LOCAL BONDING CONFIGURATIONS OF AMORPHOUS Se_xTe_{1-x} FILMS

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X-ray absorption measurements at both the Se and Te K-edges have been performed in binary chalcogenide amorphous (a-) Se_xTe_{1-x} films. The EXAFS results for the Se K-edge indicate that the number of Se-Se bonds decreases with increasing Te content, while the number of Se-Te bonds increases. However, the bonding configuration of the Te site, which consists of one Se-Te and one Te-Te bond, remains the same as a function of composition. Furthermore, contrary to several other reports, we find no evidence of two other inequivalent Te sites (i.e., Te bonded to two Se neighbors or bonded to two Te neighbors).

1. INTRODUCTION

Alloys of a-Se_xTe_{1-x} are of particular interest because of their photogeneration efficiency in the xerographic process. There are three bond types in these alloys: Se-Se, Se-Te, and Te-Te bonds. However, relatively little is known about the compositional dependence of the distribution of local bonding configurations in these alloys. Because of the significant difference of the EXAFS backscattering amplitude function and the phase shift function between Se and Te atoms, each type of bond distribution function contributing to nearest neighbors can be easily separated. For example, in a study of chemical order in the As_xS_{1-x} system, the ability of the EXAFS technique to separate two atomic pair distribution functions in the same shell has been demonstrated[1]. In this study, we describe EXAFS measurements designed to quantify the compositional dependence of local structures for a-Se_xTe_{1-x} films.

2. EXPERIMENT

The a-Se_xTe_{1-x} films were prepared by a vacuum flash evaporation method. The films were deposited onto room temperature kapton substrates. Samples of the following compositions were prepared: x=1, 0.9, 0.7, and 0.5. The thickness of the films is 10 µm. EXAFS measurements at the K edges of As and Te were made on NSLS X-11A beamline. All spectra were taken at 80 K.

3. RESULTS AND DISCUSSION

The Se-Se phase-corrected Fourier transforms (PCFT's)[1] for three samples, a-$Se_{0.9}Te_{0.1}$ (solid line), a-$Se_{0.7}Te_{0.3}$ (long dashed line), and a-$Se_{0.5}Te_{0.5}$ (short dashed line), are shown in figure 1.. The empirical Se-Se phase is determined from crystalline (c-) Se. Systematic changes can be seen in the radial structure with
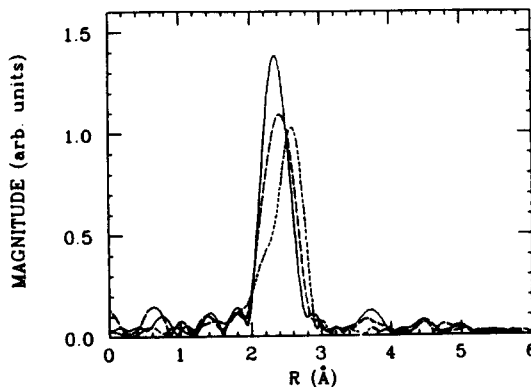

FIGURE 1
The Se-Se PCFT's for a-$Se_{0.9}Te_{0.1}$ (solid line), a-$Se_{0.7}Te_{0.3}$ (long dashed line), and a-$Se_{0.5}Te_{0.5}$ (short dashed line).

composition. The magnitude of the first peak decreases rapidly and its position also shifts to higher R site as Te content increases. The coordination number (N) of the Se-Se and Se-Te bonds and their bond lengths (R) to the first shell were determined by the PCFT method and are summarized in Table I. Structural changes associated with composition suggest increasing contributions from Se-Te bonds and decreasing contributions from Se-Se bonds with increasing Te content. As indicated in Table I, an introduction of more Te also leads to longer bond lengths of Se-Se and Se-Te.

FIGURE 2
An expanded view of the second shells of a-Se (solid line), a-$Se_{0.9}Te_{0.1}$ (dashed line), a-$Se_{0.7}Te_{0.3}$ (dot-dashed line), and a-$Se_{0.5}Te_{0.5}$ (dotted line).

TABLE I Structural Parameters of a-Se_xTe_{1-x} films at the Se site.

Sample	Se-Se N	Se-Se R (Å)	Se-Te N	Se-Te R (Å)
x=1.0	2.0	2.34	0.0	--
x=0.9	1.9	2.34	0.1	2.57
x=0.7	1.6	2.36	0.4	2.58
x=0.5	1.0	2.37	1.0	2.59
Uncertainty	±0.1	±0.02	±0.1	±0.02

The higher shells of a-Se (solid line), a-$Se_{0.9}Te_{0.1}$ (dashed line), a-$Se_{0.7}Te_{0.3}$ (dot-dashed line), and a-$Se_{0.5}Te_{0.5}$ (dotted line), are shown in figure 2. The peak A for the second neighbor Se-Se distance arises from Se-Se-Se linkages, the peak B and the peak C for the second neighbor Se-Te distances are due to contributions from Se-Se-Te linkages and Se-Te-Te linkages, respectively. It does appear that Se-Se-Se linkages are replaced by Se-Se-Te and Se-Te-Te linkages due to the formation of Se-Te bonds. We find no Se-Se-Se linkage in a-$Se_{0.5}Te_{0.5}$ film. Quantitative results for the second shell will be given in a subsequent paper.

