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## EXAFS DETERMINATION OF THE LOCAL BONDING CONFIGURATION OF P IN a-Si:H

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### ABSTRACT

We have performed EXAFS measurements at the Si and P K-edges in a-Si:H,P in order to investigate the coordination of P in an amorphous Si matrix. Samples deposited with PH<sub>3</sub> concentrations between 2 and 4% have been investigated. We find that both 3 - fold *and* 5 - fold coordinated P atoms are present. This result has important consequences for theories on the doping mechanisms in a-Si:H.

### 1. - INTRODUCTION

The nature of the doping mechanism in a-Si:H has been a long standing problem in the physics of amorphous semiconductors. While transport measurements are generally well explained by the autocompensation model<sup>1</sup> structural investigations are in apparent contradiction with it<sup>2</sup>.

There have been a number of structural studies on dopants in a-Si:H. One of the earliest<sup>3</sup> used EXAFS to measure the coordination of As impurities in a-Si:H; it was found that the mean coordination was slightly below 3, with an increase at 1% concentration which was attributed to the presence of ≈20% 4-fold coordinated As atoms. Similar results were reached by NMR<sup>4</sup>. These results indicate a much higher concentration of 4-fold coordinated P than consistent with the autocompensation model.

In order to shed light on this problem we have performed EXAFS measurements at the Si and P K-edges in a-Si:H doped with variable amounts of P (a-Si:H,P).

Samples deposited with PH<sub>3</sub> concentrations ranging between 2% and 4% have been examined. We find that both 3-fold *and* 5-fold coordinated P atoms are present and thus provide evidence that five-fold coordinated P atoms exist in a-Si:H - an apparently long neglected possibility. This observation has important implications for the doping mechanism in a-Si:H and is compatible with a modified version of the autocompensation model.

### 2. - EXPERIMENTAL AND DATA ANALYSIS

EXAFS measurements were performed on two separate runs at the ACO storage ring in Orsay, France and at the PULS facility on the ADONE storage ring in Frascati, Italy. These two runs will be termed F (Frascati) and O (Orsay) in the following. The X-ray absorption coefficient was measured by monitoring the flux before and after the sample with ionization chambers.

A total of 4 samples were measured in the two combined runs. All samples were deposited from mixtures of  $\text{SiH}_4$  and  $\text{PH}_3$  in a capacitively coupled PA-CVD apparatus in identical conditions, the only difference being the relative amount of  $\text{PH}_3$  in the discharge gas. This quantity is listed in Table I.

Si and P EXAFS signals were extracted by fitting the experimental absorption spectrum with a cubic spline curve; subsequently the spectra were normalized by  $Jx\{1-8/3[(E-E_0)/E_0]\}$  where  $J$  is the atomic absorption jump height and  $E_0$  was chosen as the maximum of the derivative of the absorption edge.

In Figure 1 we show the experimental normalized P EXAFS signals relative to three samples measured in run F. The signals have different amplitudes but are otherwise quite similar. We have performed two different and independent analyses of these spectra (and those obtained in run O) in order to estimate the local bonding parameters for P in these samples.

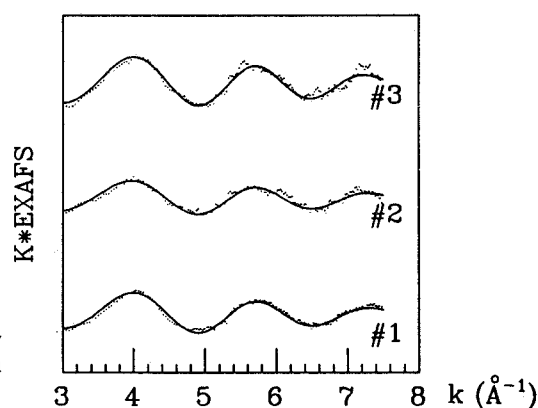


FIG. 1 - Spectra for samples in run F. Dots: raw P EXAFS; solid line: Fourier filtered signal from the first shell. Sample number is indicated.

Firstly, we have used the sample with the highest P concentration (sample #1) as a model for the other samples. The coordination number ( $N$ ), interatomic distance ( $R$ ) and mean square relative displacement ( $\Delta s^2$ ) were varied in a least-squares fitting routine until a best fit was obtained. Appreciable variations in  $N$  were obtained and are listed in column 4 of Table I and plotted in the top panel of Figure 2. This set of data has been treated self-consistently so that possible systematic errors are minimized. We find negligible variations in the interatomic bond distance and values of  $\Delta s^2$  smaller than or equal to  $10^{-3} \text{ \AA}^2$ , close to experimental sensitivity.

