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The elemental composition mixing in a Mo/Si multilayer structure under overheating

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ABSTRACT

In the present study, the overheating degradation of as-deposited Mo/Si multilayers was investigated. Technological low-temperature furnace annealing at 300 °C for 1 h was used to simulate the overheating process. A multilayer Mo/Si structure with a period of 21.7 nm was created by DC magnetron sputtering. The dopant distribution in the as-deposited and annealed multilayers was studied by the dynamic- and 3D TOF-SIMS and SNMS methods. Periodic changes in multilayers were studied by the X-ray reflectometry method. It is shown that the cause of the Mo/Si multilayers degradation are oxygen gettering by the Mo/Si interfaces and the silicon diffusion into molybdenum layers due to the Mo/Si interface deformation with the appearance of randomly located places of penetration.

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1. Introduction

The nanoscale Mo/Si multilayer periodic structures (MPS) are widely used in the extreme ultraviolet and X-rays optoelectronic devices. Their reflective properties are determined by the thickness, the periodicity, the structure and interface abruptness of deposited layers [1]. The presence of mechanical stress and structural defects at the interfaces leads to the roughness evolution, compound formation and layer interdiffusion at the heating of Mo/Si structure already at temperature of 150 °C [2,3]. Thin layers of a-$MoSi_2$ are formed at each interface already during fabrication at the room temperature [4]. The prolonged exposure to elevated temperatures will lead to crystallize of this layer and additional Mo and Si interdiffusion as result. $MoSi_2$ interlayers have different thicknesses for the Mo-on-Si and Si-on-Mo depositions [5]. This is due to easier penetration Mo in Si layer during deposition that resulting in a thicker a-$MoSi_2$ layer. The thermal stability of the interface can be improved by introducing nanometric spacer layers between the layers of Mo and Si. The spacer layers can be molybdenum silicide [6], boron carbide [7], carbon [8] and silicon dioxide [9]. The operational overheating of Mo/Si multilayer structures leads to the mirror degradation. A model annealing of Mo/Si structure was carried out to clarify the causes of such degradation. In the present study, as-deposited and annealed Mo/Si multilayer structures were investigated by high precision analytical SIMS, SNMS, XRR methods.

2. Experiment

Mo/Si multilayer periodic structures were deposited on silicon substrates with a surface roughness of 0.3–0.5 nm by successive DC magnetron sputtering from molybdenum with a purity of 99.5% and silicon with a purity of 99.99%. The deposition rate of the Mo and Si layers was maintained at 0.31 nm/s and 0.35 nm/s, respectively. The furnace annealing at 300 °C during 1 h in argon ambience was carried out to simulate the process of mirror degradation during overheating.

The element distributions in the multilayer Mo/Si structures were investigated by Dynamic (D)-SIMS, Time-of-flight (TOF)-SIMS and SNMS methods. The D-SIMS measurements were performed on a quadrupole Perkin-Elmer ATOMIKA 4000 instrument. The depth profiles were measured using 180nA O_2^+ primary ion beam with energy 7 keV. The angle of incidence was 0°. The squire raster was 500 μm × 500 μm. Analyzed area was 20%.

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The TOF-SIMS measurements were performed by TOF-SIMS IV instrument in the dual beam mode with 25 keV Bi^+ primary ion source (1.5pA) as the analysis beam and a 2 keV Cs^+ (150nA) as sputtering ion beam. The angle of incidence was 45° for both ion beams. Spectra were acquired from area of 50 μm × 50 μm and sputtering was performed with scanned over a surface of 300 μm × 300 μm.

The SNMS measurements [10] were performed on a Laybold-Heraeus INA-3 instrument in the high-frequency (HFM) sputtering mode by low-energy Ar^+ ions (the energy E = 325 eV) of a low-pressure high frequency plasma (3.26×10^{-3} mbar). The frequency of sputtering was 50 kHz with a pulse duty of 0.6. The sputtering area was restricted by tantalum diaphragms with internal diameter of 3 mm. The crater depth and shape were estimated by DEKTAK 3030 profiler. X-ray reflectivity (XRR) measurements were performed using an X-ray diffractometer DRON-3 M (at CuKalfa1 radiation with 0.154 nm).

