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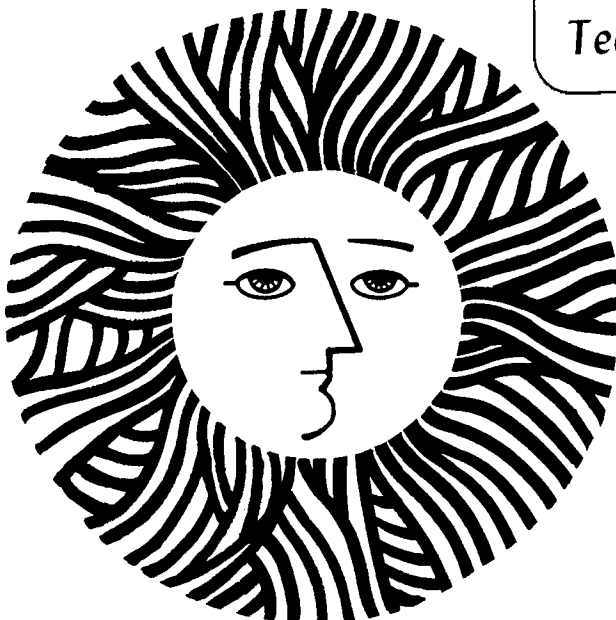
THE ENERGY DEPENDENCE OF THE EFFICIENCY-MOBILITY-LIFETIME
PRODUCT ($\eta\mu\tau$) IN HYDROGENATED AMORPHOUS SILICON

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The Energy Dependence of the Efficiency-Mobility-Lifetime
Product ($\eta\mu\tau$) in Hydrogenated Amorphous Silicon

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ABSTRACT

We report preliminary results of secondary photoconductivity and optical absorption measurements determined by photothermal deflection spectroscopy on doped and undoped hydrogenated amorphous silicon films. From these measurements, we find that, for the undoped material the efficiency-mobility-lifetime product is constant to ~ 1.5 eV and drops markedly below ~ 0.9 eV. For phosphorus doped films, $\eta\mu\tau$ is constant down to 0.9 eV. Our results are compared to primary photoconductivity measurements and a tentative model is proposed to explain the results.

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I. Introduction

Although the incorporation of hydrogen in amorphous silicon can significantly reduce the density of states within the gap, little is known about the energy distribution of the remaining states or their effect on the transport properties of this material. While conventional optical absorption measurements in hydrogenated amorphous silicon (a-Si:H) have been reported,¹⁻³ the results for gap state absorption are considered unreliable. Since the films are typically 1 μm thick and elastically scatter light, conventional reflection and transmission techniques are not adequate for determining such an absorption. Other experiments have attempted to derive the absorption from photoconductivity,³⁻¹⁰ but they required experimentally unverified assumptions about efficiency-mobility-lifetime product ($\eta\mu\tau$). Recently we have developed the technique of photothermal deflection spectroscopy (PDS)¹¹ which enables the reliable measurement of small optical absorptions down to 0.1 cm^{-1} for one micron thick films. We have employed this technique to measure gap-states and band edge absorption for undoped and doped a-Si:H films.¹²

In this paper, we present preliminary results combining absorption data from PDS with photoconductivity measurements to derive $\eta\mu\tau$ as a function of photon energy in the range of 0.7 - 2.1 eV. We find that for phosphorus-doped samples, the $\eta\mu\tau$ product is fairly constant between 2.1 and 0.9 eV. For the undoped film, this product is constant down to 1.5 eV, where it drops by a factor ~ 5 . Below 0.9 eV, $\eta\mu\tau$ drops rapidly. We propose a tentative density of states model to explain our results and results from other experiments.

II. Experimental Considerations

The films were deposited in a dc capacitively-coupled glow discharge system.¹³ The ohmic contacts were formed by depositing chromium contacts 1.5 mm apart from each other on a fused silica substrate. A small n^+ layer (500Å) was deposited, followed by either a 0.5 μm layer of a-Si:H with <1% SiF_4 or 0.19% .7 μm PH_3 doped a-Si:H film.

