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Caroline Teyssier, Etienne Quesnel, Viviane Muffato, Patrick Schiavone. Stress characteristics in EUV mask Mo/Si multilayers deposited by ion beam sputtering. *Microelectronic Engineering*, 2002, 61-62, pp.241-250. 10.1016/S0167-9317(02)00506-3 . hal-00475800

HAL Id: hal-00475800

<https://hal.science/hal-00475800>

Submitted on 28 Sep 2022

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Stress characteristics in EUV mask Mo/Si multilayers deposited by ion beam sputtering

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The stress evolution of IBS-deposited Mo and Si 100-nm-thick films has been investigated. Mo films' compressive stress decreases from -2550 MPa to -1000 MPa as the sputtering gas changes from Ar to Xe, whereas Si films' stress remains constant around -850 MPa whatever the sputtering gas. Then the stress behaviour of Mo/Si multilayers sputtered either with Ar or Xe has been observed. In both cases, the multilayer stress first becomes less compressive and then increases, as Mo thickness in the multilayer increases. However, like in the single layer case, the level of stress strongly depends on the sputtering gas. The multilayers sputtered with Xe even become tensile. Moreover, the analysis of the contraction of the multilayers led us to the conclusion that a Mo/Si interface grows, but in a different way, depending on the sputtering gas. Possible stress-generating mechanisms during growth of these multilayers as well as single layer films of Mo and Si are discussed.

Keywords: EUV; Ion beam sputtering; Stress; Multilayer; Molybdenum; Silicon

1. Introduction

The rapid advancement over the last decade in the development of faster and more powerful integrated circuits has made it necessary to reduce feature sizes. Extensions of current optical lithography are not expected to be able to print sub- 0.1 μm features. Hence, there is a need to develop new lithographic technologies. Extreme ultraviolet lithography (EUVL) is one of the technologies being developed for this purpose.

The current designs for an EUVL tool entail the use of several optics and a mask, which should reflect light in the wavelength range of 11 – 14 nm at near-normal angles of incidence. The optics of EUVL are required to be all-reflective, consisting of multilayer-coated mirrors which enhance

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reflectance by using interference of EUV light. Molybdenum/silicon (Mo/Si) multilayers are now routinely achieved with a peak reflectivity of more than 60% at 13.4 nm. Depending on the applications, optics or masks, magnetron or ion beam sputtering (IBS) deposition is used. In both cases, reduction of the deformation due to the multilayer mechanical stress remains an issue to be addressed since the internal stress may deform the multilayer to the extent that optical properties are affected. A number of investigations have been made on the mechanical properties of magnetron-sputtered Mo/Si films [1–3], others on stress in ion beam sputtered Mo/Si coatings [4,5]. Nevertheless, to our knowledge, there is no systematic approach where the stress in IBS Mo/Si multilayers is studied in relation with deposition conditions. Our first results show that Mo/Si multilayers deposited by ion beam sputtering (IBS) generally have a compressive internal stress of several hundred MPa. Therefore, our purpose is to study the influence of deposition parameters on the mechanical stress of IBS Mo/Si mirrors for EUV lithography applications.

The stresses in Mo and Si single layers (~ 100-nm-thick) have been measured. Then, the evolution of the mechanical stress within the multilayer stack has been analysed using a novel method. The idea was to keep the Si layer thickness constant (4.1 nm) and to progressively increase the Mo layer thickness from one sample to the other. In the following paragraphs, we will thus successively present the experimental procedure, then detail the obtained results and finally propose a discussion on the main characteristics of the results.

2. Experimental procedure

Mo and Si films were deposited by ion beam sputtering (IBS), using argon (Ar) or xenon (Xe) as working gas. The chamber contains a sputtering ion source and a rotating pyramidal target holder that can carry four circular targets. The substrates are mounted facing downward on a rotating substrate holder. The temperature of the substrate was not controlled during deposition but can be estimated around 60 °C. <111>-oriented-silicon substrates were used. Single layers were deposited at various sputtering pressure (5×10^{-5} to 10^{-3} mTorr) by varying the Ar or Xe flow within the chamber whereas discharge voltages ranged from 600 to 1400 V. The deposition chamber was cryo-pumped to a pressure of 5×10^{-8} mTorr. All Mo/Si multilayers have been made in the same deposition conditions: 1000 V, 5×10^{-5} mTorr. The multilayers always have the same Si thickness, but the Mo thickness changes from one sample to the other as can be seen in Fig. 1.

