Article ID: 1004-924X(2001)05-0446-05

Thermal Diffusion of Si Atoms at the Interface of Mo/Si Bilayers Studied with a Soft X-ray Emission Microscope

Yoshitaka SHITANI* , Noboru MIYATA[1], Mihiro YANAGIHARA[2], Makoto WATANABE[3]

(Institute of Multidisciplinary Research for Advanced Materials, Tokoku University
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan)
[1]*Phone:* +81-22-217-5377, *fax:* +81-22-217-5379, *e-mail: miyata@tagen.tohoku.ac.jp*
[2]*phone:* +81-22-217-5377, *fax:* +81-22-217-5379, *e-mail: m.yanagi@tagen.tohoku.ac.jp*
[3]*phone:* +81-22-217-5376, *fax:* +81-22-217-5379, *e-mail: watamako@tagen.tohokuy.ac.jp*
* *Aisin AW Co.*, 10 *Takane, Fujii-cho, Anjo, Aichi* 444-1192, *Japan*

Abstract: Thermal diffusion of Si atoms at the interface in Mo/Si multilayers was observed with an imaging-type soft-X-ray emission microscope developed by us. It was possible to observe the diffusion with 0.2nm depth resolution in the direction normal to the interface by comparing the emission intensity for exactly the same position. The diffusion coefficient of Si atoms in Mo at 600℃ was roughly estimated to be $6.0\times10^{-17}cm^2/s$.

Key words: multilayer films; thermal diffusion; soft X-ray emission microscope
CLC number: O484.4 **Document code:** A

1 Introduction

The property of the devices with a layer structure such as superlattices, multilayer coatings, and semiconductor devices is dependent upon the quality of the interface between adjacent layers. From the viewpoint of their practical usage, thermal stability of the interface is one of the essential factors. Therefore, annealing tests are often carried out to examine the thermal stability. However, it is difficult to evaluate the interface nondestructively because it is buried inside the bulk. Using soft X-ray emission spectroscopy, we are able to investigate the electronic structure of bulk materials independent of the surface state, because mean free path of the soft X-ray is in the order of 100nm. We made clear using soft X-ray emission spectroscopy that the interface of a Mo/Si multilayer coating deposited with a magnetron sputter system was Mo_3Si of about 0.8nm thick[1]. Thus the soft X-ray emission spectroscopy is a useful tool to investigate the buried interfaces. On the other hand, we have recently developed an imaging-type soft-X-ray emission microscope[2]. In this microscope the soft X-ray emissin from a sample generated with an electron beam is focused on a position-sensitive detector using a multilayer-coated Schwarzschild objective. Owing to the narrow-band reflection of the multilayer coating, we obtain a microscope image of a specific kind of atoms. Concerning the present microscope, it has been tuned to the Si $L_{2,3}$ emission. Its spatial resolution on the sample is estimated to be about 2μm. In order to demonstrate its possibilities we have lately studied the diffusion of Si atoms across the interface of a Mo/Si bilayer coating. Mo/Si multilayer coatings exhibit high reflectance at normal incidence in the 13nm wavelength region. Its application has been widely studied in the fields of EUV lithography, soft X-ray microscopy,

Received date: 2001-08-29; **revised date:** 2001-09-18

and free electron lasers. The thermal stability of the interface in the multilayer is essential to keep its performance. The Mo/Si multilayer coating is known to become unstable above 400℃[3] because of the interdiffusion and the chemical reaction to form $MoSi_2$[4]. However, this property is all the more preferable for us to observe the diffusion of Si atoms at high temperature using the soft X-ray emission microscope. We chose Mo/Si multialyer coatings to examine the performance of the soft X-ray emission microscope. On the other hand, the diffusion coefficient of Si atoms in Mo so far reported ranges from $1.3\times10^{-24}cm^2/s$[5] to $1.0\times10^{-16}cm^2/s$[6] at 400℃. The analysis of the images observed in this study will yield diffusion coefficients. It will also contribute to resolving the inconsistency in the basic data of materials.

