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Tetrahedrally bonded ternary amorphous semiconductor alloys

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The properties of tetrahedrally bonded ternary amorphous semiconductors a -CSiSn:H and a -CSiGe:H are reviewed with particular emphasis on the temperature dependence of dark conductivity and the coordination in random networks. It is shown here that the dark conductivity as a function of the temperature strongly depends on the carbon content and, more precisely, on the proportion of sp^3 and sp^2 sites in the carbon. Ternary alloys with different carbon contents are compared to binary alloys using the average coordination number. The ternary alloys have an average coordination number close to the optimal value predicted for amorphous covalent networks.

INTRODUCTION

Alloy materials can be very useful, because they allow one to realize photovoltaic and optoelectronic devices with good characteristics. Hydrogenated amorphous silicon, a -Si:H, is the most widely used semiconductor in electronic devices. However, alloys with optical gaps smaller than a -Si:H, such as a -SiSn:H (Refs. 1–5) and a -SiGe:H,^{6,7} are of interest in photovoltaic devices, since these materials improve the long-wavelength sensitivity of a -Si solar cells. On the other hand, alloys with gaps wider than a -Si:H such as a -SiC:H (Refs. 8 and 9) are promising materials for a -Si solar-cell window layers and for large-area white-luminescence devices.

Tetrahedrally bonded ternary amorphous carbon-based alloys such as a -CSiSn:H and a -CSiGe:H have been studied recently.^{10–12} Carbon, germanium, and tin atoms (group-IV elements) can be easily introduced in a -Si:H networks to make alloys. Germanium could easily produce the Si-Ge fourfold-coordinated structure, since Si has the same tetrahedrally coordinated diamond cubic crystal structure as Ge. On the contrary, Si-Sn alloys are homogeneous mixtures of Si and Sn atoms in random tetrahedral coordination. Tin atoms increase the stress in the a -Si:H network because of their large atomic radius and for the presence of oxygen in a -SiSn samples. They tend to create many dangling bonds and do not bind easily with hydrogen atoms as compared with germanium atoms.

The carbon presents peculiar characteristics. Alloys as a -Si:H, a -SiSn:H, a -SiGe:H, and the a -C:H are indeed fundamentally different from an electronic structure point of view. While silicon and germanium are fully stable only under fourfold coordination, carbon has an allotropic nature and can present three types of hybridization with comparable probability; i.e., sp^3 , sp^2 , and sp^1 . The corresponding chemical bonds are tetrahedral, trigonal, and linear. Amorphous samples contain both sp^2 - and sp^3 -bonded carbon. The proportion of sp^3 to sp^2 bonding has been widely studied. Recently arguments for the existence of π -bonded sp^2 clusters surrounded by sp^3 regions have been presented by Robertson.^{13,14} Furthermore, carbon has higher thermal stability and binding en-

ergy than silicon and germanium. The properties of the tetrahedral carbon alloys are then the result of the type of bonding of the carbon atoms and the role of hydrogen inclusion. The a -SiC:H compound and the effect of carbon in the a -Si:H network have received a great deal of attention to date. On the contrary, little work has been done on the tetrahedral ternary alloys. More information can be gained from the experimental results recently obtained on the optoelectronic properties of such alloys.^{10,15}

The main experimental observations reported in this paper concern the behavior of the dc conductivity as a function of the temperature and the coordination of the atoms in random networks. These results give a coherent picture of the structure of the ternary alloys and assess the strong influence of carbon on their physical properties. Such alloys, indeed, are expected to be a random distribution of Si,Sn,C or Si,Ge,C atoms without chemical ordering in a tetrahedral network terminated at its open bonds by hydrogen atoms. But while only one H atom is bonded to a Si or Ge atom, H atoms are bonded to carbon predominantly in the CH_n ($n=2,3$) form.

SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURES

Samples of a -CSiSn:H and a -CSiGe:H have been prepared by sputter-assisted plasma chemical-vapor deposition (SAPCVD). The magnetron cathodes used have been Sn (purity 99.9995%) or Ge (purity 99.999%) targets. A mixture of SiH_4 , CH_4 , and Ar has been introduced into the chamber controlling the flows separately. The pressure, the rf (13.56 MHz) power, and the deposition temperatures (120°C for a -CSiSn:H and 100°C for a -CSiGe:H) have been chosen to give the best optoelectronic properties.^{10,12} The substrates of the samples are different for each experiment and are described in Refs. 10 and 12. The atomic compositions have been obtained by Rutherford backscattering spectrometry and ERDA techniques.^{10,12} Infrared spectroscopy measurements have been made in the absorption mode using a single-beam Perkin Elmer 1710 Fourier spectrophotometer between 400 and 4000 cm^{-1} . The temperature dependence of the dark conductivity in the range 295–520 K has

been measured in vacuum with a Hewlett Packard high-resistance meter 4329A. Aluminum electrodes ($8 \times 1 \text{ mm}^2$) have been vacuum evaporated in a coplanar arrangement. The photoconductivity has been studied under AM2 illumination.

Samples for ir measurements were "annealed" in vacuum at 520 K, following the same temperature versus time relationship obtained during resistance measurements, for a total time (heating and cooling) of nearly 2 h.

We report the results obtained from measurements performed on sets of *a*-CSiGe:H and *a*-CSiSn:H films fabricated with similar deposition conditions. The Ar and SiH₄ flows were kept constants, while the CH₄ flow was varied. The samples are labeled CSG and CST, respectively, for the *a*-CSiGe:H and *a*-CSiSn:H sets, followed by a number indicating the CH₄ flow in sccm.

TEMPERATURE DEPENDENCE OF DARK CONDUCTIVITY

Figures 1 and 2 show plots of $\log_{10} \sigma_D$ against $1000/T$ for the two sets of samples. They exhibit a curvature in

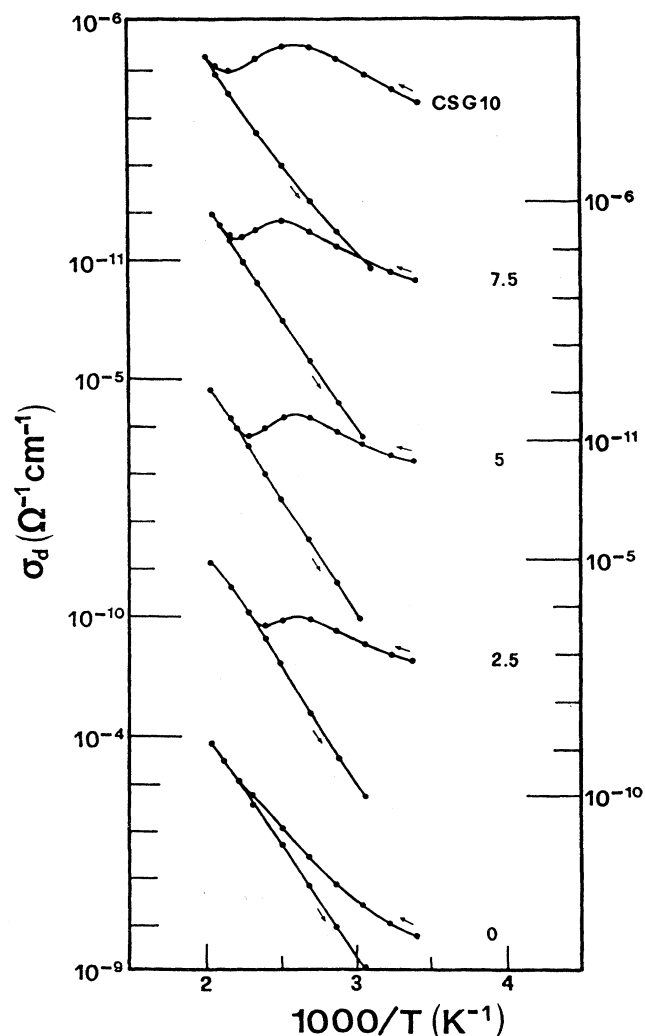


FIG. 1. Temperature dependence of dark conductivity for *a*-CSiGe:H samples.