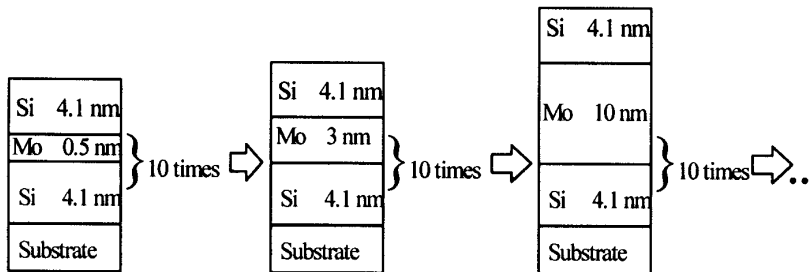


Fig. 1. A novel method to study mechanical stress within the multilayer stack.

The samples were characterized in terms of stress. X-ray reflectance measurement and Rutherford backscattering spectroscopy (RBS) analyses have been performed. Concerning the stress investigations, before describing the experimental measurement, it is useful to briefly review the definition of thin-film stress. If a film of thickness t_f having a biaxial stress σ is attached to a substrate of thickness t_s , it will cause the substrate to deform, as required by the condition of static equilibrium. If the substrate is significantly thicker than the film, the deformation will be spherical, having a radius of curvature R . The relationship between σ and R is given by the well-known Stoney equation [6]:

$$\sigma = \frac{Y_s}{6} \frac{t_s^2}{t_f} \frac{1}{R} \quad (1)$$

where Y_s is the biaxial elastic modulus of the substrate (which is related to E_s , Young's modulus, and ν_s , Poisson's ratio for the substrate by $Y_s = E_s / (1 - \nu_s)$). By convention, positive σ refers to a tensile stress state, in which the substrate is bent towards the film (concave), while negative σ corresponds to a compressive stress state, in which the substrate is bent away from the film (convex). Film stress was determined from the change in substrate's radius of curvature, before and after coating, using a Fizeau interferometer automated for curvature measurements of the substrate. The sample is a $5 \times 50 \text{ mm}^2$ $\langle 111 \rangle$ -oriented-Si substrate. As explained by Mirkarimi [3], the film stress σ can be calculated via a modified Stoney equation:

$$\sigma = \frac{Y_s}{6} \frac{t_s^2}{t_f} \left(\frac{1}{R_2} - \frac{1}{R_1} \right) \quad (2)$$

where R_1 and R_2 are the radii of curvature of the substrate before and after coating.

A value of 229 GPa for Y_s was used. We estimated that the stress measurements are accurate to $\pm 10\%$. In the case of a multilayer, t_f is taken as the total multilayer thickness.

The thicknesses were determined from grazing X-ray reflectance measurements using a SIEMENS D500 X-ray diffractometer with Cu K_α radiation (0.154 nm). This technique is conventionally used for the characterization of periodic bilayer structures as it is non-destructive and gives the multilayer period with good accuracy ($\Delta d = \pm 0.3 \text{ nm}$). Moreover we should be able to deduce the ratio Γ between the two materials in the bilayer (for Mo/Si multilayer, $\Gamma = t_{\text{Mo}} / (t_{\text{Mo}} + t_{\text{Si}})$) from RSRX measurement. However the results strongly depend on the theoretical stack used in the simulation model to fit the X-ray reflectance measurement curve. Furthermore, the very thin Mo thickness used in some stacks and the extreme sensitivity of X-ray reflectance measurements to surface roughness make a reliable determination of Mo thickness within the stack sometimes difficult. In fact, a more relevant parameter, which corresponds to the real quantity of deposited Mo, will be used. It is defined as:

$$T_{\text{Mo}} = dt_{\text{Mo}} \times V_{\text{Mo}} \quad (3)$$

where dt_{Mo} is the deposition time of Mo and V_{Mo} is the deposition rate of Mo. Finally, Rutherford backscattering spectrometry (RBS) was used to quantify the level of sputtering gas in the layers, with 2 MeV alpha particles and incidence and detection angle of 60° and 165° , respectively.

