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Disorder and absorption edges in ion-irradiated hydrogenated amorphous carbon films

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The optical properties of ion-irradiated hydrogenated amorphous carbon films in the low and medium absorption coefficient region (1–10^5 cm^{-1}) were investigated as functions of the hydrogen atomic fraction (5–50 H at. %) by using a photothermal deflection spectroscopy technique. The data are interpreted using Urbach and Tauc theories for the different spectral regions. It was found that an increase in hydrogen content induces an overall increase of order in the film, leading to a sharpening of the band edge slope, in agreement with the known tendency of trigonal carbon to cluster in ordered graphitic domains. Correspondingly a decrease of the Tauc optical energy gap (from 1.6 to 0.2 eV) was observed due to the formation of weakly bonded π electron states in these materials. The data are compared with those reported by several authors on a-Si and a-Si:H samples.

The optical properties of amorphous hydrogenated materials have been the subject of intensive research for the last 30 years.[1–4] In particular, amorphous hydrogenated covalent networks (a-Si:H, a-Ge:H, and a-C:H) provide good examples of simple amorphous semiconductors in which hydrogen plays a crucial role in determining physical and chemical properties such as energy gap, density, and room-temperature conductivity.

Amorphous hydrogenated carbons hold a special place among these materials, due to the ability of carbon to generate trigonal and tetrahedral bonds when placed in different environments. This feature has a large influence on the electronic and phononic structure of amorphous carbon samples, as was demonstrated with several spectroscopic studies.[5,6]

Moreover, in several a-C:H samples it was found that a decrease of the hydrogen atomic concentration from 50 to 0 at. % causes a decrease of room-temperature resistivity from 10^9 to 10 Ω cm and a mass density increase from 1 to 2 g/cm^3.[7,8] At the same time the samples become softer, with a dramatic drop of their hardness from values very close to that of diamond (80 GPa) to about 1 GPa for nearly hydrogen-free matrices.[9]

This is also true for ion-irradiated hydrogenated amorphous carbons, in which the hydrogen atomic fraction could be driven by irradiating with appropriate ions and fluences in order to obtain different average ion-deposited energies.[10] In fact it was found that the hydrogen content is decreased by increasing ion fluences in different ways depending on the ion stopping power cross section, without loss of massive material.[11]

The key point in the understanding of optical and transport properties of amorphous carbon consists in the study of the evolution of the amount of weakly bonded valence electrons (π electrons) resulting from trigonal carbon atoms whose positions in the electronic density of states (EDOS) are very close to the Fermi energy (E_F). The remaining σ states characteristic of both trigonal and tetrahedral sites constitute the high-energy part of the conduction and valence EDOS.

In this paper we make an extended study of the optical-absorption coefficient for ion-irradiated a-C:H as a function of the photon energy in the region where only π-π^* transitions are involved (below 7 eV), looking at the effects of different amounts of bonded hydrogen on the optical gap, and on the compositional- and structural-disorder-induced EDOS tailing in the material. The results will be compared with the different behavior found in a-Si:H.[12]

Amorphous hydrogenated films (1 μm) were obtained by high-energy ion irradiation of hydrocarbon polymers using 300-keV He$^+$ beams. In order to obtain different hydrogen concentrations the samples were subsequently irradiated with the same ion beam at different ion fluences, and details of the irradiation conditions and the processes involved during such an experimental procedure are reported elsewhere.[10]

Each amorphous film was obtained on a fused silica substrate in order to perform several optical measurements in the range of the fundamental absorption edge.

After each irradiation step, the hydrogen atomic fraction was measured by using the elastic recoil detection technique, that is, sending a 2-MeV He$^+$ beam at a glancing angle with respect to the surface ($\sim 20°$) and detecting the recoiled protons. In this way it is possible to obtain a depth profile with a sensitivity of about 5%, and a depth resolution of 60 nm.[13] All the investigated samples were found to have a uniform hydrogen atomic concentration between 5 and 45 at % (2×10^{21}–2×10^{22} H/cm^3).

