Fluorescence EXAFS Measurements of Hydrogenated Amorphous Silicon-Germanium Film Alloys

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Introduction

The optical absorption spectrum of hydrogenated amorphous silicon-germanium (a-$Si_{1-x}Ge_x$:H) alloys can be tuned by the Ge content. As a result, there is considerable interest in a-$Si_{1-x}Ge_x$:H films owing to applications in solar cell technology. However, some aspects of the relationship between microstructure and opto-electronic properties are not yet fully understood. For example, it has generally been found, independent of the method of sample preparation, that there is a significant deterioration of the photoresponse of these materials with increasing Ge alloying. This trend appears to be correlated with the concomitant appearance of film heterogeneity. Fluorescence extended x-ray absorption fine structure (EXAFS) measurements are uniquely suited for investigations of the short-range ordering in a-$Si_{1-x}Ge_x$:H films. We have used Ge K-edge EXAFS to determine the Ge environment near-neighbor coordination and bond lengths in high photovoltaic efficiency a-$Si_{1-x}Ge_x$:H films as a function of Ge content.

Methods and Materials

The a-$Si_{1-x}Ge_x$:H films were deposited onto crystalline silicon substrates by the rf glow discharge method, with film thicknesses ~1 µm. We report EXAFS measurements of five samples, with alloy content: x = {45.2, 32.5, 20.0, 13.0, 10.0} at. %. All measurements were made at the Pacific Northwest Consortium Collaborative Access Team (PNC-CAT) bending magnet beamline (sector 20-BM). Energy selection was achieved using a water-cooled double-crystal Si(111) monochromator, with the second crystal detuned ~30% for harmonic rejection. The incident signal was monitored using a nitrogen-filled ion chamber. The fluorescence yield from the sample was measured with a nitrogen/argon-filled ion chamber, in conjunction with a Ga filter and Soller slit assembly. The sample was under ambient conditions, and it was spun (~5000 rpm) in order to minimize diffraction effects from the crystalline substrate. Any Bragg peaks that remained in the spectra were eliminated by moving the sample slightly off the 45°geometry or by locating (with film) and masking them out from the detector. The effective fluorescent signal was typically ~10^6 p/s, and the measurements were obtained in a few hours per sample.

Background subtraction was performed using AUTOBK,[1] with R_{bkg} = 1.3 Å. Fourier transforms to R-space were done using k^2 weighting and Hanning windows, over a range of k = 3.3 $Å^{-1}$ up to the end of the data, typically k ~ 15 $Å^{-1}$. Theoretical phases and amplitudes were calculated using FEFF7.[2] The data were fit in R-space using FEFFIT[3] from approximately 1.6 to 2.80 Å. The total coordination number was fixed at 4, based upon the fact that these binary semiconductor systems are strongly covalently bonded in tetravalent form, even when there is significant hydrogenation. The two Debye-Waller factors (σ^2_{Ge-Ge} and σ^2_{Ge-Si}) were set equal to each other for each data set, which was found to be the case in previous investigations. Relaxing these two fitting constraints merely increases the uncertainties in the fitted parameters without altering the values.

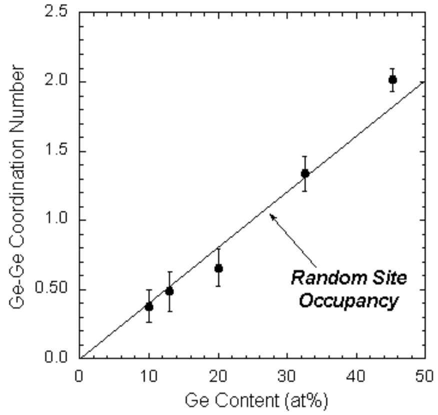

FIG. 1. Plot of Ge-Ge coordination number as a function of Ge content. The solid line is expected for a completely random Ge-Ge distribution.

Results

The agreement between data and theory is better than 2 parts in 10^3, with physically reasonable values for S_0^2 and the $\sigma^2(x)$, both of which were found to be independent of alloy composition within the uncertainty. Figure 1 shows the Ge-Ge coordination number as a function of composition. The error bars are as computed by FEFFIT, with a small additional uncertainty due to self-absorption effects in the film. The results are consistent with a random local distribution of the Ge atoms. Figure 2 shows the near-neighbor bond lengths, which are found to be independent of alloy composition within the uncertainties.

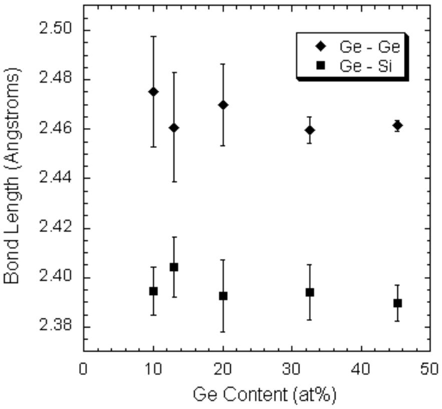

FIG. 2. Plot of near-neighbor bond lengths as a function of Ge content.

Discussion

A structural analysis of the EXAFS reveals no evidence for Ge-Ge clustering, indicating random miscibility of Ge and Si in the alloying process and little hydrogen incorporation into the local Ge environment. We also find no compositional dependence in the Ge environment near-neighbor bond lengths (Ge-Ge and Ge-Si), suggesting that there is little topological rigidity in the amorphous phase. This latter result is inconsistent with a recent EXAFS study of molecular beam epitaxy (MBE)-grown, Si ion-amorphized samples.[4]

Acknowledgments

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