

Report on the research performed at beam-line BM08 with signatures:

08-01-83 (1997)

HS-536 (1998)

08-01-161 (1999)

- 3 MAR. 2000

Title:

Local structure investigation of amorphous germanium hydrogenated thin films doped with column III and V elements.

Introduction.

One of the major debates on the amorphous semiconductor physics relies on the understanding of microscopic mechanisms of substitutional doping in hydrogenated amorphous silicon and germanium thin films doped with group III and V elements. The hydrogenated amorphous germanium (a-Ge:H) is particularly interesting, due to its narrow gap, for the production of infrared sensitive devices. Most of the potential advantages, however, rely on the ability of controlling the electronic properties of the active semi-conducting layer by chemical doping. One of the most important aspects of this process is concerned with the chemical role of the dopant species. This is an important question since most physical properties of the amorphous semiconductors are determined by the local energy minimisation involving network relaxation around individual atoms. So, it is expected that different impurities will exhibit different distribution of co-ordination states. A further aspect to be clarified is how the fraction of impurities, as well as the doping-induced effects, are related to the doping efficiency.

In this work, amorphous germanium thin films with different doping elements and concentrations have been investigated by EXAFS spectroscopy. These preliminary results constitute a first answer to the above mentioned problems. They also show the possibility to measure very diluted samples at the GILDA beam-line.

Experimental.

The a-Ge:H thin films were prepared by rf sputtering a c-Ge target in an Ar+H₂ atmosphere. The doping was performed by co-sputtering small, solid pieces of the source material together with the Ge target. Details on samples preparation can be found in ref. [1-3]. The typical thickness of the film was 3 μm . The defect density was estimated from absorption coefficient (α_n) at 0.7 eV photon energy using the calibration constant reported in the literature [4]. The total dopant concentration was inferred from proton-induced X-ray emission. Samples of a-Ge:H with the following dopant concentrations were examined : $1.5 \cdot 10^{18}$, $1.5 \cdot 10^{19}$, $5 \cdot 10^{19}$, $1.5 \cdot 10^{20}$ and $4.5 \cdot 10^{20}$ cm^{-3} . The average thickness of the films was of 3 μm with a number of doping atoms exposed to the x-ray beam (4 mm x 1.5 mm) of the order of $3 \cdot 10^{13}$ to $8 \cdot 10^{15}$. In order to determine the local order around the dopant specie a measurement of reference samples was carried out. In the case of gallium a gallium-implanted crystalline Ge sample with concentration of $4 \cdot 10^{19}$ cm^{-3} was measured. For indium two reference samples were used: a crystalline germanium with impurity concentration of 10^{18} cm^{-3} indium atoms and a InAs sample. The difficulty in obtaining a crystalline sample doped with antimony induced us to use GaSb as reference. The K-edge of the doping elements (Ga, In, Sb) has been measured in fluorescence mode, at GILDA beam line (BM08), at room temperature, by a nitrogen-cooled pure Ge multi-detector. Due to the low concentration rates

and the efficiency of the Ge detector, 15 to 20 seconds of acquisition time per point were used to record each spectrum.

Results.

The EXAFS signal has been extracted using a technique already described elsewhere [5].

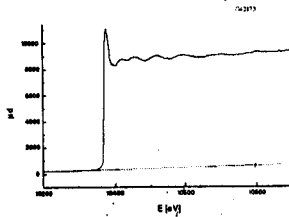


Figure 1

Fluorescence spectrum relative to the a-Ge:H film doped with Ga with a concentration of $1.5 \cdot 10^{20} \text{ cm}^{-3}$. The dotted line refers to the first degree polynomial used for the pre-edge removal.

In figure 2a is reported, as an example representative of all the measurements, the k-weighted EXAFS signal relative to the gallium-doped samples [9] and the crystalline reference sample. In the same figure (b) the corresponding Fourier transform has been reported.

The signal-to-noise ratio is satisfactory even at the smallest impurity concentration ($\sim 1.5 \cdot 10^{18} \text{ cm}^{-3}$, corresponding to $\sim 0.003\%$ at. %) even though the extension in the energy range is shorter in comparison with that of the more doped samples.

