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# Bismuth doping of hydrogenated amorphous germanium thin films

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#### Abstract

The optoelectronic properties of Bi-doped hydrogenated amorphous germanium (a-Ge:H), with relative impurity concentrations  $[N_{imp}/N_{Ge}]$  ranging between  $8 \times 10^{-6}$  and  $5.5 \times 10^{-3}$ , are reported. The incorporation of Bi produces small changes in the dark conductivity of a-Ge:H. For a three orders of magnitude change in impurity concentration the room-temperature conductivity changes by just one order of magnitude. Within this doping range no, or small, changes were measured in the values of the pseudo-gap, the Urbach energy, and the hydrogen content. The Fermi level always remains far from the conduction band edge, shifting by only 0.1 eV for the sample with the largest doping concentration. The main conclusion is that Bi is a very inefficient active donor in a-Ge:H. The likely reasons for such behavior are discussed. © 2006 Elsevier B.V. All rights reserved.

Keywords: Amorphous germanium; Hydrogenated amorphous semiconductor; Doped semiconductor; Sputtering; Extended X-ray adsorption fine structure; Conductivity

## 1. Introduction

The doping of hydrogenated amorphous group IV semiconductors (a-Ge:H, a-Si:H and their alloys) with group III or Vatoms has been thoroughly studied during past years after the demonstration of its intrinsic peculiarities as compared to the doping process in their crystalline semiconductor counterparts [1-7]. It is well known that in these materials the doping is very inefficient and accompanied by the creation of dangling bond defects [1-5]. The low efficiency can be understood if the amorphous lattice is imagined to roughly resemble a continuous random network (CRN) [8], where individual atoms are allowed to maximize the number of paired electrons in a bonding orbital, each chemical species taking its preferred coordination (i.e., the 8-N rule) [9]. Within such a model, columns III and V impurities in a tetrahedrally coordinated CRN are expected to adopt a non-active doping configuration. The low doping efficiency can then be explained by small deviations from this model. A CRN with a

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modified 8-N rule, which considers the incorporation of ionized impurities during film deposition, was proposed by Street [10]. A thermal equilibrium distribution of different possible bonding and defect states is assumed, where formation energy and hence density are mainly determined by the position of the Fermi level relative to the acceptor or donor state [1]. In a quite satisfactory way, this scheme predicted the gross features of the electronic properties of phosphorus and boron doped a-Si:H films. It should be noted, however, that in this model (and in its later modifications) the role of the chemical specificity of the doping impurity-electronegativity, electron cloud radius, etc.-is not directly considered. This fact could be at the origin of their little success in explaining the electronic properties of amorphous films doped with heavier elements. As most properties of amorphous semiconductors are determined by the minimization of the local energy involving the relaxation of the network around the impurity, it is appropriate to consider this problem. The above questions motivated our research group in Campinas to carry out a systematic study of the active doping properties of all elements of columns III and V in a-Ge:H films. The results of this research clearly indicate that different impurity contents  $(N_{\rm imp}/N_{\rm Ge})$  are needed for each specific doping element to achieve a given conductivity variation, suggesting that a different doping efficiency is associated to each element [5]. The studies of the optoelectronic properties of a-Ge: H films doped with column III metals [6], as well as the analysis of

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Fig. 1. Room temperature dark conductivity of Bi- and As-doped a-Ge:H as a function of relative impurity concentration  $[N_{imp}/N_{Ge}]$ . Note the large  $\sigma_{RT}$  variations induced by As doping in contrast with the one order of magnitude increase provoked by almost 1 at.% Bi. The dashed lines are a guide to the eyes.