3. Results and discussion

The SEM cross section image of the as-deposited Mo/Si multilayer structure is shown on Fig. 1. The dark and light bands (similar in thickness) correspond to the layers of molybdenum and silicon, respectively. It's seen the structure contains 14 periods with a total thickness of 304 ± 4 nm. Each period has a thickness of 21.7 ± 0.3 nm.

On the surface of the structure there is a silicon cap layer with a thickness of 10 nm. It is known that the deposited molybdenum penetrates into the pre-deposited silicon layer [5]. On the contrary, the penetration of silicon in molybdenum layer does not occur. This feature causes the formation of thicker interface layers of Mo-Si (indicated by U) compared with layers of Si-Mo (indicated by B).

The SIMS depth distribution for elemental composition of MPS before and after annealing is presented in Fig. 2. There are periodic changes in the intensity of the signals from silicon and molybdenum. 14 periods of such changes occur in a layer thickness of about 300 ± 4 nm. The 21.5 ± 0.3 nm period thickness was defined by the atomic force microscope. This value agrees with the results of SEM measurements. The presence of a large number of layers in the Mo/Si structure makes it possible to investigate the dopant redistribution and structural changes occurring on the surface and the depth of the mirrors during heat treatment. It's seen that there is no principal difference in the distribution of basic elements in the Mo/Si structure before (Fig. 2a) and after (Fig. 2b) annealing (300 °C, 1 h.). Only the depth resolution of the measurements was improved, but the cause of the deterioration of Mo/Si mirror is unclear.

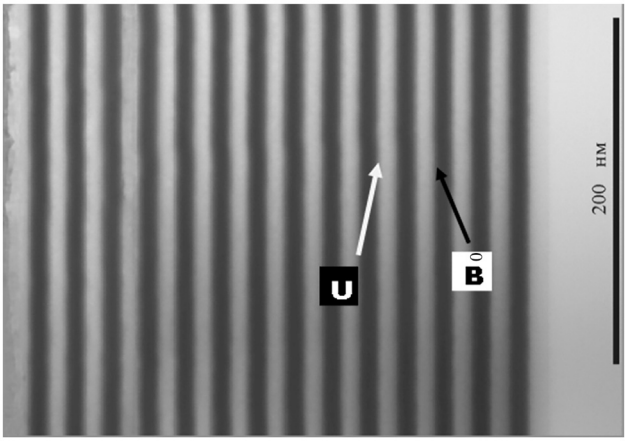

Fig. 1. Cross-section image of the as-deposited14-period multilayer Mo/Si structure.

However, some differences in the elemental distribution on the internal structure interfaces can be notice. The increasing of the $MoSi^+$ signal intensity at the interfaces indicates the presence of silicide-like transition layers that can already be created at room temperature. The intensity and width of the $MoSi^+$ peaks are different for the Mo-Si and Si-Mo interfaces and hence the silicide-like layers can be different in composition, structures and thickness.

In order to obtain additional information on the Mo/Si structure degradation during annealing, the low-energy argon plasma SNMS method was used. A feature of the method is the almost complete absence of sensitivity to the different matrix effects. SNMS profiles of the Mo^+, Si^+ and SiO^+ ions before and after annealing of MPS are shown in Fig. 3. It has seen that the increasing of signal from silicon is observed at the Mo-Si interface. SiO^+ polyatomic signal distribution indicates that silicon is partially oxidized.

That behavior of the silicon signal is due to the silicon oxidation at the interface. Obviously, molybdenum penetrates deeper into silicon during deposition and stimulates the silicon oxidation. After annealing, the oxidation of all interfaces is observed. The SiO^+ signal behavior indicates the enhanced oxide formation at the U interface in comparison with the B interface. Obviously, it's connected with an increase of tensile stresses in the mixed Mo/Si interface layer during annealing. These stresses lead to gettering of oxygen from the deposited layers due to the formation of regions with high solubility of oxygen [11,12].