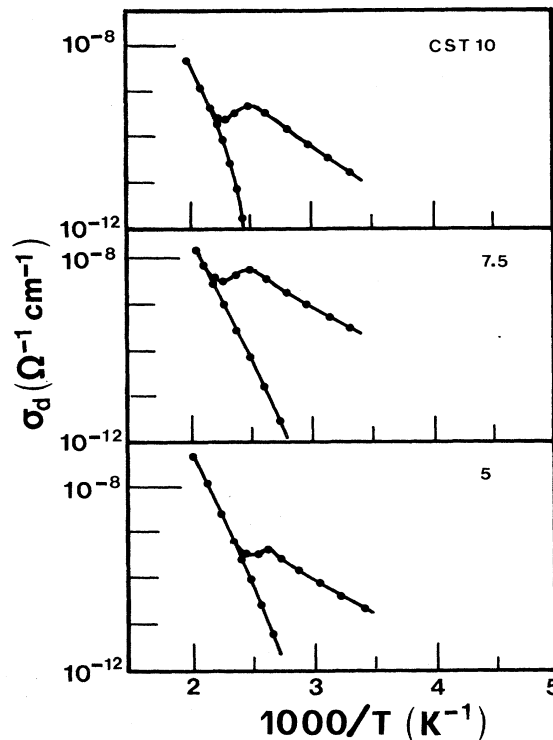


FIG. 2. Temperature dependence of dark conductivity for *a*-CSiSn:H samples.

the heating process which becomes more pronounced when the CH₄ flow increases. In each case there is a distinct hump with a change in activation energy and preexponential factor. Indeed the data of Figs. 1 and 2 show unambiguously two thermal activated conduction regimes which can both be described by the Arrhenius relation

$$\sigma_D = \sigma_0 \exp(-E_a/kT), \quad (1)$$

where σ_0 is the preexponential factor, E_a the conductivity activation energy, k the Boltzmann constant, and the temperature T is in kelvin. The activation energies and preexponential factors in low-temperature and in high-temperature regions are given in Table I together with the temperatures of the maximum and the minimum of the hump.

A tentative interpretation of the conduction mechanism could be the following. The films, as deposited, form a random tetrahedral alloy containing regions in which four atoms are bonded together. When the carbon content is high, regions of graphitic carbon (containing a considerable proportion of sp^2 sites) are more likely to be present in the network. Furthermore, it should be kept in mind that in these alloys, in addition to the normally bonded hydrogen which can be detected by ir absorption, there is a weakly bonded hydrogen which is not ir active.¹⁶ Annealing at temperatures just above the deposition temperature T_d causes the weakly bonded hydrogen to bond preferentially with carbon in the form CH_n, rather than to silicon or germanium.

TABLE I. Electrical properties. L stands for the low-, and H for the high-temperature region.

Sample	E_{aL} (eV)	σ_{0L} ($\Omega^{-1}\text{cm}^{-1}$)	E_{aH} (eV)	σ_{0H} ($\Omega^{-1}\text{cm}^{-1}$)	$T(\sigma_{\max})$ (°C)	$T(\sigma_{\min})$ (°C)	σ_{ph}/σ_d
CSG0	0.31	1.4×10^{-3}	0.95	5.9×10^5			1.3×10^3
CSG2.5	0.25	1.0×10^{-3}	0.97	9.9×10^4	110	140	4.5×10^2
CSG5	0.24	2.0×10^{-3}	0.95	3.1×10^4	110	165	1.4×10^2
CSG7.5	0.26	5.5×10^{-4}	1.00	1.2×10^4	125	180	3.2×10^1
CSG10	0.35	2.1×10^{-2}	0.96	9.5×10^2	110	190	
CST5	0.13	3.0×10^{-3}	1.39	1.4×10^6	120	160	
CST7.5	0.12	8.9×10^{-3}	1.24	1.7×10^5	125	175	
CST10	0.12	2.2×10^{-3}	1.38	1.7×10^7	115	135	

Because the introduction of hydrogen in carbon favors sp^3 over sp^2 bonding,^{17,18} its effect could lead to the reduction of π electrons and hence of the conductivity. According to Gambino and Thompson,¹⁹ the percolation theory predicts indeed that at least half of the carbon atoms must be sp^2 bonded to provide appreciable conductivity.