The secondary photoconductivity (SPC)¹⁴ was produced using the the monochromatized output (0.1 eV resolution) of a 1000W HgXe lamp. The monochromatic light intensity increased by a factor of 30 from 2 eV to 1.2 eV. The variation of the carrier generation as energy decreased was less than would be expected because the intensity increase partially offsets the film absorption decrease. The light on the sample uniformly illuminated the film between the electrodes. The source intensity was measured by a calibrated silicon photodiode and a pyroelectric detector. The sample and a load resistor were biased by 100V dc (the I-V characteristic was quite linear in this region). The dc photocurrent was measured across the load resistor using a computer-interfaced voltmeter. The current measurement was averaged for 45 seconds with illumination and then 45 seconds with the light blocked. The photocurrent was the difference between the two measurements. For the ac measurements, the exciting light was chopped and the current through the load resistor was measured using a lock-in amplifier.

A number of experiments were performed to investigate the response time and intensity effects. When the light intensity (I) was varied over 3 orders of magnitude, the dc and ac photoconductivity for the undoped film varied linearly ($I^{.98}$) for photon energies, ($h\nu$) both

above and below the band edge. In addition, some phase shifts were noted for $\hbar\omega < 1.5$ eV indicating an increase in the response time. Measurements of the SPC decay confirmed that the response time increased to about 15ms. To insure that the response time variations were not altering the SPC measurements, we measured the ac SPC at 5 Hz with a much larger dc bias light of wavelength greater than 640nm (to insure uniform carrier generation). The dc bias light insured that the ratio of trapped to free carriers was not altered by the ac probe beam.⁸ Measurements in the time domain confirmed that the response time was independent of photon energy.

For the phosphorus doped sample, the photoconductivity varied as $I^{0.8}$ at 27 Hz. The phase shifts and response time variations did not significantly alter the shape of the SPC. The optical absorption was measured using PDS as described elsewhere.¹¹ Care was taken to insure that no signal originated from absorption in the electrodes.

III. Results

The results of our SPC measurements on undoped films are shown in Fig. 1. Qualitatively, the overall shape is independent of the frequency or of the presence of dc bias light. The dependence of SPC on the chopping frequency at lower photon energies is due to the increase in response time. The dc bias light curve follows the dc measurement but is enhanced at ~ 0.9 eV and quenched at ~ 1.2 eV, an effect which has been observed in two-beam photoconductivity measurements.¹⁵ Although the response time is constant due to the dc bias light, the ac probe light periodically modulates the occupancy of trap and recombination centers, especially at low energies (< 1.2 eV). The periodic change in occupation

of these centers periodically modulates the larger dc current. The resulting ac current signal adds to the true photocurrent due to changes in the carrier density caused by absorption of the probe light. Hence, for our purposes, dc or low frequency SPC give more accurate results.

In Fig. 2, we present both dc SPC measurements and the absorption for the same film. Also plotted are the SPC and PPC results of Ref. 8. These SPC and PPC results of Ref. 8 also agree with those of Ref. 4. on undoped Schottky barrier diodes. The agreement between our SPC measurements and those on Schottky barrier diodes indicates that: (1) our undoped film with $<1\%$ SiF_4 is not significantly different than films without SiF_4 , and (2) the basic transport is the same in films produced in different laboratories. The most remarkable feature is that the shape of the absorption and the SPC curves are roughly the same until ~ 0.9 eV, where the SPC measurement begins to decrease. The deviation between SPC and PPC on the Schottky diode is an important indication that transport properties are changing in this region. The SPC and PPC Schottky results have a different slope probably due to photoemission and are offset from one another because only a fraction of the carriers are collected. If corrections for the collection efficiency and photoemission are made, the SPC and PPC curves are equal to ~ 1.5 eV.⁷ When corrected for photoemission, the PPC curve continues with the same exponential slope below 1.5 eV. In Fig. 3, we show absorption and SPC of our phosphorus doped film along with PPC measurements of a phosphorus film in a Schottky barrier configuration.⁵ Again the agreement demonstrates that these films are representative of films produced elsewhere. Unlike the undoped case, the absorption follows the SPC closely throughout the energy range $0.9 \text{ eV} < h\nu < 2.5 \text{ eV}$ for doped films.

