

# Modification of the Local Structure of Ga in Amorphous Silicon by Synchrotron X-ray Irradiation

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## INTRODUCTION

Achieving high efficiency n- and p-type doping in amorphous silicon materials (a-Si) has been reported to be difficult. According to the “8-N” rule proposed by Mott in 1975, the dopant element in covalent amorphous semiconductors takes on its natural coordination.<sup>1</sup> Consequently group III (B, Ga) and V (P, As) elements will not contribute free holes or electrons in a-Si, suggesting that substitutional doping cannot be realized in covalent amorphous semiconductors.

Experimental evidence for n- and p-type doping (with much lower doping efficiency than crystalline Si) by the incorporation of phosphorus and boron in hydrogenated amorphous silicon (a-Si:H) over a wide resistivity range<sup>2,3</sup> indicates that at least a small fraction of these impurities are tetrahedrally coordinated in a-Si:H. Street proposed an autocompensation model which suggested that doping in a-Si:H can only occur in the presence of gap states that maintain ionized donor levels.<sup>4,5</sup>

Recently, we have studied the effects of intense x-ray irradiation on the structure and the crystallization of amorphous Si films.<sup>6-9</sup> Our results strongly suggest that a-Si structures are unstable and when irradiated by large x-ray doses, the unstable amorphous network can locally rearrange to a relaxed configuration through the excitation of the  $sp^3$  and  $sp^2$ -like bi-stable dangling bond.<sup>10</sup> In this paper, we report the modification of the local bonding structures, with the aim to increase the doping efficiency of Ga dopants in both hydrogenated (a-Si:H) and hydrogen-free amorphous silicon (a-Si) thin films by exposing the samples to high x-ray doses generated by a synchrotron source.

## EXPERIMENT

Hydrogen free and hydrogenated a-Si thin films ( $\sim 2\mu\text{m}$ ) were deposited on oxidized Si wafers by dc reactive magnetron sputtering of a Si target and plasma enhanced chemical vapor deposition (PECVD) methods, respectively. The hydrogen content in the a-Si:H films was determined to be  $\sim 8$  at. % by the elastic recoil detection method. Both types of films were grown on thermally oxidized silicon wafers. Ga ions were implanted into the a-Si and a-Si:H thin films with multiple energies (550 keV to 2.1 MeV) creating a relatively uniform Ga distribution of  $\sim 1 \times 10^{20} \text{cm}^{-3}$  throughout the  $2\mu\text{m}$  films.

The Ga implanted samples were irradiated with intense x-rays at beamline 3.3.2 at the Advance Light Source (ALS) at the Lawrence Berkeley National Laboratory. The peak x-ray energy delivered to the beamline was  $\sim 4.0$  keV. The total x-ray dose was  $4.6 \times 10^3$  mA-min., corresponding roughly to 1 photon/Si atom. It has been concluded from our previous study that this x-ray dose results in a maximum relaxation in a-Si thin film.<sup>9</sup>

EXAFS measurements were carried out at 20K using beamline 4-3 at the Stanford Synchrotron Radiation Laboratory. The Ga  $K_{\alpha}$  fluorescence signals from the implanted films were collected by a 13-element Ge x-ray spectrometer. The raw EXAFS data were analyzed by the SPLINE and XFIT code<sup>11</sup> using backscattering amplitudes and phase shifts determined from ab-initio calculations (FEFF4.0).<sup>12</sup>

## RESULTS AND DISCUSSION

Fig. 1 shows the back-transformed EXAFS isolated for the nearest neighbor (NN) for Ga implanted a-Si and a-Si:H (without x-ray treatment). The difference of the two EXAFS curves as well as the root mean square (RMS) noise of the EXAFS data are also plotted in Fig. 1. Fig. 1 clearly

shows that the difference curve exceeds the RMS noise level up to  $k = 9 \text{ \AA}^{-1}$  indicating a substantial difference in the structure of the NN around the Ga atoms in the hydrogenated and hydrogen-free samples. Structural parameters obtained by fitting the EXAFS curves using the XFIT code are listed in Table I. The structural parameters for a Ga in c-Si taken from reference 13 are also included in the Table for comparison. The high  $\sigma^2$  value for the c-Si:Ga is due to thermal vibration since these data were taken at room temperature. We have also performed EXAFS on crystalline GaP standard at 20K and found that the  $\sigma^2=0.024 \text{ \AA}^2$ .

