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Ion beam modification of Mo–Si multilayer systems for X-ray reflection

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The influence of the impact of 300 as well as 800 eV Ar^+ ions on the surface and interface roughness of a bilayer of Mo on top of Si is reported. The materials are deposited by electron beam evaporation. X-ray reflection and Auger electron spectroscopy are used as diagnostic tools. After initial smoothing of the Mo surface, roughening is observed after a dose of 2×10^{19} Ar^+ ions/cm^2 for both ion energies. Etching with 800 eV ions improves the surface smoothness a factor of two more than using 300 eV ions. For 300 eV Ar^+ ions interface mixing is observed at a Mo film thickness < 2.7 nm; 800 eV ions cause interface mixing at a film thickness < 4 nm.

1. Introduction

Reflection of X-rays by a multilayer coating is based on interference of radiation reflected by each interface. Multilayer coatings applied for this purpose consist usually of a low mass (carbon, boron or silicon) and a high mass (metals) component. The roughness of the interfaces reduces the reflection of the stack [1]. Interface roughness can be caused by interdiffusion of the materials used, which is a slow process. One material can grow on top of another substrate material in the form of islands. This results in a rough top surface of the deposited film, which is the next interface [2]. It has previously been demonstrated [3,4,7] that ion etching with low energy ions improves the smoothness of a surface. An increase in the reflection of X-rays by a factor of 3 has been observed after etching each tungsten layer of a W/C multilayer with 10 periods of 2.7 nm by 200 eV Ar^+ ions [5].

As Mo/Si multilayers are of interest for X-ray lithography purposes, we investigated the possibility of improving the reflectivity of a Mo/Si multilayer by ion beam etching. We report on the effect of ion bombardment on the surface roughness of a Mo film and on intermixing of the Mo/Si interface.

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2. Experimental

The experiments are done in a system with an ultimate vacuum of 10^{-8} Pa. We deposited the materials by electron beam evaporation in a working pressure of 10^{-6} Pa. For ion beam etching the system is provided with a differentially pumped Kaufman ion source. During ion bombardment the residual argon pressure was 10^{-3} Pa. We used interference between reflections of N$K\alpha$ radiation by the interfaces to measure in real time the thickness of the layers during deposition as well as during etching [3,4]. The interference periodicity was 2.7 nm. This technique gives also information about the relative changes in the surface roughness [1] and in the roughness changes of deeper interfaces induced by ion beam intermixing.

For the determination of the chemical composition of the first monolayers during deposition and ion beam etching we applied Auger electron spectroscopy (AES). The retarding field analyser we used has an energy resolution of 0.3% and is described elsewhere [6]. Si(111) wafers were used as substrates, from which we did not remove the native oxide layer.

We produced some preliminary Mo/Si samples for transmission electron microscopy (TEM), to investigate the applicability of this technique to obtain additional information about the growth and the etching effects. The samples consisted of 5.4 nm Si, grown on rock-salt samples, followed by Mo films of various thicknesses and treatments. The samples were sealed by a 15 nm thick C film, to prevent atmospheric influences during transport through air.

With the Monte Carlo program TRIM [9] as well as the analytical program VG SUSPRE [10] we obtained an indication of the maximum penetration depth of the ions and the etch rate.

3. Results and discussion

The results of our investigations are presented in figs. 1 to 5. We deposited 2.7 nm Si on top of the substrate, with another 10.8 nm Mo on top of the Si film. This was followed by an etch procedure, using 30 $\mu A/cm^2$ Ar^+ ions of 300 or 800 eV under an angle of 45°. Fig. 1a shows the reflection of N$K\alpha$ radiation during deposition and etching with 300 eV ions. The initial 2.7 nm Si is represented by the first interference peak, caused by reflection from the Si/SiO_2 interface and the top surface. The next four interference peak (2–5) represent the growth of 10.8 nm Mo on top. The decrease of the average reflectivity can be ascribed to an increasing roughness of the Mo surface [1]. The increased average reflection represented by the higher interference peak (5′) during removal of the first 2.7 nm Mo by 300 eV Ar^+ ion bombardment is an indication of a reduced surface roughness. The decreasing amplitude of the next interference peak (4′, represent-

