

1-1-2015

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Publication Information

Ailavajhala, M.; Latif, M.R.; Wolf, K.; Mitkova, M.; and Skoda, M.W.A. (2015). "Dynamics of Silver Photo-Diffusion into Ge-Chalcogenide Films: Time-Resolved Neutron Reflectometry". *Journal of Physics: Conference Series*, 619, 012046-1 - 012046-4. <http://dx.doi.org/10.1088/1742-6596/619/1/012046>



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Dynamics of silver photo-diffusion into Ge-chalcogenide films: time-resolved neutron reflectometry

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Abstract. Silver diffuses into an amorphous (a-) chalcogenide layer while visible light illuminates Ag/a-chalcogenide films and neutron reflectometry is a suitable technique probing time evolution of the depth profiles without damaging the sample by the probe beam itself. In this paper, we report the results of time-resolved neutron reflectivity measurements of a-Ge₄₀Se₆₀/Ag/Si films taken while the films are exposed to visible light. From the measurements, we found enormous changes in the neutron reflectivity profile, including a loss of total reflection region, with continuous illumination even after forming one homogeneous layer, which occurred about 50 min after starting illumination. At this stage, a clear off-specular scattering was observed by a linear detector and a surface roughness was observed with naked eyes.

1. Introduction

Silver photo-diffusion in amorphous (a-) chalcogenide films such as a-As₂S₃ and a-GeSe₂ has attracted much interest because of the potential applications in, for example, photo-lithography [1, 2] and non-volatile memory devices [3]. Investigation of the dynamics of the silver photo-diffusion is considered to be quite important in order to get good performance in devices, and in fact, previous numerous studies have shown that this diffusion exhibits unique behaviour in the dynamical process. According to Rutherford Backscattering (RBS) studies [4, 5, 6], there is a step-like silver concentration in the depth profile after the silver diffusion takes place. This feature is different from typical diffusion processes in which the concentration gradually decreases or fades out. Although RBS is a powerful non-destructive technique for determining depth profiles, the experiments in this case were very challenging because a strong He⁺ beam can also induce silver diffusion in the films. For this reason, a lower He⁺ beam intensity was used in the reported experiments and the time-evolution measurement was not successful. Considering such a situation, Wagner et al. performed a combinational method using RBS and modified optical reflectivity measurements [6]. In the modified optical reflectivity measurement, they measured the reflected beam from the film irradiated from the chalcogenide side as a function of time. It resulted in an oscillatory change due to interference with the



optical path in the film and the wavelength of the probe laser beam. From the result, they estimated the thickness of the chalcogenide layer as a function of time. After that, they selected several illumination times in order to see all the features of the diffusion process, and prepared several films with different illumination times. For these films, they measured RBS with an appropriate He^+ beam intensity and found the dynamics of the depth profile. According to their conclusion, there is a step-like silver concentration profile in the silver reaction layer, and the reaction layer proceeds to the chalcogenide layer, resulting in the disappearance of the chalcogenide layer in the final stage. Of course, there is no doubt that their carefully treated measurements provide a conclusive picture on silver diffusion dynamics. However, there is one unanswered question in their treatment: Is the diffusion process really frozen by stopping the illumination? In this sense, it is desirable to measure the depth profile *in situ* during exposure of the sample to light. X-ray and Neutron reflectivity are powerful techniques that can be used to reveal such transient depth profiles. Of these, synchrotron radiation provides brilliant photon fluxes for time-resolved X-ray reflectivity measurements and can readily discern small changes in surface or interface structure. However, it is known that X-rays can induce silver diffusion in chalcogenide materials [7] and the strong possibility of rapid sample decomposition due to the synchrotron radiation beam – even before any data can be collected – cannot be overlooked. Neutrons, on the other hand, offer a safer approach by excluding the possibility of changes induced by the probe beam and, the use of an intense pulsed neutron source is well-suited to realize time-resolved measurements. So far, we have applied time-resolved neutron reflectivity technique for the investigation on the silver diffusion dynamics into germanium sulphide films and obtained successful results to reveal the diffusion process [8]. In this paper, we report our recent results of time-resolved neutron reflectivity measurement for Ag/Ge-Se films while being exposed to visible light, and discuss the silver photo-diffusion process into the films.

2. Experimental

The neutron reflectivity measurements of Ag/Ge-Se films were carried out on INTER [9, 10] at ISIS (UK). Pulsed neutrons are provided at a 10Hz repetition rate. The specular reflectivity was measured with a ^3He detector with the time-of-flight technique. The available wavelength range was 1.5 to 15 Å. The kinetic data were measured at an incident angle of 0.55° , resulting in a Q range from 0.008 to 0.05 \AA^{-1} . The full profile before and after illumination was measured at two angles, 0.55° and 1.6° , resulting in a Q range from 0.008 to 0.23 \AA^{-1} . The data were acquired within a 30 second interval and they were averaged to improve their statistics. In addition, a linear detector was used to measure off-specular scattering for a specific case. White light from a 300 W xenon lamp (MAX-303, ASAHI Spectra, Co., Ltd.) was used as an excitation light source, and the exposure of the sample was under computer-control. The samples were prepared using thermal evaporation. The thicknesses were estimated using the output from a quartz crystal microbalance.

