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T. Datta

University of South Carolina, Columbia, South Carolina

John A. Woollam

University of Nebraska-Lincoln, jwoollam1@unl.edu

W. Notohamiprodjo

University of Nebraska - Lincoln

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Optical-absorption edge and disorder effects in hydrogenated amorphous diamondlike carbon films

T. Datta

Physics and Astronomy Department, University of South Carolina, Columbia, South Carolina 29208

John A. Woollam and W. Notohamiprodjo

Department of Electrical Engineering, University of Nebraska, Lincoln, Nebraska 68588-0511

Optical absorption ($\sim 1\text{--}5$ eV) in rf-deposited hydrogenated (20–40 at. %) amorphous “diamondlike” carbon films has been studied as a function of heat treatment. For $E > \sim 2.5$ eV a Tauc behavior is exhibited. Optical band gaps E_g are $< \sim 2.4$ eV. At lower energies, band tailing with an Urbach focus is found. E_0 , the width of the tail, is quantitatively explained in terms of the annealing temperature T_H . Increasing T_H (< 700 K) reduces the hydrogen content, lowers E_g , and appears to harden the films. E_g is determined to be a linear function of E_0 . Additional analysis was performed in terms of a divergence temperature, T_0 ; the results of this analysis are comparable to those observed in $a\text{-Si:H}$.

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T. Datta

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INTRODUCTION

Semitransparent diamondlike carbon (DLC) films have attracted world-wide attention,^{1–10} in part because of the potential technological usefulness of these materials. The desirable properties of DLC include hardness, chemical inactivity, and infrared transparency. There are also many fundamental physical questions of interest, such as understanding the relationship between disorder and the electronic properties, the density of states (DOS) tailing, the optical gap, and the mobility edge. Optical absorption is a powerful diagnostic tool to investigate some of these issues.

In this paper we discuss the near-band-gap optical-absorption coefficient α in DLC films. The purpose is to understand the effect of compositional and structural disorder and DOS tailing in these materials. When applicable, comparison is made between results on DLC and known properties of the amorphous hydrogenated silicon (*a*-Si:H) system.

EXPERIMENT

These films were 13 MHz rf plasma deposited (~ 15 Å/min) at ambient temperature on $0.1 \times 1.0 \times 2.5$ cm³ substrates of fused quartz with a 50:50 (volume percent) argon and methane mixture. A dc electric field of ~ 0.5 kV/m was applied. As deposited, the films (~ 400 Å thick) were amorphous with 30 to 40 at. % incorporated hydrogen. As determined earlier,¹¹ the mass density was $(1.7-1.8) \times 10^3$ kg/m³, and from Raman scattering results¹² the average nearest-neighbor distance was estimated to be 1.5 Å. The details of the rf deposition apparatus, procedure, and material parameters have been reported earlier.^{2,5,11–15}

Measurements were performed on virgin as-deposited specimens, as well as on specimens subjected to successive thermal annealings. A total of nine films were stud-

ied. All samples showed similar behavior, but to minimize systematic error introduced by uncertainties in film thickness the data from a single batch of films will be presented and discussed.

Standard room-temperature optical-transmission data between the wavelengths of 250 and 700 nm were obtained using an HP-8450A UV/VIS spectrophotometer. The heat treatments were performed in a microprocessor controlled, quartz-lined furnace, and specimens were isochronally heated at the desired fixed temperatures (450–650 K). Both the temperature T_H and the exposure time (30 min) were controlled to better than $\pm 5\%$. Some of the treatments were done in vacuum and the remainder in a small [~ 2 sccm (cm³/min at STP)] flow of high-purity argon. No systematic differences were noticed between the samples annealed in vacuum, as opposed to those annealed in an argon flow.

