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Complex Dielectric Function of
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Pulsed Excimer (ArF) Laser Ablation of Graphite

by

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COMPLEX DIELECTRIC FUNCTION OF AMORPHOUS DIAMOND FILMS DEPOSITED BY PULSED EXCIMER LASER ABLATION OF GRAPHITE

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ABSTRACT

Amorphous diamond films have been synthesized by pulsed excimer (ArF) laser ablation of graphite at room temperature. Detailed studies of the energy-dependent complex dielectric function in the energy range up to 40 eV have been carried out by Kramers-Kronig dispersion analysis of transmission electron energy loss spectroscopy and spectroscopic ellipsometry. Distinct from those of graphitic amorphous carbon and diamond-like carbon, the optical constants of amorphous diamond films are closely related to that of crystalline diamond, but with a smooth band structure, a decrease in the magnitude strength, and band shift towards lower energies. The variation of dielectric function from crystalline diamond to amorphous diamond is analogue to those of crystalline and amorphous semiconductors such as Si and Ge. The extracted optical energy band gap reaches 2.6 eV, the highest value among the reported results for amorphous carbon films. The implication of dielectric function to the bond structure analysis of a-D films has also confirmed its diamond character. All of these provide further evidence of the existence of amorphous diamond.

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I. INTRODUCTION

Diamond and graphite are two basic allotropic crystalline structural forms of elemental carbon,¹ though a variety of cluster forms (fullerenes) have been discovered recently. In diamond, carbon atoms are connected in four-fold-coordinated tetrahedral bonding structure (sp^3 hybrids, four σ bonds per carbon atom); while in graphite, the atoms are in three-fold-coordinated hexagonal bonding planar structure (sp^2 hybrids, three σ bonds plus one π bond per carbon atom). These two bonding structures give distinct properties in all aspects for the two crystalline carbon forms. Graphite is thermodynamically stable with respect to diamond at standard temperature and pressure (for the transition from diamond to graphite, $\Delta H = -2.1 \text{ kJ/mol}$).¹ As a consequence, amorphous carbon (a-C), a common carbon form, is mostly a disordered graphitic network. Both theoretical study and experimental evidence have shown that over 80% of the carbon atoms in thermally evaporated a-C films are in sp^2 bonding²⁻³. An amorphous form of diamond or completely tetrahedrally bonded amorphous carbon network was previously thought to be unlikely to exist because of the presumed bonding constraints imposed on carbon network⁴⁻⁵, even though such a tetrahedral amorphous structure is common in other IV column elemental semiconductors, such as Si and Ge.

During the course of synthesis of polycrystalline diamond by low temperature and low pressure chemical vapor deposition process, amorphous diamond-like carbon (DLC) has attracted renewed attention^{4,6} because this material has been found to have similar physical, chemical, and mechanical properties with those of crystalline diamond. Early attempts to make diamondlike carbon films is to introduce hydrogen atoms (20%-60%) to saturate the dangling bonds of carbon atoms, so that the sp^3 character in the films is due to C-H bonds instead of C-C bonds. Although the hydrogenated amorphous carbon films have a large optical energy band gap (1~2 eV) and high mechanical hardness, heating of the films causes hydrogen to escape and results in soft graphitic carbon films.^{7,8}

Recently, a variety of techniques, such as pulsed laser deposition,⁹⁻¹³ filtered arc

deposition,¹⁴⁻¹⁵ and ion beam deposition,¹⁶⁻¹⁷ have been used for deposition of diamond like carbon films without incorporated hydrogen. Such films with a high degree of diamond character are referred as amorphous diamond (a-D).^{18,19} It was suspected that in this material, though lack of the long range order of crystalline structure, the local bonding structure is retained closely to sp^3 rather than sp^2 . This has been revealed in the neutron diffraction and electron energy loss spectroscopy analysis.^{18,19} However, Raman spectroscopy measurement of this material does not show the distinct feature appearing in crystalline diamond. Due to these conflicting experimental evidences, it is still arguable whether this newly developed material is amorphous diamond with its local bonding structure in an sp^3 form.

We have deposited amorphous diamond films by pulsed ArF excimer laser ablation of graphite at room temperature.¹³ In this paper we present a detailed study of the energy-dependent complex dielectric function of the a-D films in the energy range to 40 eV. The dielectric function provides not only the corresponding optical constants of the material, but also gives additional information about electronic band structure of the material. The dielectric function of the films is determined by Kramers-Kronig (K-K) dispersion analysis, transmission high electron energy loss spectroscopy (EELS) and spectroscopic ellipsometry. The results are compared with dielectric function of crystalline diamond. Analogous to the relationship between dielectric functions of amorphous and crystalline silicon and germanium, we show further evidence of the existence of amorphous diamond and the sp^3 local structure in the films.

II. EXPERIMENTAL

The a-D films in this study were deposited by pulsed ArF (193 nm wavelength) excimer laser ablation of pyrolytic graphite (PG) at room temperature in a high vacuum chamber. The detailed description of the deposition system and process conditions was described elsewhere.^{13,20} Si(100) substrates were cleaned through a standard degreasing process and finally dipped in diluted HF acid to remove SiO_2 before loading into the chamber. The as-deposited films on Si wafers were mirror-like smooth. After removing

the substrates, the free-standing films were transparent. General properties of a-D films have been characterized by a variety of analytic techniques,¹³ which we summarize briefly here. The plan-view transmission electron microscopy and selected area electron diffraction indicated that the films were homogenous and in an amorphous phase. The films were tested to be chemically inert, electrical resistant, and optical transparent in the IR and visible regions. High energy ion elastic forward scattering spectroscopy revealed that the films were free of hydrogen, a distinct difference from diamond-like hydrocarbon films. Nanoindentation measurement showed a microhardness close to 40 GPa (80-100 GPa for crystal diamond) and Young's modulus value of about 220~230 GPa. The optical energy gap was found to be 2.6 eV, the highest value reported for a-D or DLC films prepared by pulsed laser deposition and filtered cathode arc deposition. The a-D films also exhibited excellent thermal stability, and the optical energy band gap remained unchanged upon the annealing up to 800 °C in vacuum. This is in contrast to the hydrogenated diamondlike carbon films which upon heating turn to soot. Films deposited on Si(100) with a thickness about 150 nm were used for ellipsometry measurements and the films deposited on Si or fresh cleaved NaCl crystalline substrates with a thickness of 30-50 nm were used for EELS analysis. The specimen were made by lifting the film on to a Cu grid after removing the Si substrates by chemical etching or dissolving NaCl into water.

Spectroscopic ellipsometry measurement was performed on a rotating analyzing ellipsometry system (SOPRA, Inc) for the films deposited on Si(100). Spectroscopic scanning covered a range from 1.5 to 5 eV. A microspot of a size of 150x100 μm^2 was used to eliminate the effect of thickness non-uniformity of the films. The incident angle of 75° with respect to the sample surface normal was used. The optical properties of the films, the complex refractive index ($N=n+ik$) were obtained by polynomial fitting of the experimental curves in a 3-layer (air-film-substrate) structure with the Cauchy model,²¹

$$\begin{aligned} n &= A_1 + A_2/\lambda^2 + A_3/\lambda^4, \\ k &= B_1 + B_2/\lambda + B_3/\lambda^3, \end{aligned} \quad (1)$$

where λ is the photon wavelength, and A_i and B_i are the coefficients determined by the

least square fit to the spectroscopic ellipsometry spectra. The complex dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) was derived through the relation,

$$\epsilon = N^2 = (n + ik)^2 = (n^2 - k^2) + i2nk. \quad (2)$$

Based on the dielectric theory,²² the electron energy loss spectrum can be quantitatively described by

$$dI(\Delta\omega, \Delta\theta)/d\omega d\theta \propto \text{Im}(-1/\epsilon(\omega)) = \epsilon_2/(\epsilon_1^2 + \epsilon_2^2). \quad (3)$$

The dielectric function of an isotropic solid can be readily determined from an EELS spectrum^{23,24} through the K-K dispersion analysis:

$$\text{Re}[1/\epsilon(\omega)] = 1 - (2/\pi) \int_0^\infty [\xi/(\xi^2 - \omega^2)] \text{Im}[-1/\epsilon(\xi)] d\xi. \quad (4)$$

At $\omega=0$, Eq. 4 gives a normalization condition for the energy loss spectra providing ϵ_0 is known. EELS measurements were carried out on a Hitach H-2000 analytical transmission electron microscopy, operated at an accelerating voltage of 100 keV. The microscope was equipped with a cold field-emission gun with an energy spread of about 0.5 eV (FWHM), and with a Gatan-666 parallel electron energy loss spectrometer. Two regions of EELS spectra were collected, the low energy valence excitation loss spectra (0-80 eV) and the high energy carbon K-edge core-loss spectra (250-400 eV). The low loss spectrum was taken in an off-angle scattering angle with a momentum transfer at $0.1 \text{ \AA}^{-1}$ in order to avoid complications of the contribution of surface plasmon, Cerenkov radiation, and energy dependent factor. The energy loss function was obtained from the low loss spectra by the zero loss peak remove with a Lorentzian function fitting, and the multiple scattering correction up to the 3rd order.²⁵ In the calculation, the loss function was extended to infinite energy as $1/E^3$ for $E > 80 \text{ eV}$.^{23,24} The dielectric function were calculated from the electron loss function by K-K analysis in conjunction with the spectroscopic ellipsometry result for the normalization constant, ϵ_0 .