Significant differences in the structural parameters between the Ga impurity in a-Si and a-Si:H are observed. First, we notice that the  $R_{\text{Ga-Si}}$  is slightly shorter in the hydrogenated sample (0.8%). The Ga CN in both the a-Si and a-Si:H samples are less than four, indicating only a fraction of the Ga atoms are occupying a tetrahedral doping site while the rest assume threefold alloying sites. Since hydrogen has a negligible scattering cross section, it effectively reduces the Ga CN in the a-Si:H sample. Assuming that the hydrogen in the a-Si:H are randomly distributed, we calculate the fraction of tetrahedral Ga in a-Si and a-Si:H from the Ga CN measured by EXAFS to be 46% and 64%, respectively. Moreover, we observe that the mean square displacement of the bondlength  $\sigma^2$  for the a-Si:H sample is smaller than that in the a-Si

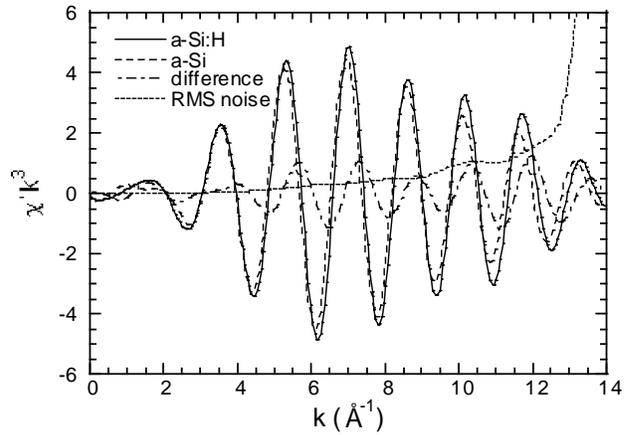


Fig.2 A comparison between the EXAFS oscillations from the Ga implanted a-Si and a-Si:H thin films. The difference curve between the two EXAFS spectra and the RMS noise level curve are also shown in the figure.

Table I. A summary of the structural parameters, bondlength  $R_{\text{Ga-Si}}$ , coordination number CN and Debye-Waller factor  $\sigma^2$ , extracted from the EXAFS data for the Ga implanted a-Si and a-Si:H samples with and without x-ray treatment.

Sample	x-ray treatment	$R_{\text{Ga-Si}}$ ( $\text{\AA}$ )	CN	$\sigma^2$ ( $\text{\AA}^2$ )
a-Si	No	$2.414 \pm 0.002$	$3.46 \pm 0.3$	$0.0050 \pm 0.0009$
	Irradiated	$2.407 \pm 0.003$	$3.80 \pm 0.4$	$0.0059 \pm 0.0012$
a-Si:H	No	$2.395 \pm 0.002$	$3.35 \pm 0.23$	$0.0041 \pm 0.00065$
	Irradiated	$2.405 \pm 0.002$	$3.82 \pm 0.2$	$0.0054 \pm 0.00045$
c-Si:Ga	--	$2.38 \pm 0.01$	$4.2 \pm 0.5$	$0.004 \pm 0.0004$

sample suggesting that the hydrogen reduces the static disorder in the amorphous structure. Most obvious is the longer  $R_{\text{Ga-Si}}$  and larger  $\sigma^2$  in a-Si and a-Si:H as compared to c-Si. The longer  $R_{\text{Ga-Si}}$  of a-Si results in the lower density of the amorphous material while the larger  $\sigma^2$  comes from the larger inherent structural disorders incorporated in amorphous structures.

