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Electron-Irradiation-Induced Amorphization in Mo/Si Nano-Multilayer Material

Etsuko Shioya[1, *], Takanori Suda[1], Seiichi Watanabe[1], Somei Ohnuki[1], Masahiko Ishino[2], Osamu Yoda[2], Hiroaki Abe[3] and Fritz Phillip[4]

[1]*Materials Science Division, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan*
[2]*Kansai Research Establishment, Japan Atomic Energy Research Institute, Kizu 619-0215, Japan*
[3]*Takasaki Research Establishment, Japan Atomic Energy Research Institute, Takasaki 370-1292, Japan*
[4]*Max-Planck-Institut fur Metallforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

In the Mo–Si system, there are three typical intermetallic compounds. In order to get insight into the phase stability under irradiation, interface structure and non-equilibrium phase formation in multilayer materials with several nanometers scale were investigated by means of high-voltage electron microscope. The initial structure was composed of crystalline Mo and amorphous Si layers, and transition layer existed at the interfaces. The thickness of transition layers is thicker at the Mo-on-Si than at the Si-on-Mo interface. While those structures were basically stable after thermal annealing up to 773 K, two types of amorphous layers developed during electron irradiation at room temperature: one is an amorphous-Si layer and the other is a Mo–Si mixing layer. And the radiation-induced amorphization was accompanied by anomalous shrinkage in the thickness of layers. It is suggested that those phenomena are related to non-equilibrium phase formation and biased diffusion process during irradiation.

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1. Introduction

Multilayer materials with the alternation of heavy and light elements in nano-scale have been used for soft X-ray optical elements in physics and astronomy.[1,2)] Especially Mo–Si multilayers are recognized as the material combination providing the largest theoretical reflectivity in multilayered mirrors working in the extreme ultraviolet (EUV) region at around 13 nm wavelength. The main reason to the decrease in reflectivity comes from the roughness of the interface and the heterogeneity of the period.[3)] High-resolution transmission electron microscopy (HRTEM)[4)] reveals that the Mo and Si layers are separated by interlayers composed of an amorphous mixture of Mo and Si. The nature of the interfaces in Mo–Si multilayers is of considerable practical interests, because they reduce the reflectivity of the coating by several percent. An important material issue is the stability of such nano-scale structure. For comparing with bulk materials, atomic diffusion in the multilayer materials should be enhanced by high-energy particle irradiation. Therefore, the stability of nano-multilayer can be studied by thermal annealing and high energy particle irradiation.

In the Mo–Si system, there are three typical intermetallic compounds of $MoSi_2$, Mo_5Si_3 and Mo_3Si, which are different in crystal structure and composition, but the phase stability under irradiation is not surveyed in nano-scale. In this study, we focused on the non-equilibrium phase formation and diffusion process in multilayer materials by using high-resolution microscopy. We performed the electron irradiation to study the electron-irradiation-induced amorphization.

*Graduate Student, Hokkaido University.

2. Experimental Procedure

Multilayer samples of alternation of Mo and Si were prepared by ion beam sputtering method on Si substrates.[5)] The thickness of each layer with typically less than 10 nm and the total thickness with 100 nm were selected for having nominal compositions of intermetallic compounds in the Mo–Si system.

TEM specimens were prepared by the conventional cross-sectional method using ion-thinning technique. Thinning was performed in a Gatan Dual Ion Mill with a beam consisting of Ar ions. Gun voltage and current were 4 kV and 0.4 mA per gun. The cross-sectional observation was performed with 200 kV transition electron microscope (2000FX), and the high-resolution electron microscope (JEM-2010F). "*In-situ*" observation of microstructure during electron-irradiation was carried out in a 1250 kV HVEM (JEM-ARM 1300) with a dose rate of $1 \times 10^{20}\,\mathrm{cm^{-2}{\cdot}s^{-1}}$ at room temperature.

3. Results and Discussion

3.1 Multilayer structure

Figure 1 shows the cross-sectional structure in the specimen, Mo_3Si. The dark and bright contrasts are corresponding to Mo layers with thickness of 7.1 nm and Si layers with thickness of 2.2 nm, respectively. Selected area diffraction patterns (SAD) show preferential orientation ⟨110⟩ in Mo crystal, and superlattice diffraction comes from Mo layers.