III. RESULTS

The experimental spectroscopic ellipsometry spectra ($\tan\Psi$, $\cos\Delta$) of a film deposited on Si(100) are given in Fig. 1. From the spectra, the oscillation strength of $\cos(\Delta)$ between -1 and +1 indicates the film is smooth on the surface and optically

transparent. The best fit spectra from Cauchy polynomial approximation are also plotted as the solid line in Fig. 1. The derived refraction index spectra for this film are shown in Fig. 2. The n spectra for diamond²⁶ and graphite²⁷ are also plotted in the same figure for comparison. The real part of the index of refraction (n) had a similar trend to that of diamond, but different from that of graphite. Its values range between 2.5 to 2.8, slightly higher than diamond. The k value is very low in this region with a cut off at 1.8 eV, implying a high optical energy band gap. A linear extension of the n spectrum to the zero energy gives $n_0=2.45$, resulting in $\epsilon_0=6.0$, slightly high than that of c-D.

Fig. 3 shows a low loss EELS spectrum of an a-D film. The spectrum gives distinct features from that of graphite, consisting of only a single broaden plasmon peak centered at 29.5 eV (compared to 26 eV for graphite and 33 eV for crystalline diamond). The peak at 60 eV is the second order plasmon loss. The $\pi-\pi^*$ antibond transition peak (about 6-7 eV as is present in the spectra of graphite and evaporated a-C films) is completely disappeared, giving a sign of the lacking of sp^2 bonding in the film. Inserted in Fig. 3 is the corresponding carbon K-edge loss spectrum after removal of the background. The spectrum of our film gives a broad peak centered at 296 eV, a smearing out of the fine transition structures from $1s$ to σ^* states, with the overall structure close to that of diamond.¹³ A very small shoulder at the low energy edge of the carbon K-edge loss band indicates the existence of a small fraction of π band-like transition in the film. The estimated sp^3 bond fraction in the film is greater than 95%.

The energy loss function of the a-D reduced from the EELS low loss spectra is shown in Fig. 4. The low energy region has been modified according to the loss function spectrum calculated from the ellipsometry result. The dashed line refers to the case before multiple scattering is made. The resulting real and imaginary parts of dielectric function of a-D by the K-K analysis are given in Fig. 5. The dielectric function from spectroscopic ellipsometry measurement in the energy range of 1.5 - 5 eV is also plotted. Two results are in good consistency in the energy range that the ellipsometry covers. For comparison, the plots of the energy-dependent complex dielectric function of crystalline

diamond from Ref. 26 are also given in Fig. 5. For a comparison purpose, the spectra of dielectric function of crystalline and amorphous silicon^{32,33} are also inserted in Fig. 5.

The main feature in the spectra of a-D shows smooth single bands with the overall structure close to c-D, but distinct to that of graphite.³⁰ The position of the peaks shift to lower energies, with a peak broadening and a magnitude drop. The $\epsilon_{1,\max}$ of 8 occurs at 4.5 eV, which is 1.5 eV lower than the energy position in c-D. This has been revealed in the SE result. In ϵ_2 the absorption band is peaked at 9 eV, shifted by about 3 eV from the maximum position of the c-D. The magnitude of the band drops to 7.2 with a width of 8 eV in FWHM, comparing to a peak value of 18.5 and a width of 2.5 eV in FWHM for c-D. In the energy region higher than 20 eV, both ϵ_1 and ϵ_2 values approach closely to those of c-D. The overall view of dielectric function explains why the refractive index in the visible region measured by ellipsometry is always higher than that of c-D.

IV. DISCUSSION

The overall features of the dielectric function of an a-D film we obtained possess common characteristic of amorphous semiconductors. Such a spectroscopic variation of dielectric function from crystalline to amorphous are present clearly in a-Si (Fig. 5b) and a-Ge.³¹ It results in smoothly varying spectra, a magnitude decrease and a band shift towards lower energies. It is generally agreed that the variation of dielectric function from amorphous to crystalline materials is attributed to the loss of long-range order in the amorphous state which leads to the relaxation of the k-conservation selection rule, resulting in smoothing out of the fine band structure in dielectric function spectra.

We consider the optical transition strength $\omega^2\epsilon_2(\omega)$ which is related to the density of states of the valence and conduction bands, $g_c(E)$ and $g_v(E-E_g)$,^{32,33} as

$$\omega^2\epsilon_2(\omega) = \text{constant} \int_0^{\hbar\omega} g_c(E) g_v(E-E_g) dE. \quad (5)$$

In an amorphous semiconductor, the conduction band density of states $g_c(E)$ should be smooth and featureless and can be reasonably taken as a step function at an energy above the valence band mobility edge.³⁴ Thus, from Eq. 5, the optical transition strength

$\omega^2\epsilon_2(\omega)$ is proportional to the integral of the density of valence-band states, implying the dependence of the absorption band (or ϵ_2) on the density of the valence states. Though this correlation cannot give an exact representation of the valence band density of states, it exhibits their major features. The plots of the quantity of the optical transition strength $\omega^2\epsilon_2(\omega)$ in term of the transition energy for a-D and c-D are shown in Fig. 6. The remarkable structural differences between them are obvious. These indicate a reduction and different distribution of the density of valence band states and weakening in the valence electron bonding strength in a-D. We have also noticed the absorption mobility edge shift towards to the low energy edge with a broaden diffuse tail. This is directly attributed from its amorphous structure. The presence of a great number of voids and dangling bonds as well as changes in bonding in the first and second nearest neighbor region may result in such a shift and magnitude drop. The broad tail in the low energy region suggests that there may exist defects-related states in the valence band tail, possibly extending into the band gap. Theoretical considerations of such sp^2 -free a-D carbon networks by Robertson and O'Reilly in a calculation of the local density of states of electrons by the recursion method revealed a smoothing of features and a shift of the leading edge of the valence band. The results are consistent with our perception of transition strength obtained from dielectric function of a-D.

As an implication of the connection of the band structure with dielectric function, the optical energy band gap can be determined from the relation^{33,36}

$$\omega^2\epsilon_2(\omega) = \text{constant} (E - E_g)^2, \quad (6)$$

assuming the band edges are parabolic. We have determined the optical energy band gap to be 2.6 eV for our a-D films from spectroscopic ellipsometry results.¹³ In Fig. 7, we extend this plot to a higher energy region from the ϵ_2 spectrum of a-D. There, the extrapolation by a straight line along the edge indicates the satisfaction of the square power law. This result indicates the consistency between EELE and ellipsometry measurements.

