Selscted Properties of Hydrogenated Silicon Carbon Alloys with Very Low Densities of States*

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A great deal of attention has been dedicated to tlie growth of amorphous silicon carbon alloy (a-SiC$_x$:H) films because of potential applications in the electronic industry, as electrolumi-rescent and solar cell devices. In this paper tlie main concepts of amorphous tetrahedrally l onded seinicoiiductors are reviewed with einphasis in some selccted properties of amorphous silicon carbon alloys.

I. Introduction

The amoi phous materials are well known since long time ago and glass, perhaps, is the more conspicuous example. Re :ently, however, the study of their proper-ties and applications to microelectronics has been dra-matically increased. This followed tlie success of Spear and LeComber[1] ill controlling the electrical and opti-cal propertie:; of hydrogenated [2] amorphous silicon (a-Si:II) by tlie inclusion of boron and phosphorous tetra-hedrally bonded. The inclusion of the impurity in a crystalline nttwork leave a free electron (phosphorous) or a hole borcn) provided tliat the foreign atom is tetra-hedially bon led. Conversely, it was suggested that in amorphous niaterials the lack of topological constraints allows tlie iripurity to be incorporated satisfying its own valence, i.e. the so called "8-Z=N rule" is met and consequently no doping effects should be observed. Here Z and N are tlie valence and coordination number of the impuri :y, respectively. In tlie attempts to explain the doping sensitivity of a-Si:H, Spear and LeComber concluded th it the low density of states (DOS) within the pseudo gip of tlie material was responsible for the efficiency in the observed doping. Moreover, tlie hydro-gen incorporated into the semiconductor was playing a twofold role, namely, passivation of the dangling bonds and decreasing tlie disorder. The efficient doping was explained as follows. Assuming a.density of states $g(E)$,

*Invited talk.

a density of ionized donor impurities Nd^+ and neglect-ing tlie free-electron contribution as compared with the trapped charge, the new position of the Fermi level is fixed by tlie neutrality conditions, i.e., in the zero tem-perature approximation:

$$N_d \approx g(E_0)(E_f - E_{f0}) = g(E_0)\Delta f . \qquad (1)$$

Where we have assumed $N_d^+ \approx N_d$, $\mathbf{Af} = E_f - E_{f0}$ is tlie Fermi level shift and E_{f0} is the Fermi level posi-tion of the intrinsic material. From this equation it is evident that a large displaceinent of the Fermi level is conditioned to a low DOS near the intrinsic Fermi level position. We remark, also, the conceptual differences of doping effects between crystalline materials and amor-phous semiconductors. In the former, the extra elec-tron (liole) introduced by the impurity is thermally promoted to the conduction (valence) band produc-ing changes in the material conductivity. In the latter, oii the other hand, the phenomenon occurs as follows. The extra electron (hole) drops to states deeper in the pseudo-gap moving up (down) the Fermi level. Thus, the maximum of the convolution of $g(E)$ aiid the Fermi occupation probability distribution shifts up (down) in-creasing the population of charge in extended states at the conduction (valence) band and consequently, vary-ing tlie conductivity of the material.

Other important properties of a-Si:H is its remark-able high absorption coefficient and photoconductivity. The first property is due to the lack of symmetry which

prevents the conservation of tlie quantum number k. Consequently, more optical transitions for incident photoll are allowed and tlie absorptioii coefficieiit in the region of interest is larger than in crystalline silicon. The good photoconductivity properties are due to tlie large band gap, low density of gap states and relative large diffusion length obtained in the materials. Indeed, in the dark (at room temperature) a larger band gap material is depleted of carriers in extended states, preventing tlie electrical conduction. Shining light upon the semiconductor increases the electron-hole population in extended states. Subsequently, the cairiers separate by diffusion, increasing tlie conductivity of tlie material. The Iiigh absorptioii coefficient together with its excellent photoconductivity makes the material adequate for inexpensive large area solar cells. Other applications are electrophotography copiers, radiation sensors, Vidicons, etc. and recently, tlie a-Si:H thin film transistor seems to he tlie tcclinological solutions for addressing liquid crystal display[2]. Indeed, the unique possibility of depositing large areas of the material iii almost any available substrate supporting 200-300 °C of temperature, makes tlie semiconductor suitable in electronic devices having human dimensions, such as display panels.