At higher temperatures ($T \sim 180^\circ\text{C}$) a new increase in σ_D is observed. After the maximum measurement temperature is reached, the cooling seems to “freeze” the atomic configuration corresponding at the maximum temperature. Subsequent thermal cycles, indeed, show that heating and cooling curves become indistinguishable from the first cooling, indicating that an irreversible change has occurred. When the sp^2 to sp^3 ratio for carbon bonds drops below the threshold for percolative conduction, the σ_D behavior becomes characteristic of the host material, as confirmed by the values of σ_0 and E_a in Table I and by the comparison with the σ_D behavior of non-carbon-based alloys.

To give value to our hypothesis we have calculated, for a -CSiGe:H samples, the integrated intensities of the different deconvoluted peaks of the vibration bands in the ir transmission spectra before and after the annealing cycle. We have observed no change in the 2100-cm^{-1} SiH stretching mode, a reduction of $\sim 17\%$ in the 650-cm^{-1} GeH wagging mode in the sample richer in carbon and hydrogen and a corresponding increase of $\sim 27\%$ in 1030-cm^{-1} CH_2 rocking (and/or wagging) vibrations.

Further considerations can be deduced from the values of σ_{ph}/σ_D measured at 295 K after annealing. The main result is that there is a decrease by about only 1 order of magnitude when carbon is introduced into the a -SiGe:H network (CSG0, composition in at. %, Ge 30.7, Si 35.5, H 33.8; CSG5, composition in at. %, Ge 18.3, Si 25.6, C 11.0, H 45.1).

Compared to these ternary alloys, a -SiC:H shows a much more rapid drop in photoconductivity as the amount of carbon in the solid gradually increases.^{20,21} Bullot *et al.*²² report a decrease in the absolute value of photoconductivity of about 8 orders of magnitude when the composition $\text{SiH}_4/(\text{SiH}_4 + \text{CH}_4)$ decreases from 1 to ~ 0.3 . The introduction of carbon in ternary alloys does not decrease the photoconductivity as much. Moreover, it improves the optical properties of the films.^{10,11,16}

COORDINATION IN RANDOM NETWORKS

Recent theories^{23,24} point out that an optimum average coordination is realized which balances the stabilizing influence of bondings and the destabilizing influence of strains in a covalent random network.

Phillips²⁴ considered the mismatch between bonding constraints and the degree of freedom in three dimensions and introduced a convenient parameter, the average coordination number \bar{m} , showing that a value of $\bar{m} = 2.45$ represents the best compromise between mechanical stability, due to cross-linking, and stress minimization, due to minimal bond length and bond-angle disorder.

Following Thorpe, we consider a random network with N atoms in a valence force field of only nearest-neighbor bond-stretching and bond-bending forces, while Van der Waals forces and dihedral angle constraints are of second order with respect to them. If in the network with N atoms the number of atoms having r bonds is represented by n_r , the average coordination number is defined as

$$\bar{m} = \frac{\left[\sum_r r n_r \right]}{N} \quad (2)$$

Calculating the fraction f of vibration modes with zero frequency that corresponds to the ways in which the network can be continuously deformed at no cost in energy, one obtains¹³

$$f = 2 - \frac{5\bar{m}}{6} \quad (3)$$

Setting $f=0$ we see that the optimum value of the average coordination number, for atoms with a number of degrees of freedom $N_f=3$, is $\bar{m}_0 = 2.4$.

For $\bar{m} > \bar{m}_0$ the rigid regions²⁵ percolate and we have an “overconstrained” rigid solid. For $\bar{m} < \bar{m}_0$ the network is not rigid, can be macroscopically deformed, and we have an “underconstrained” polymeric glass with rigid and floppy regions in which the rigid regions do not percolate.

The amorphous tetrahedral networks of a -Si and a -Ge might be regarded as prototypes of random covalent networks. According to Phillips, for $\bar{m}=4$ the glass conditions can be satisfied only by embedding the network in an eight-dimensional space. On the other hand, the more

TABLE II. Composition and average coordination number. The first column of \bar{m} is calculated assuming for carbon $r=4$, the second assuming that the sp^3 -to- sp^2 ratio is 2:1.