THEORY

In the one-electron approximation the imaginary part of the dielectric function $\epsilon_2(\omega)$ is given by

$$\omega^2 \epsilon_2(\omega) = \text{const} \sum \hat{\mathbf{n}} \cdot \mathbf{P}_{ij}^2 \delta(E_f - E_i - \hbar\omega). \quad (1)$$

In Eq. (1) ω is the photon frequency, E_i and E_f are the initial and final energies, $\hat{\mathbf{n}}$ the light polarization unit vector, and \mathbf{P}_{ij} the momentum matrix element. Approximating \mathbf{P}_{ij} by a constant, one obtains,

$$\omega^2 \epsilon_2(\omega) \propto \int^{\hbar\omega} N_c(E) N_v(E - \hbar\omega) d\omega, \quad (2)$$

where N_c and N_v are the conduction- and valence-band densities of states (DOS). We assume a parabolic-band DOS, and an absorption coefficient $\alpha(t)$ given by

$$\alpha = \omega \epsilon_2 / nc, \quad (3)$$

where n is the refractive index and c the speed of light in

vacuum. Tauc *et al.*¹⁶ have shown that

$$(\alpha E_n)^{1/2} \propto (E - E_g). \quad (4)$$

However, in the energies of experimental interest $n(E)$ is nearly independent of energy, hence it may be approximated by the average value n . In this approximation, Eq. (4) leads to

$$(\alpha E)^{1/2} = \beta(E - E_g). \quad (5)$$

Equation (5) is a well-known formula often employed to determine the optical gap E_g from the experimental data $\alpha(E)$. Cody *et al.*¹⁷ have argued that for these systems a more justifiable approximation is to treat the dipole matrix elements (r_{if}) as being independent of energy. In this case one obtains the Cody formula, given by

$$(\alpha/E)^{1/2} = \beta_C(E - E_g). \quad (6)$$

The slope β_C and the "Cody gap" E_{Cg} are not the same as those obtained from the Tauc model, i.e., Eq. (5). Often $E_{Cb} < E_g$.

The exact physical meaning of both the slope and the gap has been questioned.^{18,19} However, either of the behaviors (for $E < E_g$) is almost universally observed in amorphous thin films. The lack of a clear interpretation notwithstanding, the slope and the intercept of Eq. (5) or (6) -type plots are two important measurable optical parameters for these systems.

EXPERIMENTAL RESULTS AND ANALYSIS

The $\alpha(E)$ data for the present films were analyzed via both Tauc and Cody approximations. At least above certain (~ 2 eV) energy, and within some energy region, both methods of analysis fit the data. Figure 1 shows the fit to Eq. (5), and Fig. 2 shows the results of the Cody plot, for the same specimen. Data from as-deposited specimens, as well as those obtained after successive annealing, are exhibited.

Notice the qualitative effects of the heat treatment. To the unaided eyes the as-deposited films appear pale yellow. Upon annealing to higher temperatures the films become brownish. Proton-recoil studies reported earlier¹³ indicate that the hydrogen concentration is progressively reduced by the annealing. At the maximum annealing temperature (623 K) in this work, the hydrogen concentration goes down to about 20 at. %. We believe that the hydrogen reduces the number of dangling bonds and the strain in the DLC films. Removal of hydrogen makes them less pliable, but harder. On heating above 650 K the films appear to deteriorate.

Quantitatively, upon heat treating to 623 K the optical gap E_g decreases from ~ 2.5 eV for the as-deposited film to ~ 1.5 eV after annealing. The slope β appears to be rather insensitive to the heat treatment and is nearly constant. Similar behaviors are observed on the Cody plots of Fig. 2. The differences between them are (i) the lower estimates for the optical gap E_g , and (ii) the unexpected nonlinear turn down of $(\alpha/E)^{1/2}$ at high energies for the annealed films. This latter behavior is not seen in *a*-Si:H. Although some *a*-Si:H researchers report β values in-