The success obtained with a-Si:H encouraged the researchers to look for other elemental amorphous semiconductors and alloys potentially useful for optoelectronic applications. Among them, amorphous silicon-carbon alloys is one of tlie most interesting material-to be used in several applications. This is so because its particular properties such as controllable band gap with carbon content, hardness, and what is very important, controllability of its conductivity by substitutional doping. The material lias been used successfully as "window" contact ill amorphous silicon solar cells, light emitting diodes and blocking contact in electrophotographic cylinders[3]. However, although the band gap of the material can be varied over a large range of energies (1.7 eV to ~3 eV) there is a concomitant detriment in its transport properties. In ordei to avoid it, attempts have been made to find particular deposition conditions to improve tlie material.

Recently, Matsuda and Tanaka[4] reported encouraging results obtained diluting heavily with hydrogen the gaseous mixture of [CH_4 + SiH_4] during the glow discharge deposition of tlie material. According to these autliors, tlie amorphous network is determined by the energy relaxation process of the absorbed species at the surface of the growing film. Moreover, a disconnected structure is formed if the surface-diffusion length is so sliort that tlie absorbed fragments are frozen on the landing site before they can find a more appropriate position. Thus, a larger diffusion length could be obtained selecting the less reactive radicals arriving to the growing film and covering the surface with hydrogen, i.e. make passive the surface dangling bonds with hydrogen. Furthermore, it is experimentally verified that the plasma structure strongly depends on tlie proportion of the gaseous mixture (methane-silane-hydrogen, in our case), adding one more complication to the preparation process. Consequently, the appropriate conditions for a-SiCx:H preparation are different than those used in a-Si:H. It is not surprising, for instance, that higher substrate temperatures produce better results than in a-Si:H.

In this work, the influence of hydrogen on some optical properties of tlie silicon-carbon alloy is reviewed by studying the sub-gap absorption, Urbach tail, infrared spectra, and low temperature pliotoluminescence emission. In section II the preparation method and experimental techiiiques used to characterize tlie material are discussed. In section III the optical properties are discussed. Finally, in section IV the conclusions are presented.

II. Sample preparation and experimental techniques

Plasma enhanced chemical vapor deposition (glow discharge) has proven to produce the best hydrogenated amorphous silicon (a-Si:H). Pure silane or diluted in hydrogen is let into a vacuum chamber and a radiofrequency (rf) plasma is generated in close contact to the substrate. Different ionized fragments produced by electrons colliding with neutral species of the gaseous

mixture are deposited onto a heated substrate forming the amorpl ous semiconductor. The large amount of work dedicated to this material have allowed to find well established conditions of substrate temperature, rf power, fluxes, hydrogen dilution, reactor geometry, etc. producing the best a-Si:H.

In the case of amorphous silicon-carbon alloys our best results were obtained in samples deposited from a constant ratio of gaseous given by $[H_2/[H_2 + CH_4 + SiH_4]$ of ~95-97% (HD, "high dilution") on substrates maintained at 320 °C[5]. Therefore, different materials were obtain changing the gaseous mixture maintaining its ratio constant. As it was remarked in tlic introduction, temperature is an important parameter and we found that, samples deposited with tlie same gaseous mixtures but at 260°C, do not present good properties. "Standard" samples aro normally deposited on substrate maintained at ~260°C from gaseous mixtures containing few or none percentages of hydrogen (LD, "low dilution").