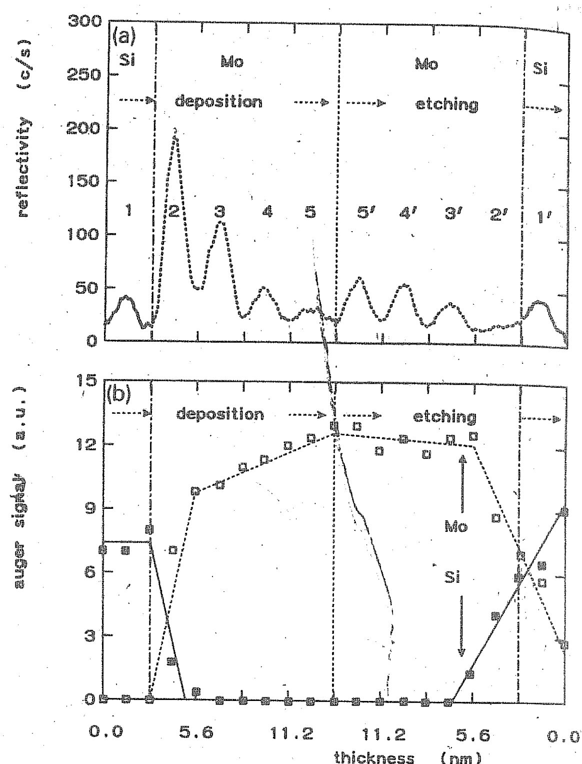
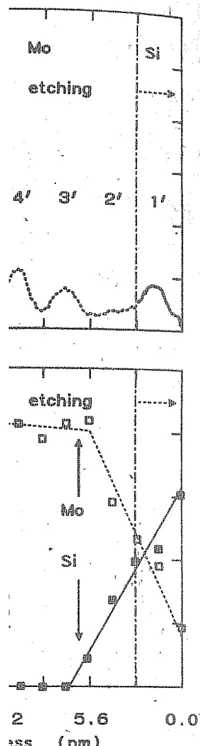


Fig. 1. (a) Reflectivity of N$K\alpha$ radiation as a function of layer thickness during deposition of 2.7 nm Si and 10.5 nm Mo on top, followed by etching with Ar^+ ions of 300 eV. (b) Auger MNN peak of Mo and the LMM peak of Si as a function of layer thickness during deposition of 2.7 nm Si and 10.8 nm Mo on top, followed by etching with Ar^+ ions of 300 eV.



ing the Mo film between 5.4 and 8.1 nm) cannot be explained by ion beam mixing of the Mo/Si interface, according to the maximum penetration depth < 2.5 nm as obtained by TRIM calculations. We propose an increasing surface roughness. The disappearance of the interference peak (2′) which represents 2.7 nm Mo on top of 2.7 nm Si is caused by interface mixing. It is striking that the peak (1′) representing 2.7 nm Si does not disappear, as also intermixing of the Si/SiO_2 interface can be expected. The explanation is an increasing density of the Si layer due to intermixing with Mo which compensates reflection losses due to intermixing of the Si/SiO_2 interface. The height of peak 1′ does not only depend on the density of the Si film and the roughness of the Si/SiO_2 interface due to intermixing. It should also be taken into account that intermixing of Mo and amorphous Si and SiO_2 will reduce the crystallinity effect of surface roughening and lead again to surface smoothing. A similar effect was recently observed in sputter profiling of Cr/NiO multilayers by Hofmann [11].

From the distance between the maxima of the interference features in relation to the time we calculated the etch rate, resulting in ~ 0.3 Mo atoms/incoming ion. VG SUSPRE calculations result in 0.228 atoms/ion.

