Study of photoexpansion and photocontraction in chalcogenide glass films by *in-situ* EXAFS

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Introduction

Germanium chalcogenide glasses show a volume contraction with illumination, whereas the volume of arsenic chalcogenide glasses expands with illumination. The contrasting effects are generally explained in terms of different structural units in these chalcogenides. Here, we attempt to establish an atomistic understanding of their opposite behaviors by studying the local structure before, during and after illumation of a-$GeSe_2$ and a-As_2S_3 films by *in-situ* EXAFS.

Methods and Materials

Thin films of a-$GeSe_2$ and a-As_2S_3 (thickness, d~1 μm) were deposited on glass substrates in vacuum from respective bulk materials. In-situ EXAFS experiments were done at X18B and X19A beamlines at NSLS, BNL at Ge and Se K-edges and at As and S K-edges, respectively. The EXAFS spectra before, during and after laser irradiation were collected in the fluorescence mode. Samples were illuminated with bandgap light from a 633 nm diode laser ($GeSe_2$) or a 488 nm Ar ion laser (As_2S_3).

Results

From the EXAFS data at Ge and Se K-edges for a-$GeSe_2$ and from As and S K-edges for a-As_2S_3 films before, during and after illumination, we obtain the partial radial distribution function (PRDF) for Ge and Se K-edges. Fitting the experimentally obtained PRDF, we estimate the nearest neighbor distance (NN) and Debye-Waller factor for Ge and Se in a-$GeSe_2$ films and for As and S in a-As_2S_3 for various stages of exposure, viz. as prepared films (AP), during (ON) and after (OFF) illumination. For example, the changes in the NN distances are shown in fig. 1 (a) and (b) for Ge and Se and As and S, respectively.

Discussion

Figure 1(a) shows a contraction in the local structure around Ge as well as Se nearest neighbors in a-$GeSe_2$ films. It consists of a transient and a metastable part induced by illumination. The former vanishes to leave behind only the metastable part of the chenges when the illumination is switched off, as is evident from a slight increase in NN distances from the ON to OFF stage. The Debye-Waller factor for both Ge and Se decreases with illumination (not shown here), but increases slightly after the laser is switched off, indicating a transient recovery of the ordering of the structure upon removal of illumination.

The overall volume contraction with illumination may suggest the creation of thermally stable Ge-Se bonds from less stable homopolar Ge-Ge and Se-Se bonds present in the as prepared films (similar to annealing). The contraction in the Ge NN distance with illumination supports this hypothesis, but the contraction in the Se NN distances contradicts this hypothesis since Ge-Ge bond distance > Ge-Se bond distance > Se-Se bond distance. So we suggest that there are additional stresses present in the as-prepared films which relax during illumination.

For the case of a-As_2S_3 films (fig. 1(b)), we see a contraction in the As NN distances and an expansion in the S NN distances with illumination, which reverse after the illumination is switched off. The Debye-Waller factor shows ordering of the structure with illumination. These results can also be understood in terms of ordering of the structure by the formation of heteropolar As-S bonds from hompolar As-As and S-S bonds present in the as-prepared films (As-As bond length > As-S bond length > S-S bond length). The expansion around S induced by the formation of As-S bonds appears to dominate the overall expansion seen in As-S films.

In conclusion, we have identified the source of contraction in Ge-Se films and exapansion in As-S films at an atomic level.

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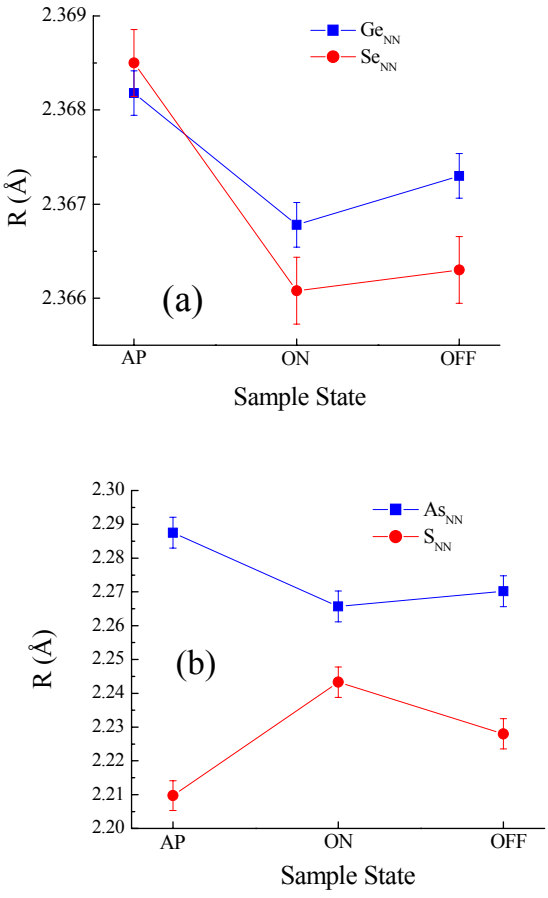

Fig. 1: The changes in the NN distances for (a) Ge and Se and (b) As and S for various sample stages. Details are in the text.