3. Results

The effect of Ar and Xe pressure on the level of stress of thin Mo and Si single layers is presented in Fig. 2. As can be seen from this plot, all the films present a compressive stress which does not vary

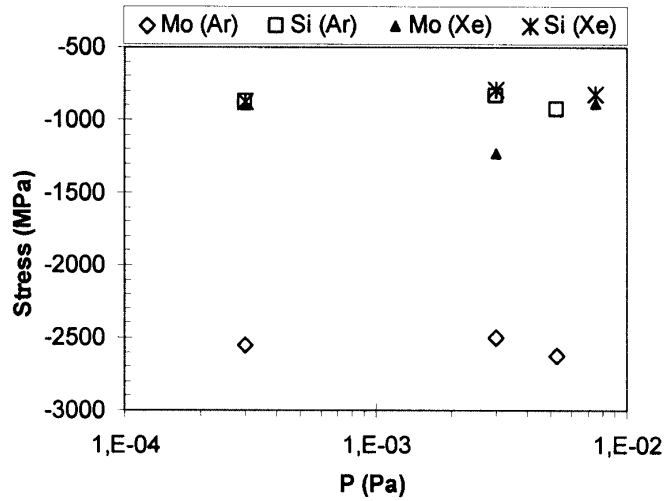


Fig. 2. Measured stress vs. sputtering pressure in ~ 100 nm Mo or Si films for different working gases.

with the deposition pressure. The only significant difference in these data between Ar and Xe gas, is that the compressive stress of Mo varies from approximately -2550 MPa in Ar to -1000 MPa in Xe. On the other hand, the average stress of Si films is roughly the same for Ar (-880 MPa) and Xe (-830 MPa). RBS analysis shows that sputtered films contain some amount of sputtering gases (Fig. 3). Ar contents remain constant at 1 at.% in Mo and increases from 0.2 at.% at 4×10^{-5} mTorr to 0.5 at.% at 7×10^{-4} in Si. Xe content is much lower (up to 0.1 at.% in Si at high pressure) and becomes even smaller than the detection limit in Mo (0.02%).

The significant stress difference between the Mo single layers deposited either by Ar or Xe led us to fabricate Mo/Si multilayers with these two sputtering gases. Fig. 1 shows the stack design of the multilayers we have studied. The evolution of stress in the multilayers is shown in Fig. 4 for thickness T_{Mo} ranging from 0.5 nm to 25 nm. From $T_{\text{Mo}}=0$, the initial compressive multilayer stress begins to decrease and then increases in both cases, Ar or Xe. The Ar–Mo/Si-multilayers are however in a

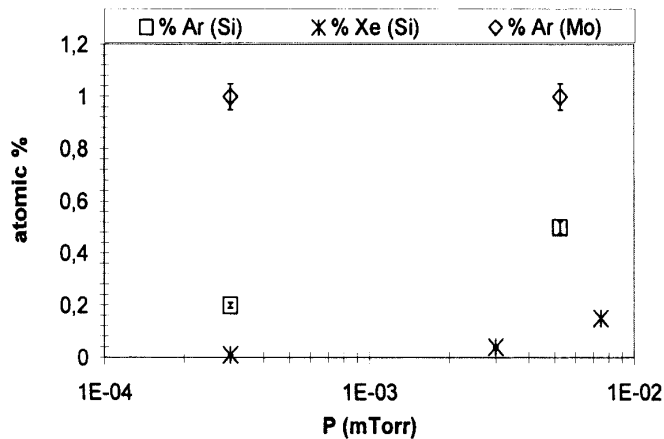


Fig. 3. Ar and Xe content in IBS-sputtered Mo and Si as a function of sputtering pressure.

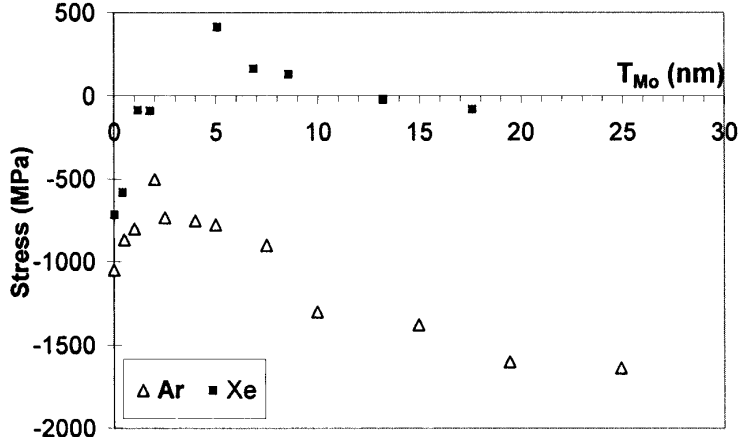


Fig. 4. Stress evolution with Mo film thickness T_{Mo} ($T_{\text{Mo}} = dt_{\text{Mo}} \times V_{\text{Mo}}$ cf. Eq. (3)) in Mo/Si multilayers of different period.