Tlic sub-gap absorption strongly depends on tlie dangling bonds, i.e. on the material defects. Two things preve it the use of standard techniques (transmission) to measure the sub-gap absorption coefficient, namely the low sub-gap absorption coefficient and small thickness of tlie samples. Photo-thermal deflection spectroscopy (PDS)[6] and photoconductivity[7] are sensible techniques adequate to measure very low absorption coefficie its. PDS consists of the following. Tlie sample is immersed in a liquid which is transparent in tlie spectrum region of interest. A chopped monochromatic beam is shined perpendicular to the sample while a helium laser beam gocs nearby to the surface of the material. The absorbed radiation heat up the sample. Tlie heat is subsequently transferred to tlic liquid by diffusion generating a temperature profile. The temperature changes locally tlie liquid refractive, index deflecting tlie laser beam proportional to the transferred heat, i.e. proportional to tlic absorption coefficient. Care should be taken with tlie sample thickness. Indeed, very thin samples have surface DOS comparable to tlie bulk DOS[5]. However, the Urbach tail, i.e. the exponential part of the absorption coefficient, is fairly independent

on tlic surfaces states. Therefore, even in thin samples, PDS is a powerful tool for analyzing this parameter associated with disorder, i.e. tlie Urbach energy. An alternative technique which is quite insensitive to surfaces states is the constant photocurrent method (CPM) or shortly, photoconductivity inethod. The method takes advantage of the correlation between the sub-gap absorption coefficient and the generated photocurrent. In order to maintain the recombination kinetics invariant, the intensity of tlie monochromatic illumination is varied in such a way to'maintain a constant photocurrent for all incident photon frequencies. A disadvantage of this method in relation to PDS resides in the necessity of electrical contacts. Furthermore, a photoconductive material is obviously necessary, a condition not always met. We remark that both techniques do not give absolute values of a and normalization procedures are necessary to obtain meaningful results.

The absorption coefficient corresponding to high energies ($> 10^4$ cm^{-1}) is obtained by standard transmission procedures and used to define the optical gap. In amorphous semiconductors the optical gap is usually obtained by plotting $(\hbar\nu\alpha)^{1/2}$ vs. $h\nu$. The interception of a generally well defined straight line with the hv axis define the optical gap of Tauc[8]. As remarked above, PDS and CPM are not absolute measures of a. Therefore, the absorption coefficient ohtained by standard procedures is also used to scale tlie sub-gap value of by matching both curves in tlie region were they overlap.

Tlie infra-red (ir) absorption spectra is a valuable tool in the determination of the local vibrations in the amorphous structure. Indeed, hydrogen atoms bonded to silicon (carbon) dangling bonds are the cause of the low DOS observed in the alloy. Furthermore, the ratio of the integrated areas of the stretching absorption vibrations (Si-H)/(Si-H$_2$) is a figure of merit of the material quality.

Although the photoluminescence (PL) emission spectra. in amorphous materials are featureless, the technique proved to give information about band tails, disorder and electron-phonon interaction. The PL intensity as function of temperature $I(T)$ is generally ex-

pressed in the form:

$$I(T) = I_0 \mathbf{P}R(T)/[PR(T) + PNR(T)] , \qquad (2)$$

where $PR(T)$ and $PNR(T)$ are the radiative and non-radiative transitions probabilities respectively, and I_0 is the PL intensity at zero temperature. Therefore, a plot of $I_0/I(T) - 1 = PNR(T)/PR(T)$ can be used to determine the P L quenching with temperature. In a-Si:H a good fitting to the experimental data is obtained with $PNR(T)/PR(T) \sim \exp(T/To)$[9]. Sliis temperature behavior is found iii chalcolgenide materials and is explained in terms of tunneling recombination of carriers to non-radiative centers. To is a material parameter which depend of the Urbach band tail, Eu[10]:

