

## CHALCOGENIDE AMORPHOUS SEMICONDUCTORS: CHEMICAL MODIFICATION OR DOPING?

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The incorporation of high concentrations of different additives in the amorphous chalcogenide semiconductors can affect drastically their electronic properties. The effect is known as 'modification', but sometimes is called 'doping', which could be misleading. This paper reviews some of the more important aspects of the development of the field and attempts to bring up some points that may need more attention.

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### 1. Introduction

The year 1955 may be considered as the origin of the field of amorphous materials. It was in 1955 when Kolomiets and his collaborators [1] have shown that amorphous chalcogenide glasses are semiconductors. It was difficult at that time to understand why amorphous materials, like window glasses or the chalcogenide alloys, characterised by the lack of lattice periodicity, have an energy gap. Only in 1960, Ioffe and Regel [2] realised that the band gap depends on the existence of short-range order rather than on the long-range order of the lattice and suggested that the first coordination number of the corresponding crystal (if it exists) is preserved in the amorphous structure. At about the same time, in his effort to explain hopping conduction on compensated crystalline semiconductors, Anderson [3] introduced the concept of localisation with his classic paper 'On the absence of diffusion in certain random lattices'. Soon after Mott and Twose [4] showed that, as soon as disorder was introduced, all states in one dimensional energy band became localised and thus the concept of a sharp 'mobility edge',  $E_C$ , that separates a range of localised energy states from the extended electronic states, was first introduced by Cohen, Fritzsche and Ovshinsky [5]. In their energy band model, the well-known CFO model, the bands were extended to wide ranges of the localised states that overlap in the centre of the mobility gap. In contrast, Davis and Mott [6] suggested a model where the geometrical disorder of the material, forms a short range of localised states at the band edges while the neutral dangling bonds give rise a well-separated narrow band of localised states, at the centre of the gap where the  $E_F$  lies. In the case of charge dangling bonds [7], two narrow bands are formed, proportional to the concentration of the  $D^+$  and  $D^-$  centres that are located around  $E_F$ . The tools for the theoretical understanding of the amorphous materials were created.

On the other hand, the pioneer experimental work of Ovshinsky [8] on electrical switching and memory has already shown that amorphous materials have a bright future with a lot of useful potential applications. Soon, the Ovonic Electrically Erasable Programmable Read Only Memory for computer data storage was fabricated. The device is continuously developed and Ovshinsky's goal for the near future is to fabricate a single device, called Ovonic Unified Memory [9], in order to replace the multiple memory types of devices used in today's personal computers. In the early 70's, the sensitivity of the chalcogenide alloys to the light have been already recognized [10, 11] and Xerography was widely used [12]. The importance of the photocrystallization [10] and the ability of Ovshinsky to foresee future applications make him to hold the world patent on the rewritable optical memory technology that practically developed more than a decade later!

In the early days one of the many puzzles was that amorphous semiconductors were not possible to be doped. It was understood at the time that the existing very high concentration of states in the energy gap of evaporated a-Si and a-Ge films [12] prevents the doping. The challenge for researchers was to invent ways to reduce the high density of dangling bonds. In the case of chalcogenide glasses the picture was more confused, as the concentration of states inside the energy gap was very low. The introduction of low, or even of high concentrations, of impurities was not able to change the sign of the majority carriers. Why doping was not possible for the chalcogenide semiconductors?

In the middle 70's, the introduction of hydrogen in the lattice of a-Si, by the decomposition of  $\text{SiH}_4$  [13] or with the incorporation of  $\text{H}_2$  in the sputtering gas [14] reduced drastically the middle gap states, improved the photoconductive properties and made possible the doping of a-Si:H. Soon the industrial production of large area, thin-film photovoltaic solar cells with relative high efficiencies became available [9]. In the present paper we re-consider existing data in an attempt to understand better the observed changes in the electronic properties of the chalcogenide alloys when different additives are introduced in the host lattice during gas phase deposition.