The magnitudes of the Te-Se PCFT's of the samples, a-$Se_{0.5}Te_{0.5}$ (solid line), a-$Se_{0.7}Te_{0.3}$ (long dashed line), and a-$Se_{0.9}Te_{0.1}$ (short dashed line), are shown in figure 3. The empirical Te-Se phase is determined from c-AsI_3. As shown in figure 3, the PCFT's in the first shell region show asymmetric patterns which result from the
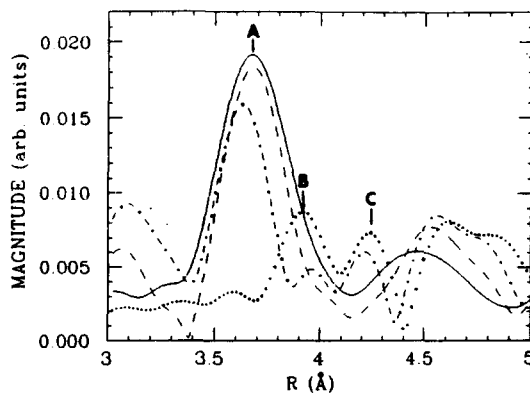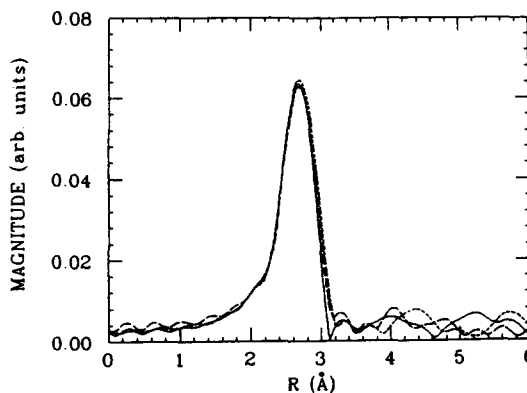

FIGURE 3
The Te-Se PCFT's for a-Se_xTe_{1-x} films: $Se_{0.5}Te_{0.5}$ (solid line), $Se_{0.7}Te_{0.3}$ (long dashed line), and $Se_{0.9}Te_{0.1}$ (short dashed line).

contributions of the Te-Se and Te-Te bonds. Unlike the Se site, the first shells of a-Se_xTe_{1-x} films at the Te site are fairly similar with respect to their shapes and magnitudes. This indicates that a-Se_xTe_{1-x} films on the Te site have similar bonding configurations. However, the first peak positions are systematically shifted toward higher R site with increasing Te content. A quantitative analysis of the

structural parameters for the first shell were performed using the same PCFT procedure.[1] We find that the first coordination number corresponding to one Te-Te (R=2.72Å) and one Te-Se (the bond distance increases slightly with increasing Te content) pair does not change with composition.

The c-semiconductors Se and Te are isomorphic; their atoms are arranged in spiral chains with axes parallel to the c-axis. An x-ray diffraction study of $c-Se_x Te_{1-x}$ alloys indicates[2] that the alloys are true copolymers with compound chains containing covalent Se-Te bonds. Other studies[3-4] suggest that the covalent Se-Te bond is stronger than the average of the Se-Se and Te-Te bonds. Therefore, it has been inferred that the distribution of the Se-Te bonds is a predominant contribution. But, in this work, we show that Se-Se and Se-Te bonds are randomly distributed at the Se site, while the Se and Te atoms are arranged in an alternating manner at the Te site. Boolchand and Suranyi[4] interpret their Mössbauer spectra by suggesting that there are three types of inequivalent Te sites, i.e., Te bonded to two Te neighbors, or two Se neighbors, or one Te and one Se neighbor. Contrary to their report, we find only one Te site, which consists of one Se-Te and one Te-Te bond at all compositions, and no evidence of other two Te sites. Several studies[5-6] have shown that a-Se film comprises a mixture of rings and chains. Our study suggests that Te may be incorporated into Se chains because of the evidence of Se-Se-Se linkages being replaced by Se-Se-Te and Se-Te-Te linkages. Furthermore, the structure of $a-Se_{0.5}Te_{0.5}$ film is built up of chains involving alternating Se and Te atoms. Further study is needed to confirm this view.

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