The experimental and simulated XRR spectra from the as-deposited and annealed Mo/Si MPS are shown in Fig. 4a and 4b respectively. The X'Pert Reflectivity software from Phillips Analytical was used to simulate the XRR spectra of the investigated structures.

The simulation of XRR spectra from the as-deposited multilayers (Fig. 4a) showed minor changes in simulated spectra taking into account the presence of an additional transition MoSiO layer at the interfaces and without it. This may indicate that the densities of the "lower" transition MoSi layers and MoSiO layers have close values. During the modeling process the presence of different transition MoSi layers on the B and U interfaces, "lower" and "upper" MoSi layers, respectively, had been taken into account. When the Mo layer is deposited on the Si layer, the density of the "lower" transition MoSi layer is about 4.9 g/cm^3 and when the Si layer is deposited on the Mo layer, the density of the "upper" transition MoSi layer is about ~9 g/cm^3. This indicates on various component composition in "lower" and "upper" transition layers. The density of "upper" transition MoSi layer is close to density of Mo layer. This explains the results of SEM analysis that show sharper B interfaces. The best-fit parameters for as-deposited multilayers are shown in Table 1.

In the experimental XRR spectra of annealed Mo/Si multilayers (Fig. 4b) there is present a split of oscillation peaks, which is more pronounced for peaks located at larger angles. It should be noted, that on the spectra from the as-deposited multilayers, there is also the broadening of the peaks located in the region of larger angles. The fitting of the XRR spectra for the annealed multilayers (Fig. 4b) shows the existence of two slightly various superlattice structures, which have different thicknesses of Mo, Si, transition MoSi layers and period's thicknesses the values of which are ~20.9 nm and 21.6 nm, respectively. Annealing also affects on the densities and, hence, the composition of the transition MoSi layers. If before the annealing, the"lower" transition MoSi and MoSiO layers had a lower density value (~5 g/cm^3), and the "upper" transition MoSi layers has larger value (~9 g/cm^3), then after the annealing the density value of the "lower" MoSi layers increased (~8 g/cm^3 for

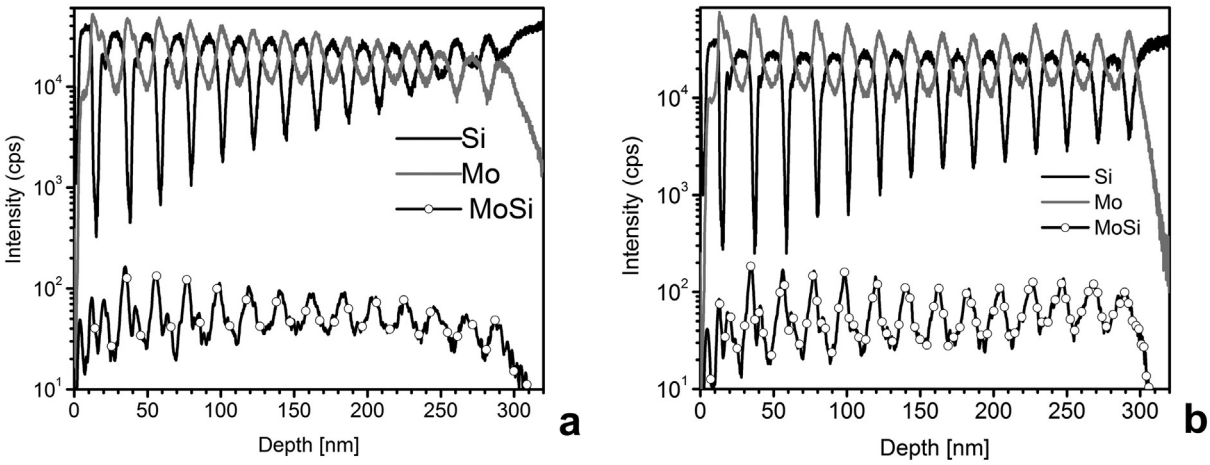

Fig. 2. SIMS depth profiles of the as-deposited (a) and annealed (b) Mo/Si structure.