## 2. Why chemical modification and not doping?

For the early days [15] the effect of impurities to the electronic properties of the chalcogenide alloys was studied systematically. It was proved experimentally that the addition of impurities was not able to shift the energy Fermi,  $E_F$ , and dope the amorphous chalcogenide semiconductors. The 'pinning of the  $E_F$ ' in the middle of the gap was explained by the 8-N rule, according to which all the available electrons of the impurity made covalent bonds with the surrounding atoms. Nevertheless, some exceptions to the rule were reported at which the electrical conductivity increases by 4-5 orders of magnitude, when relative small concentrations of Cu, Mn, Ag, In or few more elements were added in melt quenched  $\text{As}_2\text{Se}_3$  and other ternary chalcogenide amorphous alloys (for relative references see [12]).

In 1977 Ovshinsky [16] pointed out that the incorporation of significant amount of elements that preferably make directional bonding with d- or f-orbitals, could affect the local environment and modify the electronic properties of the host material. In the following years the incorporation of transition metals or rare earth elements in amorphous chalcogenides became a popular topic. A number of different transition and non-transition elements were added, by co-sputtering, in amorphous  $\text{As}_2\text{Se}_3$  [17, 18], in multi-component chalcogenides [17, 19] and pure a-As [20] films. It had pointed out that the modification is much more efficient if the impurity is added below the glass transition temperature or the melting point of the host material [16], as the equilibrium between the charged additives and the valance alternation centers is prevented. It was also argued that crystallization or phase separation is more difficult to occur when the incorporation of the additive is made during the gas phase deposition, onto low temperature substrates. Experimentally it was proved that the efficiency of the doping is higher in films than in bulk samples [17, 19]. ESR measurements [21] have shown that the bonding scheme of Ni atoms is different between bulk and thin films.

Even though the influence on the electronic properties depends on the impurity, the host material and the sample preparation technique [16, 17], the general features of all data could be summarized as follows: the addition of up to 10 to 15 at. % of the transition metals into the amorphous chalcogenide films [16-20],

- increases the room temperature electrical conductivity by 8-10 orders of magnitude,
- induces a strong contribution of variable range hopping conduction at low temperatures,
- decreases considerable, the activation energy,  $E_\sigma$ , and the intercept of the dark conductivity at the high temperature regime [17, 18, 20],
- induces relative small variations on the optical band gap,  $E_o$ , while the energy dependence of the absorption coefficient becomes less steep [18],
- reduces drastically the magnitude of the thermopower from few mV/K to hundred  $\mu\text{V/K}$  [17-20].

Indicatively, in Fig. 1a are plotted the optical band gap,  $E_o/2$ , and the conductivity activation energy,  $E_\sigma$ , of  $\text{As}_2\text{Se}_3$  [17, 18] and of pure a-As [20] films co-sputtered with Ni and Fe. The activation energy for conduction of pure a-As is 0.6 eV and the optical gap, determined by the energy at which

the absorption coefficient equals to  $3 \times 10^4 \text{ cm}^{-1}$ , is 1.3 eV. For better comparison in Fig. 1a, all values have been normalized to that of  $\text{As}_2\text{Se}_3$  [17]. The relative small decrease of the optical gap is the result of alloying and depends on the material. In contrast, the activation energy,  $E_\sigma$ , that is determined by the conduction path and the position of the Fermi level, decreases by about 80% with the addition of only 2% of the transition element. The observed simultaneous decrease of the intercept [17, 18, 20] indicates that the main conduction path may be shifted from the extended to the localized states. At impurity concentrations higher than 4% the activation energy shows a leveling-off. At this region, the variable range hopping dominates the electronic conduction even at room temperature. The linear region is reduced or in some cases, is limited to the temperature range where the transition from the variable range hopping to band conduction occurs. In this region the meaning of the activation energy, calculated from a straight line, raises some questions and the values will be, at least, underestimated. Even under these experimental difficulties the results, from different laboratories on various alloys with a range of additives, show a remarkable agreement. We may notice that even though a-As is not a chalcogenide element, the effect is very similar.