The similar character of tetrahedral bonding in a-D to c-D can be also recognized

by examining the oscillator strength, n_{eff} , the effective number of valence electrons per carbon atom which take part in optical transition^{37,38} up to an energy E_0

$$n_{\text{eff}} = (m/2\pi^2 N e^2 \hbar^2) \int_0^{E_0} E \epsilon_2(E) dE, \quad (7)$$

where N is the atomic density of the material. For the 4th column elemental atoms such as silicon and carbon, there are four valence electrons per atom available for bonding. If they were all to take part in interband optical transitions, we would expect n_{eff} to take a value of 4 at sufficiently high energy, providing that all the possible optical transitions are exhausted and the transitions involving the core states are negligible. Both crystalline and amorphous silicon closely follow this tendency.³⁹ In the materials of carbon, however, the behavior is different between diamond and graphite. In diamond, four sp^3 -bonded σ electrons are available for valence-to-conduction band transitions. Thus, n_{eff} would have rapidly steeper rise after passing through a bandgap threshold and approaches a value of four at a sufficiently large energy. This is shown in Fig. 8. It is calculated from the dielectric function shown in Fig. 5b from Ref. 26. Below 7 eV, n_{eff} is zero, indicating a wide band gap for c-D. There is a rapid increase at 10 eV and n_{eff} reaches 3 at 30 eV. It tends to approach 4 at higher energies. In contrast, for graphite, because of its sp^2 bond, the π - π^* transitions result in a plateau with n_{eff} as 0.6 electron below 9 eV. This spectrum is illustrated in Fig. 9, which is calculated from the data given in Ref. 27. Although there is one π electron and three σ electrons involved in the transition, the fact that the number of electrons below 9 eV is about 0.6 indicates that the π - π^* transition has not saturated at 9 eV. From our experimental results given in Fig. 6, the n_{eff} for a-D as a function of the energy is calculated and shown as the solid curve in Fig. 8. The behavior of n_{eff} for a-D is very similar to that of diamond and clearly different from that of graphitic carbon since there is no evidence of the existence of a plateau at low energies. In a-D, $n_{\text{eff}}=0$ for energies below the absorption edge. It rises less rapidly and reaches a value of 3.5 at the energy of 40 eV. It is also expected to reach a value of 4 at sufficient high energies.

We note that an error of a missing factor of $\pi/2$ has been found^{3,26,40} in the report of Taft and Pillipp,³⁰ where it was shown that the π - π^* electron oscillator strength in

graphite saturated at 9 eV with 1 electron/atom, instead of 0.6 electron/atom. Taft and Phillip's result was widely quoted by later publications with an implication for the quantitative determination of the relative fraction of sp^2 and sp^3 bonds from the behavior of the complex dielectric function below 9 eV.^{8,33} However, because of π electron transition does not saturate at 9 eV, contrary to what was believed earlier, it is clear that the relative fraction of sp^2 and sp^3 bonds cannot be simply determined from the behavior of the oscillator strength below 9 eV. This view is also supported by theoretic calculations of the distribution of density of states for graphite by Robertson and O'Reilly³⁵, which indicates that the transition for π electrons can be extended in the energy region more than 9 eV.

From the electron energy loss function and dielectric function, the density of the film can be estimated from the plasmon energy in the "free-electron gas" model for the valence electrons²² as

$$\omega_p^2 = \omega_p'^2 - \omega_n^2 = 4\pi N e^2 / m. \quad (8)$$

where $\omega_p'^2$ is the valence plasmon energy observed in EELS and ω_n is the center of valence band excitation in the dielectric function ϵ_2 . Assuming 4 electrons per carbon atom participating in the plasma transition, we estimate the density of our films as 2.95 g/cm³, providing the valence plasmon energy at 30 eV and the center of the excitation at 9 eV. This density is about 18% lower than that of crystalline diamond (3.515 g/cm³), but 30% higher than that of graphite (2.26 g/cm³). A similar value has been found for the films deposited by other methods such as filtered arc deposition,^{18,41} pulsed laser deposition,¹² and ion beam deposition.¹⁷ Reduction of the mass density from that of its crystalline form can be found in most solids. It is mainly due to the reduction of its atomic coordination number in the amorphous random network and the existence of a large fraction of voids.

The dielectric function of our films presented above as well as their implication to band structure analysis have provided further evidence for confirmation of the reality of a-D films. Upon its hydrogen-free character, fulfilled sp^3 bonding structure, many

unique physical, chemical and mechanical properties, and the analogous transition changes of dielectric function and optical properties from its counterpart of c-D to those of a-Si and c-Si, the designation of amorphous diamond is completely satisfied. However, we have noticed that the detailed properties of this material can be varied, depending strongly on the preparation conditions, especially the energetic sources for deposition. As the energy of the depositing carbon species spans the range from thermal to high energy (a few tens eV), the films can span the range from the completely graphitic a-C, diamond-like, to a-D. In our case, ArF excimer laser we used with a short UV wavelength (193 nm, 6.2 eV) and a short pulse width provides a high efficiency of ionization and excitation for atomic carbon deposited species with a high kinetic energy (up to 50 eV), ensuring properties of the deposited films near those of diamond.

The properties of a-D and diamondlike a-C films have been extensively studied and characterized in many aspects. The main effort has emphasized on physical property, mechanical hardness and the bonding structure determination. Among a variety of techniques for deposition of carbon films with a tendency towards a-D films, pulsed excimer laser deposition^{12,13} and filtered arc deposition^{14,15} have shown great promise. Plasma arc deposited hard carbon films (referred as a-D) have been extensively studied by McKenzie, Saced and their co-workers.^{18,19,41-43} They show the amorphous films have structures essentially analogous to the other elemental amorphous semiconductors (Si and Ge). The predominant tetrahedral bonding up to 85% has been found with the rest in trigonal bonding. The films have found to contain hydrogen up to 11%. The residual sp^2 π -bonding has shown significantly in the EELS spectra. Hard hydrocarbon films from a gas plasma deposition have been studied by Fink, et al. with EELS.⁸ Though the film had optical energy band gap of 2.05 eV, the appearance of sp^2 bands in the EELS spectra and degrading of diamond-like properties upon annealing exclude them from the a-D category. Ion beam sputtering deposited films by Cuomo, et. al.¹⁷ have shown a strong dependence of the sp^3/sp^2 ratio and mass density on deposition conditions, while a graphitic character has been shown in the ion beam sputtering deposited films by Savvides.³⁰ The films deposited by pulsed excimer laser ablation with KrF (248 nm) beam

by Pappas et al¹² showed to have an sp^3 bond fraction up to 75 % on non-diamond substrates with the optical energy band gap up to 1.8 eV. In comparison, our films prepared by pulsed excimer laser deposition with ArF beam gives the superior quality with the highest optical energy band gap (2.6 eV) obtained so far.

Common critical features for the formation of a-D are believed to rely on non-equilibrium feature in the deposition process,⁴⁴ in which the carbon species impact the substrate at energies well above thermal and quickly quenched down to the comparatively lower substrate temperatures, referring as an energy condensation process. We suggest that in the formation and structural phase stability of this a-D material, the initial atomic ionization and excitation of deposited carbon species and their kinetic energy range are very important factors, which provides the pre-condition for bonding structural transition from the planar sp^2 to 3-dimensional sp^3 . After these carbon species are accommodated on the substrate surface through the energy condensation process, the compressive stress in the film generated would further stabilize the sp^3 bonding structure. This effective pressure and temperature condition in the film could match a condition falling inside the diamond stable zone as is proposed by McKenzie et. al.^{18,19}

By reviewing the reported results on a-C films prepared by laser ablation methods, we have found⁴⁵ that there is a strong correlation between the wavelength of lasers used for ablation and one of film properties, optical energy band gap. As the laser wavelength changes from the IR region (the photon energy of ~ 1 eV) to UV region ($\sim 5-6$ eV), the optical energy band gap of the films increases consistently from 0 up to 2.6 eV. We suspect that upon the laser impact on a graphite target, the original sp^2 C-C bonding in the target material would be destroyed due to laser-induced high temperature rapid heating, ionization and excitation. A plasma plume with highly ionization and high energetic carbon species is generated. Depending on the laser photon energy used, carbon species in the plume can be at different excitation states, ejecting in cluster forms with the kinetic energy of a few eV for IR laser sources to an mostly atomic ionized form with the kinetic energy of a few tens eV for UV excimer lasers.⁴⁶⁻⁴⁸ Based on this pre-

condition, these ionized or excited carbon species have a tendency in a different degree to reconstruct themselves into the sp^3 C-C bonding. Thus, in the deposited films prepared by different laser sources, instead of a simple mixing of standard sp^2 and sp^3 bonds, there may exist an evolutionary transition in the bonding structure formation from the planar sp^2 to 3-dimensional sp^3 in respect of changes of the bond angle and length or bond interaction strength. In turn, this evolution leads to film property change from graphitic to diamond-like. The supporting experimental evidence has been illustrated in plasma arc deposited amorphous carbon films by McKenzie.¹⁸ As the plasma energy spans from 22 to 33 eV, the nearest C-C distance, measured by neutron scattering, changes from 0.142 nm (for graphite) to 0.154 nm (for diamond). In the (e,2e) analysis,³ it is also demonstrated that there is a rehybridization between π and σ electrons in ion beam deposited DLC films due to the bending of the planar σ bonds. More theoretical and experimental studies need to confirm this suspect regarding pulsed excimer laser deposition of a-D films.