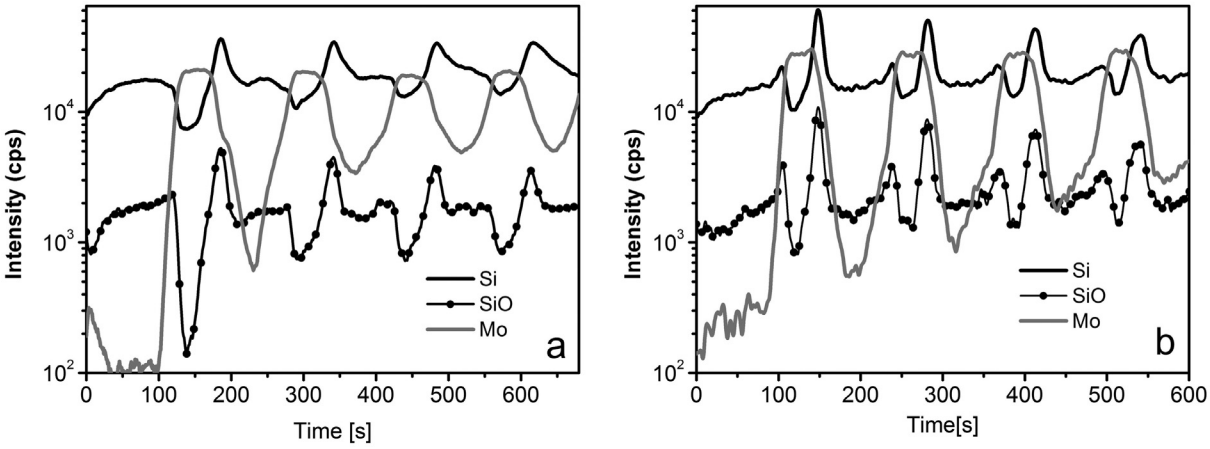

Fig. 3. SNMS element depth profiles of Mo/Si structure before (a) and after annealing (b).

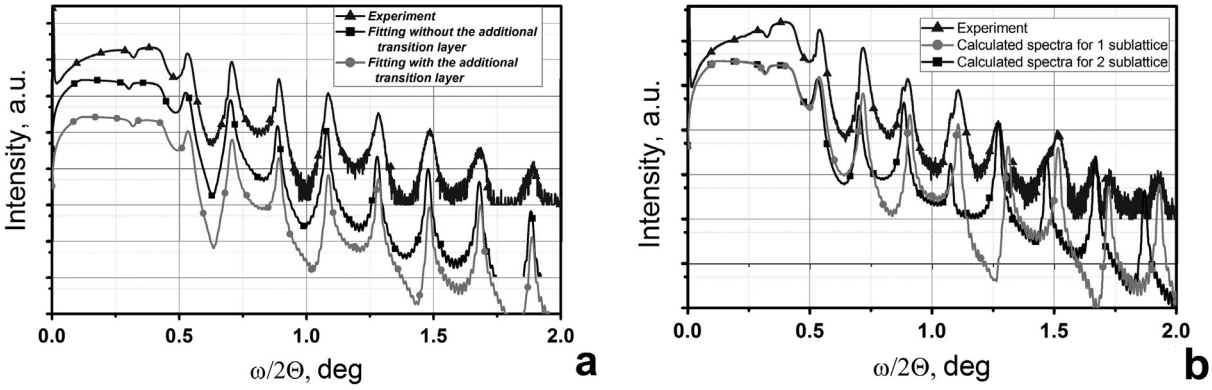

Fig. 4. XRR profiles for the as-deposited (a) and annealed (b) Mo/Si multilayer structure with the simulated spectra.