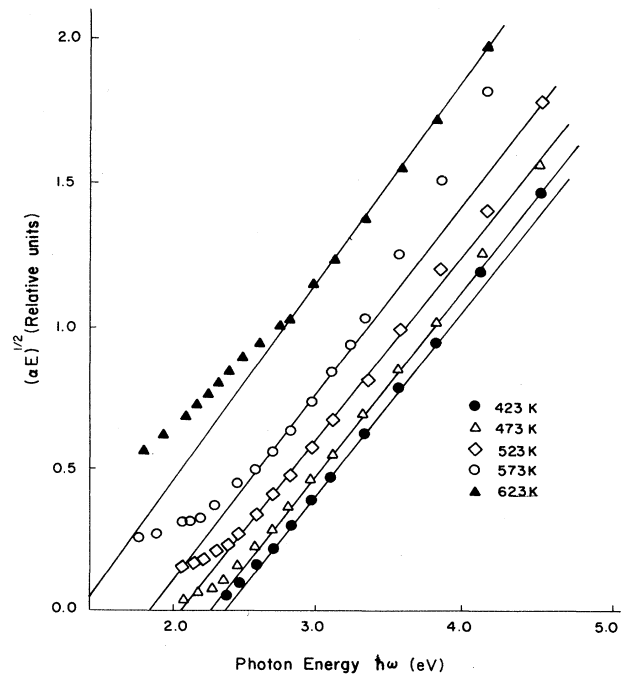


FIG. 1. Tauc plot for a DLC film and the effects of annealing at different temperatures is shown.

dependent of T_H , and hence E_g , others such as Frova and co-workers^{19,20} expostulate that because of the conservation of the total number of states, a monotonically increasing relationship between E_g and β is to be expected. The observed constancy of β in these DLC films is thus evidence that the total number of states observed in these optical-transitions changes with annealing.

The response in the subband gap region may be more conveniently analyzed using a semilog plot. The data from samples of Figs. 1 and 2 are shown in Fig. 3. Three

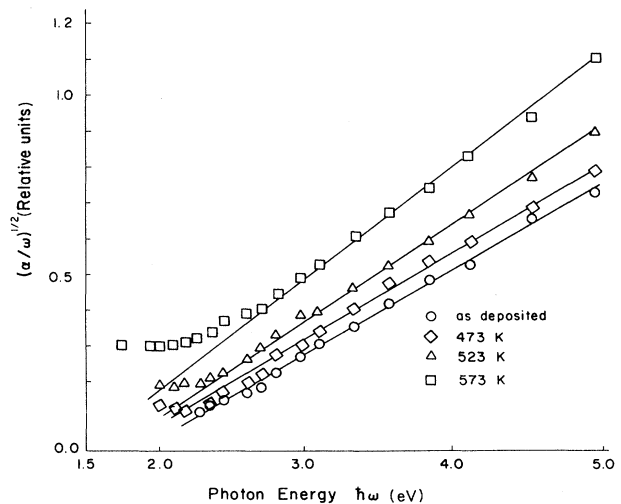


FIG. 2. Cody plot and the effects of annealing for the film of Fig. 1.