V. CONCLUSIONS

Amorphous diamond has been synthesized by pulsed excimer laser deposition. Its dielectric function we have obtained have provided further evidence to confirm its existence. The dielectric function of a-D presents a typical characteristic of tetrahedrally bonded semiconductors. Loss of a long-range periodic crystalline structure in a-D leads to a smooth band feature. Its overall behavior is contrast to graphite, but similar to that of crystalline diamond. The peak position in the dielectric function shifts to low energy region, with a magnitude drop and band width broadening, leading to a narrow optical band gap and an absorption tail at low energies. The measured optical energy band gap of our films is 2.6 eV, the highest value reported so far for pulsed laser deposited amorphous carbon films. The variation of dielectric function from crystalline to amorphous diamond are analogous to dielectric function of amorphous and crystalline semiconductors such as Si and Ge. Implication of dielectric function of a-D has further shown that the transition strength and oscillator strength of a-D are very much in connection with those of c-D. The films we obtained have shown a high degree of

diamond character upon the retaining of the sp^3 bonding in a short range order.

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REFERENCES

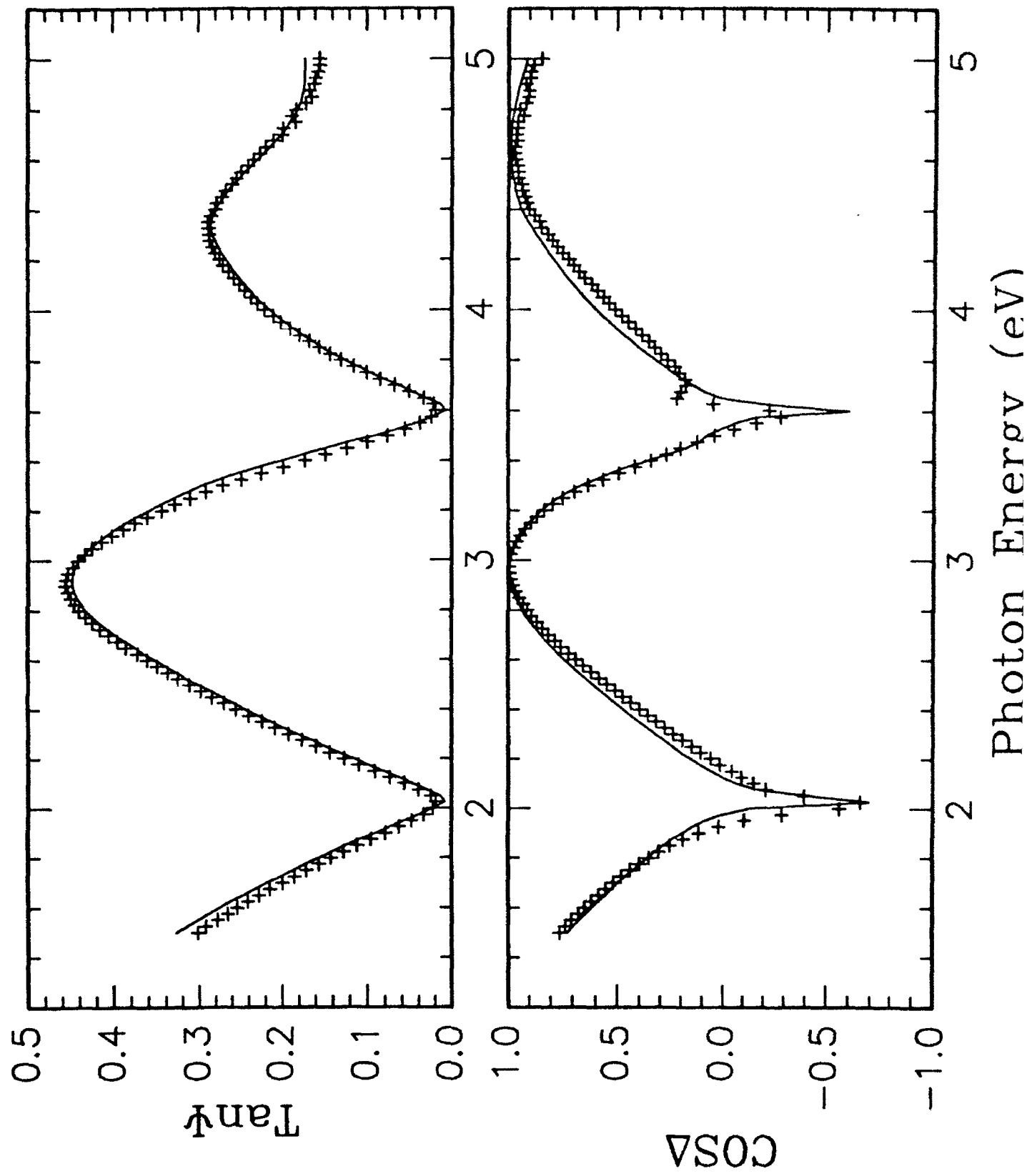
1. H. Marsh, *Introduction to Carbon Science* (Butterworths, London, 1989).
2. J. Robertson, *Adv. Phys.* **35**, 317 (1986).
3. G. Gao, Y. Y. Wang, and A. R. Dennison, *Phys. Rev. Lett.* **62**, 945 (1989).
4. J. C. Angus and C. C. Hayman, *Science* **241**, 913 (1988).
5. J. C. Angus and F. Jansen, *J. Vac. Sci. Technol.* **A6**, 1778 (1988).
6. *Properties and Characterization of Amorphous Carbon Films*, ed. J. J. Pouch and S. A. Alterovitz, *Materials Science Forum*, Vol. 52&53 (Trans. Tech. Publications, Switzerland, 1990).
7. F. W. Smith, *J. Appl. Phys.* **55**, 764 (1984).
8. J. Fink, Th. Muller-Heinzerling, J. Pfluger, B. Scheerer, B. Dichler, P. Koidl, A. Bubenzer, and R. E. Sah, *Phys. Rev.* **B30**, 4713 (1984).
9. C. L. Marquardt, R. T. Williams, and D. J. Nagel, *Mat. Res. Soc. Symp. Proc.* Vol. **38**, 325 (1985).
10. F. Davanloo, E. M. Juengerman, D. R. Jander, T. J. Lee, and C. B. Collins, *J. Appl. Phys.* **67**, 2081 (1990); C. B. Collins, F. Davanloo, D. R. Jander, T. J. Lee, H. Park, and J. H. You, *J. Appl. Phys.* **69**, 7862 (1991).
11. J. Krishnaswamy, A. Rengan, J. Narayan, K. Vedam, and C. J. Mchargue, *Appl. Phys. Lett.* **54**, 2455 (1989).
12. D. L. Pappas, K. L. Saenger, J. Bruley, W. Krakow, J. J. Cuomo, T. Gu, R. W. Collins, *J. Appl. Phys.* **71**, 5675 (1992).
13. F. Xiong, Y. Y. Wang, V. Leppert, and R. P. H. Chang, *J. Mat. Res.* (in press, 1992).
14. S. D. Berger, D. R. McKenzie, and P. J. Martin, *Phil. Mag. Lett.* **57**, 285 (1988).
15. R. Lossy, D. L. Pappas, R. A. Roy, J. J. Cuomo, *Appl. Phys. Lett.* **61**, 171 (1992).
16. C. Weissmantel, C. Shurer, F. Frohlich, P. Grau, and H. Lehmann, *Thin Solid Films* **61**, L5 (1979)
17. J. J. Cuomo, J. P. Doyle, J. Bruley, and J. C. Liu, *Appl. Phys. Lett.* **58**, 1 (1991); and *J. Vac. Sci. Tech.* **A9** (1991) 2210.
18. D. R. McKenzie, D. A. Muller, E. Kravchinskaia, D. Segel, D. J. H. Cockayne,