The effects of x-ray irradiation on the local structure of the Ga atoms in a-Si and a-Si:H are shown in Fig. 2. The difference between in the EXAFS of samples with and without x-ray exposure is readily observable. Structural parameters obtained by fitting the EXAFS oscillations listed in Table I show that after x-ray exposure, all of the structural parameters,  $R_{\text{Ga-Si}}$ , CN and  $\sigma^2$  for the a-Si sample are similar to those of the a-Si:H. This suggests that while the local structure around the Ga atoms in a-Si:H and a-Si varies substantially, x-ray excitations modified this variation and transforms it into a structurally similar state with  $R_{\text{Ga-Si}} \approx 2.405 \text{ \AA}$ ,  $\text{CN} \approx 3.8$  and  $\sigma^2 \approx 0.0055 \text{ \AA}^2$ .

In particular, the Ga CNs in the a-Si and a-Si:H samples increase by 10 and 14%, respectively after x-ray irradiation. For the a-Si sample, this corresponds to 80% of the Ga atoms in tetrahedral sites, more than a 70% increase in fourfold coordination. In the case of the a-Si:H, the increase in Ga CN due to x-ray excitations is even more pronounced (from 3.35 to 3.82). Such increase four-fold coordination for Ga in a-Si materials suggests that electrical activation can be improved by x-ray exposure.

## SUMMARY

In summary we have determined that hydrogen in a-Si reduces the static disorder of the local structures around the Ga atoms. High dose x-ray irradiation modified the Ga local structures in both the a-Si and a-Si:H samples. In particular the Ga coordination increases from  $<3.5$  to  $\sim 3.80$  in both hydrogenated and H-free a-Si, suggesting that x-ray excitation promotes tetrahedral bonding of Ga atoms in a-Si. Moreover we also observed more structural disorder around Ga after x-ray treatment, suggesting that fourfold coordinated Ga is less ordered than Ga on the threefold coordinated sites.

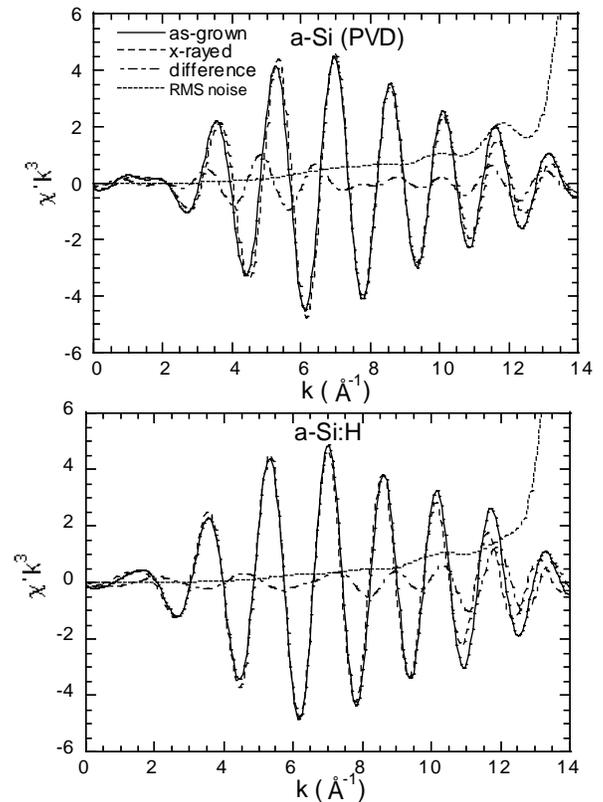


Fig.3 The EXAFS spectra from the Ga implanted a-Si and a-Si:H samples as-implanted and after x-ray treatment. The difference and RMS noise curves are also shown.

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