We performed optical-absorption spectra in the range

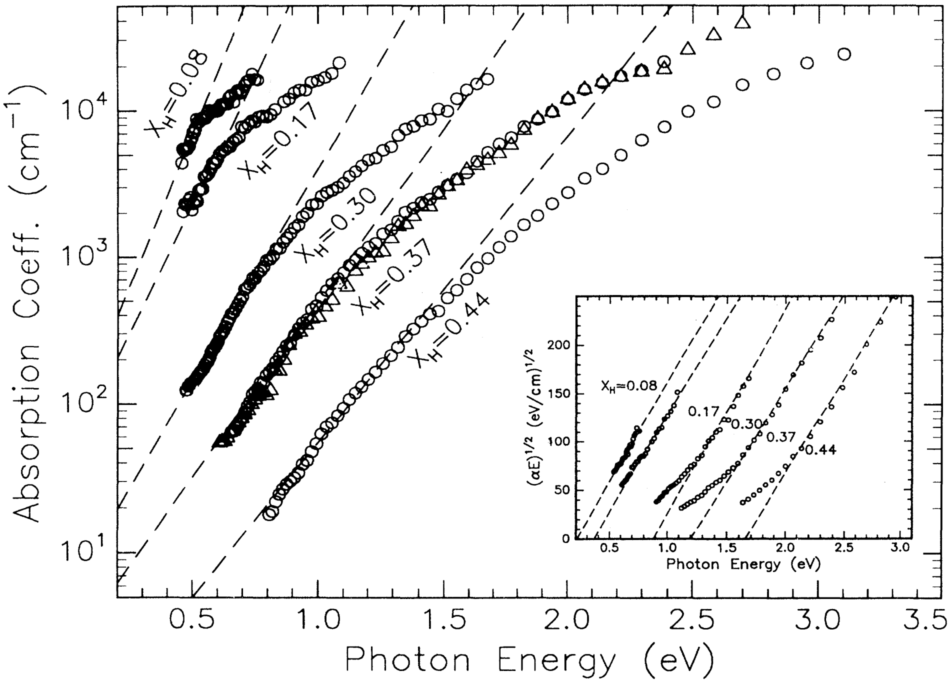

FIG. 1. Experimental absorption coefficient for several ion-irradiated hydrogenated amorphous carbon samples with different hydrogen atomic fractions, and for a plasma-deposited sample ($x_H \sim 0.32$, open triangles). The inset shows a typical fit in the Urbach and Tauc regions to obtain optical energy gaps and Urbach tails.

0.48–3 eV using a photothermal deflection spectroscopy (PDS) technique which is highly sensitive at low levels of absorption ($\alpha d \sim 10^{-5}$, where α is the absorption coefficient and d is the thickness of the sample) typical of the subgap spectral region for most semiconductors.[14] For instance, using a sample whose thickness is about 1 μm it is possible to estimate absorption coefficients down to 10^{-1} cm^{-1}.

The low-energy limit in the current measurements was imposed by the onset of a strong substrate absorption in the range 2.6–2.8 μm (0.47–0.44 eV) which overshadowed the film absorption. The absolute absorption values were obtained by normalizing the PDS signal with respect to values measured in a spectral region where the samples are opaque.

Figure 1 shows the absorption coefficient for five different ion-irradiated samples with different hydrogen concentrations in the region of the fundamental absorption edge together with a rf plasma-deposited sample (open triangles) whose hydrogen content was found to be very close to one of the ion-irradiated samples ($x_H = 0.37$). The first observation concerns the overall trend of the experimental data for the investigated samples; that is, an increase of the absorption values with decreasing hydrogen concentration, in agreement with the known growing of the trigonal carbon component. Moreover the fundamental absorption edge is observed both to shift progressively to lower energies and to sharpen with decreasing hydrogen content in agreement with previous optical transmission measurements.[10]

A close inspection of each absorption spectra shows two main absorption regions: The first is located at the low absorption coefficient, in the low photon energy part, and is termed the Urbach region, in which α varies exponentially with photon energy. The second (the Tauc region) is located at larger energies and manifests a smoother variation of the absorption coefficient. Tauc[15] suggested that the high absorption part of the spectra can be used to define an optical energy gap E_g through the use of the empirical law

$$\alpha E = A(E - E_g)^2 ,$$

which finds its justification in the parabolic behavior of the electronic valence and conduction densities of states near the Fermi energy. It must be pointed out that the Tauc optical energy gap represents only an estimation of the separation between the valence and conduction bands because of the uncertainty in the EDOS behavior near Fermi energy.

In Fig. 1 the dashed lines represent the results of fits performed on the band-edge region of each data set according to the exponential dependence suggested by Urbach,[16]

$$\alpha = \alpha_0 \exp(E/E_0) ,$$

while in the inset $(\alpha E)^{1/2}$ is reported as a function of E to obtain the Tauc optical gap.

The values of the fits for both Urbach and Tauc regions are summarized in Table I, and reported in Fig. 2 as a function of the hydrogen content in the films.

In the top part of the same figure the trigonal carbon

TABLE I. Values of the fits of the experimental data in the investigated absorption regions as discussed in the text.