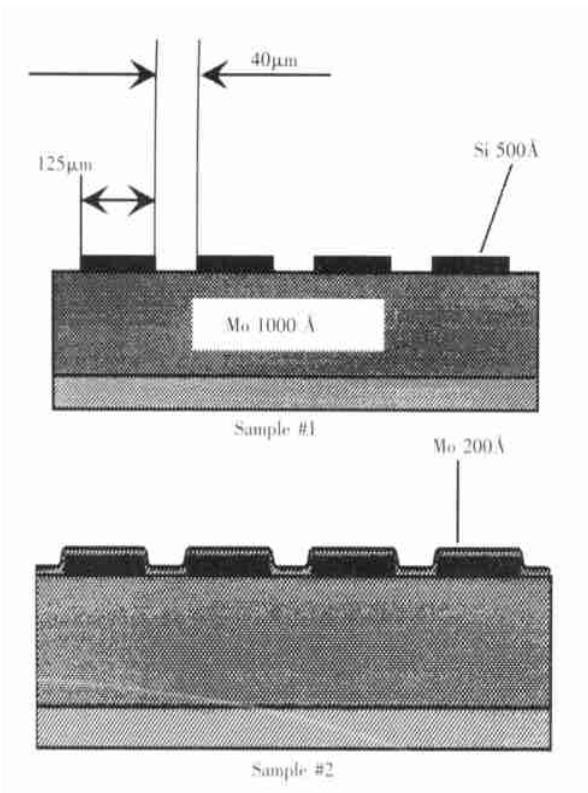


Fig. 1 Schematic cross sections of the samples # 1 and # 2.

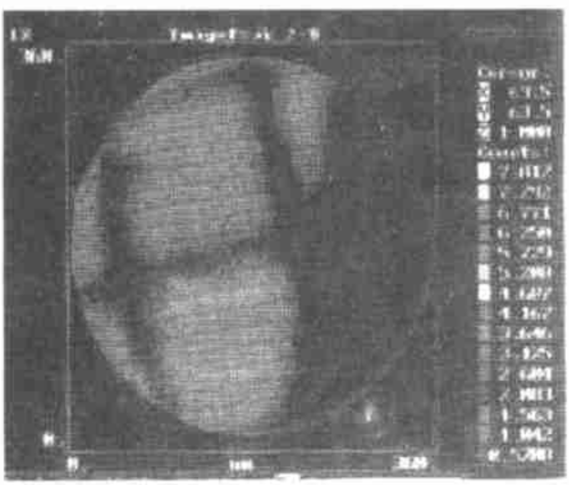
2 Experiments

The samples used in this study were prepared using a magnetron sputter system as follows. A Mo buffer layer of 100nm thick was once deposited on a Si wafer. A Si layer of 50nm thick was patterned using a Cu mesh of # 150 on the Mo buffer layer (sample # 1). Then a Mo topmost layer of 20nm thick was deposited on the sample # 1(sample # 2). The samples were once exposed to the atmosphere when attaching and removing the Cu mesh. The cross section of the samples is schematically illustrated in Fig. 1. It is expected to observe diffusion of Si atoms from the Si layer through into the Mo layer. If the diffusion proceeds more than the resolving power of the microscope, we can expect to observe it at the boundary for both samples. On the contrary, if the degree of the diffusion is lower than the resolving power, it is expected to observe the diffusion in the direction normal to the interface at the plateau for the sample # 2 as an increment in the emission intensity. The sample holder was remade to in situ observe a sample under annealing. The temperature was ascertained to rise to 700℃. A shutter was installed between the sample and the objective to avoid deposition onto the objective mirror during annealing at high temperature. In this study annealing was carried out at 600℃ for 10 hours with the shutter closed. The samples were excited with an electron beam of 1.4μA accelerated to 2.5kV.

3 Results and discussion

Figures 2a and 2b show images of the sample # 1 observed before and after annealing, respectively. Both images were recorded for 80 sec at room temperature. The bright tone shows Si to be rich, while the dark tone shows to be poor. The image shows a boundary of the Si layer patterned using the Cu mesh. The image of Fig. 2b looks slightly unclear. Except for a small dark spot seen in the lower part Fig. 2b, both images look much alike. The small spot was probably generated by desorption of Si atoms during the annealing. In order to estimate the diffusion length we compared the emission intensity profiles of the same position. Figure 3 shows the emission intensity profiles taken across a wire pattern as shown in the upper column of the figure. In order to increase the S/N ratio all the profiles taken inside the rectangular were added up. The high intensity region on both sides of Fig. 3 is the Si layer. As is seen, there seems to be no difference between the two profiles, suggesting that the diffusion was too microscopic to observe with the present microscope even if the diffusion occurred.