Figure 2 shows lattice image of Mo–Si multilayer material, where Mo layers are poly-crystalline and show a preferential orientation of ⟨110⟩ direction, while Si layers are amorphous structure. It can be noted that extra layers (here called transition layers) exist at each interface about 1 nm in thickness. The thickness of these layers are thicker at the Mo-on-Si than

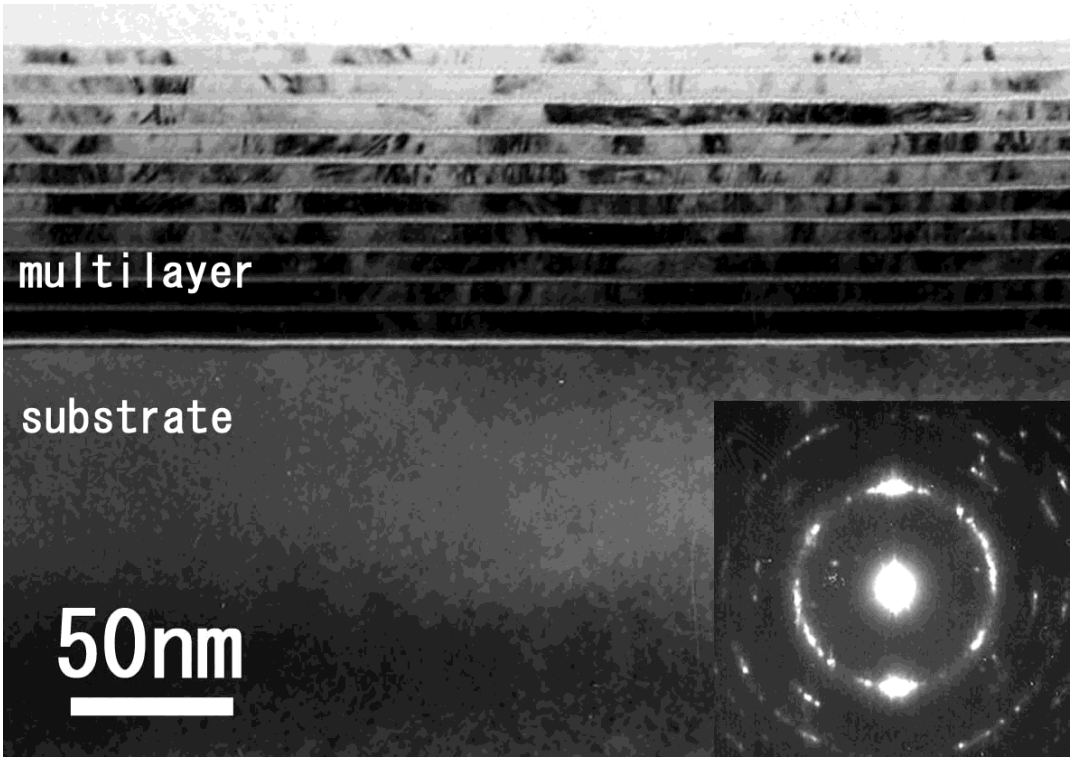

Fig. 1 The cross-sectional TEM image of the Mo–Si multilayer.

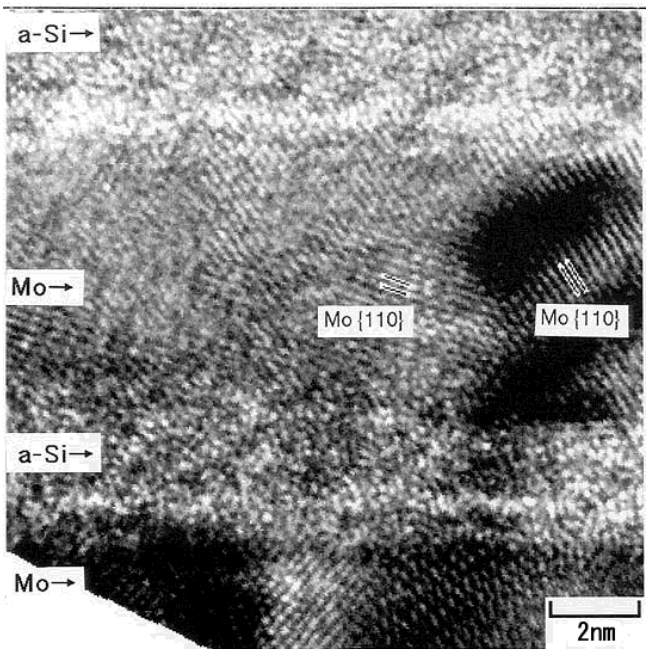

Fig. 2 The high-resolution TEM image from Fig. 1.

at the Si-on-Mo interface.[6,7] A possible reason for the formation of the transition layer is physical mixing or chemical combination during the sputter deposition process.

