SIMS, a SOLVER by NT-MDT in contact mode for the TOF-SIMS, and a NT-MDT NTegra Prima in contact mode for the samples analyzed by pulsed RF GDOES.

3. RESULTS AND DISCUSSION

Raw depth profiles, in a semi-logarithmic scale, obtained by pulsed RF GDOES and SIMS are shown in Fig. 2 for the sample PM596 and in Fig. 3 for the sample PM615. In the case of pulsed RF GDOES (Fig. 2a and Fig. 3a), the bombarding ions were Ar^+ with mean impact energy of 50 eV. We measured the intensity of the light emission of excited sputtered atoms at wavelengths of 381.411 nm (Mo), 251.611 nm (Si), 249.678 nm (B), and 156.144 nm (C).

For the PM596 sample (Fig. 2a), the number of fully-resolved periods was estimated to be 59. With deeper penetration into the sample structure only the depth profile of carbon exhibits a continuous decrease in intensity, however without decay of the signal oscillations. In our opinion this profile can be considered as a result of two contributions - one of them relating to carbon originating from the B_4C barrier layers and the other one from contamination. For the PM615 sample (without the B_4C barrier layers), an evident degradation of both Mo and Si profiles versus the sputter time (the depth of

sputtering) is observed (Fig. 3a).

For the TOF-SIMS, only the first 10 periods of the structures were analyzed (Fig. 2b and Fig. 3b). The depth distributions of positively charged atomic Mo^+ (sum of all isotopes), $Cs_2{}^{11}B^+$ and $^{28}Si^+$ secondary ions are shown in Fig. 2b (PM596) and Fig. 3b (PM615). As compared with pulse RF GDOES, the introduction of B_4C layers does not induce significant difference between the measured profiles.

For CAMECA IMS7f with a magnetic sector mass analyzer (hereinafter this instrument will be called the magnetic SIMS or M-SIMS) we chose molecular ions MCs^+ (where M is B, Si or Mo) as the characteristic ions. In spite of the fact that the mechanisms of secondary ion formation under Cs^+ bombardment and deposition are still debated, Cs-based SIMS allows for the minimization of matrix effects, which greatly influence the secondary ion yields. In our case, non-degraded profiles were obtained for both samples with 58 resolved periods (Fig. 2c and Fig. 3c). No significant difference between the data of the PM596 and PM615 samples was observed. However, the signals of Si and Mo within each period overlapped, and in case of $SiCs^+$ were split into two parts (see the inserts in Fig. 2c and 3c) – phenomena which was not observed for pulsed RF GDOES and TOF-SIMS. One possible explanation could be the ion-induced distortion of the interfacial region by Cs^+ ions with high impact energy (5.8 keV) – the highest in our experiments. In principle, in CAMECA IMS7f this energy can be reduced to 1 keV or lower, however, it results in the decrease of the sputter rate and increase of the analysis time.

The final crater depth in the magnetic SIMS was measured for both samples using an AMBIOS XP-1 profilometer. Assuming a constant sputter rate, we obtained the values of 5.71 and 6.88 nm/min for the PM596 and PM615 samples, respectively. This is only average since for our samples the sputter rate of individual layers varies significantly from each to other. The B_4C layers in the sample PM596 cause a decrease of the overall sputter rate as compared to the sample PM615. Using this data, we converted sputter time into depth of sputtering in Fig. 2c and Fig. 3c (upper X-axis).

The initial surface roughness R_a of the both samples is found to be similar, within the range from 0.13 nm to 0.22 nm. For the PM596 sample (with B_4C barrier layers) after the depth profiling using magnetic SIMS, the average roughness increased by a factor of 1.7, and for the PM615 sample (without B_4C barrier layers) the roughness increased 9 times. For the samples analyzed by TOF-SIMS using 1 keV Cs^+ sputter ions, no significant difference in the roughness before and after depth profiling was observed.