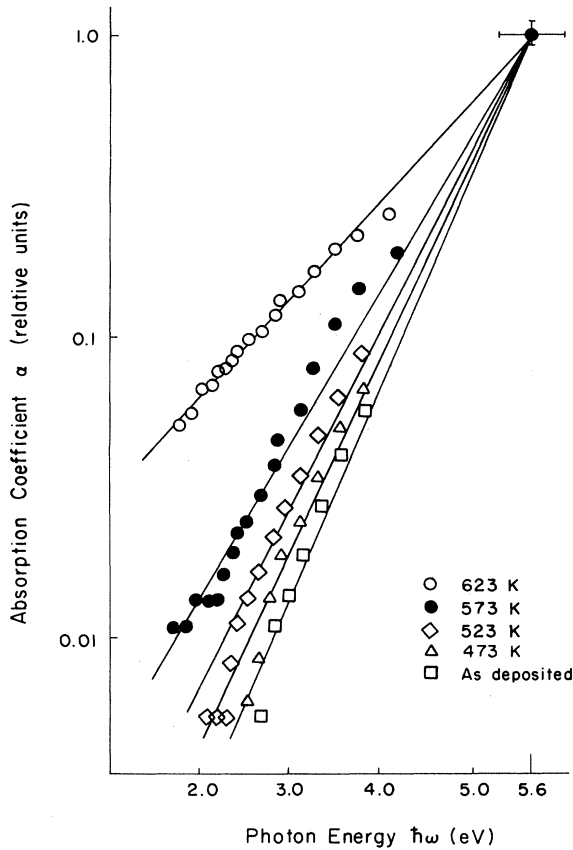


FIG. 3. Urbach tail absorption in DLC for the specimen of Fig. 1; the "Urbach focus" $E_{00} = 5.6$ eV is clearly shown.

energy regions can be identified.³ The high energy region ($E = 3$ eV) is where Tauc-type behavior is evidenced. The lowest energy region is where the absorption is not Tauc- (or Cody-) like, nor does it have an exponential dependence. In the intermediate energy range a linear semilog $\alpha(E)$ versus E dependence is observed. For each "annealed state," $\alpha(E)$ in this energy range is thermally activated. The activation energy is T_H dependent. Furthermore, collectively all these different $\ln\alpha$ versus E straight lines converge to an extrapolated high-energy focal point at $E = E_{00}$. We determine that

$$\alpha(E) = \alpha_{00} \exp[(E - E_{00})/E_0] \quad (E \lesssim E_g). \quad (7)$$

Equation (7) is the well-known Urbach-edge absorption. It is commonly observed in both crystalline and disordered systems. E_{00} is often termed the Urbach focus,^{21,22} and E_0 the width of the absorption tail or edge. For DLC this behavior has recently been reported by us.³

In the absence of crystalline order the absorption edge is not sharp. Because of the disorder the DOS in the pseudogap is not zero, and these states contribute towards photon absorption. In the one electron picture as in Eq. (2), a "smoothly tailing" exponential $\alpha(E)$ will arise if the DOS is exponential. Arguably, disorder induced DOS in the band edges may be represented by exponential functions. Even in the crystalline case at abso-

lute zero the zero-point motion of the atoms, and at finite temperatures the phonons, may produce sufficient disorder to show some band tailing.

Cody and co-workers¹⁸ have proposed that the effects of different types of disorder, viz., thermal, structural (topological), compositional, etc., are similar and are linearly superposable. In this model E_0 is a direct measure of the net disorder. They argue that the calculation of E_0 is similar to that used for finding the Debye-Waller factor. So in the harmonic approximation, they show

$$E_0(\omega) = \frac{1}{2} \sum_i K_i W_i^2, \quad (8)$$

where the W_i^2 , are the squares of averages of the atomic displacements from their equilibrium positions. The subscript $i = X, T_H, H$, etc. represents a disorder contribution due to structural, annealing, and hydrogen incorporation, respectively. It is also shown that

$$E_g = A/BE_0, \quad (9)$$

where A is the Abe-Toyazawa parameter. In this approximation the slope B is a constant. However, in a real system B may be expected to depend on E_0 .

The optical (Tauc) band-gap data for all specimens studied exhibit a monotonic variation with E_0 . The high band-gap films show smaller band tailing, and E_g decreases as E_0 increases. Data from three samples are exhibited in Fig. 5. A linear fit $E_g = 3.54 - 1.84E_0$ was obtained. This is similar to that obtained for a -Si:H data,¹⁸ but the slope B for a -Si is -6 . Hence in DLC the influence of E_0 is about $\frac{1}{3}$ of that in Si.