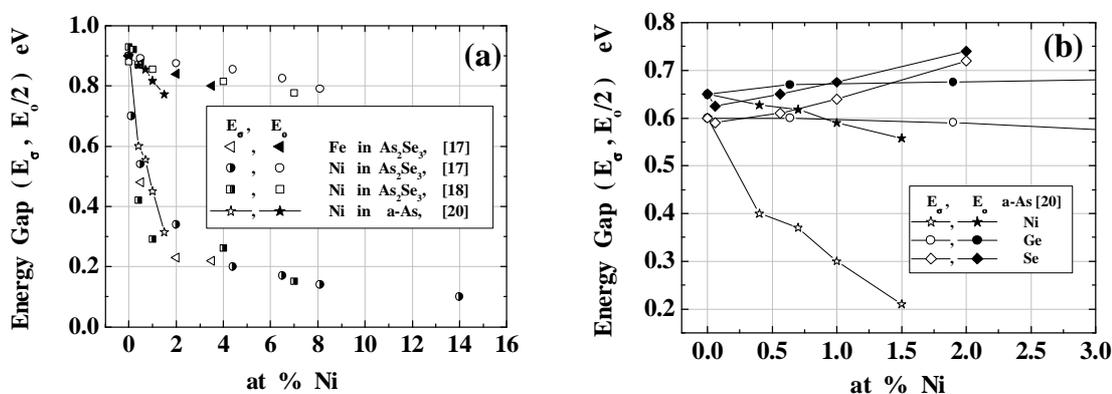


Fig. 1. The conductivity activation energy,  $E_\sigma$ , and (half) the optical band gap,  $E_0/2$ ; a) for  $\text{As}_2\text{Se}_3$  [17, 18] and for pure a-As [20] films co-sputtered with Ni and Fe and b) for pure a-As [20a] films co-sputtered with Ni, Ge and Se.

In the literature, most of the publications have focused on high concentrations of additives, as the observed increase of the conductivity was the main topic. But, if the goal is to understand the mechanisms responsible for the modification effects, it seems more interesting to study alloys with concentrations less than 1-2 % at. of the additive, where most of the observed changes occur. An elementary amorphous semiconductor, a-As, was studied extensively [20]. Low concentrations from three different groups of additives, a transition metal (Ni), a tetrahedral element (Ge) and the chalcogenide elements (S, Se and Te) were used. The addition of each element affects the electrical conductivity and the optical band gap in a very different and characteristic way.

The effect of Ni has been already described above. The addition of up to 12% of Ge has no effect on the magnitude of the room temperature conductivity, while, up to 4% Ge, the activation energy and the intercept show only a small variation and then decrease with increasing the Ge content. At low temperatures, a strong contribution of variable range hopping conduction is induced. The optical gap increases slightly. The addition of any of the three different chalcogenide elements into a-As, causes exactly the same effects. At very low chalcogen concentrations ( $< 0.4\%$ ) the magnitude of the room temperature conductivity increases slightly and then decreases by one order of magnitude with the addition of 1% of the chalcogen atom while the activation energy,  $E_\sigma$ , first decreases and then increases. No variable range hopping is introduced; in contrast the observed small departure from the linearity in the conductivity of pure a-As [20b], at low temperatures, is completely removed with the addition of  $>0.4\%$  of the chalcogens. Similarly, the optical gap, first decrease slightly and then increases. The variations observed in the optical gap,  $E_0$  and the activation energy for conduction,  $E_\sigma$ , are plotted in Fig. 1b. It is obvious that Ni induces the more profound changes to the  $E_\sigma$  than the other elements. Ge introduces a high concentration of dangling bonds in the center of gap, while the chalcogens are mainly alloying with the As, as  $E_0$  and  $E_\sigma$  follow an almost parallel variation [20]. We

may notice that very low concentrations (< 0.4 %) of a chalcogen additive are necessary for removing As-dangling bonds from the gap.