$$kTo = Eu/ln(\tau/\tau_0) , \qquad (3)$$

where k is the Boltzman constant, τ_0 and τ are the "attempt to tunnel pre-factor" antl radiative recombination characteristic time of the material, respectively. The recombination time is expressed by $\tau(r_c) = \tau_0 \exp(\alpha r_c)$, where Lo $= 2/\alpha$ a. is the effective Bolir radius (localizatioii distance) and r_c is the electron-hole distance. In hydrogenated amorphous silicon these quantities are estimated to be $\sim$ 10-12 Å and $\tau_0 \approx 10^{-12}$ s, respectively[11]. The critical distance r, between tlie electron and defect is defiiied in such a way that a carrier having $r < r_c (r > r,)$ will recombine non-radiatively (radiatively). This critical distance is estimated considering the mean value $r_= < r >$ of a distribution of randomly dispersed defects[10] $G(r) = 4\pi r^2 N \exp(-4\pi r^3 N/3)$, where N is tlie DOS. Combining these equations the localization distance of trapped carricrs in samples with different carbon concentration is estimated by[12]

$$Lo \approx 0.5(kTo/N^{1/3}Eu) . \qquad (4)$$

In the next section we 1\41 discuss the experimental results aiid tlie interpretations of them.

III. Experimental results and discussion

Figure 1 (a) represents the absorption coefficient obtained by ÇPM of two representative materials, corresponding to IID (1.93 eV optical gap) and LD (standard, 1.00 eV optical gap) samples. A reduction of
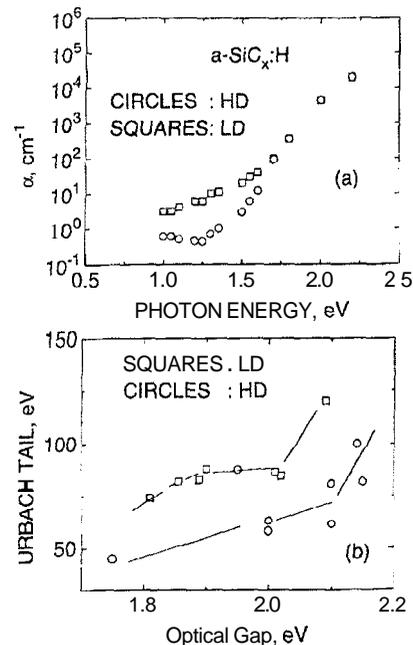

Figure 1: (a) Absorption coefficient a vs photon energy for BD (1.95 eV) and LD (1.90 eV). (b) Urbach energy vs Optical gap for both type of samples.

approximately one order of magnitude in the absorption coefficient due to defects is quite evident. Also, smaller Urbach tails are observed (Figure 1 (h)) indicating smaller disorder in HD than in LD samples with similar gaps. Also, tlie DOS is smaller in HD than LD samples (non represented).

In tlie attempt to correlate the good optoelectronic properties of tlie HD material to the local structure, the ir spectrum of materials deposited simultaneously on a crystalline substrate is normally studied. These spectra are very rich in structures. The studied samples present bands which are commonly associated with carbon coinplex vibrations and the dependence with optical gap is in agreement with results found in tlie literature[13]. Unfortunately, the overlapping of rnost of the bands prevents a clear individualization of possible atomic local arrangements. Tliere are two exceptions, namely tlie stretching modes C-H and Si-H bonds. The formcr, however, is extreniely weak and no clear conclusions can be obtained from it. The Si-H band, on the contrary, proved to be relatively easy to analyze. The stretching Si-H band of a-SiC$_x$:H with x < 0.4 can be interpreted in terms of only two independent vibrating contributions localized approximately at 2000 and 2100 cm^{-1}, respectively[13]. These two contribution are

due to Si-H and Si-Hn complex, where n is an integer greater thar one. The higher order hydrides are typical of porous ar d less compact structures which are associated to poor optoelectronic properties[14,15]. In order to compare thc influence of tlie *hydrogen dilution on the* structural cliaracteristic of the material, the Si-H absorptioii bar ds of the studied samples were fitted with two Gaussians centerecl at 2000 and 2085 cm^{-1}. The ratio of the integrated absorption coefficient of those bands as a function of the optical gap were studied (non represented). It was observed relatively smaller values of the ratio in LD than in JID samples. This result is indica;ive of a porous structure aiicl l e s eompact structures of LD samples.