Recently, we have proposed that the contribution $E_0(T_H)$ due to structural disorder after annealing at T_H is proportional to the corresponding thermal energy. It was shown that²³

$$E_0(T_H) = (\gamma T_H)/(1 - T_H/T_0), \quad (10)$$

where γ is the proportionality constant and T_0 is a characteristic temperature. Hence from Eqs. (7) and (10) the absorption coefficient after annealing may be expressed as

$$\alpha(T_H, E) = \alpha_{00} \exp(E - E_{00})/\gamma T_H (1 - T_H/T_0) \quad (11)$$

which after regrouping gives,

$$\alpha(T_H) = \alpha_0 \exp(-\Delta/T_H), \quad (12)$$

where $\Delta(E) = -(E - E_{00})/\gamma$ and

$$\alpha_0 = \alpha_{00} \exp(-\Delta/T_0). \quad (13)$$

From Eq. (13) it follows that

$$\ln\alpha_0 = \ln\alpha_{00} - \Delta/T_0. \quad (14)$$

Both the exponential factor α and the Urbach tail E_0 were determined from our data. We observe a linear behavior Fig. 3 between $\ln\alpha_0$ and Δ , as required by Eq. (14). Similar behavior is observed in the conductivity of many thin films in different activated states.²⁴ This is indicative of the similarity between optical and transport properties of these systems. The direct proportionality between E_0

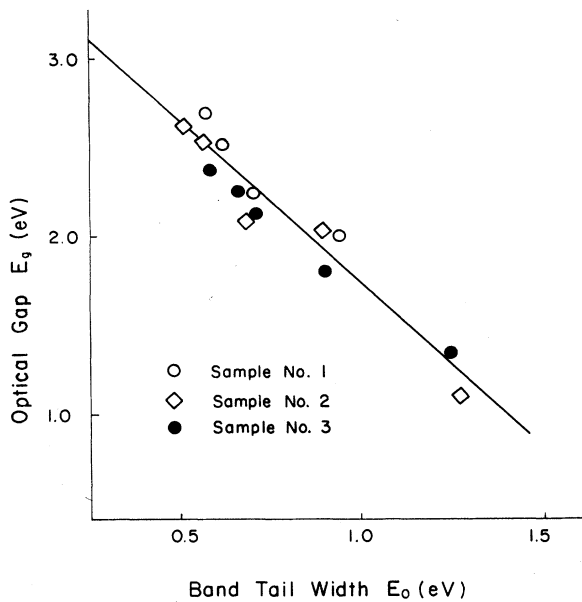


FIG. 4. Linear dependence of the optical gap on band-tail width. Data from three different specimens from the same deposition run are displayed. Points with same shape represents the effect of annealing.

and γ expressed by Eq. (10) was also observed. Evidence for this is shown in Fig. 4. The characteristic temperature T_0 or the value of T_H at the focus was estimated to be 950 K. This is in surprisingly good agreement with the temperature onset of graphite crystallite formation determined by Raman scattering.¹² Not surprisingly, T_0 was observed to be sample dependent, with $850 < T_0 < 1050$ K for the samples of Figs. 5 and 6.

FURTHER DISCUSSION

As was stated earlier, annealing reduces the amount of hydrogen in the film. Hydrogen is incorporated from the plasma while the films are being formed. Presumably the hydrogen is dissociated from the parent CH_4 present in the gas mixture. The presence of hydrogen in DLC creates compositional disorder but reduces structural dis-

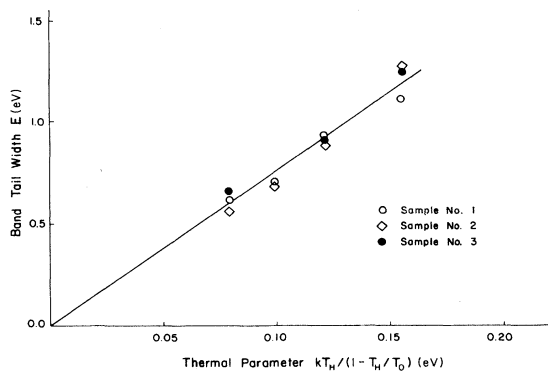


FIG. 5. Test of Eq. (10). Data from the samples of Fig. 4 are shown.