higher compressive stress state than the Xe–Mo/Si-multilayers which become even tensile. One can see that the original value of stress (i.e. when the multilayer is in fact only composed of 11 Si-layers) is not exactly the value of one single layer of Si around -850 MPa) but remains in the same range (between -700 and -1000 MPa). In Ar-sputtering, the compressive stress first decreases and then increases after a given T_{Mo} which is not far from 2 nm. One can expect that the stress value reaches the Mo single layer stress value for very high T_{Mo} . In Xe-sputtering, the curve presents the same trends with some differences. For instance, the maximum of the stress curve is placed at a higher value of T_{Mo} . The same decrease of compressive stress can be observed but the difference between the lowest level of stress and the initial stress is much higher in Xe (1200 MPa) than in Ar (600 MPa). The multilayers become nearly free of stress for T_{Mo} between 10 and 20 nm.

4. Discussion

4.1. Single layers

First of all, it is interesting to compare our results to published data for Ar-sputtering only. To our knowledge, no systematic investigation has been previously made for Xe. Some results available in the open literature are summarized in Table 1. Whatever the deposition system, Si film stress is found

Table 1
Some published values of stress

Reference	1	2	3	5	7	8		Present results
Process	Magnetron	Magnetron	Magnetron	Magnetron	IBS	IBS		IBS
Mo (nm)	100	/	/	1.5	/	200	1.5	100
Mo (GPa)	-2	/	/	+4.9	/	-2.86	+3.6	-3
Si (nm)	100	110	10	500	280	/		100
Si (GPa)	-1	-1.36	-1.3	-1.2	-1.35	/		-0.9

to be around -1.2 GPa. On the other hand, Mo film stress strongly depends on the deposition process and film thickness. As a comparison, our experimental results are in a rather good agreement with published data. The question however is to understand why the Mo stress is so process- and thickness-dependent. Several possible origins of stress can be suspected. Firstly, stress can change because of thermalization of arriving particles. Secondly, the presence of inert gases may cause internal stress. And thirdly, one should consider the very high energy of sputtered particles in IBS.

As can be seen in Fig. 2, in our experiment, the stress does not vary with the log of background pressure. The thermalization distance is indeed always higher than the distance between the target and the substrate (42 cm) in our chamber. This means that the particles, as they arrive on the substrate, have all of their kinetic (there is no loss of energy by collisions). That explains why stress does not vary with sputtering pressure.

Another explanation for high level of compressive stress can be the presence of inert gas in the layer as shown by Fig. 3. However, the link between inert gas entrapment and stress remains controversial [7], as it is not obvious why gas inclusion should cause compressive (as well as tensile) stress. In Fig. 3, the RBS analysis shows that the sputtering gas contents are very low. By comparison to Fig. 2, no direct correlation between stress values and level of gas contamination can be highlighted.

The third concept invoked to explain the compressive stress is atomic peening. D’Heurle et al. [8] explained that atomic density is higher in a growing film submitted to peening than in those obtained otherwise. In such a film the number of bonds under compression might be relatively higher than those in tension, putting the whole film under a state of compression. During deposition, the main sources of particle bombardment are sputtered target atoms and backscattered ions reflected on the target. The relative contribution of each source depends on the sputtering process and especially on the mass ratio between sputtering gas and target atoms.