(a) before annealing



(b) after annealing

Fig. 2 Si $L_{2,3}$ emission images of the sample # 1 observed (a) before and (b) after annealing at 600℃ for 10h.

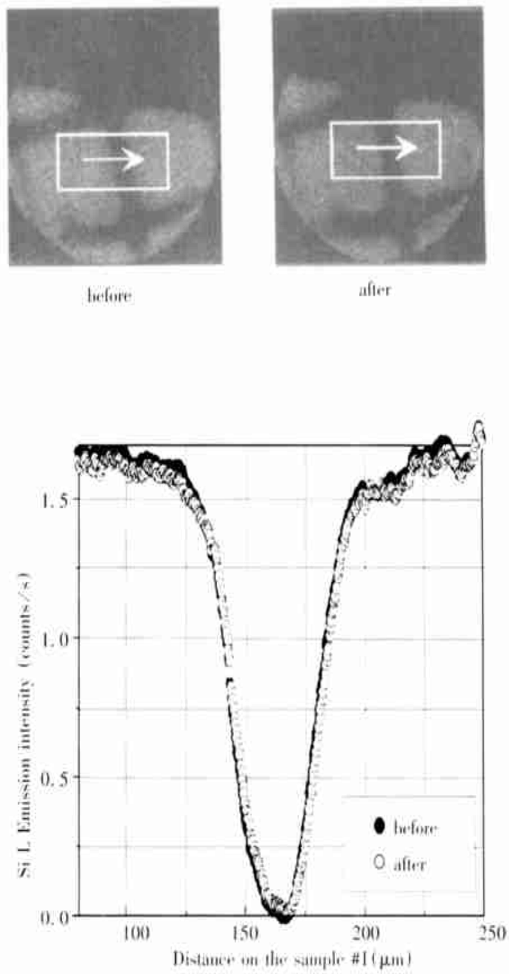
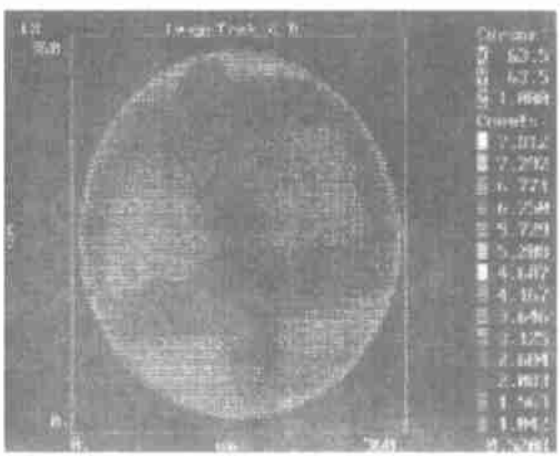
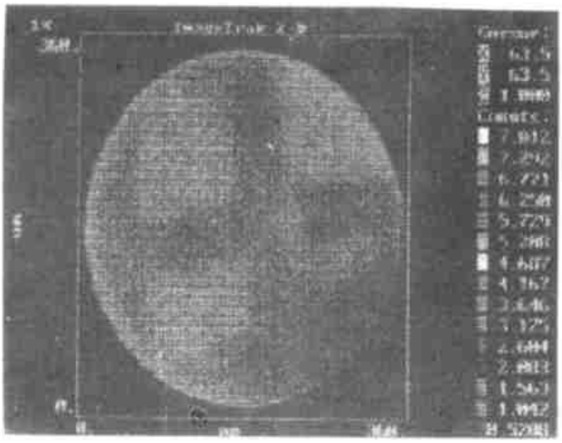


Fig. 3 Emission intensity profiles of Fig. 2(a) (solid circles) and 2(b) (open circles). They are taken at the same position as illustrated in the upper column.



(a) before annealing



(b) after annealing

Fig. 4 Si $L_{2,3}$ emission images of the sample # 2 observed (a) before and (b) after annealing at 600℃ for 10h.