extended X-ray absorption fine structure (EXAFS) data [7], clearly demonstrated that the thermal equilibrium models of doping based on the modified 8-N rule are not applicable to Al, Ga, and In impurities. In particular, the increased defect density associated with doping does not appear to be connected to the Fermi energy. Moreover, EXAFS data indicate that practically all highly diluted impurities, i.e., Ga and In concentrations smaller than ca.  $1.5 \times 10^{18}$  cm<sup>-3</sup>, adopt the four-fold coordination of the a-Ge host network. However, as  $N_{\text{Ga}}/N_{\text{Ge}}$  and  $N_{\text{In}}/N_{\text{Ge}}$  increase, the impurity coordination N rapidly decreases from 4 to less than 3 for a doping level which is an order-of-magnitude higher for Ga than for In, in consistency with conductivity data. From the overall analysis of first-shell Ga-Ge and In-Ge distances, and the disorder around the impurity, it was proposed that the rapid change of impurity coordination originates from a process of relaxation of the compressive stress accumulated in the a-Ge:H network due to the increasing incorporation of substitutional impurities. As a consequence, the "size" of the impurity element appears also to play a fundamental role in the process of active electronic doping.

The present contribution extends the above studies to the case of the column V metal Bi. The results of Bi doping are compared with those obtained with arsenic impurity [6]. We find that, differently from all other column V elements studied, bismuth is a very poor electronic dopant in a-Ge:H [11]. The reason for this different behavior appears to be related to the size of the electron cloud radius of bismuth, as can be deduced by correlating the present results with recent extended X-ray absorption fine structure (EXAFS) data [12]. The results on impurity coordination and local order around Bi in a-Ge:H suggest that the large electron cloud radius of Bi, relative to the atoms of the host network, prevents the four-fold coordination of most impurities in the amorphous network and, consequently, any reasonable active doping.

#### 2. Experimental details

The a-Ge:H films were prepared by radio-frequency sputtering a c-Ge target in an Ar+H<sub>2</sub> atmosphere. The doping was performed by co-sputtering small, solid pieces of Bi together with the Ge target. Details on sample deposition parameters and film characterization are given in previous publications of the Campinas group [13,14]. Films of  $10^{-4}$  cm typical thickness were deposited onto Corning 7059 glass and onto crystalline silicon substrates. Optical transmittance data and photo-thermal deflection spectroscopy measurements were combined to yield the optical pseudogap and the characteristic energy of the exponential absorption edge, or Urbach energy ( $E_{\rm U}$ ). The defect density  $N_{\rm D}$  was estimated from the absorption coefficient at a photon energy of 0.7 eV ( $\alpha_{0.7}$ ) [15].

The conductivity measurements were performed in a way described in Refs. [13,14]. Thermopower data indicate that Bi impurity always induces a dominant electron conduction, implying an n-type doping, as expected from a column V element [11]. The total impurity concentration in the films was inferred from Rutherford back-scattering (RBS) measurements. Most data of As-doped a-Ge:H samples are from Ref. [16]. The hydrogen content ( $\sim 10$  at.%) was determined from the integrated infrared absorption of the wagging vibration mode of the Ge–H dipole [17].

# 3. Results

Fig. 1 shows the room temperature conductivity,  $\sigma_{\rm RT}$ , as a function of Bi impurity concentration. For comparison purposes, the conductivity variations induced by similar concentrations of arsenic impurity are also shown. Fig. 1 clearly indicates that, within the considered doping concentration range, i.e.,  $N_{\rm imp}/N_{\rm Ge} < 10^{-2}$ , *arsenic* induces a three orders of magnitude increase



Fig. 2. Activation energy of the Bi- and As-doped a-Ge:H as a function of relative impurity concentration  $[N_{\rm imp}/N_{\rm Ge}]$ , as measured in the 200–400 K range. Note the very small variation of  $E_{\rm A}$  induced by Bi doping. The dashed lines are a guide to the eyes.

of  $\sigma_{\text{RT}}$  whereas Bi only provokes one order of magnitude increase. Note that the dark conductivity of all samples is thermally activated down to 200 K. The values of the activation energy of the dark conductivity ( $E_A$ ) induced by Bi doping, as derived from the log  $\sigma(T)$  vs. (1/T) Arrhenius plots, are shown in Fig. 2. Arsenic doping induces a large  $E_A$  decrease, a typical situation of an efficient n-type doping. In contrast, the small  $E_A$  decrements induced by Bi impurity confirm the poorness of this heavy column V metal as an n-type doping element. We conclude that Bi is an n-type doping element in a-Ge:H but having a very poor active doping efficiency.

