(※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。)

TOKAI CROSS Experimental Report J-PARC	提出日 Date of Report 2013/05/21
課題番号 Project No. 2012B0163 実験課題名 Title of experiment Investigations on oxygen-assisted photoinduced structural transformation in amorphous Ge-S films by means of neutron reflectometry 実験責任者名 Name of principal investigator Yoshifumi Sakaguchi 所属 Affiliation CROSS	装置責任者 Name of responsible person Masayasu Takeda 装置名 Name of Instrument/(BL No.) SHARAKU (BL 17) 実施日時 Date and time of Experiment 2012/12/17-12/19 2012/12/20-12/23 2013/02/07-02/09

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

$Ge_{40}S_{60}$ films

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。)
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Experimental method:

Recently, we have found oxygen-assisted photoinduced structural transformation in amorphous (a-) Ge-S films by Laser Raman spectroscopy in which the laser with 441.6nm illuminates the sample in air [1]. The obvious change in the Raman spectrum suggested that there is a structural transformation from double-layer structure to GeS_4 tetrahedral units. Also, we have observed the presence of oxygen on the films by EDS measurements. However, we have not obtained yet an experimental evidence to show "where" the oxygen exists. We can easily imagine that GeO_2 layer is formed on top and that the $Ge_{40}S_{60}$ layer changes to be $Ge_{33}S_{67}$ layer plus GeO_2 layer. To observe the presence of the oxide layer and changes in the Ge-S layer, neutron reflectometry is very powerful technique.

In the experiment, we used a xenon lamp unit (MAX-303, ASAHI SPECTRA) as an excitation light source. The white light has a spectrum in ultra-violet region (254-385nm). The illumination area on the film was 25mm x 25mm. Neutron reflectivity measurements have been made on BL17 (SHARAKU) with unpolarized neutron beam mode. We measured neutron reflectivity of the sample before light exposure and after reaching the saturation of changes in the Q-region up to 0.08 $Å^{-1}$. The light was exposed on the film for 90 minutes and neutron reflectivity measurements have also been made during the light exposure, fixing the angle of a detector.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

Experimental results:

Fig.1 shows the neutron reflectivity of a-$Ge_{40}S_{60}$ 2000Å film before light exposure and after reaching the saturation of the photoinduced changes. The dots show the experimental data while the solid curve shows the result of fitting. There is a small, but certain difference in the neutron reflectivity and this indicates that the layer structure changes by the light illumination. We have tried to make fitting by assuming the presence of oxide layer, for instance, GeO_2. However, we have failed to fit by assuming the oxide layer. Table 1shows the summary of the fitting parameters, in which only one layer is assumed. Considering the changes in the scattering length density (SLD) and the thickness (d), it seems that the layer expands and the mass density decreases by the light illumination. The change in the roughness (σ) to be larger can also support our idea that a reaction occurs by the light illumination.

	SLD (x 10^{-6} Å $^{-2}$)	d (Å)	σ (Å)
Before	2.005	2175	6.501
After	1.945	2203	14.998

Table 1 (above) Summary of the fitting parameter

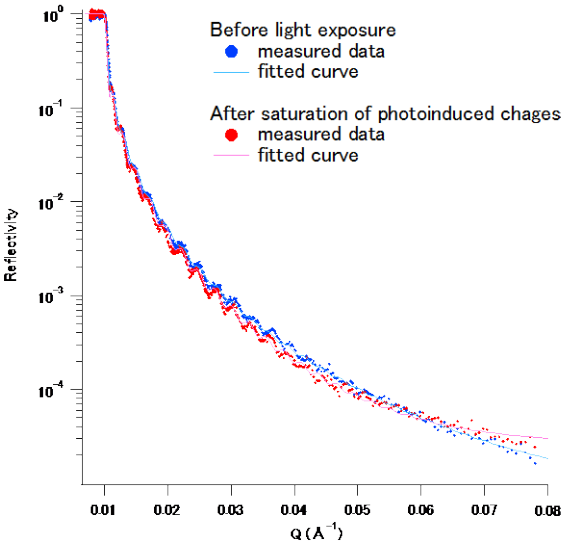

Fig.1(right) Neutron reflectivity of a-$Ge_{40}S_{60}$ 2000Å film before light exposure and after reaching the saturation of the photoinduced changes.

Fig.3 shows the time evolution of neutron reflectivity during light exposure. As shown in the figure, we could observe the neutron reflectivity in the photoinduced changes from an initial state every 10 minute. There are small changes in the reflectivity curve. Especially, a portion indicated by an arrow is distinct. The time evolutional changes can show the dynamical changes of the layer structure in terms of thickness, mass density, or chemical composition. To clarify the changes, we are now making further analysis.

In summary, we have not found a clear evidence of the presence of the surface oxide layer, which was supposed to be formed in the oxygen-assisted photoinduced structural transformation in a-Ge-S films. However, we have observed changes in the neutron reflectivity under light exposure. We believe that the result would be a key to draw a realistic picture of the photoinduced changes.

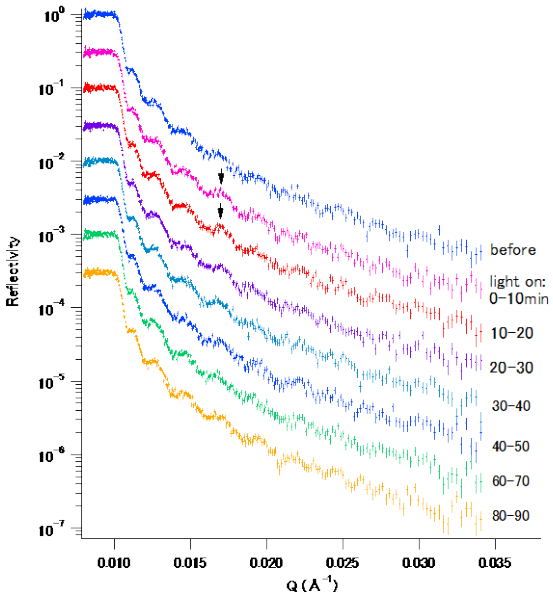

Fig. 3 Time evolution of neutron reflectivity

[1] Y. Sakaguchi, D. A. Tenne and M. Mitkova, Physica Status Solidi B 246 (2009) 1813.