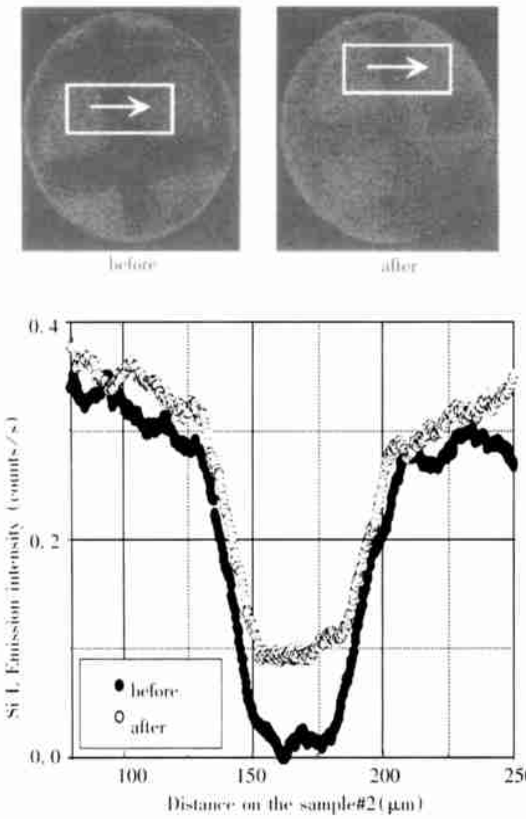


Fig. 5 Emission intensity profiles of Fig. 4(a) (solid circles) and 4(b) (open circles). They are taken at the same position as illustrated in the upper column.

Figures 4a and 4b show images of the sample # 2 observed before and after annealing, respectively. The acquisition time was 300 sec for the Mo cover layer. As is seen, contrast of the image evidently degraded after annealing. Figure 5 shows the emission intensity profiles taken for the same area shown in the upper part of the figure. As for the middle region, some amount of Si atoms were observed after annealing, while almost no Si atoms were observed before annealing. Si atoms were not deposited onto the middle region because the Si layer was covered with the Mo layer for the sample # 2. Besides, the sample # 1 offers another evidence that Si deposition did not occur at all, where the Si layer was not covered. It may be explained as follows. Contamination caused by the atmosphere resulted in defects at the area sandwiched between the bottom and the top Mo layers, thus Si atoms efficiencly diffused laterally into the defect layer. It may be possible to observe this effect under an appropriate condition using the microscope. We thus pay no more attention to the middle area but to the Si layer region. As is seen, the emission intensity increased after annealing. The increment was not caused by the Si deposition onto the Mo layer from the same reasons as described above. The increment in the emission intensity suggests strongly that Si atoms diffused upward into the Mo layer at the topmost interface. The ratio of the emission intensity before and after annealing averaged over the Si layer region is 1. 18. Using a diffusion model and the penetration depth of an electron beam formalized by Castaing[7] we roughly estimated the diffusion coefficient of Si atom in Mo at 600 ℃ to be 3.4×10^{-17} cm^2/s. Averaging over the diffusion coefficients obtained from the images observed after several annealing periods, we finally estimated it to be $6.0(\pm0.5)\times10^{-17}$ cm^2/s. This value is roughly consistent with 1.0×10^{-18} cm^2/s at 400 ℃ recently obtained by Miyata et al. using soft X-ray emission spectroscopy[4]. Stearns et al. reported 4×10^{-18} cm^2/s at 400℃ measured using a high-resolution electron microscope[8]. If our estimated value is correct, the diffusion length for 10 hours is about 20 nm, which is too small for the microscope to observe the Si diffusion in the lateral direction. However, it was found to be possible to observe diffusion of about 0.2 nm in the direction normal to the interface. This result owes much to the fact that the emission microscope enables us to compare the emission intensity for exactly the same position. The present result demonstrates that the soft X-ray emission microscope has the capability of evaluating the thermal stability of the buried interfaces.

4 Summary

Thermal diffusion of Si atoms at the interface in Mo/Si multilayers has been observed with an imaging-type soft-X-ray emission microscope developed by us. It has been found to be possible to observe the diffusion with 0.2nm depth resolution in the normal to the interface because we can compare the emission intensity for exactly the same position using the emission microscope. On the contrary, the diffusion was too small for the microscope to observe in the lateral direction. We have roughly estimated that the diffusion coefficient of Si atoms in Mo at 600℃ is $6.0\times10^{-17}cm^2/s$.

Acknowledgements

The authors would like to thank Y. Fuda for preparing the sample holder equipped with an annealing heater. This work was supported in part by Grant-in-aid for Scientific Research (B) (Contract No. 10555012) from Japan Society for the Promotion of Science. This work was also supported in part by the Mitsubishi Foundation.

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