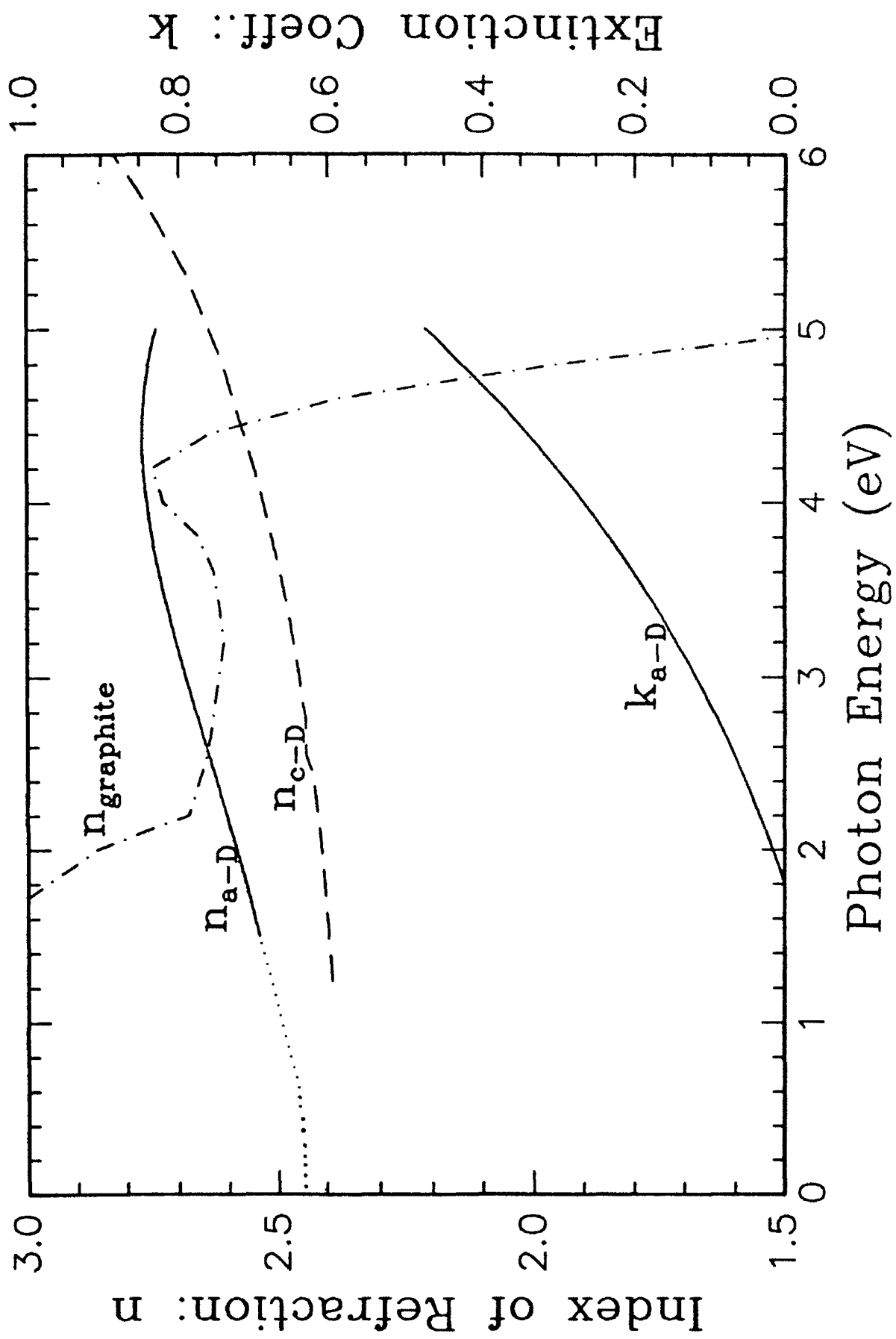
- G. Amaratunga, R. Silva, *Thin Solid Films* **206**, 198 (1991).
19. D. R. McKenzie, D. A. Muller, and B. A. Pailthorpe, *Phys. Rev. Lett.* **67**, 773 (1991).
 20. F. Xiong and R. P. H. Chang, *Mat. Res. Soc. Symp. Proc.* Vol. **299** (in press, 1992).
 21. R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light*, North-Holland, Amsterdam, 1989.
 22. H. Raether, *Excitation of Plasmons and Interband Transitions by Electrons*, in *Springer Tracts in Modern Physics*, ed. G. Hohler (Springer-Verlag, Berlin, 1980), Vol. **88**, p.1.
 23. J. Daniels, C. V. Festenberg, H. Raether, and K. Zeppenfeld, in *Springer Tracts in Modern Physics*, ed. by G. Hohler (Springer-Verlag, Berlin, 1970), Vol. **54**, p.77.
 24. J. Pfluger and J. Fink, *Handbook of Optical Constants of Solids II*, ed. E. D. Palik, (Academic Press, Inc., San Diego, 1991) p. 293.
 25. Y. Y. Wang, *Ultramicroscopy* **33**, 385 (1990).
 26. D. F. Edwards and H. R. Philipp, *Handbook of Optical Constants of Solids*, ed. E. D. Palik, (Academic Press, San Diego, 1985) p. 665.
 27. A. Borghesi and G. Guizzetti, *Handbook of Optical Constants of Solids II*, ed. E. D. Palik, (Academic Press, Inc., San Diego, 1991) p. 449.
 28. D. F. Edwards, *Handbook of Optical Constants of Solids*, ed. E. D. Palik, (Academic Press, San Diego, 1985) p. 547.
 29. H. Piller, *Handbook of Optical Constants of Solids*, ed. E. D. Palik, (Academic Press, San Diego, 1985) p. 571.
 30. E. A. Taft and H. R. Philipp, *Phys. Rev.* **138**, A197 (1965).
 31. T. M. Donovan and W. E. Spicer, J. M. Bennett, and E. J. Ashley, *Phys. Rev.* **B2**, 397 (1970).
 32. G. A. N. Connell, *Amorphous Semiconductors*, ed. by M. H. Brodsky, *Topic in Applied Physics* (Springer, Berlin, 1979) Vol. **36**, p. 73.
 33. N. Savvides, *J. Appl. Phys.* **59**, 4133 (1986).
 34. J. D. Hoannopoulos and M. . Cohen, *Phys. Rev.* **B8**, 2733 (1973).