MoSi and ~5 g/cm^3 for MoSiO) and the density of "upper" ones slightly decreased to ~8 g/cm^3. This is evidence of the redistribution of elements in the transition layers and their mutual diffusion. More detailed the parameters of annealed multilayers are shown in Table 2.

The appearance of double superlattice structure in annealed Mo/Si multilayers can be explained by the heterogeneity of thicknesses of the layers over the sample area because the XRR is integral method of analysis. These results indicate on a deterioration of structure of Mo/Si multilayers after annealing.

The investigation of homogeneity of the spatial dopant distribution in the layers of the Mo/Si structure after annealing has been carried out with the ToF-SIMS 3D analysis. The 3D secondary ion images were reconstructed from the depth profile data. These ion images map the spatial variations in the element distributions throughout the multilayer systems. Fig. 5 presents the spatial dis-

Table.1
Parameters of as-deposited Mo/Si MPS obtained by simulation with and without additional transition layer MoSiO.

Layer	Density, g/cm^3		Thickness, nm		Roughness, nm	
Interface	With	Without	With	Without	With	Without
Cap SiO2	2.58	2.56	3.245	2.634	0.614	0.789
Si	2.05	2.15	9.196	10.1	0.87	0.834
"upper" MoSi	9.498	8.79	1.584	1.482	0.67	0.68-
Mo	10.19	10.1956	8.5	8.6	0.84	1.02
MoSiO	3.89	–	1.1	–	0.66	–
"lower" MoSi	4.924	4.9	1.128	1.239	0.58	0.66
Si-substrate	–	–	–	–	0.57	0.713

Table.2
Parameters of annealed Mo/Si MPS obtained by simulation as sum of two MPS.

layer	Density, g/cm^3		Thickness, nm		Roughness, nm	
MPS	1	2	1	2	1	2
Cap SiO2	2.1047	2.572	4.571	3.2	0.563	0.56
Si	2.2	2	10	9.178	0.77	0.87
"upper" MoSi	9	7.729	0.935	1.384	0.609	0.73
Mo	10.2	10.2	7.5	8.45	0.725	0.8
MoSiO	5.63	3.5	1.267	1.267	0.66	0.65
"lower" MoSi	8	8.0	1.191	1.327	0.576	0.472
Si –substrate	–		–	–	0.585	0.585