3.2 Structural change under electron-irradiation

"*In-situ*" high-resolution observation was performed under electron-irradiation at an ambient temperature. Figure 3 shows an example of mixing process under electron irradiation. Although periodic structures were basically stable after thermal annealing up to 773 K, we can observe that c-Mo layers mixed with a-Si layers, and all of the area turned to amorphous structure with homogeneous contrast after irradiation. It should be noted that the position of the layers shifted to the substrate side after irradiation, which means the shrinkage due to irradiation. The thickness of the transition layer increased with decreasing in the specimen thickness, which means the transition layer is sensitive to the damage for ion-thinning.

Figure 4 shows the shrinkage as a function of irradiation time. The shrinkage finished very quickly and the reduction rate was almost 10%. In general, amorphization induced an increase in volume of the samples. It seems that this phenomenon related to the mixing process between the larger size atom and the smaller size atom. In Ti/TiC multilayer, the value of the interdiffusion coefficient is higher by many orders of magnitude than expected one from extrapolation of high temperature bulk data.[8]

Figure 5 shows a high-resolution image from Fig. 3. Two types of amorphous layers were observable with dark contrast and with bright contrast. The mean distance of dots in the dark area is smaller than in the bright area, which means that the atomic density in the mixed layer should be high comparing with bright area of amorphous Si. Those phenomena under irradiation could be related to the atomic behavior in the system composed of heavy and light elements.

4. Conclusion

Microstructure and amorphization process of Mo–Si multilayers in nano-scale were investigated by cross-sectional TEM and in-situ observation under electron-irradiation.