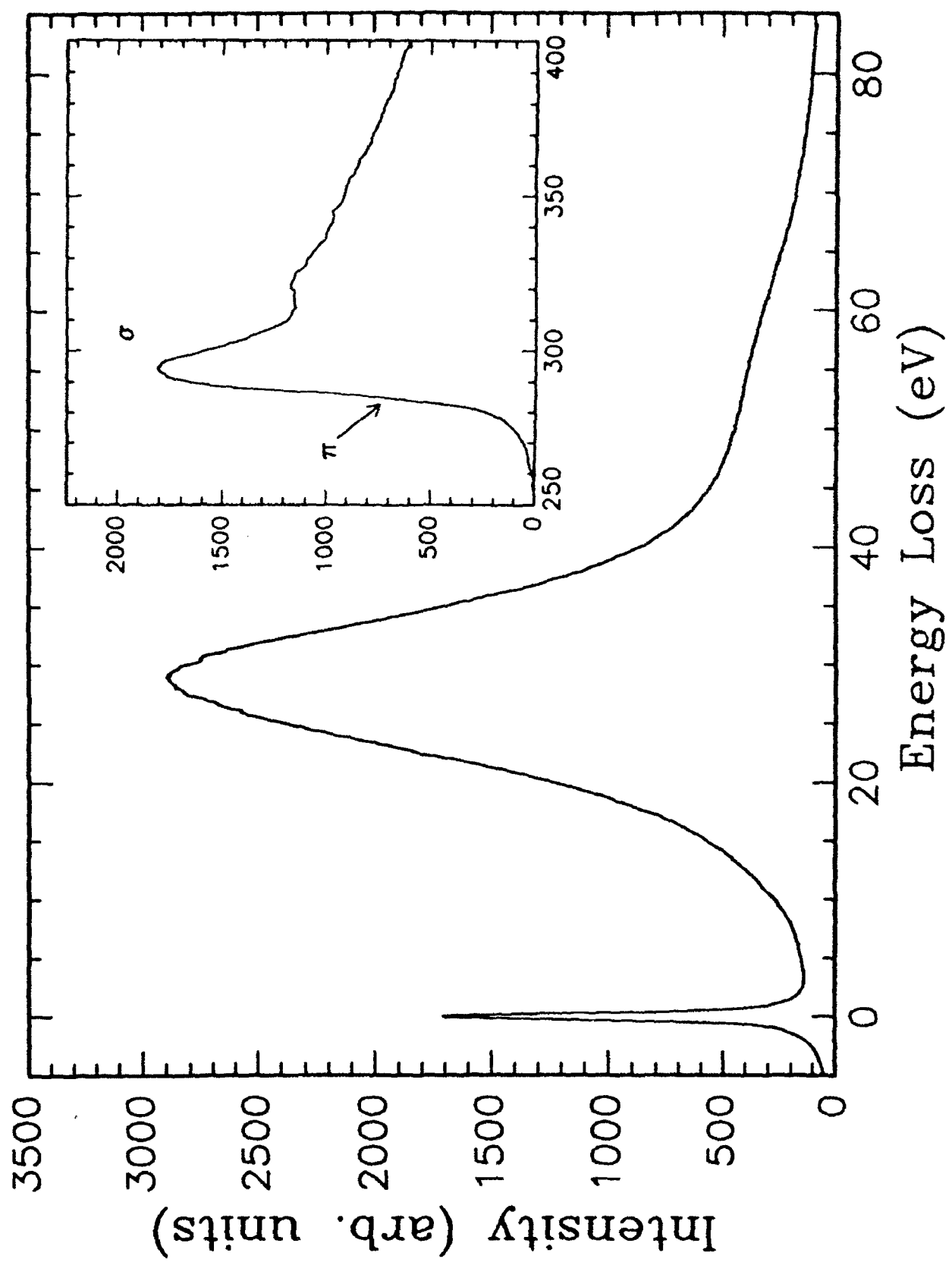
35. J. Robertson and E. P. O'Reilly, Phys. Rev. B35, 2946 (1987).
36. J. Tauc, R. Grigorovici, and A. Vancu, Phys. Status Solidi 15, 627 (1966).
37. H. R. Phillipp and H. Ehrenreich, Phys. Rev. 129, 1550 (1963).
38. D. Y. Smith, *Handbook of Optical Constants of Solids*, ed. E. D. Palik, (Academic Press, San Diego, 1985) p. 35.
39. N. Savvides, D. R. McKenzie and R. C. McPhedran, Solid State Communications, 48, 189 (1983).
40. Sonenschein, M. Hanfland, and K. Syassen, Phys. Rev. B38, 3152 (1988). See Footnote 30 therein.
41. A. Saeed, P. H. Gaskell, and D. A. Jefferson, Philosophical Magazine B66, 171 (1992).
42. P. H. Gaskell, A. Saeed, P. Chieux, and D. R. Mckenzie, Philosophical Magazine B66, 155 (1992).
43. J. Yuan, A. Saeed, L. M. Brown, and P. H. Gaskell, Philosophical Magazine B66, 187 (1992).
44. J. J. Cuomo, D. L. Pappas, J. Bruley, J. P. Doyle, and K. L. Senger, J. Appl. Phys. 10, 1706 (1991).
45. F. Xiong and Y. Y. Wang (to be published, 1993).
46. D. L. Pappas, K. L. Saenger, J. J. Cuomo, and R. W. Dreyfus (preprint, 1992).
47. P. T. Murray, and D. V. Dempsey, Mat. Res. Soc. 1991 Fall Meeting Presentation Abstract, B9.3/A16.3.
48. P. T. Murray, private communication.