The characteristic energy of the Urbach tail  $E_{\rm U}$ , which correlates with disorder, is shown in Fig. 3.  $E_{\rm U}$  does not appreciably change with increasing Bi concentration. In contrast, note the important  $E_{\rm U}$  variations provoked by As in the a-Ge:H network within the same impurity concentration range. The figure indicates that the addition of Bi into the amorphous network does not influence very much the overall topological disorder, i.e., Ge–Ge bond angle and length distributions. We note at this point that other column III and column V elements provoke a considerable increase of  $E_{\rm U}$  as the impurity concentration increases (see Refs. [5,6], and the changes of  $E_{\rm U}$  induced by As doping shown in Fig. 3).

The density of deep defects induced by an increasing Bi concentration, shown in Fig. 4, changes by no more than a factor of two within the studied impurity concentration range. This is also a surprising finding that indicates small impurity-induced structural changes, but correlates with the little change of  $E_U$  as seen in Fig. 3. As a consequence, all experimental data indicate that, either from the point of view of electronic conduction or from the structural aspects, Bi disturbs very little the properties of amorphous hydrogenated germanium.



Fig. 3. Characteristic energy of the Urbach edge of Bi- and As-doped a-Ge:H as a function of relative impurity concentration  $[N_{imp}/N_{Ge}]$ . The Urbach energy remains constant for Bi-doped samples whereas large changes are experienced by As-doped samples. Arsenic behaves as a classical doping element in a-Ge:H. The dashed lines are a guide to the eyes.



Fig. 4. Deep defect density generated in a-Ge:H by Bi and As doping as a function of relative impurity concentration  $[N_{\rm imp}/N_{\rm Ge}]$ . The small change of  $N_{\rm D}$  with Bi concentration suggests a small density of ionized four-fold Bi, in agreement with electrical and EXAFS data. The dashed lines are a guide to the eyes.

Finally, it is important to mention here that the  $E_{04}$  optical gap-photon energy at which the absorption coefficient equals  $10^4 \text{ cm}^{-1}$ -and the hydrogen concentration in the samples, stay almost unchanged within the studied doping range [11]. We concluded, then, that the small conductivity changes induced by Bi doping, as seen in Fig. 1, do not originate from optical gap and/or variations of the concentration of hydrogen, but from active Bi centers that induce a small shift of the Fermi energy.

## 4. Discussion

The results indicate that Bi is an inefficient electronic n-type doping element in a-Ge:H. Note that all other group V elements (N, P, As, and Sb) are very efficient donors: they produce a several orders of magnitude increase of  $\sigma_{\rm RT}$ , decrease considerably  $E_{\rm A}$ , and push  $E_{\rm F}$  toward the conduction band edge [6]. The ionization energy of Bi impurity in crystalline Ge is nearly the same as that of other column V elements (P: 12.36 meV; As: 13.65 meV; Sb: 9.66 meV and Bi: 12.15 meV) [18]. It is known, however, that in the amorphous network lattice relaxation effects tend to push donor (or acceptor) states deeper away from the conduction (or valence) band edges [2]. Hence, a larger activation energy of a given doping center is expected for a-Ge:H than for c-Ge, the difference depending on the chemical specificity of the impurity. This aspect is not sufficiently considered by the existing models of doping [1,4,10]. The question in order is then—why Bi is such an inefficient donor in a-Ge:H? In what follows we explore different possible causes.

One possibility would be Bi atoms not being randomly distributed in the network but aggregated forming metallic Bi clusters in the film. However, EXAFS data on the coordination number of Bi in the a-Ge:H network do not support the hypothesis of metal aggregates [12]. Furthermore, the sputter deposition process occurs at a relatively low temperature, hence Bi precipitation in clusters is not expected.