(1) The multilayer structure was composed of c-Mo and

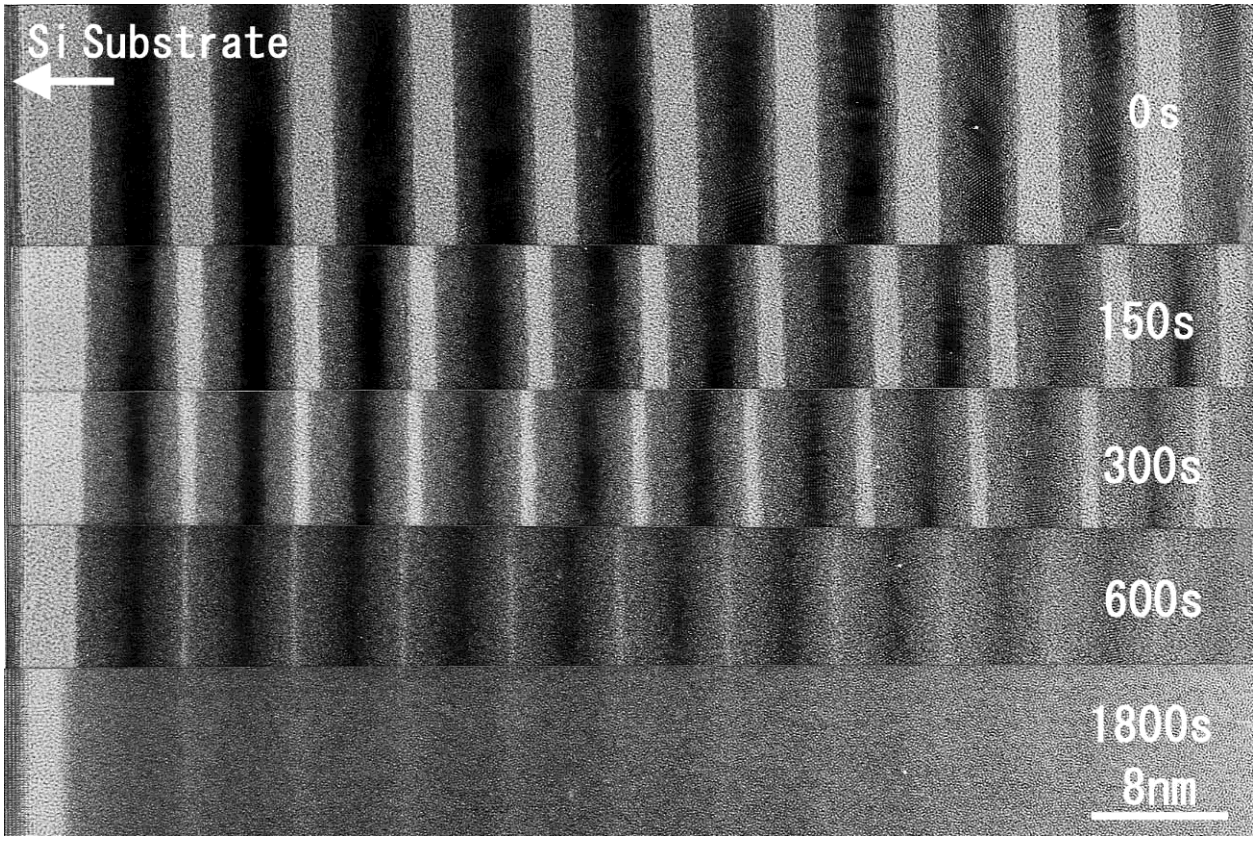

Fig. 3 *In-situ* observation of the multilayer during electron-irradiation.

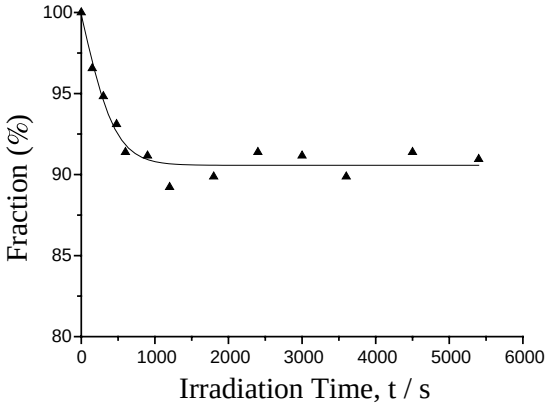

Fig. 4 The relation between the fraction of layer thickness and irradiation time.

a-Si in several nanometer levels. The transition layers of amorphous structure exist at each interface in as-deposited sample.

(2) Electron-irradiation enhanced to extend rapidly the transition layer, which is an amorphous structure with dark contrast.

(3) Extreme shrinkage of 10% was observed during irradiation, which means the amorphous phase has high density structure as similar as an ideal glass.

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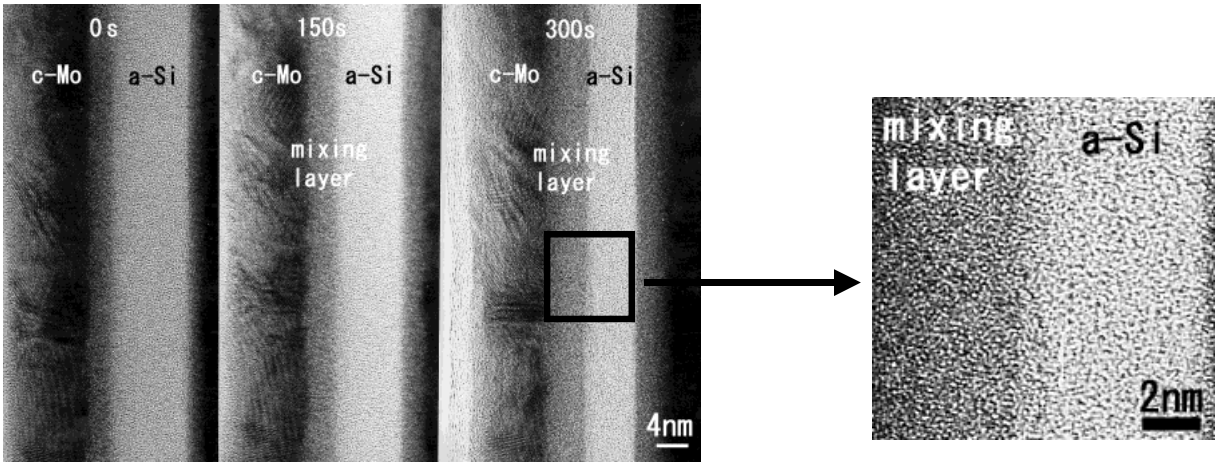

Fig. 5 Two types of amorphous layers.

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