The PL emission spectra of the alloys are broad bands centered at energies around 0.4 eV below the energy of the conduction band. There is general consensus tliat the emission is due to recombination between carriers iocalized in band-tail states. However, a controversy about tlie origin of tlie full width at the half maximum (FWHM) and the energy sliift between the absorption spectra and the PL emission still exists. In a-Si:H, and using cletailed balance arguments which consider tlie absorption and emission spectra, Street[16] has concludec that the large energy difference between the absorption and emission a.swell a.sthe spectra width is mainly due to electron-phonon interaction. Furthermore! Street has estimated a Stokes shift of 0.4 eV and a FWHM of 0.25 eV. Dustan and Boulitrop[11], however, claim that the main causes of the PL broadening and shifting between the absorption and emission, are disorder and carriers thermalization in band tails states, respectively. Both models describe the PL as radiative tunneling recombination between trapped carriers in band-tail states. Moreover, in both models the non radiative recombination is explained a.s tunneling recombination to defect states (dangling bonds) within the gap. Receiitly, Searle and Jackson[17] have contributed to this debate stuclying the PL in hydrogenated silicon nitride concluding that disorder is the main cause for the pointed discrepancies. We shall return to this point later.
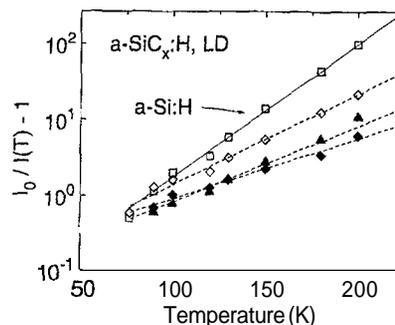
The lowest temperatiire reachecl in our experiments

Figure 2: Plot of $I_0(T)/I(T) - 1$ vs. T. For the sake of clarity we have plotted only a few curves corresponding to LD sainples. Similar curves are obtained for HD samples.
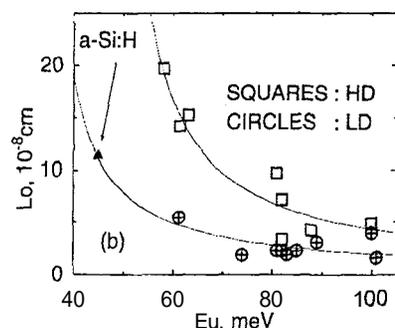

Figure 3: Localization length Lo vs Urbach tail for HD and LD samples. The valne for a-Si:H is also indicated.

was 77 K. Therefore, errors in the determination of the To parameter are minimized if I_0 is determined as an adjustable parameter[18]. Figure 2 shows the best fit of the expression $I_0/I(T) - 1 = PNR(T)/PR(T) \sim \exp(T/To)$ applying this procedure.

Figure 3 are the curves obtained by substituting the experimental values of To, E u and DOS in equation 4. The dashed curves are fits of $A/(Eu - Eo)$ hyperbolic functions, with A and Eo being adjustable parameters. Several conclusions are obtained from this graph. First, the shorter localization lengths obtained for LD samples suggest stronger disorder than in HD samples. Second, the fabrication parameters used in the deposition of the LD material seem to produce a material with properties similar those of a-Si:H. Therefore, fabrication conditions producing good a-Si:H are not necessarily the best conditions to be used in the fabrication of a-SiCx:H. Third, the relatively large valnes of Lo in HD sainples with E u < 65 meV suggest the existence of micro-crystals.