Fig. 1b shows the Auger MNN peak of Mo and the Auger Si LMM peak in various stages of layer growth and etching by 300 eV Ar^+ ions. We were not able to detect peak shifts from which we might have concluded about silicide formation. The Si LMM signal is roughly reduced to 20% after 1.3 nm and disappears after deposition of 4 nm Mo. For 90 eV electrons ($\sim$ Si LMM energy), the average escape depth is on the order of 0.5 nm [8]. For an exponential attenuation we can calculate that an overlayer of 1.3 nm reduces the signal to $\sim 1\%$, which we estimate to be the sensitivity of our analyser. From this we can conclude that 1.3 nm Mo is not a homogeneously closed film, but that islands are formed.

From the very onset of the Si LMM signal during ion etching we cannot conclude that ion-beam-induced intermixing takes place. However, the Si LMM signal at a remaining Mo thickness of 2.7 nm in the etch procedure is roughly the same as for 1.3 nm after growth. For 1.3 nm this signal is a factor of ~ 2.5 higher than for 1.3 nm during growth. Since the maximum penetration depth of argon ions of 300 eV is roughly 2.5 nm according to TRIM calculations, we expect that this difference in the Si LMM signal is caused by intermixing. We roughly estimate a penetration depth of 3 nm for 300 eV Ar^+ ions.

We ascribe the discontinuity at 2.7 nm in the Mo MNN curve as a function of layer thickness during deposition to the formation of Mo islands which initially does not result in a closed film, as discussed before. Intermixing is clearly demonstrated by the presence of Mo in the Si overlayer, confirming our idea of the influence of an increasing layer density on the reflectivity, as stated before. It is striking that also after removing all Si

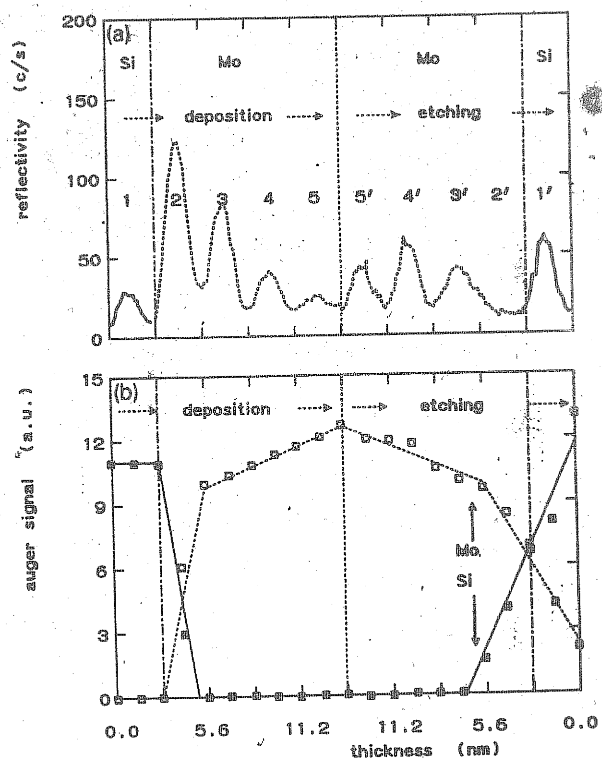


Fig. 2. (a) Reflectivity of N Kα radiation as a function of layer thickness during deposition of 2.7 nm Si and 10.5 nm Mo on top, followed by etching with Ar^+ ions of 800 eV. (b) Auger MNN peak of Mo and the LMM peak of Si as a function of layer thickness during deposition of 2.7 nm Si and 10.8 nm Mo on top, followed by etching with Ar^+ ions of 800 eV.