3. Results and Discussion

Figure 1 shows the time evolution of the neutron reflectivity profiles of a- $\text{Ge}_{40}\text{Se}_{60}$ 1500Å / Ag 500 Å / Si substrate film. At the initial stage, before light exposure, we confirmed that silver diffusion had already taken place forming a reaction layer with about 250Å thickness, and leaving a thin Ag layer with 30Å thickness (see, Table 1). After starting light exposure, silver diffusion proceeds further, and one homogenous layer was formed at 20.5-25.5 min as shown in Table 1. Usually, the diffusion dynamics are completed at this stage. However, further changes in the neutron reflectivity profile have been observed. Firstly, the intensity at total reflection region decreased around 50 min, and the flat total reflectivity region was totally lost at 76 min. Secondly, the fringes in the neutron reflectivity profile also changed after 50 min and the oscillated pattern was totally lost at 76 min. Such a situation cannot be followed as long as only a typical specular scattering is assumed. Therefore, we used a linear detector instead of a point ^3He detector and measured the intensities as a function of neutron wavelength and scattering angle. Figure 2 shows a scattering angle-wavelength map for the film after

having the unusual changes, together with a “usual” map obtained from Ag 500Å film. In the map of Ag 500Å film, scattered neutrons are observed at the same angle as the incident angle, 0.55° , suggesting specular scattering. At the angle, a bright yellow line (6-15 Å), indicating a total reflection, and repeated light blue-bright blue pattern (1.75-6 Å), indicating fringes on the reflectivity profiles, are observed. On the other hand, in the map of a-Ge₄₀Se₆₀ 1500Å / Ag 500Å /Si substrate film, the scattered neutrons are diffused from 0.1° to 1.0° around 0.55° . It is apparent that the losses of the total reflection region and the fringes, observed in Fig.1, result from the off-specular scattering, and this is attributed to a large (e.g. micrometer-size) surface roughness. In fact, the surface roughness is visible even with the naked eyes as shown in Figure 3(a). Also, the image of an optical microscope in Figure 3 (b) shows that there are inhomogeneous patterns on micrometer-scales on the surface.

Considering the change in the depth profiles (Table 1), the enormous surface roughness is caused by a photo-induced structural change on a homogeneous silver-diffused film. The further light illumination must trigger a structural transformation from the homogeneous Ag-Ge-Se layer to more stable state. Also, it is noted that the change occurred only when the Ge composition is 40% and the Ge₄₀Se₆₀ layer was on top. Such change was not observed for other films; Ag/Ge₂₀Se₈₀/Si, Ag/Ge₄₀Se₆₀/Si, and Ge₂₀Se₈₀/Ag/Si. Therefore, the occurrence of this phenomenon seems to be composition-sensitive and the compositional stability must be related to the change. At present, we cannot conclude what the more stable state is. However, there are some candidates to explain the results. The first possibility is a photo-induced surface deposition, in which silver particles appear [11]. This is the opposite process to photo-diffusion. The second possibility is a photo-induced phase separation, in which Ag-rich stable domains and Ag-poor stable domains co-exist. The third possibility is particle-formation, in which self-aggregation takes place. In any case, further investigations are required to understand the physical origin of the surface roughness.

4. Conclusion

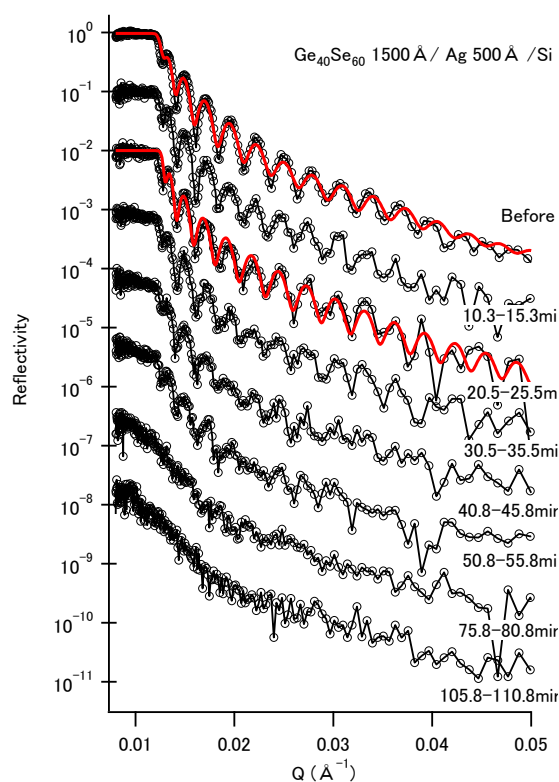


Figure 1 Time evolution of the neutron reflectivity profile of a-Ge₄₀Se₆₀ 1500Å / Ag 500Å / Si substrate film. Thick red curves indicate the fitted curves using the parameters in Table 1.

	thickness	SLD	roughness
Ge ₄₀ Se ₆₀	1594	3.01	15.3
Ag-Ge ₄₀ Se ₆₀	252	3.24	2.1
Ag	30	3.47	0.5

Before light illumination

	thickness	SLD	roughness
Ag-Ge ₄₀ Se ₆₀	1943	3.13	18.0

At 20.5-25.5 min

Table 1 Parameters used for curve fitting; thickness (Å), scattering length density (SLD) ($\times 10^{-6} \text{ \AA}^{-2}$), and roughness (Å).