How it is possible to explain all these different features within a unified way? According to the ideas of the charge defect model [7, 12], in the amorphous semiconductors there are equal concentrations of positive and negatively charged point defects of all the components of the alloy; for example, it is believed that in  $\text{As}_2\text{Se}_3$  the concentrations of  $[\text{P}_4^+][\text{C}_3^+]=[\text{P}_2^-][\text{C}_1^-]$  where the superscript denotes the charge and the subscript the coordination number. The introduction of a charged additive disturbs the concentration of the native charged defects, but keeps the charge neutrality. Ovshinsky and Adler [23] suggested that transition metals in amorphous semiconductors exist in different oxidation states, indeed ESR [21] and Mössbauer spectra [24] on Ni and Fe modified chalcogenide alloys, confirmed the existence of  $(\text{Ni or Fe})^{+3}$  and/or  $(\text{Ni or Fe})^{+2}$  ions. It is expected that low concentrations of Ni positive charged sites would reduce greatly the concentration of all positively charged native defects. When their density would exceed the concentration of  $[\text{P}_4^+][\text{C}_3^+]$  sites, the concentration of the  $[\text{P}_2^-][\text{C}_1^-]$  will increase but remains always somewhat larger than the concentration of the Ni ions [17, 20, 23]. If a sufficient concentration of Ni is present, the Fermi energy rises until it enters the band arising from the modifier, as it is suggested by the appearance of variable range hopping. The Ni bands will be located at the upper half of the gap, as is indicated by their charge [17, 20, 23]. In the case of a-As that is an n-type semiconductor, the shift of  $E_F$  inside it, addresses no questions about change of the conduction type; but in the case of  $\text{As}_2\text{Se}_3$  and the other ternary alloys that are p-type semiconductors, the suggestion that the  $E_F$  moves inside a positive Ni band raises some very important questions. Does the materials become n-type, as it has been argued [17, 23]? Unfortunately, the predominant variable range hopping conduction do not allow the determination of the sign of the free majority carries by the usual experimental methods, as it will be discussed later. In contrast, some researchers proposed [18] that Ni forms negative ions when added in  $\text{As}_2\text{Se}_3$ , the acceptor level lies at 0.22 eV above the valence band.

In all the cases where the thermopower of amorphous chalcogenides modified by Ni is reported [17-20], the values were of the order of few hundreds  $\mu\text{V}/\text{K}$ , being consistent with the observation of variable range hopping conduction in this temperature regime [12]. Increasing the concentration of the transition element in the chalcogenide alloys, the sign of the thermopower changed from positive to negative [17, 19], while in the case of pure a-As, which is an n-type intrinsic semiconductor [22], the thermopower always remains negative, with values around  $-100 \mu\text{V}/\text{K}$  for all the alloys [20]. An important point to be brought up is the relation between the sign of the thermoelectric power and the sign of the majority carriers. In the case where the electronic conduction takes place by variable range hopping, the  $E_F$  lies inside a band of localized states; the sign of the thermopower is then determined by the energy variation of the density of states at  $E_F$  and does not give information about the sign of the free majority carriers [12]. Often in the literature the observed sign reverse have been misinterpreted as a change in the conduction type of the modified material that was characterized as an n-type chalcogenide semiconductor.

To our knowledge, the more sensitive substance to ‘doping’ seems to be a-Se. Only few hundreds ppm of O, K or Cl [25] introduced in the melt, increase the dark conductivity by several orders of magnitude. With some reservation, due to the low conductivity of the material, a change to n-type conduction was reported when traces of Cl were added. A detailed explanation has been given by Mott [12] who assumed that  $\text{O}^-$ ,  $\text{Cl}^-$  or  $\text{K}^+$  ions were compensated by the  $\text{D}^+$  or the  $\text{D}^-$  native defects respectively.

The only amorphous alloys where transition from p- to n-type conduction observed without any doubt, are alloys of Ge-Se or Ge-S, with different of Ge/Se(S), when relative high concentrations of Bi were added in the melt [26] or by co-sputtering [27]. At around 9-10% Bi a change in the conduction type occurs, as the thermoelectric power becomes negative with values between  $-0.5$  to  $-1 \text{ mV}/\text{deg}$  depending on the alloy. The dark conductivity increases by 10 orders of magnitude, without any indication of variable range hopping conduction at all concentrations up to 16% Bi. The optical gap decreases with the addition of Bi. Calculation of the quantity  $(E_o/2-E_\sigma)$  indicates that the Fermi energy is shifted from 0.1 eV below to 0.1 eV above the center of the energy gap [26, 27].