These results are similar to those in Reference 16.

These curves can be used to deduce information about the transport properties of the films. The secondary photoconductivity, $\Delta\sigma$, is given by

$$\Delta\sigma = ef (\eta_h \tau_h \mu_h + \eta_e \tau_e \mu_e) \quad (1)$$

where

$$f = F (1-R)(1-e^{-\alpha l})/l$$

is the number of photons absorbed /cc/sec, F is the flux of photon/cm²/sec, l is the film thickness, R is the surface reflection of the film, α is the absorption coefficient, η is the efficiency of carrier generation, τ is the free carrier lifetime, μ is the free carrier mobility, and e is the electron charge. The subscripts e and h refer to electrons and holes, respectively. We also have⁴ $\mu\tau = \mu_D \tau_R$ where τ_R is the trap dominated response time and μ_D is the trap dominated drift mobility.

Because the occupation of traps and recombination centers depend on the carrier generation rates, the photocurrent changes as the intensity and absorption change. By noting empirically that $\Delta\sigma \propto I^\gamma$ where $\gamma = 0.8$ for the phosphorus doped films, we may approximately correct for this effect by normalizing the photoconductivity by⁹

$$\Delta\sigma = \Delta\sigma_0 (f/f_0)^\gamma \quad (2)$$

where

$$\Delta\sigma_0 = ef_0 (\eta_h \tau_h \mu_h + \eta_e \tau_e \mu_e)$$

and the subscript o denotes values at an arbitrary but fixed generation rate/cc, f_o . Hence,

$$(\eta_h \tau_h \mu_h + \eta_e \tau_e \mu_e) = \frac{\Delta \sigma}{e f_o} \left(\frac{f_o}{f} \right)^\gamma \quad (3)$$

This neglects changes in the carrier density due to changes in η and τ . However, this effect is small. For the computation of $\eta\mu\tau$, it is found that the overall shape does not depend significantly on the value of γ .

PDS theory shows that the deflection signal is given by¹¹

$$S_{PDS} = S (1 - e^{-\alpha \ell}) \quad (4)$$

where S is determined from the saturation of the signal at large energies. Hence,

$$f = F (1-R) S_{PDS} / (\ell S)$$

giving

$$\eta_h \tau_h \mu_h + \eta_e \tau_e \mu_e = \frac{\Delta I}{e f_o} \left(\frac{F_o S_o PDS}{F S_{PDS}} \right)^\gamma \frac{L}{VA} \quad (5)$$

where L is the electrode spacing, V is the applied bias.

Using Eq. (5), we obtain the results shown in Fig. 4. The magnitude for the undoped film at 2.0 eV agrees with values measured by other investigators.¹⁰ The error bars conservatively estimate the error of one part of the curve relative to another due to noise, lamp and electronic drifts, and possible nonlinearities in the electronics. Hence, we believe that the structure shown in the undoped film is significant. Fig. 4 shows that for undoped films, the $\eta\mu\tau$ product is independent of energy to 1.5 eV. At this point it drops by a factor of 5 until ~0.9 eV

whereupon it rapidly decreases. The general shape approximately agrees with the results of Ref. 1.

For the doped sample, the product is constant throughout the energy range. Supporting evidence for these results can be found in the data of a number of researchers who have reported deviations between PC and absorption measurements at low energies for undoped samples^{2,7,16} and good agreement between the measurements at high energies for doped sample. Because of the limitations of conventional optical measurements and the possibility that the signal was due to scattering, these deviations were not considered significant.

IV. Discussion

By combining our measurements with results of other experiments, we arrive at the tentative model described below. In the following discussion it is convenient to divide the spectra into three regions: Region A -- $\hbar\omega > 1.5$ eV, Region B -- $0.9 \leq \hbar\omega \leq 1.5$ eV, and Region C -- $\hbar\omega < 0.9$ eV.