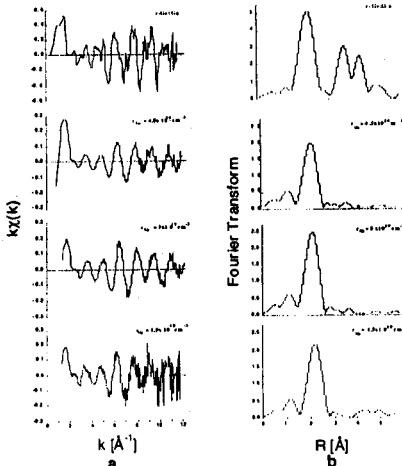


Figure 2

a) Extracted EXAFS signal $\chi(k) \cdot k$ relative to the Ga doped samples in order of increasing concentration (the most diluted is in the lowermost figure) and the crystalline reference sample (the uppermost figure). The signal-to-noise ratio for a concentration of ~ 0.003 at. % is satisfactory. b) The corresponding Fourier transform. The same Hanning window was applied to all the data before the transformation.

The Fourier transform indicates that, as expected, the peaks relative to the second and third shell are absent in all the amorphous samples. To extract the information on the local structure around the dopant specie, the EXAFS signal of the X-Ge first shell were Fourier back-transformed (X refers to the Ga, In and Sb). The information regarding the co-ordination number and the local order around the impurity atom of the investigated sample were extracted by a reference signal obtained from a crystal.

Co-ordination number and $\Delta\sigma^2$ (sample-model Debye-Waller difference) are summarised for all the dopant species in figure 3.

It is apparent from such figure that a similar behaviour of the co-ordination number as a function of impurity concentration can be deduced (solid symbols). The effect of rising doping concentration is a general lowering in co-ordination of the dopant atom. For Ga and In a four-fold co-ordination is apparent while for Sb a slightly less value is reported at the lowest concentrations. Values close to 2 are relative to the highest concentrations for all the impurity atoms. The abrupt decrease in co-ordination doesn't follow a model proposed by Street [6] ("the modified 8-N Mott's rule") which was well attained for P and B impurities in a-Si:H. Beside, only 1% of four-fold co-ordinated sites was found electrically active. Moreover, the comparison between conductivity and co-ordination shows only a partial agreement, from which one can deduce that the conduction mechanism is not completely related to the substitutional doping.

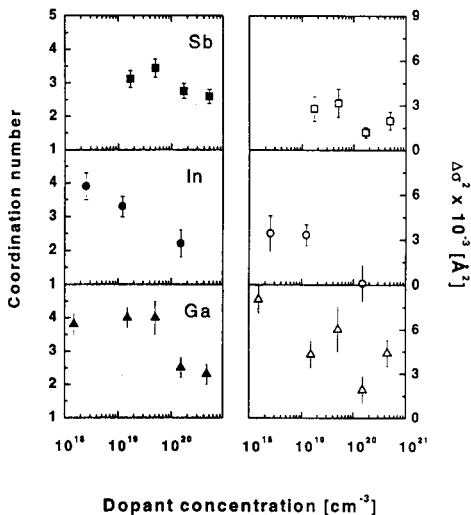


Figure 3

Co-ordination number and Debye-Waller factor difference between sample and model for all the measured dopant species.

For an estimation of the disorder induced by the doping process was used a comparison method, with a crystal as reference sample, based on the cumulant expansion where the

second cumulant represent the Debye-Waller factor. By this method it is possible to estimate the variation of the second cumulant which is related to the overall disorder of the sample under investigation with respect to the reference model. The outcomes of this investigation shows that hydrogen can reduce the effect of the doping-induced network stress by completing dangling bonds [7]. The adding of chemical impurities surprisingly reduce further the disorder as can be seen in the fig. 3 (open symbols).

On the basis of these first results we proposed a new model to explain the doping properties of group III metals in a-Ge:H [8]. The mechanism proposed is not related to the fraction of four-fold co-ordinated doping atoms only, but it considers the compressive stress induced by the atomic and ionic size differences between the germanium atom and the four-fold co-ordinated impurity and its effect on the co-ordination and electrical conductivity.

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Publications related to the research.

1) G. Dalba, P. Fornasini, R. Grisenti, F. Rocca, D. Comedi and I. Chambouleyron, Local coordination of Ga impurity in hydrogenated amorphous germanium studied by EXAFS *Appl. Phys. Lett.* 74 2, 281-283 (1999)

2) I. Chambouleyron, D. Comedi, G. Dalba, P. Fornasini, R. Grisenti and F. Rocca *J. Non-Cryst. Solids* (in press) 2000.

Presentations at international conferences.

"Local Coordination and Electronic Doping of Column III Metals in Hydrogenated Amorphous Germanium"

I. Chambouleyron, D. Comedi, G. Dalba, P. Fornasini, R. Grisenti, and F. Rocca
ICAMS 18 - International Conference on Amorphous and Crystalline Semiconductors, Utah (USA) 1999.