In case of pulsed RF GDOES, we measured the roughness after sputtering of 30 periods since with completing depth profiling the bottom of crater was deep in Si substrate. The average roughness of both initially flat samples increased and reached 0.7 nm and 1.0 nm for the PM596 and PM615 samples, respectively. However, such little difference in our opinion cannot be considered the only root of the abovementioned difference between the depth profiles of these samples shown in Fig. 2a and Fig. 3a.
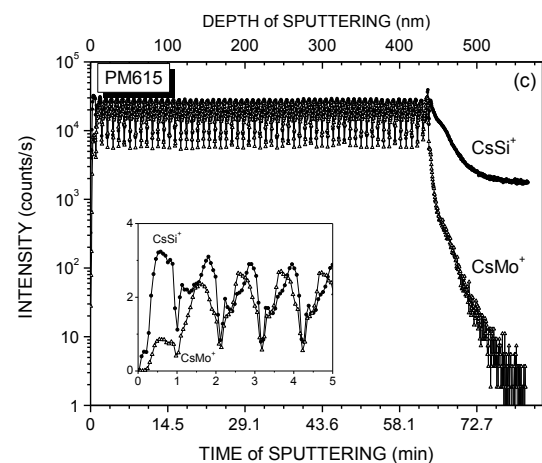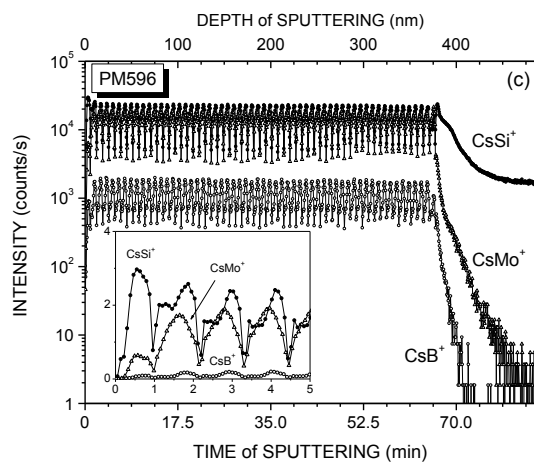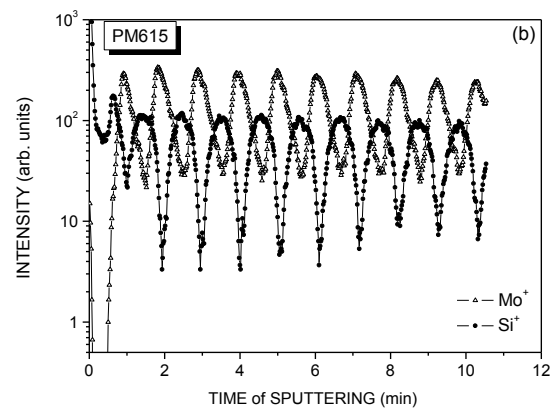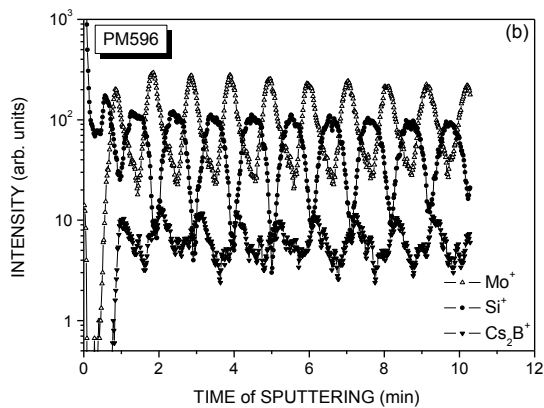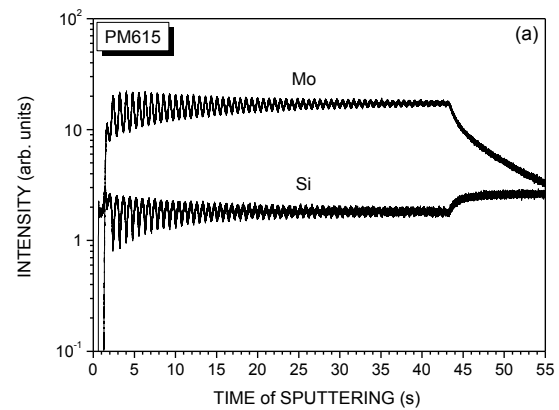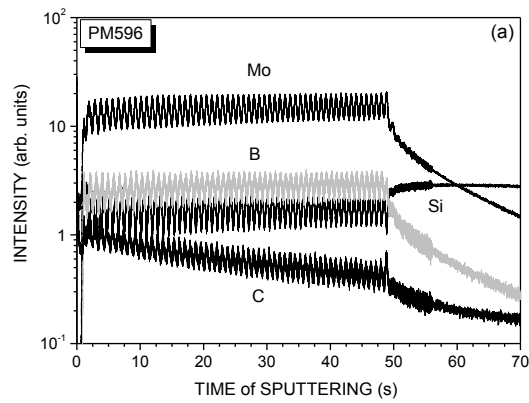
Fig. 2 − Depth profiles of the PM596 sample by pulsed RF GDOES (a), TOF-SIMS (b) and magnetic SIMS (c)