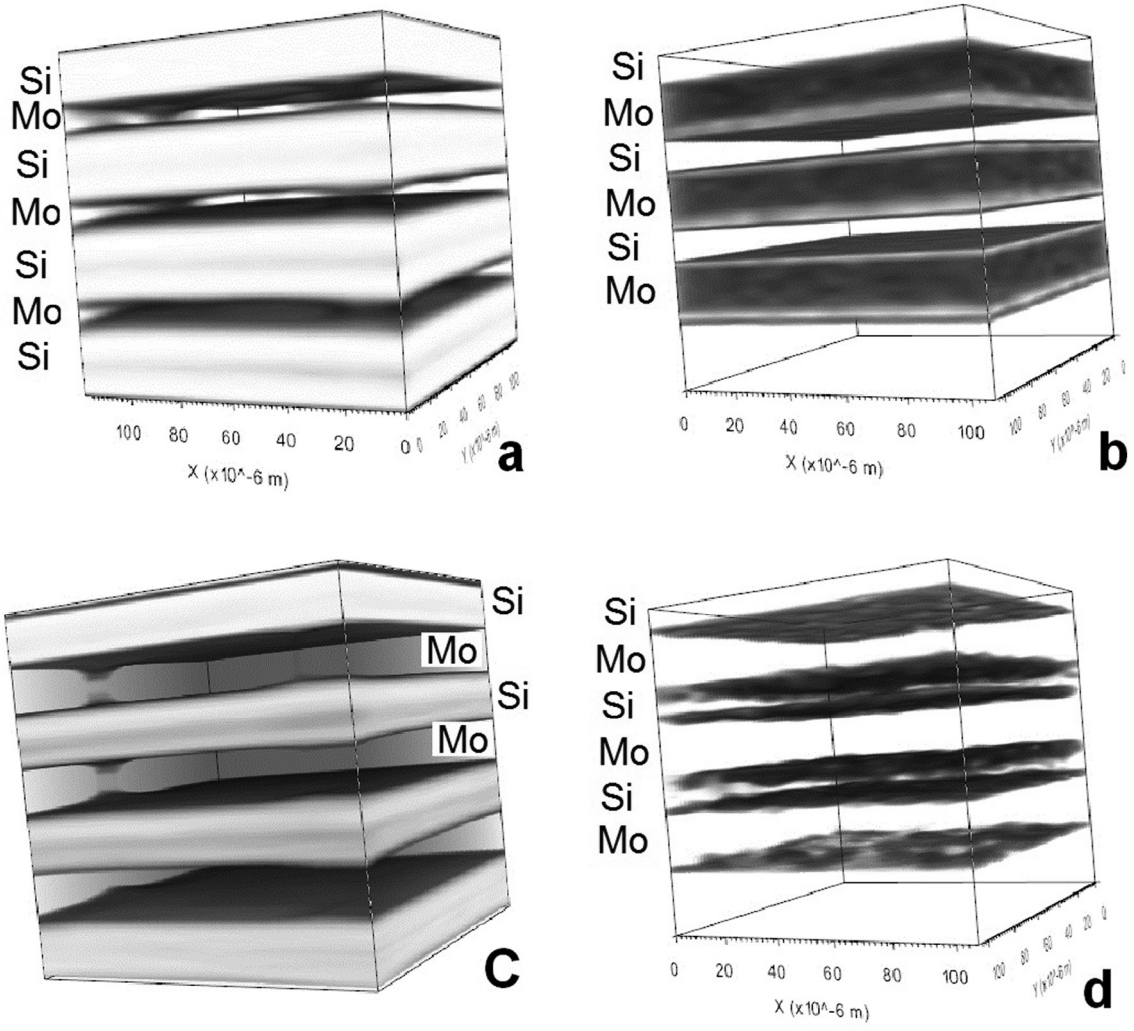

Fig. 5. Reconstructed 3D TOF-SIMS images of Si^- (a), Mo^+ (b), O^- (c) and $MoSi^+$ (d) ions from depth profiles of Mo/Si multilayer structure after annealing at 300 °C during 1 h in argon ambience.

tribution of basic elements and molybdenum monosilicide in the 110 μm × 110 μm × 50 nm volume. The images in silicon (Fig. 5a) and oxygen (Fig. 5c) ions demonstrate the presence of local places of penetration of silicon and oxygen atoms into the depth of molybdenum layers. It can be seen that silicon can locally penetrate the entire thickness of the molybdenum layer. The lateral dimensions of the penetration areas are about 10 μm. At the same time, the image in molybdenum ions (Fig. 5b) demonstrates the edge sharpness of layers. The image in MoSi (Fug.5d) ions contains information about the quality of the interface after thermal annealing. It is seen that the interfaces have a well-developed relief with many recesses and protrusions, which indicates the presence of degradation process during annealing.

4. Conclusion

A multilayer Mo/Si structure with a period of 21.7 nm was created by DC magnetron sputtering. The redistribution of elements and the change in periodicity in Mo/Si multilayers during 300 °C furnace annealing for 1 h were investigated. SNMS measurements show oxygen gettering at the Mo/Si interfaces during annealing. At the same time, the appearance of a double superlattice pattern in the XRR spectrum indicates that the transformation of the Mo/Si interfaces takes place. It is obvious that the simultaneous accumulation of oxygen and the lattice transformation lead to the broadening and spatially inhomogeneous deformation of the Mo/Si interfaces. Since the described processes may not be dynamic at such a low annealing temperature, the places of silicon penetration into molybdenum are randomly located, which is confirmed by 3D TOF-SIMS measurements. Obviously, this is one of the main reasons for the degradation of a multilayer structure during overheating.

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