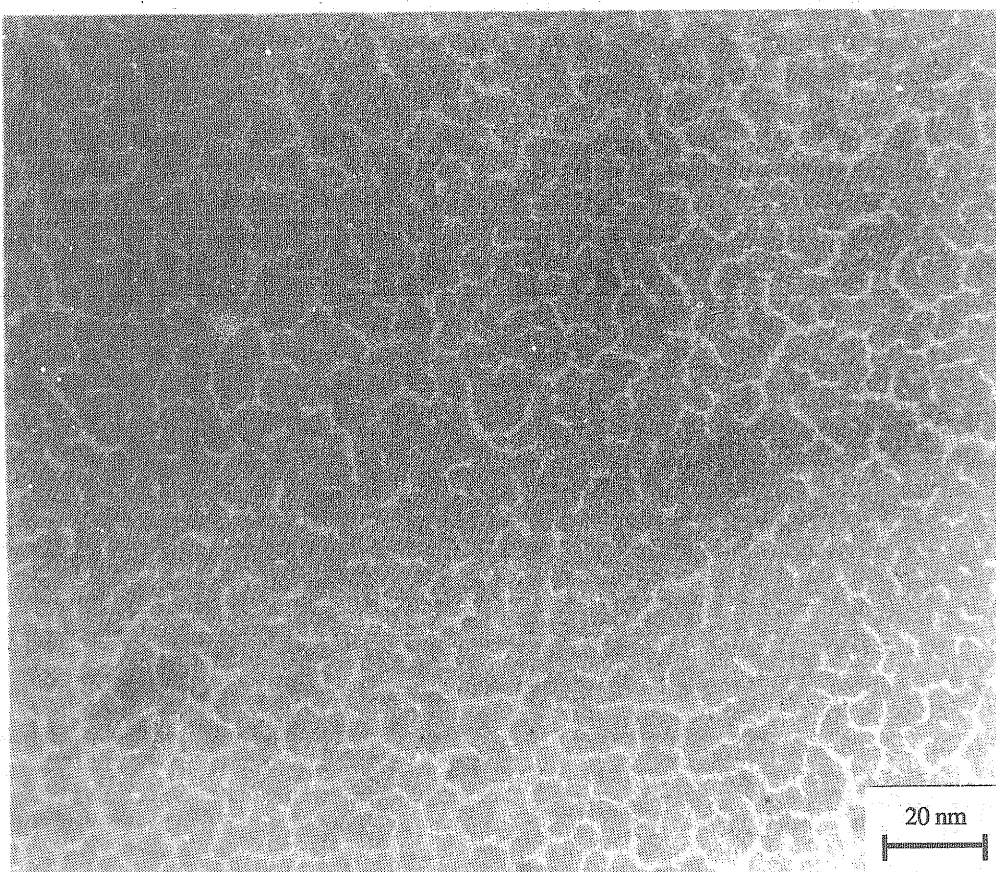


Fig. 3. Bright-field TEM photograph of 5.4 nm Si with 2.7 nm Mo on top.

on top of the SiO_2 substrate, Mo can still be observed. This can be explained by selective sputtering of Si in competition with recoil implantation of Mo.

Fig. 2a shows the growth of the same layer pair as in fig. 1a, however etching is performed using 800 eV Ar^+ ions. The etch rate is calculated as mentioned before and results in ~ 0.6 Mo atoms/incoming ion. According to VG SUSPRE calculations this would be 0.582 atom/ion. The reflectivity is higher for the two interference peaks (5′ and 4′) (factor of 2) compared to etching by 300 eV ions, before roughening takes place. If we compare the etch rate for the two ion energies, we can conclude that roughening occurs at the same ion dose, being $\sim 6 \times 10^{19}$ ions/cm^2. The shape of the reflectivity curve during sputtering, for Mo thicknesses smaller than 4 nm suggests that intermixing occurs at a larger depth than for 300 eV ions. From this we can conclude that the penetration depth of 800 eV Ar^+ ions in a Mo layer is < 4 nm. According to TRIM calculations the maximum penetration depth should be 4.5 nm. The high peak, representing the initial Si film (1′) demonstrates, even more clearly than for 300 eV ions, the density increase due to intermixing with Mo as mentioned before. However, from a larger penetration depth on the ions more intermixing of the Si/SiO_2 interface and a smaller interference peak would be expected. Also the AES curves in fig. 2b cannot answer this question. For that, more accurately quantified data are needed.