TABLE I - Concentrations of  $\text{PH}_3$  during deposition and results for coordination numbers.

SAMPLE	$[\text{PH}_3]$	RUN	$N^* = N/N_{4\%}$	$N$
1	4%	F	-	$3.64 \pm 0.15$
1	4%	O	-	$3.36 \pm 0.40$
2	3%	F	$0.80 \pm 0.03$	$3.14 \pm 0.15$
3	2%	F	$1.24 \pm 0.03$	$4.62 \pm 0.15$
4	2%	O	$1.42 \pm 0.1$	$4.20 \pm 0.40$

In an attempt to obtain an absolute determination of bonding parameters we have also fitted the P EXAFS using the signal from the Si edge in a-Si:H as a model. This choice is not expected to cause large errors in the analysis because of the chemical similarity the EXAFS signal from Si-Si and P-Si pairs, as was confirmed by spherical wave calculations we have

performed. The results of this analysis also shows appreciable variations in coordination number which are qualitatively similar to those obtained from the first type of analysis. By using the experimental value of the average coordination number in a-Si:H deposited under identical conditions as those used in the present investigation we obtain values of  $N$  as listed in column 5 of table 1 and plotted in the bottom panel of figure 2. The values we obtain for  $R$  are in the range 2.27 - 2.29 Å, with a possible slight increase at low  $P$  concentrations. Again, negligible values for  $\Delta s^2$  were found.

Some caution is necessary in the interpretation of these results. The *absolute* values of the coordination number of all the samples is subject to a possible common systematic error ( $\approx 0.4$  atoms in the same direction) which is possibly different for runs O and F. Also, the absolute value of  $R$  has a relatively large error ( $\approx 0.03$  Å). These observations, however, do not invalidate our conclusion that large variations in the coordination of  $P$  are present in the samples investigated.

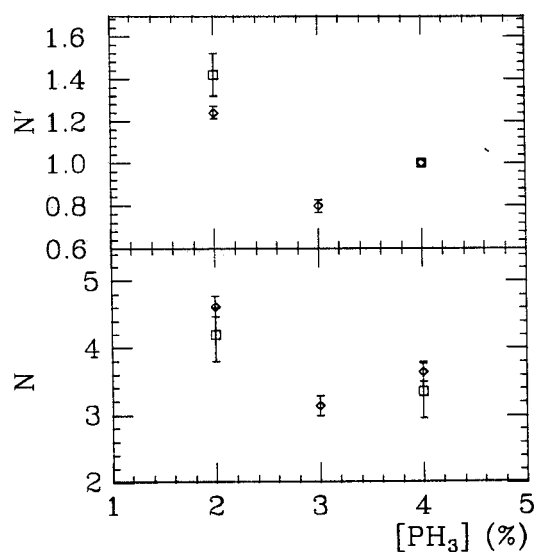


FIG. 2 - Results of the coordination number analyses, as described in the text.

### 3. - DISCUSSION

We interpret the data presented so far as clear evidence that the absolute value of the mean coordination number of  $P$  in a-Si:H varies between 3 and 5. As a coordination number of 4 would imply a doping state for  $P$ , which is untenable because transport measurements indicate very limited doping efficiency at these concentrations, we conclude that  $P$  is present in two distinct bonding configurations, three-fold and five-fold coordinated to Si; these configurations will be termed  $P_3$  and  $P_5$ . Mean coordination numbers between 3 and 5 are to be thought as resulting from different proportions of  $P_3$  and  $P_5$ . A definite trend of this relative proportion with concentration cannot, however, be established at the moment, in our opinion.

The presence of  $P_5$  sites is compatible with the general properties of  $P^5$  and, in fact, had been suggested by Mott and Davis<sup>6</sup> for  $P$  sites in amorphous Ge. Moreover, it has been recently pointed out<sup>7</sup> that an overcoordination of Si (in an a-Si matrix, i.e. a "floating bond") should not be energetically more unfavorable than an undercoordination (a dangling bond), a situation which might also apply to the case of  $P$  in amorphous silicon.

This set of data can also explain the discrepancy between the EXAFS measurements on As in a-Si:H and transport measurements if the increase in mean coordination number at low concentrations for that data set is interpreted as arising from combined presence of  $P_3$  and  $P_5$  sites rather than  $P_3$  and  $P_4$ .

Lastly, we would like to point out that the presence of  $P_5$  sites is compatible with a modified version of the autocompensation model for doping in a-Si:H. Moreover it provides

the means for a local (and possibly reversible) transition between a non-doping configuration on the one hand and a doping state plus a doubly occupied dangling bond on the other via the breaking of one of the five bonds.

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