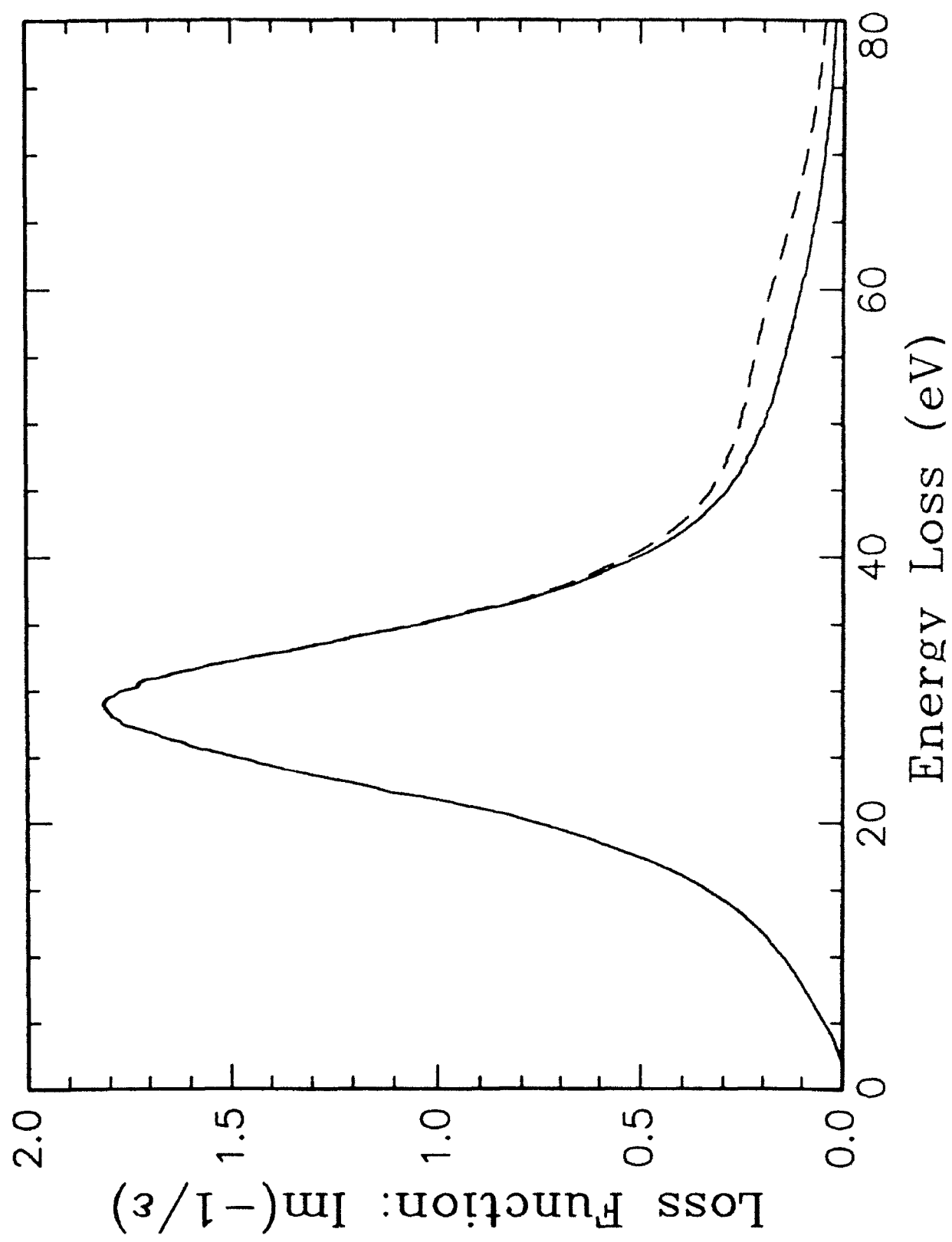
FIGURE CAPTIONS

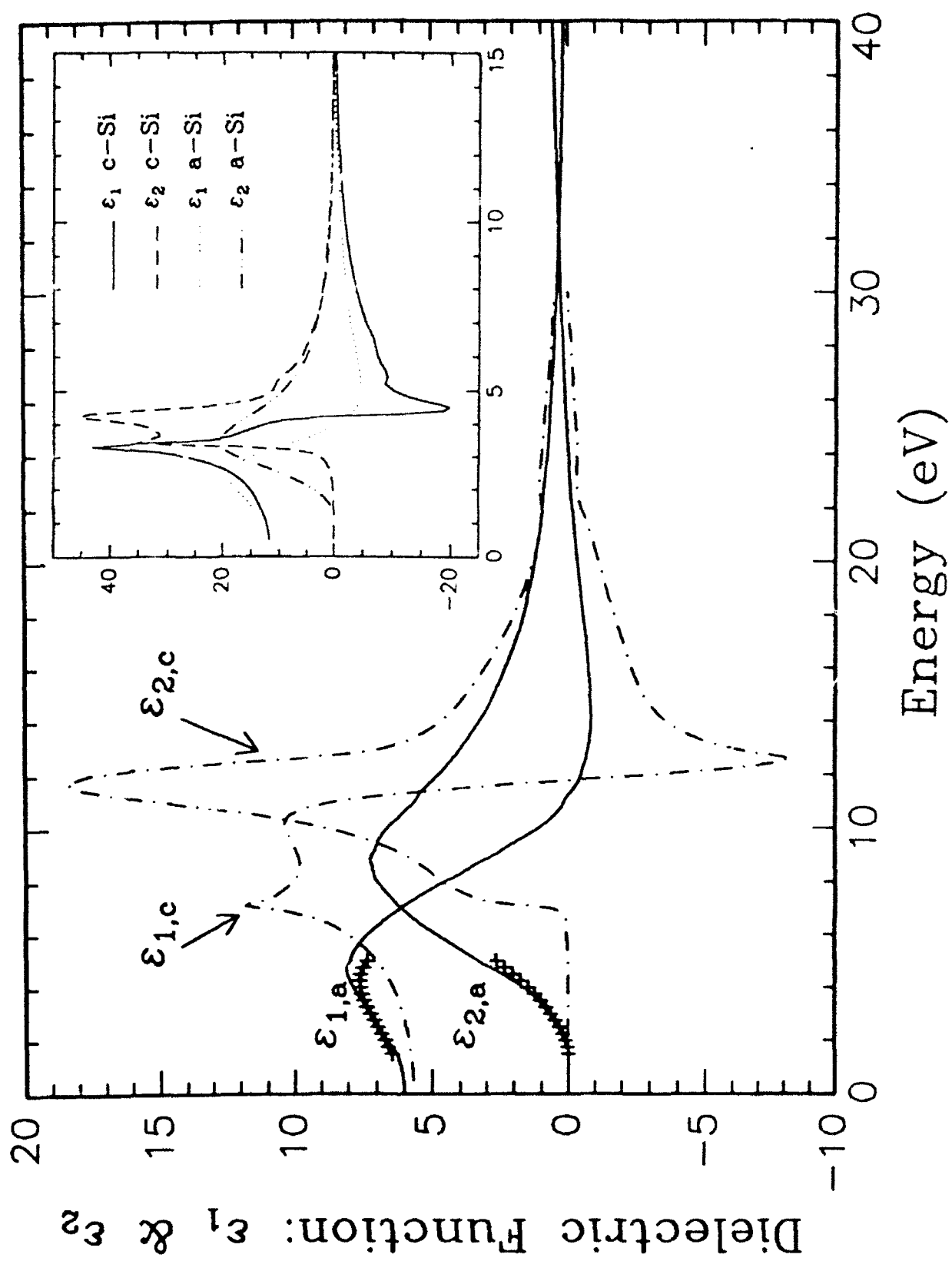
- Fig 1.** Spectroscopic ellipsometry spectra of amorphous diamond on Si(100) prepared by pulsed excimer laser ablation. Solid curves are the best fits of a polynomial function using the Cauchy model.
- Fig 2.** Real part (n) and imaginary part (k) of the complex refractive index of an a-D film, reduced from the spectroscopic ellipsometry measurement shown in Figure 1. The n values for diamond (from Ref. 15) and graphite (from Ref. 16) are also plotted for comparison.
- Fig 3.** Low energy loss spectrum of electron energy loss spectroscopy of an a-D film on Si(100). Inserted is the corresponding carbon K-edge core loss spectrum after removing the background.
- Fig 4.** Energy loss function of amorphous diamond, reduced from EELS spectrum shown in Figure 4. Dashed curve is before multiple scattering correction.
- Fig 5.** Complex dielectric function of amorphous diamond reduced from the energy loss function shown in Figure 4 through K-K analysis (solid curves, $\epsilon_{1,a}$ and $\epsilon_{2,a}$). Cross symbols are the results from SE shown in Figure 2. Complex dielectric function of crystalline diamond from Ref. 20 are also plotted as dot-dashed curves. Inserted are plots of complex dielectric function of crystalline and amorphous silicon, for comparison.
- Fig 6.** The energy-dependent optical transition strength of amorphous diamond and crystalline diamond.
- Fig 7.** Plot of the quantity $E\epsilon_i^{1/2}$ versus the photon energy, E , from the data shown in Figure 6 for an amorphous diamond film.
- Fig 8.** The energy-dependent oscillator strength or the effective number of valence electron per atom contributing to interband transitions in amorphous diamond, crystalline diamond, and graphite.