X_H	E_0 (meV)	α_0 (cm^{-1})	A (eV^{-1} cm^{-1})	E_g (eV)
0.44	208	0.45	3.8×10^4	1.65
0.37	183	2.09	3.8×10^4	1.2
0.3	150	5.15	4.5×10^4	0.85
0.17	125	41.6	4.0×10^4	0.36
0.08	105	59.4	4.2×10^4	0.21

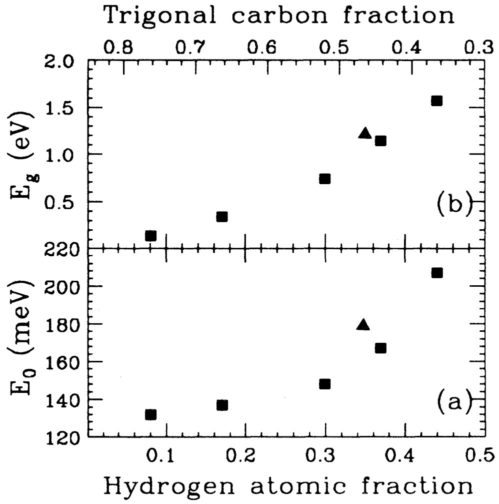

FIG. 2. Optical energy gaps (a) and Urbach tail parameters (b) for the investigated carbon samples as functions of both the hydrogen atomic fraction and the trigonal carbon fraction. The filled triangle refers to the plasma-deposited sample.

fraction is displayed for each sample, as deduced by optical and electron-energy-loss measurements.[3] These data suggest that a decrease of the hydrogen atomic fraction in the analyzed samples, accompanied by an increase of the trigonal carbon component, causes both a decrease of the optical gap and the sharpening of the Urbach slope E_0. Moreover we reported values of E_0 and E_g for the plasma-deposited sample, showing a deviation from the curve obtained for the ion irradiated samples. However, this discrepancy remains within 5%, revealing that plasma-deposited samples possess optical and structural properties very close to ion-irradiated *a*-C:H, at least for the reported x_H value.

Theories developed about Urbach behavior of the optical-absorption spectra in amorphous semiconductors[17] are based on the idea that the absorption edge is broadened by some mechanisms, and that the broadening is manifested through an increase of the parameter E_0. The main factors which determine the broadening of the exponential tails are those which contribute to the disorder in the atomic structure of the sample, as was suggested by Cody *et al.* for several *a*-Si samples.[12] In particular they assumed that E_0 is a measure of the disorder contained in the sample, and they consider thermal and structural contributions to disorder such that

$$E_0(T,X)=K[\langle U^2\rangle_T+\langle U^2\rangle_X] ,$$

where $\langle U^2\rangle_X$ and $\langle U^2\rangle_T$, respectively, are structural- and thermal-induced mean-square deviations of the atomic position from a perfectly ordered configuration. The same authors showed that in *a*-Si:H both thermal and structural terms contribute to increase E_0, while preliminary low-temperature measurements performed on one of our *a*-C:H samples ($X_H=0.17$) result in a negligible difference in the whole absorption spectra until 80 K, and indicate that only structural mean-square deviations are to be considered. This may be attributed to a higher Debye temperature for our samples (~800 K) compared to that of *a*-Si:H (~600 K).

The progressive decrease of E_0 with decreasing H content in the film [Fig. 2(b)] may thus be attributed to disorder and strain reduction in the film. In fact, samples with a low hydrogen atomic fraction contain a high fraction of trigonal carbon atoms with respect to the amount of tetrahedral sites,[18] and overall this causes a more ordered structure.

This is due both to the tendency of trigonal carbon to cluster in ordered graphitic domains and to the ability of atoms with lowered coordination to give rise to amorphous networks with lower amounts of structural defects and voids, and to a smaller departure from optimum covalent lengths and angles.[17]

Indeed it was found[19] that clusters of ordered sixfold benzoic rings are energetically strongly favored in *a*-C:H, suggesting a medium-range order behavior for the structure of carbons containing a large amount of sp^2 sites. This establishes the main difference between amorphous carbons with respect to other amorphous covalent semiconductors.

At the same time [Fig. 2(a)] E_g also increases with H content, and this is related to the considerable number of π states which are introduced in the gap following the increased fraction of the trigonal carbon component. In particular, Robertson suggested that[19] a decrease of the optical energy gap can be related in a quantitative way to the increase in the graphitic cluster dimensions:

$$M=36/E_g^2 \quad (E_g \text{ in eV}) .$$

Here M represents the number of benzoic rings in the largest clusters present in the amorphous matrix, and this means that in our samples the cluster dimensions range between 1 and 10 nm.