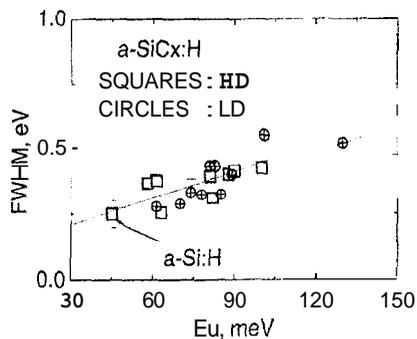We return to the problem of the origin of the PL width. Following a similar analysis applied to silicon

Figure 4: Full width at the half maximum, FWHM vs. the Urbach tail of RD and LD samples. The dashed line is the best fitting to the experimental data. The straight line interpolation intercepts the y axis at 90 meV.

nitride by Searle and Jackson[17], we have plotted (Figure 4) the FWHM vs the Urbach tail for different samples. We note that the FWHM is determined at 77 K while Eu is obtained at room temperature. However, we think that temperature corrections will not change the main conclusions. The accumulation of the LD and HD experimental data on an unique straight line strongly supports the assumption of tail to tail radiative recombination.

From this graph is concluded that the **PWHM, A**, is proportional to the Urbach energy. Furthermore, the quadratic value of the FWHM, Δ^2, could be envisaged as the sum of two quadratic contributions, i.e. disorder and electron- phonon interaction[10]. Calling σ_{ep} and σ_d to these contributions, $A^2 = \sigma_{ep}^2 + \sigma_d^2$. If we associate the disorder to the Urbach tail, **Eu**, the linearity of Figure **3** suggests that the first term in this equation must be rather small. Assuming that the σ_{ep} contribution is at most the value obtained by the extrapolation to zero disorder, i.e. $Eu = 0$, the maximum contribution to the electron-phonon interaction is around 90 meV. The electron phonon broadening is given by $\sigma_{ep}^2 = 4ln(2)\ Es\hbar\omega$, where Es is the Stokes Shift and $\hbar\omega$ is the most probable phonon energy.[17] Assuming $\hbar\omega = 70$ meV (the average phonon energy between 60 meV of silicon and 80 meV of silicon carbide) a Stokes shift of $Es \approx 0.040$ eV is obtained. This value is smaller than 0.4-0.5 eV estimated by Street[17] but nevertheless twice the result of 0.020 eV obtained by Searle and Jackson in silicon nitride[17]. We remark, however, that the scattering in our experimental data

prevents a straight forward comparison and more work is necessary before final conclusions are pursued.

IV. Summary and conclusions

Some optical and structural properties of amorphous silicon carbon alloys prepared by glow discharge from different hydrogen dilution conditions were studied.

The density of gap states and Urbach energies of samples with optical gaps between 1.9-2.15 eV are smaller in samples produced by heavily diluting with hydrogen the methane-silane gaseous mixture. Infrared absorption spectra of high diluted with hydrogen deposited samples showed that high order hydrides Si-Hn does not increase too much as a function of the optical gap, i.e with carbon content. On the contrary, in the standard material the ratio of [Si-H]/[Si-Hn] decreases as a function of the optical gap, suggesting a less compact structure.

Photoluminescence studies allowed to gain inside about questions like disorder and its influence on the emission line width. Indeed, the low temperature line width of the PL spectra turned out to be proportional to the Urbach energy, a parameter related to disorder.

The PL dependence on temperature in both types of sample (diluted and non diluted prepared material) is similar to that observed in amorphous silicon.[9] Combined results of PL, Urbach tail and density of states show stronger localization of carriers in standard samples. Furthermore, some diluted deposited samples show larger localization length, suggesting the existence of micro-crystals.

In conclusion, by diluting the gaseous mixture with hydrogen the optoelectronic properties of the alloy improve. This is probably due to an increasing surface diffusing-length of the starting fragments forming the film. A larger diffusion-length allows the fragments to move around on the growing film before finding an energetically more favorable site. However, we remark that the structure of the plasma is also changed rendering difficult in this stage to know the exact role of hydrogen in the improvement of the material.

Acknowledgments

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