Fig. 3 − Depth profiles of the PM615 sample by pulsed RF GDOES (a), TOF-SIMS (b) and magnetic SIMS (c)

The pulsed RF GDOES and TOF-SIMS data show that the relative depth resolution (interface width) is better for the layers composed of light atoms (B and Si) than heavier one (Mo), especially for the 2^d period, which is less contaminated. This confirms the influence of cascade collision anisotropy on the sputtering of multilayer stacks. One should take into account that the cascade anisotropy results in recoil implantation (Mo in Si and vice versa). Our rough estimate using the SRIM-2008.04 code [7] shows that 0.3 nm-thick B_4C layer can fully suppress such implantation in the case of the pulsed RF GDOES

experiments. Besides, the analyzed samples may be heated by the intense bombardment from the plasma, and B_4C layers can also suppress interlayer diffusion.

Overall, the mechanism(s) of sputtering with ultra-low energy particles (ion and neutrals from the plasma) differs from the mechanism of isotropic linear cascade collisions that dominate at bombarding energies above 300-500 eV. This is one of the reasons why for the more energetic bombarding ions (1 keV and 5.8 keV Cs^+) used in the TOF- and magnetic SIMS, respectively, this layer cannot serve as an anti-mixing barrier to suppress broadening of the

interfaces with deeper penetration into the sample structure.

4. CONCLUSIONS

Comparative sputter depth profiling of the periodic nanometer-thick $Mo/B_4C/Si$ and Mo/Si multilayers has been carried out at three laboratories using two different commercial SIMS instruments and a pulsed RF GDOES. The pros and cons of each instrumental approach can be summarized as follows:

(1) The modified glow discharge optical emission spectrometer GD-Profiler 2 from Horiba Jobin Yvon with pulsed RF operation provides a rapid (less than minute for the complete profiling) and sensitive analysis. The fully resolved signal oscillations with approximately constant relative peak width were obtained for $Mo/B_4C/Si$ structure (the PM596 sample); in case of Mo/Si stack (the PM615 sample) damped profiles were observed. In our opinion, B_4C layers act as a barrier for the ballistic atomic mixing and ion-simulated interlayer diffusion, suppressing progressive broadening of the interfaces with deeper penetration into the PM596 sample.

(2) Using a TOF.SIMS-5 by IONTOF with 1 keV Cs^+ for sputtering and 25 keV Bi^{3+} for analysis, the best modulation for the surface peaks was obtained. However, the complete depth profiling of both samples was not carried out; only the first 10 periods were analyzed, and no significant difference between the data of the PM596 (with B_4C layers) and PM615 samples was observed. Since the modulation and relative layer thickness were becoming worse with deeper penetration into the samples structure, their final values (close to Si substrate) remain unknown.

(3) A Cameca IMS7f with 5.8 keV Cs^+ primary ions took approximately 70 minutes for the completion of the depth profiling of each sample. All peaks in the profiles of cesiated secondary ions were resolved. However, the peaks pertaining to different layers were overlapped, and in the case of $SiCs^+$ were split. It is evident that the Cs^+ impact energy should be lowered in order to minimize ion-induced atomic mixing.

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