Another possibility would be an amphoteric behavior of Bi, i.e., the simultaneous existence of both, n-type and p-type active doping centers, where p-type doping would result from a defectimpurity complex formation. Reports on compensated a-Si:H samples, in which P and B were included simultaneously, indicate that compensated samples exhibit a small density of deep states, but display a significantly increased Urbach edge energy, a consequence of the long-range potential fluctuations of both types of ionized impurities [1]. In the present case, however, an increased Bi concentration does not alter significantly either the characteristic energy of the Urbach edge or the  $E_{04}$  optical gap. Then, we conclude that an amphoteric behavior of Bi is not likely to be the cause of the poor doping activity.

A self-compensation mechanism via the creation deep gap states resulting from Bi atoms in a certain bonding configuration might also result in a very poor doping activity. However, this mechanism would imply a correlation between the density of deep defects and the impurity concentration. Fig. 4 shows, on the contrary, that the density of deep states hardly changes for increasing Bi concentrations, i.e., the self-compensation mechanism can possibly be excluded.

It may also occur that hydrogen passivates some active Bi centers, as reported to be the case for some dopants in a-Si:H [19]. While, as will be shown below, there are good reasons to believe that this possibility plays a role, we believe that the low doping efficiency of Bi principally results from two other main causes: a very small density of active four-fold coordinated Bi atoms  $(Bi_4^+)$  and a rather large activation energy of the donor state in the Bi<sub>4</sub> configuration. EXAFS studies of Bi-doped a-Ge: H films [12] have found that the coordination number of Bi increases from  $\sim 2.5$  up to  $\sim 3.4$  as the impurity concentration increases in the network. Within the same impurity concentration range, the disorder around Bi (i.e., Bi displacements with respect to its mean atomic position as referenced to its nearest Ge neighbors) increases as well. While the explanation of the structural behavior revealed by the EXAFS measurements is considered to be out of the scope of the present work, an attempt is made here to interpret their results in the context of the data presented here. First, it can be seen that the mean coordination of Bi changes only slightly across the expected (from the 8-N rule) preferred coordination number of three. This indicates that most Bi atoms are three-fold coordinated (i.e., the density of  $Bi_4^+$ is always low). Also noted is that some Bi atoms are probably bonded to H, as evidenced by the coordination number lower than 3 reported for low  $N_{\rm Bi}/N_{\rm Ge}$ .

Therefore, it can be seen that the low density of  $Bi_4^+$  as deduced from EXAFS is consistent with the present data, which show a small doping efficiency and small Bi induced effects on the Urbach tail parameter (see Figs. 2 and 3). In any case, the flexibility of the amorphous network allows the inclusion of a small fraction of  $Bi_4$  centers, as evidenced from the mean coordination number larger than 3 as deduced from EXAFS. Hence, we attribute the decrease of the conductivity activation energy with increasing  $N_{\rm Bi}/N_{\rm Ge}$  to the creation of such Bi<sup>+</sup><sub>4</sub> centers.

The increasing disorder around Bi as observed by EXAFS indicates that large lattice relaxation occurs around Bi atoms, which should contribute to a rather deep donor state and to the very poor electronic activity of this impurity, as observed. It is interesting to note that the density of deep defects increases only slightly as a function of  $N_{\rm Bi}/N_{\rm Ge}$  (Fig. 4) despite the fact that the Bi atomic ratio is considerably larger than that of Ge. From the EXAFS data, it seems that the network prefers to accommodate this size difference by lattice relaxation and not by dangling bond formation. Previous studies of doping of a-Ge:H have shown a lack of correlation between dangling bond formation and doping efficiency for heavy Group III impurities [5,6], but did not show it for n-type dopants [6]. It is interesting to note that for the case shown here, the small number of dangling bond defects induced by the Bi n-type doping of a-Ge:H appears to be correlated by the very small doping efficiency exhibited by this impurity. This would tentatively suggest a general picture where doping-induced defects and the doping efficiency are indeed interconnected for the case of Group V impurity doping of a-Ge:H.

# 5. Conclusions

The doping properties of bismuth in a-Ge:H have been studied. It has been shown that Bi, in contrast to As and other column V elements [6,16], is an extremely poor active donor; the reasons probably stemming from its large electron cloud radius. The comparison between the structural, electrical, and optical data suggest that the low doping efficiency is due to highly diluted Bi going preferentially three-fold coordinated and a large ionization energy of the donor state.

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