Sample	Ge (at. %)	Si (at. %)	C (at. %)	H (at. %)	O (at. %)	\bar{m}	\bar{m}
CSG0	30.7	35.5		33.8		2.99	
CSG2.5	23.1	28.9	8.1	39.9		2.80	2.77
CSG5	18.3	25.6	11.0	45.1		2.65	2.61
CSG7.5	12.8	24.7	14.0	48.5		2.54	2.50
CSG10	10.6	22.6	16.7	50.1		2.50	2.44

Sample	Sn (at. %)	Si (at. %)	C (at. %)	H (at. %)	O (at. %)	\bar{m}	\bar{m}
CST2.5	46.3	14.4	9.2	18.5	11.6	3.21	3.00
CST10	34.6	7.6	20.8	31.1	5.9	3.00	2.88

commonly used alloys are hydrogenated amorphous silicon (a -Si:H) and germanium (a -Ge:H), where the average coordination number can be reduced by the addition of hydrogen ($\bar{m}=1$). If we apply the Phillips-Thorpe model to the a -Si:H network, we deduce that the average coordination number cannot be reduced near its optimum value. For an hydrogen content of 0.25 the \bar{m} value is only reduced to 3.25.

The case of a -C is of particular interest. A hypothetical defect-free amorphous carbon network with diamond-like bonding ($\bar{m}=4$) would be highly overconstrained. The average coordination number of a -C can be reduced both by the addition of hydrogen, as for Si and Ge, and by the presence of a significant amount of sp^2 bonding ($\bar{m}=3$). The carbon network can become more "diamondlike," that is dominated by sp^3 bondings, as the hydrogen content increases.

Now we apply the Phillips-Thorpe model to calculate the hydrogen content in order to have weak polymeric a -C:H. Assuming that all carbon sites are sp^3 and imposing that the average coordination number of the a -C:H network satisfies the condition of optimum value ($\bar{m}=2.45$), a hydrogen content over 0.51 is required. Taking into account the experimental results obtained by Dischler *et al.*²⁵ that for polymeric a -C:H the proportion of sp^3 , sp^2 , and sp^1 equal to 53:54:2 yields, the strength of glassy carbon drop to zero for hydrogen content of 0.43.

It has been suggested by Phillips that strain relief in a -Si:H and a -C:H is achieved by forming small islands of Si or C surrounded by dangling bonds, which could be saturated by hydrogen. He suggested that the majority of these dangling bonds would be transformed into weak bonds. Robertson¹³ and Robertson and O'Reilly¹⁴ proposed to modify the model of Phillips by including the presence of σ and π bondings. In this case it is possible to diminish strain either by breaking σ bonds or π bonds. Since the breaking of π bonds requires less energy, these bonds can be broken at the island edges either by the presence of sp^3 sites or by aligning the sp^2 sites with a dihedral angle along the bond $\phi \sim 90^\circ$. An application of the model to the ternary alloy Ge-Se-Te studied by Sarach *et al.*²⁶ was performed by Phillips.

Considering that said above, we now apply the Phillips-Thorpe model to our ternary carbon-based alloys. The deposition of the films realized by using CH_4 and SiH_4 flows has the aim to include in the SiGe or SiSn tetrahedral networks both carbon (a mixture of sp^3 and sp^2 sites) and a great deal of hydrogen.

In Table II the calculated average coordination numbers are reported together with the atomic composition of our alloys.^{11,16} One set of values is calculated assuming $r=4$ for carbon, the other assuming the sp^3 -to- sp^2 ratio to be 2:1.¹³ We can observe that, as CH_4 increases, the average coordination number decreases, approaching the optimum value. We can deduce that these materials have an average coordination number close to the optimal value predicted for amorphous covalent networks. In this they differ remarkably from binary a -SiGe and a -SiSn.

CONCLUSIONS

The temperature dependence of conductivity and the average coordination number of ternary alloys have been discussed. The results emphasize that tetrahedrally bonded ternary alloys containing carbon have characteristic structure strongly affected by the carbon content. The presence of sp^2 sites in carbon bond (i) strongly affects the dark conductivity, as deduced from the dependence of σ_D upon the temperature, and (ii) remarkably reduces the average coordination number of the alloys, up to approaching the optimal value of 2.45.

The unusual behavior of ternary carbon-based alloys is explained by the presence of sp^2 sites, which dominates the physical properties of such alloys.

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