We performed time-resolved neutron reflectivity measurements for Ag/Ge₄₀Se₆₀ films at ISIS to clarify the silver photo-diffusion into amorphous chalcogenide. From the measurement of the Ge₄₀Se₆₀/Ag film, we found that enormous surface roughness appeared with continuous light illumination even after completing the silver diffusion. The structural origin of this change is not clear. However, other techniques such as X-ray diffraction, scanning electron microscope, and atomic force microscopy would be useful to clarify the origin.

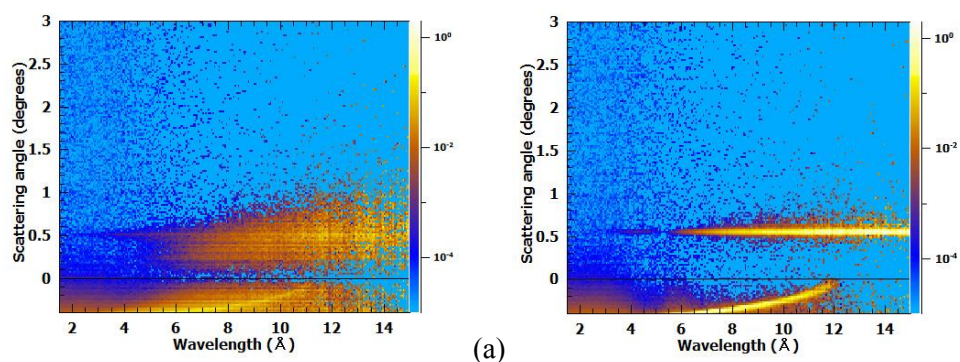


Figure 2 Scattering angle-wavelength maps obtained by a linear detector. (a) a-Ge₄₀Se₆₀ 1500Å / Ag 500Å / Si substrate, (b) Ag 500Å / Si substrate. The incident angle was 0.55°.

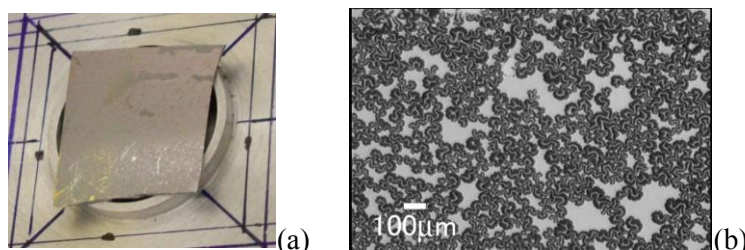


Figure 3 (a) Photograph of a-Ge₄₀Se₆₀ 1500Å / Ag 500Å / Si substrate, taken after the whole neutron reflectivity measurements, in which a large off-specular scattering was observed by a linear detector. The film on a Si wafer is about 30mm x 30mm. (b) Image of an optical microscope.

Acknowledgements

This work was supported by JSPS Grant-in-Aid for Scientific Research (C) Grant Number 25400435 and by Defense Threat Reduction Agency under Grant HDTRA 1-11-1-0055R. The neutron reflectivity measurements were performed on INTER in ISIS under Project No. RB1320307. We would like to thank Dr. G. Foran (CROSS) for valuable discussions

References

- [1] Yoshikawa A, Nagai H and Mizushima Y 1976 *Jpn. J. Appl. Phys.* **16** Suppl .16-1 67
- [2] Leung W, Cheung N W and Neureuther A R 1985 *Appl. Phys. Lett.* **46** 481
- [3] Mitkova M and Kozicki M N 2002 *J. Non-Cryst. Solids* **299-302** 1023
- [4] Yamamoto Y, Itoh T, Hirose Y and Hirose H 1976 *J. Appl. Phys.* **47** 3603
- [5] Rennie J, Elliott S R and Jeynes C 1986 *Appl. Phys. Lett.* **48** 1430
- [6] Wagner T, Peřina V, Vlček M, *et al.* 1997 *J. Non-Cryst. Solids* **212** 157
- [7] Kovalskiy A, Miller A C and Jain H 2008 *J. Am. Ceram. Soc.* **91** 760
- [8] Sakaguchi Y, Asaoka H, Uozumi Y, *et al.* 2014 *Can. J. Phys.* **92** 654
- [9] Webster J, Holt S and Dalgliesh R 2006 *Physica B* **385-386** 1164
- [10] Webster J R P, Langridge S, Dalgliesh R M, and Charlton T R 2011 *Eur. Phys. J. Plus* **126** 112
- [11] Kawaguchi T, Maruno S, and Elliott S R 1996 *J. Appl. Phys.* **79** 9096