Mo nanocrystals nucleation in Mo/B4C/Si multilayers for EUV mirrors

A. Patelli1, J. Ravagnan1, V. Rigato1, G. Salmaso1, N. Carvalho3, J. Th. De Hosson3

1 INFN, Laboratori Nazionali di Legnaro, 2 Dip. Ingegneria dell’Informazione – Università di Padova, I. 3 Netherlands Institute for Metals Research, Dept. Of Applied Physics – Univ. of Groeningen (NL)

I. INTRODUCTION

Mo/Si multilayer mirrors have been used in the last decade in different fields such as astrophysics [1] and lithography [2]. In the last years it has been shown that the use of a very thin boron carbide interlayer between Si and Mo can increase the mirror reflectance to values higher than 70% [3]. This reflectance increase is principally due to the reduced thickness of the Mo and Si interdiffused layer, in particular of the Mo-on-Si interface. As a matter of fact boron carbide acts as a diffusion barrier between the layers leading to a sharper change in refractive index. On the other hand the presence of such an interlayer can influence the growth of the Si and Mo layers and in particular the crystal nano-structure of Mo. This particular aspect is highly relevant since the Mo crystals play a central role in the interface roughness development in the multilayer structure. In particular near the transition from amorphous to crystalline phase an evident increase in roughness has been shown in Mo/Si structures [4]. In the present report the attention has been focused on the study of the dependency of the critical amount of Mo (in Mo/B4C/Si/B4C multilayers) that must be deposited before Mo nano-crystals start to form, as a function of the deposition parameters (in particular of the ion Ar energy of bombardment).

II. EXPERIMENTAL

The experimental apparatus used at LNL for producing the X-Ray/EUV mirrors consists of three planar 2” UHV type II unbalanced magnetron sputter sources and a biasable sample holder. The deposition process is static and in a sputtering up-ward configuration. The deposition process and apparatus is described in more detail in [5].

Plasma diagnostics has been performed close to the substrate by means of a cylindrical Langmuir probe (Scientific Systems SmartProbe™) in order to know the Ar+ energy and bombardment flux of the growing layers.

For the analysis of Si, Mo and Ar, RBS measurements have been performed using the HVEC 2.5 MV and CN 7.0 MV Van de Graaff accelerators at the LNL – INFN. 2.2 MeV α-beams at the scattering angle of 170° has typically been used. The stoichiometry of boron carbide has been obtained by α-1.85 MeV RBS analysis at the scattering angle of 165° where both C and B are essentially constant [6,7] and by nuclear reaction analysis, using 11B(p,α)8Be [8], 11B(d,α)nBe and 12C(d,p)13C reactions.

III. RESULTS

For the investigation of the Mo nucleation film thickness threshold two samples with different ion energies bombardment conditions (about 24eV and 74eV) have been produced. The multilayers have been purposely designed for High Resolution TEM analyses with graded Mo layers thickness. The nominal Mo layer thickness has been varied starting from the Si(100) substrate from 1.7nm to 3.5 nm and than down to 1.7nm in steps of 0.3 nm to check that Mo crystallisation is not induced by stress or temperature effects. For every Mo thickness a stack of three Si/Mo bi-layers has been produced to increase the statistics. The Si layer between the Mo layers had a constant thickness of 4.4nm (22·1015at/cm2). At every Mo and Si interface a 0.4nm (4.0·1015at/cm2) B4C layer has been introduced. As a check for composition and thickness all the Mo/B4C/Si/B4C multilayers deposited were characterised by Ion Beam Analysis. The analyses performed on thick boron carbide films (~1500Å) and on the Mo/B4C/Si/B4C multilayers reveal a boron/carbon ratio of 4.8±0.2, while the oxygen and nitrogen contents are lower than 1at%. The bias applied to the samples during the growth doesn’t influence the stoichiometry of the carbide layers.

Plasma diagnostics, performed close to sample surface at the ground potential, indicates a plasma potential Vp = 24±1V, electron temperature Te = 4.3±0.1eV and the ion flux on the sample surface of about 4.0±0.2·1014at/cm²s. Since the deposition rates of B4C, Si and Mo are of about 2.7·1014at/cm²s, the estimated ion-to-atom flux ratio on the growing surface is of about 1.5. Negative biases applied to the sample don’t influence the plasma characteristics.

From the TEM analysis in bright and dark field imaging (Fig. 1), it can be observed that for the Mo layers with a nominal 20Å thickness are amorphous. The nano-crystal formation appears in dark field by the presence of the white spot in Mo layers that are obtained by selecting the electron diffraction peak due to the Mo(110) reflection and in the bright field by the presence of the darker regions and moiré patterns. For both the growth conditions it can be clearly observed a threshold thickness for molybdenum nano-crystals formations at about 25Å (for the 24eV ion energy).
bombardment) and at about 23Å for the 74eV bombardment. In any case what is interesting to observe is that the presence of the thin boron carbide layer seems to increase the amount of molybdenum that must be deposited before crystallisation takes place relative to conventional Mo/Si multilayers. As a matter of fact in Mo/Si multilayers the transition thickness has been found to be about 20 Å. It has been explained by the presence of the intermixed Si-Mo interface: the nucleation of Mo crystals is thought to begin at Si concentrations lower than solubility limit of 7 at%[4]. The higher Mo thickness in our case may be due to a thicker interface characterized by a deeper concentration profile of boron and carbon within the Mo layer. As a confirmation of this hypothesis, in the electron diffraction patterns obtained in cross section it can be observed a ring at about 35° that in the Mo/Si multilayer structure have never been observed and that can be attributed to the formation of a Mo-B-C phase. This signal can be observed also in X-ray analysis, not shown here [5]. No stable phase between boron and silicon should be expected since, by phase diagrams, B-Mo compounds are thermodynamically promoted [9]. As a further confirmation, by bright field HRTEM images of the molybdenum layers it can be highlighted the presence of dark interlayer regions between Mo and Si layer that can be attributed to the presence of a mixed Mo-B-C compound. The thickness of this interface is different for the two different ion bombardment conditions. In fact, the increase in the ion energy produces a bigger mixing of the layers, increasing the thickness of the interfaces from about 0.4nm (24eV) to about 1.0nm (74eV).

On the other hand also the Mo grains crystal nano-structure is really influenced by the ion bombardment. As it can be clearly observed from Fig 1, at low energy bombardment the crystallisation starts smoothly starting from about 25Å: here more than a half of the Mo still remains TEM amorphous. At 28Å the layer appears mostly crystallised. On the contrary at higher ion energy bombardment the crystallisation appears to be more abrupt. This effect can be attributed to a higher degree of crystallisation induced by a higher surface mobility of Mo atoms during the film growth.

IV. CONCLUSIONS

The results obtained show that the introduction of a very small quantity of B,C at the Si/Mo interfaces besides determining sharper and more stable interfaces, affects the molybdenum crystal nano-structure. The nucleation of the Mo grains has been shown to appear at thicker Mo thickness between 23 and 25Å for multilayers prepared at different ion energy bombardment (24eV and 74eV) than in the case of standard Mo/Si multilayer. Electron diffraction patterns and HRTEM images reveal the presence of different Mo-B-C phases. On the other hand the most evident effect of the bombardment energy is the enhanced nano-crystal preferred orientation and the sharper evolution of the crystallization at the higher energy.

1 Delaboudiniére et al., SPIE Proceedings 1742, (1992) 296