Could this type of sign reversal be characterized as doping or still it could be considered as modification? What actually happens in the states in the gap with the addition of Bi that causes the small shift of the  $E_F$ , without inducing variable range hopping? Two very sensitive techniques that are

used extensively to measure deep band gap states in a-Si:H, namely the constant photocurrent method (CPM) and the modulated photocurrent method (MPC) have been used to study the density of states (DOS) in the band gap of the Ge-Se-Bi ternary films [28]. The two methods measure the DOS distribution at the opposite sides of the energy bands. Applying, both of them at the same alloy we are able to get a complete picture of the entire DOS distribution of defects in the energy gap. One of the main assumptions of the CPM is that the photogeneration quantum efficiency must remain constant in the energy range of the measurements. The comparison of the photosensitivity with the optical absorption indicates that, in our alloys, the quantum efficiency is constant and close to unity, a fact that allows us to use the CPM method to characterize the chalcogenide semiconductors. The results are shown in Fig. 2. For each alloy, the Fermi level lies always in the minimum of the DOS. At each band side, the measured DOS have been fitted with two Gaussian defect distributions and an exponential tail [28]. The very smooth and consistent variation of the DOS among the different alloys indicates that, with the increase of the Bi concentration, the defect density above the center of the gap diminishes, while the defect density below the center of the gap increases. As a result, the minimum of the DOS is gradually shifted towards the conduction band side and n-type conduction dominates at Bi concentrations higher than 9%. The  $E_F$  remains always in the minimum of the DOS, as no variable range hopping conduction was observed.

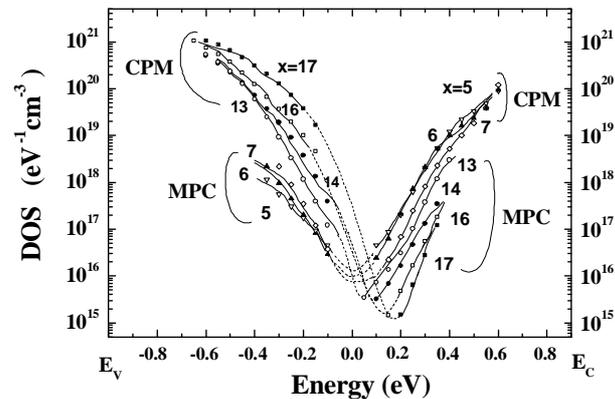


Fig. 2. The defect DOS of  $\text{Ge}_{25}\text{Se}_{75-x}\text{Bi}_x$  films, with  $x=0-15.6$  from [28]. The solid lines are the experimental data; the points are theoretical fittings; the dashed lines are guides to the eye.

It is noteworthy that detailed study of the x-ray photo-emission spectroscopy (XPS) made on the co-sputtered  $\text{Ge}_{25}\text{Se}_{75-x}\text{Bi}_x$  films, with  $x = 0-15.6$  [27], clearly demonstrates that the chemical states of all the Ge-Se-Bi alloys are mixtures of two different bonding environments on a local atomic scale. Macroscopically, they are homogeneous ternary films, as the Se states exhibit only one component and not two as in the characteristic case of a diphasic material. In contrast it has found that the melt quenched material [26] consists of a mixture of  $\text{GeSe}(\text{S})_2$  and  $\text{Bi}_2\text{Se}(\text{S})_3$  phases. In this case the change in the conduction type was explained with the percolation theory, as the  $\text{Bi}_2\text{Se}(\text{S})_3$  phase is an n-type semiconductor.

### 3. Conclusions

The reported data on a variety of chalcogenide semiconductors show that certain additives can cause large increases in the electrical conductivity. Different types of modifications have been reported: In a-As or in chalcogenide alloys with high concentrations of transition metals, the  $E_F$  is shifted inside a band induced by the additives, making variable range hopping the dominant conduction mechanism and the determination of the conduction type not possible with the usual methods. In alloys like Ge-Se(S)-Bi, where the conduction type change from p- to n-type at 9-10% of Bi, the  $E_F$  remains in the minimum of the DOS, close to the centre of the energy gap. It seems that only pure a-Se could be considered as the unique case of a truly doped chalcogenide semiconductor

as, only few hundred ppm of chlorine increase the conductivity by orders of magnitude and probably change the conduction type.

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