The Monte Carlo program TRIM [9] was used to determine yields, energy and angular distributions of sputtered and backscattered particles. We will first consider the simulations of sputtered atoms from the target. Simulations were made with 10,000 incident ions (Ar^+ or Xe^+) of 1 keV with an angle of incidence of 60° , as used in the experiments. As can be seen from the plot of Fig. 5, whatever the working gas, the Si peak of distribution is around 2 eV, whereas the Mo peak of distribution is higher,

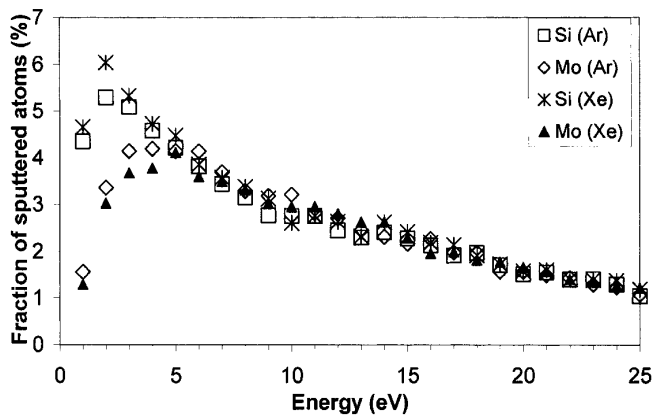


Fig. 5. Energy distribution of the Mo or Si sputtered atoms. Energy step is 1 eV.

around 5 eV. The distribution seems to be linked to the material rather than to the sputtering gas. However we have seen that the level of stress is linked to the sputtering gas. Thus, the study of sputtered particles do not provide a satisfactory explanation for the differences in the levels of stress, as measured.

The number of sputtering ions reflected from the target was then simulated, using the same parameters as for sputtered atoms (see Fig. 6). Whereas the energy distributions of sputtered atoms' curves are globally the same, the energy distribution of backscattered ions noticeably changes from one ion/target couple to another. Nearly none of the Xe reflected by Si has energy higher than 50 eV. Moreover, since their backscattering yield is also very low ($Y_b = 1\%$), their effect can be neglected. Whatever the sputtering gas, Si stress remains the same whereas the corresponding energy distribution seems to differ. This is however not so surprising since the literature always gives the same value of stress for Si (around -1.2 GPa) whatever the deposition process or thickness. On the other hand, the energy distribution of Ar backscattered ions on Mo is in contrast with the other ones. It seems that Ar backscattered ions have a rather flat energy distribution and that even Ar with a high energy (higher than 450 eV) are present. The observed increase of stress level in Mo sputtered by Ar (-2.5 GPa) seems to be due to a process akin to atomic peening by reflected flux of Ar.

Consequently, these results imply that, for our deposition conditions, the bombardment-induced compressive stress may be predominantly produced by the backscattered fraction of incident ions. The sputtered atoms play a secondary role.

4.2. Multilayers

We have seen on 100-nm-thick single layers of Mo and Si that sputtering with Ar or Xe does not lead to the same stress level. The study of multilayers, as they are presented in Fig. 1, aims at showing what happens when the thicknesses of layers decrease and when Mo and Si are superposed. In fact, according to published results and to our own experience, it seems that stress of Si films is constant

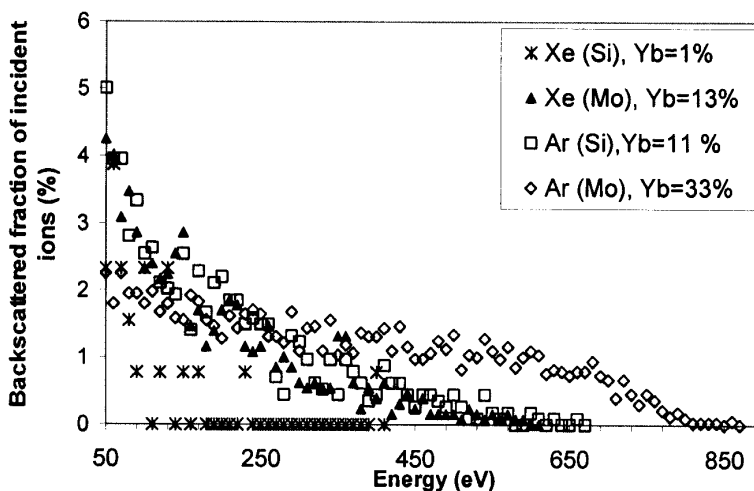


Fig. 6. Energy of Ar or Xe ions after reflexion on Si or Mo target. Y_b is the backscattering yield.

with thickness. Freitag [5] has measured a compressive stress of -1200 MPa nearly constant during growth of a 50-nm Si film. If we assume that Si film stress does not change with the thickness, there is no need in varying it within the multilayer stack. The idea was to keep the Si layer thickness constant (4.1 nm) but to progressively increase the Mo layer thickness from one sample to the other, in order to point out the Mo layer. The chosen structure is composed of 10 Mo/Si bilayers covered by a last Si layer which acts as capping layer. As can be seen in Fig. 4, the level of stress in the multilayers really changes from Ar to Xe sputtering and as Mo thickness increases.