Our results for the values of the Urbach tail parameter are in strong contradiction with the ones reported by Datta, Woollam, and Notohamiprodjo.[20] In fact they obtain much larger values for E_0 (0.5–1.5 eV), and find an increase in E_0 values with decreasing hydrogen content in the film. We believe that, although their samples were synthesized in a different way, this discrepancy arises because they obtained their E_0 values in the same spectral range where they obtained E_g, while, as reported earlier on, the Urbach tail region lies at lower energies with respect to the region where a Tauc behavior is expected. Moreover the E_0 values obtained seem unrealistically large. In particular for one sample they obtain a value of ~1.2 eV for both E_0 and E_g. This would mean that the exponential band-edge region would extend across the entire subgap absorption region. Their data cannot confirm or contradict this result since, with conventional transmission measurements performed on thin films, they have no access to the subgap region where absorption is particularly small.

The correlation between the optical energy gap and the Urbach tail in our samples can be observed directly in Fig. 3, where the data for *a*-C:H are also compared with some of the values obtained by Cody for *a*-Si:H (Ref. 12) in which all phenomena related to the above-mentioned clustering and to the change in the bonding behavior cannot be applied.

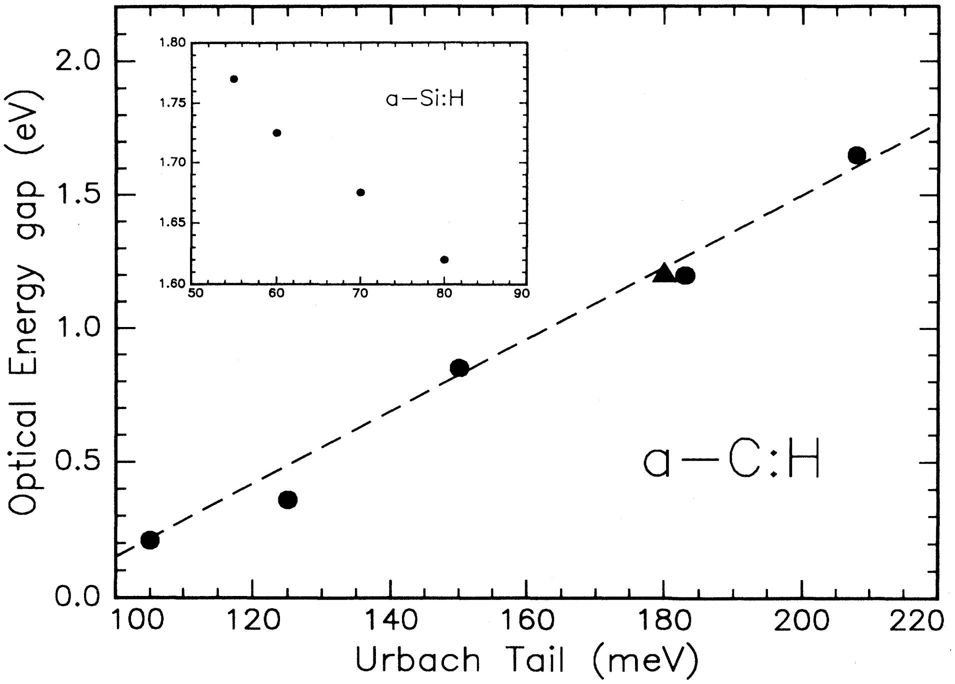

FIG. 3. Comparison between the behavior of the optical parameters (E_0 and E_g) for *a*-C:H and *a*-Si:H, showing different trends due to the different ordering disordering evolution of the two amorphous structures. The filled triangle refers to the plasma-deposited sample.

It was suggested that, for *a*-Si:H samples, the optical band gap as well as the Urbach parameter are influenced by the degree of disorder in the lattice, and that hydrogen affects the band gap only indirectly through its ability to relieve strain in the tetrahedral network. Moreover, other studies carried out during structural relaxation of ion-implanted *a*-Si confirm that strain reduction leads to an increase of the optical gap and to a decrease of the Urbach tail parameter values.[21]

The situation is somehow different in ion-irradiated *a*-C:H as well as in other *a*-C:H samples where the removal of hydrogen leads to a reduction in the strain and therefore of E_0 due to the increase in the trigonal carbon component, and to a reduction in E_g whose behavior is mainly influenced by the introduction of π electronic states in the gap. These differences could be attributed to the different bonding behavior of silicon and carbon in their own amorphous networks.

In summary, the data reported in this paper give support to the graphitic cluster theory in ion-irradiated *a*-C:H because they reveal that the introduction of a greater amount of trigonal carbon sites creates more ordered samples with a sharpening of the fundamental absorption edge, and an increase of π states near the Fermi energy responsible for the decrease of the optical energy gap.

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