In Fig. 5, we depict the approximate density of states for doped and undoped material, as measured by deep level transient spectroscopy (DLTS),¹⁸ capacitance,¹⁹ and conductivity measurements.²⁰ Recent absorption measurements have shown that the density of states maximum above the valence band (see Fig. 5) is in large part due to dangling silicon bonds for the undoped material¹² and that the maximum is strongly correlated with the LESR signal for the phosphorus doped material.¹² A maximum 0.3 eV below the conduction band is not shown in the density of states. There is evidence from field effect and luminescence measure-

ments supporting the existence of this maximum.²¹ While some photoconductivity measurements support the existence of the maximum, others do not.²⁰ DLTS,¹⁸ capacitance¹⁹ measurements do not exhibit this feature. Our results, to date, do not resolve the question of whether the maximum exists. The explanation for our results proposed below, however, does not depend on the existence or absence of this maximum.

In Region A, the transitions in both phosphorus and undoped films are band-to-band transitions resulting in free or shallow-trapped electrons and holes. These trapped carriers can be thermally excited above the mobility edges. In SPC, the current is carried by the electrons because of their greater mobility. In PPC, the mobility of the holes is sufficient to allow collection of most of the holes. Consequently, the absorption, the secondary photoconductivity, and the primary photoconductivity show the same wavelength dependence.

In Region B, the transitions are from the gap-state maximum to the conduction band. The generated electrons conduct above the conduction band mobility edge. Because most of the current is carried by electrons in Regions A and B, SPC is largely independent of photon energy, while PPC falls rapidly due to the trapping of the holes.

In the doped film, PPC does not decrease in Region B. This could be an indication that the holes deep in the gap are mobile. If the density of states within the gap is sufficiently high, the holes could tunnel or hop through the collection region. An alternative explanation is that the shoulder in PPC is due to photoemission.^{7,22} In Fig. 6, we see that the absorption shoulder differs from the PPC shoulder as doping decreases. This has been interpreted as an increase of the built-in

potential causing different photoemission contributions.²² If this shoulder in PPC is due to photoemission, then the data indicates that the free pair generation decreases rapidly for photon energies less than 1.5 eV.

The drop of the η_{PT} for undoped films compared with doped films in Region B could be explained by various mechanisms. First, the defects of the films may be quite different. Consequently, the matrix element of the transition for the undoped defect may be small compared to the band-to-band transitions or the phosphorus defect transitions. Second, there may be geminate recombination which differs between the undoped and doped films. Third, the transitions labeled B^1 in Fig. 5 may significantly increase the absorption in the undoped films without generating more mobile electrons. Fourth, the density of defects in the phosphorus films may be so great that a band begins to form. This causes a delocalization of the wave function for states in the 1.3 eV density of states maximum and results in a larger matrix element for heavy doping. For heavy doping, the matrix element could approximately equal the band-to-band matrix element. In the undoped film, the initial state at 1.3 eV below the conduction band is more localized, resulting in a reduced matrix element.

Finally, in Region C, light does not generate either mobile holes or electrons for undoped films causing both SPC and PPC to decrease sharply. The optical absorption, however, remains high due to transitions between localized states. The absorption in doped films may not remain as high as in undoped films due to the absence of transition B^1 . There is experimental evidence that such transitions are possible in the

case of amorphous arsenic.²³ Since the localized states in the tail below the mobility edge still may extend over many atomic sites, there can be a finite transition probability. Another possibility is that the absorption arises from the ground to excited state transition of defect state. This would explain the luminescence evidence for states 0.3 eV below the mobility edge, which give rise to 0.9 eV luminescence. A final possibility is that absorption in Region C may be due to surface states.

The above model provides a possible explanation for the experimental results presented in this paper and the results of other experiments. A systematic study on co-deposited material may confirm this model.

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Figure Captions

Fig.1 Secondary photoconductivity vs. photon energy for an undoped film. DC SPC without dc bias light (—), Hz SPC with dc bias light (-■-), 27 Hz SPC without dc bias light(-●-). Conductivity has been normalized by the light intensity.