According to numerous published results [2,10,11], Ar-sputtered-Mo/Si multilayers usually present an interface between the two materials, deeper when Mo is sputtered on Si (~ 1 nm) than when Si is sputtered on Mo (~ 0.5 nm). As can be seen in Fig. 4, stress values decrease until a given T_{Mo} value that is not far from the total interface thickness (1.5 nm). What can be suggested is that this first part of the curve illustrates the formation of the interface. Mo sputtered atoms mix with the Si layer allowing the stress to relax in the interface. For thicker T_{Mo} , when the first layer of pure Mo is formed, the stress in the multilayer stack first keeps on decreasing. Mo indeed apparently initially grows in tension as shown in Freitag's experiments [5]. It is suggested by the Volmer-Weber growth mode that the Mo films grow as isolated islands. Grain boundary cohesion induces a tensile stress in the film, as the islands coalesce. Then Mo film stress is supposed to become compressive (after 4 nm in Freitag's experiment). This seems in good agreement with our results as the stress increases for thicker T_{Mo} . The curve is expected to progressively reach the stress value of a thick Mo film.

Another noteworthy point is that the level of stress is really different between Ar and Xe. The Ar curve is always in the compressive stress part of the graph, whereas the Xe curve shows a tensile stress for the multilayers. As the level of stress in Si is the same whatever the sputtering gas (around -800 MPa), this indicates that Mo should be in higher tension in Xe than in Ar. What can be suggested is that, in the case of Xe-sputtering, films grow in the columnar mode coming from the above-mentioned growth mechanism. But, in Ar-sputtering, where Ar-backscattered flux is significant, the tensile state is less pronounced, just as if atomic peening causes the isolated islands to coalesce in a different way.

Additional information can be deduced from X-ray reflectance measurement. As we define the parameter $T_{\text{Mo}} = dt_{\text{Mo}} \times V_{\text{Mo}}$ where dt_{Mo} is the deposition time of Mo and V_{Mo} is the deposition rate of Mo, we can use the parameter $T_{\text{Si}} = dt_{\text{Si}} \times V_{\text{Si}}$ where dt_{Si} is the deposition time of Si and V_{Si} is the deposition rate of Si. The quantity $P = T_{\text{Mo}} + T_{\text{Si}}$ corresponds to the real quantity of molybdenum and silicon that was deposited, expressed in length units. The period p deduced from X-ray reflectance measurements should be slightly different if a contraction occurs during the multilayer formation. The contraction calculated as $P - p$ is shown in Fig. 7. It is assumed that it is intermixing and reaction at the interface of Mo/Si multilayers that lead to a volume contraction and consequently to a contraction of the bilayer period. The silicide resulting from chemical diffusion between the layers is generally supposed to be MoSi_2 . The silicide density is higher than that of an amorphous phase composed by $\text{Mo} + 2\text{Si}$. We calculated that the contraction induced by this difference of density is 28%. In a usual multilayer, the bilayer period is 7 nm and the interface formed is around 1.5 nm; 1.5 nm is in fact the thickness of the interface after contraction. In that case, we calculate that the total period contraction is 0.5 nm. This contraction value is consistent with the one found in Xe-sputtering. The Ar-contraction however is much more significant (see in Fig. 7). Since the difference between Ar- and Xe-sputtering deals with atomic peening, this suggests that Ar-contraction is not only due to silicide formation, but