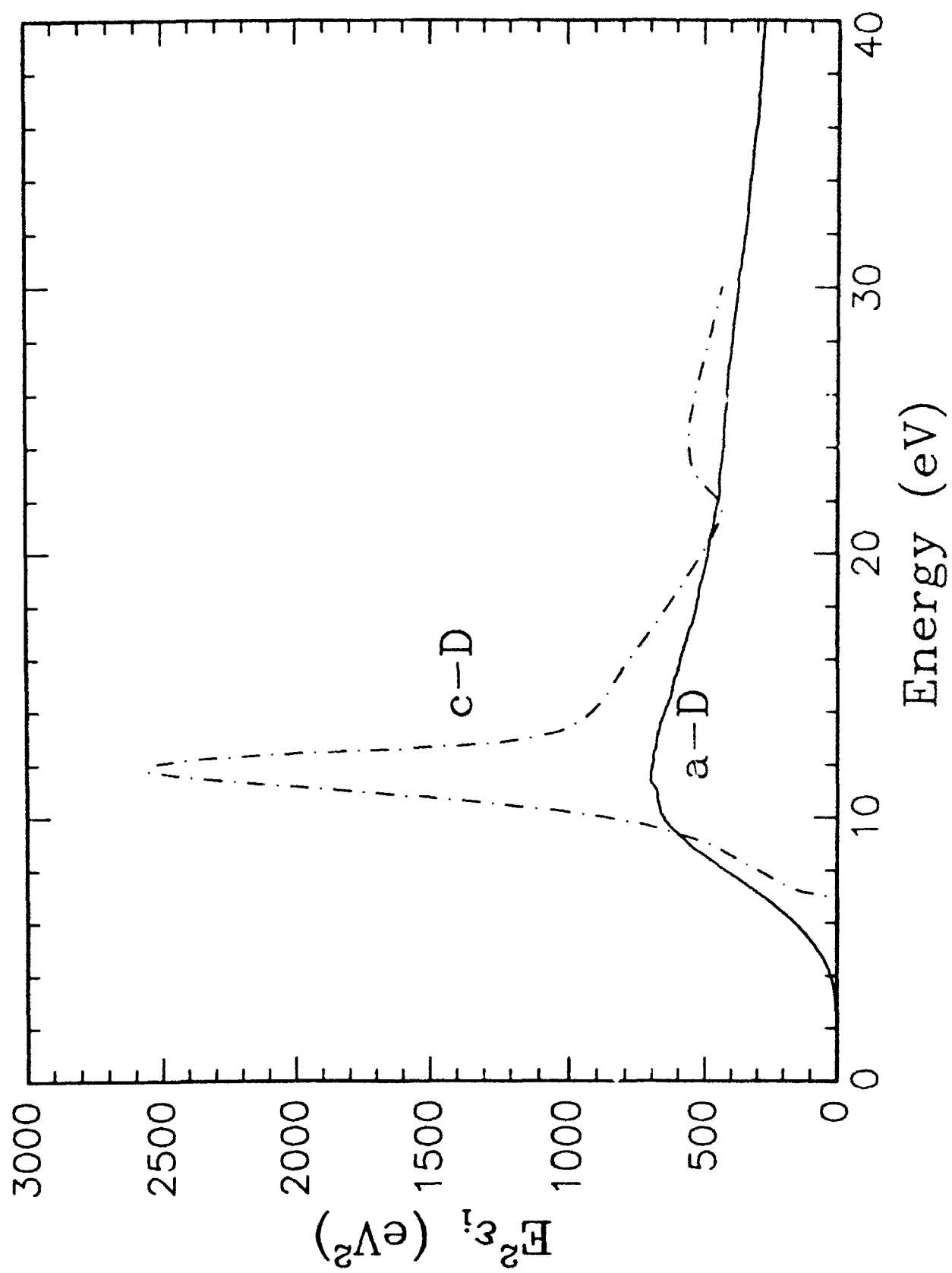


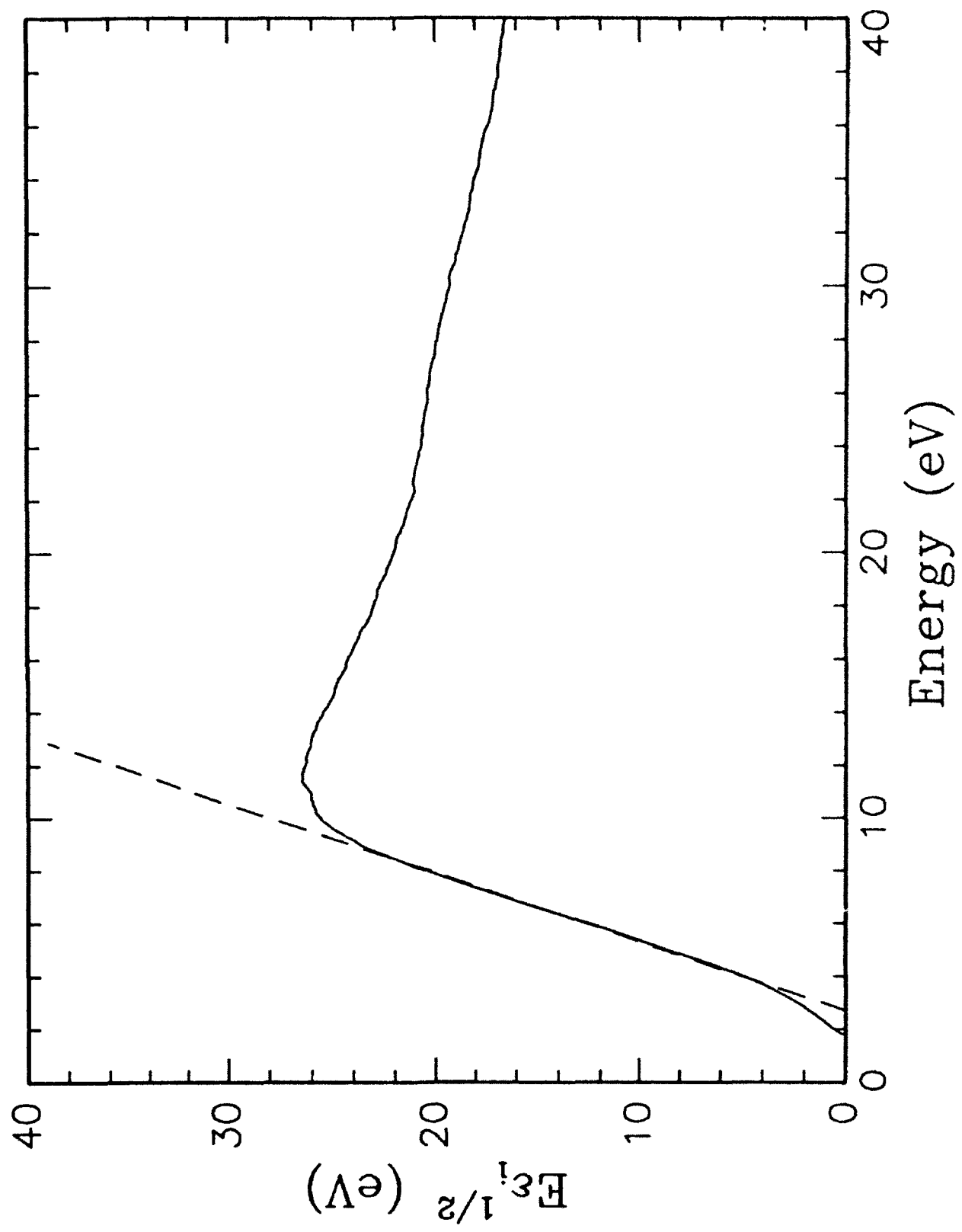




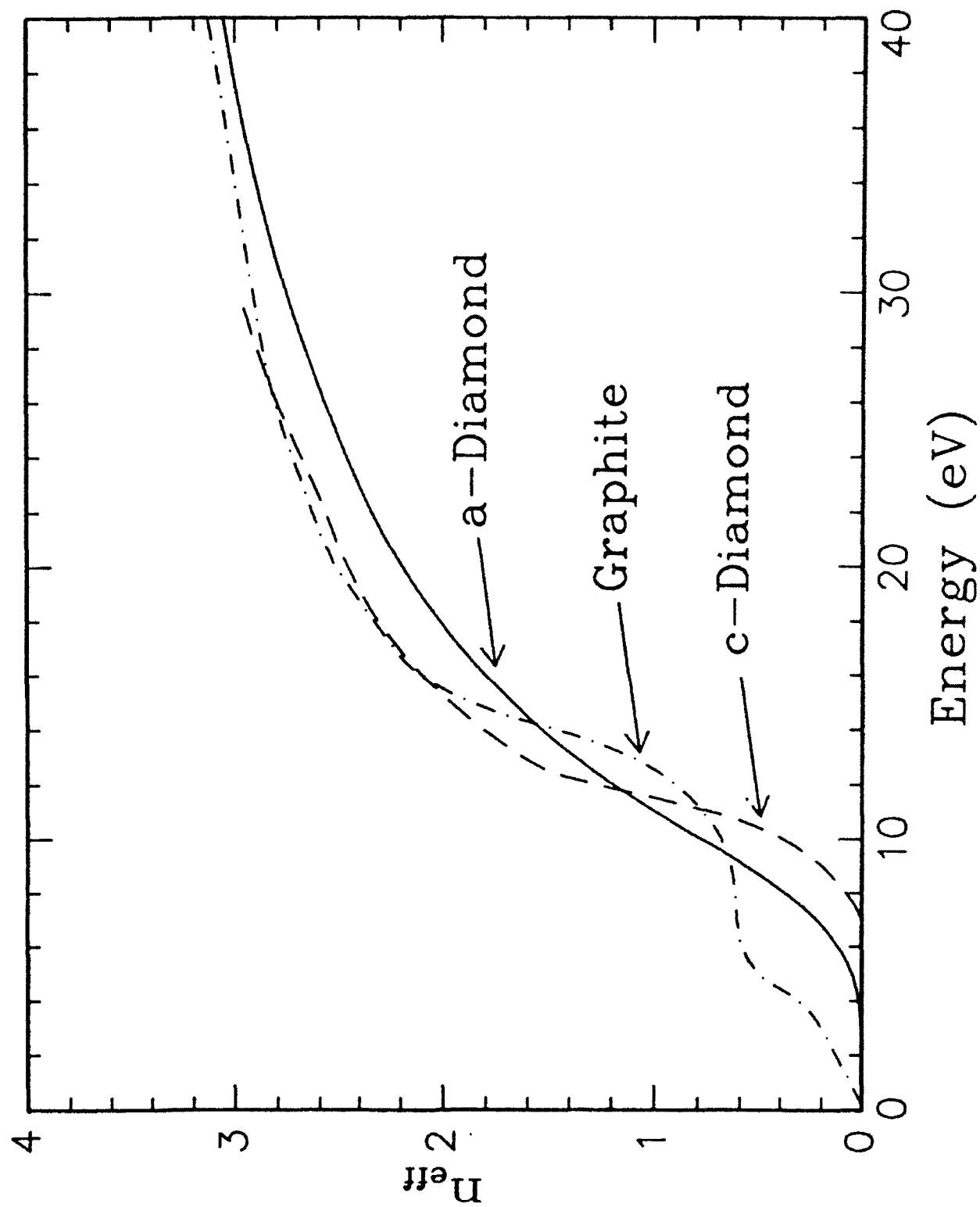








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