We made three TEM samples. The first con-

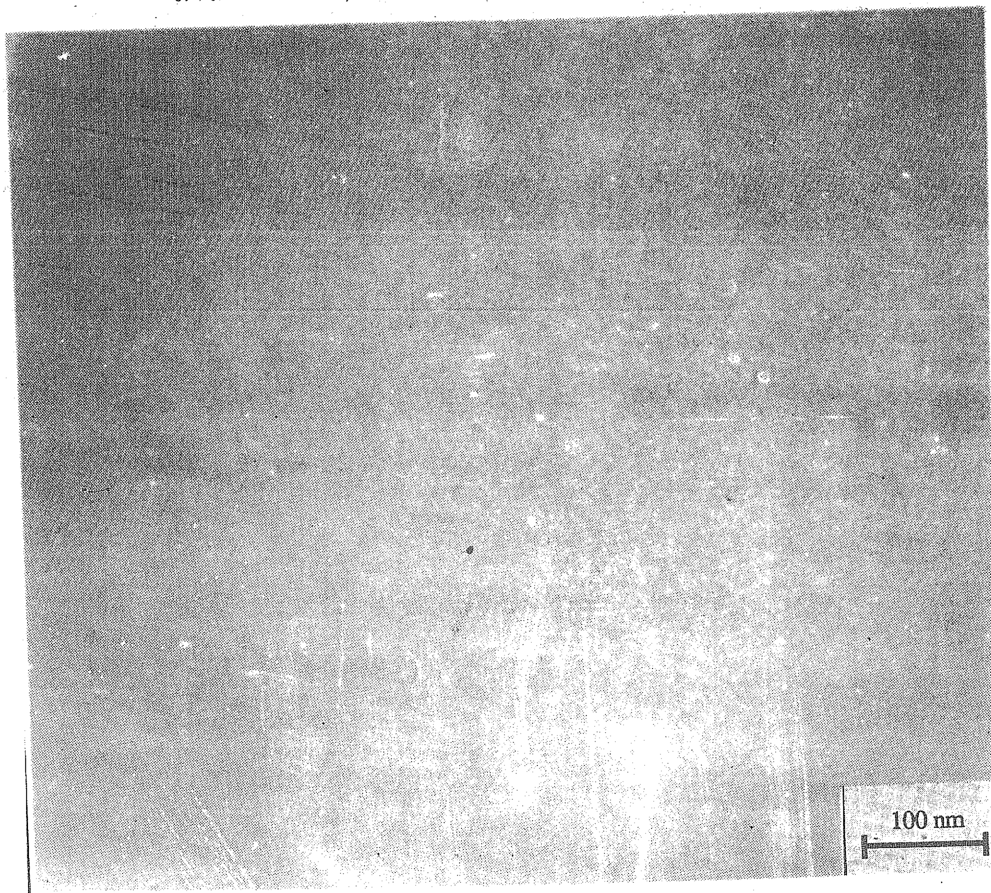


Fig. 4. Dark-field TEM photograph of 5.4 nm Si with 2.7 nm Mo on top, obtained by growing 5.4 nm Mo followed by an etch procedure with 300 eV Ar^+ ions, down to 2.7 nm.

sisted of 5.4 nm Si with 2.7 nm Mo grown on top, covered by 15 nm carbon to prevent atmospheric influence during transport to the microscope.

Fig. 3 shows a bright-field picture, which confirms the island growth as suggested before. In the next sample 5.4 nm Mo is grown on 5.4 nm Si, after which 2.7 nm Mo is removed by 300 eV Ar^+ ions. So the final Mo film thickness is the same as for the first sample. A closed layer consisting of small crystallites with a size of ~ 8 nm can be observed in fig. 4, presenting a TEM dark-field photograph. Fig. 5 shows a sample of 5.4 nm Mo on 5.4 nm Si, obtained by deposition of 10.8 nm Mo of which 5.4 nm is removed by sputtering with 300 eV Ar^+ ions. We observe clearly the formation of larger Mo crystals with a size of ~ 18 nm. A possible solution of roughening after initial smoothing is the formation larger crystals in the Mo film induced by ion bombardment. Due to crystal orientation-dependent preferential sputtering, the roughness increases. Finally, TEM diffraction patterns have not revealed the formation of any silicide. A more through investigation on a range of TEM samples is currently under investigation.