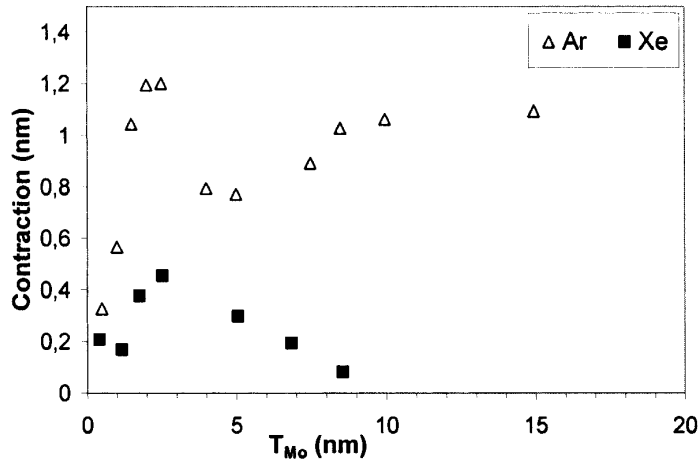


Fig. 7. Contraction of Mo/Si multilayers by Ar- and Xe-sputtering versus Mo film thickness T_{Mo} ($T_{Mo} = dt_{Mo} \times V_{Mo}$ cf. Eq. (3)).

may also result from a second mechanism which would enhance the contraction. A backsputtering of the depositing coating by the backscattered Ar can be conceivable.

5. Conclusion

The stress behaviour of 100-nm-thick Mo and Si single layers, and Mo/Si multilayers has been observed. A low-stress-state condition with Xe-sputtering has been found for Mo single layers. It is explained in terms of atomic peening by Ar-backscattered flux. In the case of Mo/Si multilayers, a modulation of stress has been observed as the thickness of Mo from a multilayer to another increases. Compressive stress first decreases, until a given value of Mo thickness, and then increases. For the increasing part, two steps are considered. The stress is first relaxed in the interface. Then Mo grows in tension in a columnar mode until the isolated islands coalesce. Furthermore a difference in level of stress in multilayers sputtered by Ar or Xe has been highlighted. We suggest that Ar-backscattered flux induces changes in the column growth. Additional information has been given by the study of multilayer period contraction. Xe-multilayer contraction is consistent with the contraction of 0.5 nm we calculated. On the other hand, Ar-multilayer contraction is more significant, resulting in an additional mechanism, namely a backscattering by the reflected flux of Ar. It is expected that HRTEM images from multilayer samples and additional TRIM calculations will help to go further in the understanding of these results.

Acknowledgements

The authors wish to thank G. Rolland and D. Muyard (LETI/CEA.G-DTS) for the grazing X-ray reflectance measurements and F. Pierre (LETI/CEA.G-DTS) for the RBS results.

References

- [1] R.R. Kola et al., Stress relaxation in Mo/Si multilayer structures, *Appl. Phys. Lett.* 60 (25) (1992) 3120–3122.
- [2] M.E. Kassner, F.J. Weber, J. Koike, R.S. Rosen, Structural and residual stress changes in Mo/a-Si multilayer thin films with annealing, *J. Mater. Sci.* 31 (1996) 2291–2299.
- [3] P.B. Mirkarimi, Stress, reflectance, and temporal stability of sputter-deposited Mo/Si and Mo/Be multilayer films for EUV lithography, *Opt. Eng.* 38 (7) (1999) 1246–1259.
- [4] T.D. Nguyen, C. Kahn-Malek, J.H. Underwood, Achievement of low stress in Mo/Si multilayer mirrors, in: *OSA Proceedings on EUV*, Vol. 23, 1994.
- [5] J.M. Freitag, B.M. Clemens, Stress evolution in Mo/Si multilayers for high-reflectivity extreme ultraviolet mirrors, *Appl. Phys. Lett.* 73 (1) (1998) 43–45.
- [6] G.G. Stoney, The tension of metallic films deposited by electrolysis, *Proc. R. Soc. Lond.* (1909) 172–175.
- [7] J.A. Thornton, The influence of bias sputter parameters on thick copper coatings deposited using a hollow cathode, *Thin Solid Films* 40 (1977) 335–344.
- [8] F.M. D’Heurle, J.M.E. Harper, Note on the origin of intrinsic stresses in films deposited via evaporation and sputtering, *Thin Solid Films* 171 (1989) 81–92.
- [9] SRIM-98, version 98,01.
- [10] D.G. Stearns, M.B. Stearns, Y. Cheng, J.H. Stith, N.M. Ceglio, Thermally induced structural modification of Mo–Si multilayers, *J. Appl. Phys.* 67 (5) (1990) 2415–2427.
- [11] D.G. Stearns, S.P. Vernon, R.S. Rosen, Fabrication of high-reflectance Mo/Si multilayer mirrors by planar magnetron sputtering, *J. Vac. Sci. Technol. A* 9 (5) (1991) 2662–2669.