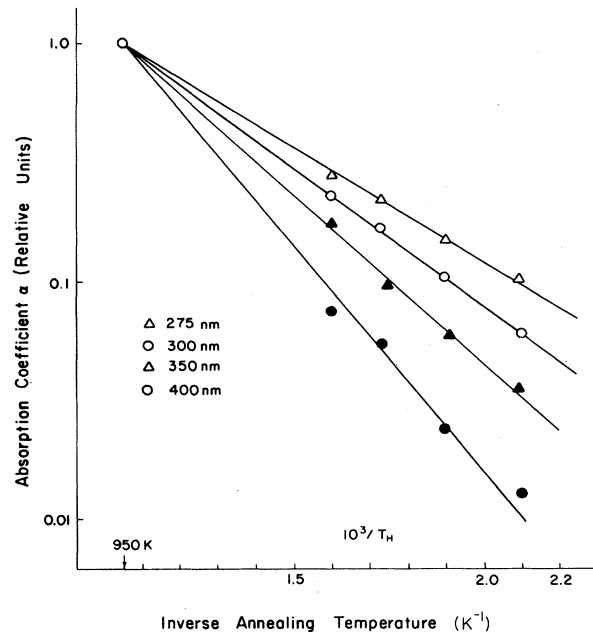


FIG. 6. Exponential dependence of a preexponential factor and activation energy. The data are selected from Fig. 3. Different samples show similar “temperature focus” behavior $T_0 = 950$ K for this specimen.

order. When the sample is annealed the opposite happens as the hydrogen is driven out. The observed increase in the band-tail width with annealing temperature T_H implies that the increased structural disorder dominates over the reduced composition disorder contribution. This gives rise to a net increase in the disorder and hence E_0 as given by Eq. (10). It may also be said that the *subgap* optical absorption is determined by the structural disorder rather than by the chemical composition and disorder. Similar behavior has been reported for *a*-Si:H.^{18,19} The scale of the band gap (~ 2 eV) and the characteristic temperature ($\sim 10^3$ K) obtained for DLC as well are comparable to those seen in the amorphous silicon system.^{18,19,23}

However, we observe important differences between the carbon and silicon systems. We have already remarked on the smaller slope of the E_g vs E_0 curves for DLC. Another point of difference is that for comparable hydrogen concentrations, band tailing in the carbon films is about an order of magnitude wider. Namely, compared with $E_0 \sim 50$ meV in silicon, we observe $E_0 \sim 500$ meV in DLC. A close examination of the data reveals that for some samples $E_0 \sim E_g$. This makes the question of the physical significance of E_g in the Tauc (or Cody) equations even more unclear. It appears that in the presence of strong disorder, the concept of E_g as the band gap that would have been operative if disorder were absent ceases to be meaningful. Furthermore, the transition may not be occurring between delocalized electron and hole states, and most certainly the DOS is not free-particle-like. Clearly in Figs. 1 and 2 at $E = E_g/2$ the absorption is not zero. The absorption $\alpha(E_g)$ appears to in-

crease with annealing, indicating a rise in the DOS. This large pseudogap DOS will reduce the chances for chemical doping by pinning the Fermi energy.

SUMMARY

We have observed that the hydrogen incorporated into diamondlike carbon films reduces structural disorder and midgap density of states. The structural disorder dominates compositional disorder for the 20 to 40 at. % hydrogen concentration range. This behavior is similar to that observed in *a*-Si:H film. However, the absolute magnitude of disorder effects is an order of magnitude stronger in DLC. We have proposed that this is because of the weaker dielectric screening. The screening is weaker because the value of the dielectric constant ϵ in carbon films is roughly 40% of that for *a*-Si films. We

speculate that a CFO type model may be appropriate for the DLC system.²⁵

Technologically, the large pseudogap density of states will discourage chemical doping.⁶ The incorporation of hydrogen opens up the gap energy. It also makes the films more pliable but less hard by relieving internal strain.

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