We propose a model in which Mo grows as islands on a Si surface. After formation of a closed layer the surface roughness of Mo increases further. Ion bombardment removes preferentially the tops of the roughness features, which results in a reduction of the roughness. After a certain ion dose ($\sim 6 \times 10^{19}$) the formation of larger crystals in the Mo film takes place. Due to preferential sputtering of certain crystal

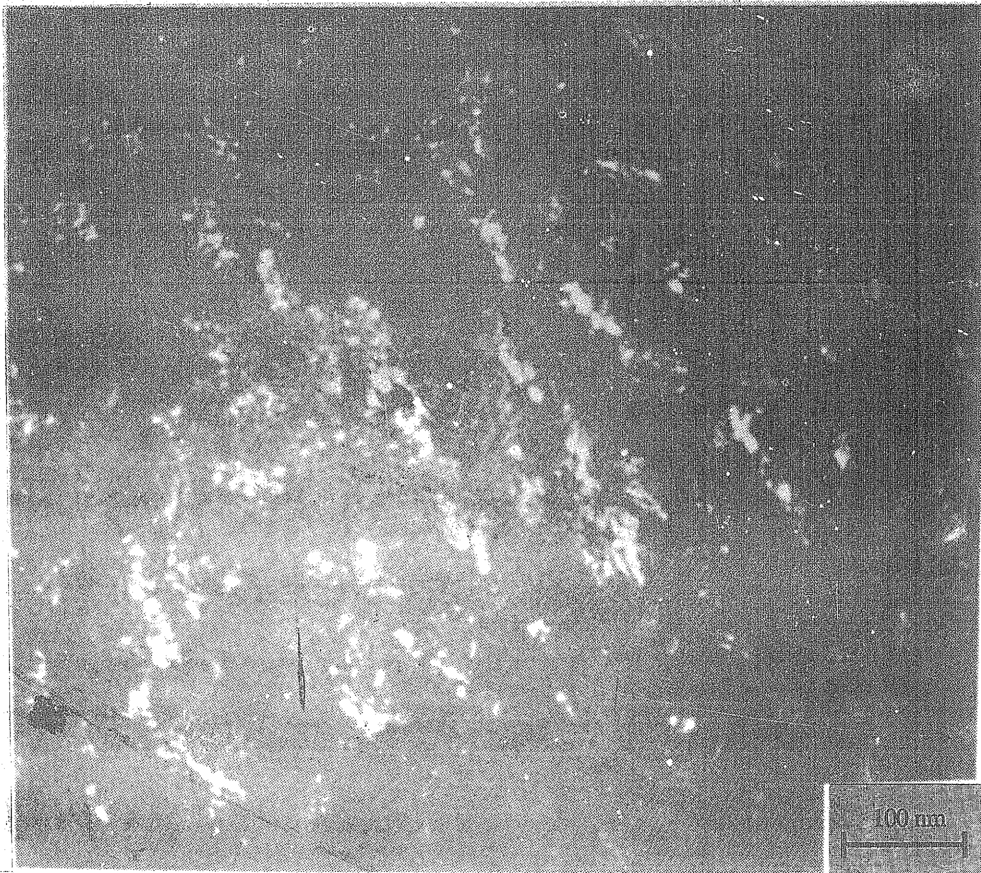


Fig. 5. Dark-field TEM photograph of 5.4 nm Si with 5.4 nm Mo on top, obtained by growing 10.8 nm Mo followed by an etch procedure with 300 eV Ar^+ ions, down to 5.4 nm.

orientations, the surface roughness increases again.

4. Conclusions

In conclusion we summarize:
(a) Sputtering by ions reduces the roughness of a vapour-deposited Mo surface.
(b) Smoothing appears to be limited by the formation of larger crystals, after which roughness increases due to preferential sputtering.
(c) Formation of larger crystals in the Mo film is observed after a dose of $\sim 6 \times 10^{19}$ ions for both ion energies.
(d) For optimum smoothing the ion mass as well as the energy has to be chosen properly, in order to optimize the etch rate with penetration depth as small as possible in order to prevent interface mixing.

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