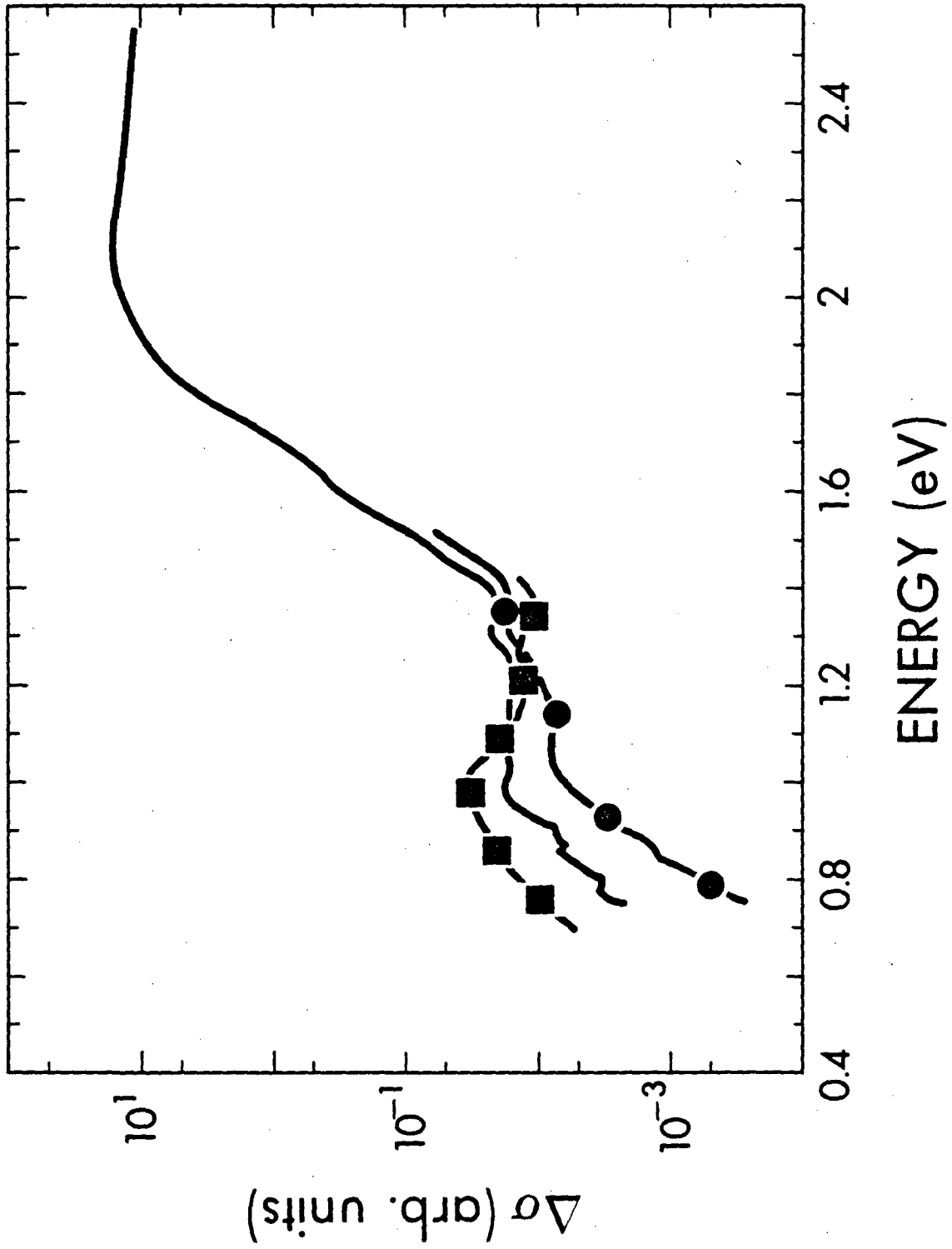
Fig.2 Photoconductivity (primary and secondary) and absorption vs. photon energy for an undoped film. (—) (lower solid line), dc SPC measured in this experiment (no dc bias light). (- - -) ac SPC measured in a Schottky barrier with dc bias light (Ref. 8). (-·-) PPC on the same Schottky barrier with dc bias light (Ref.8). (—) (upper solid line) Absorption is measured by PDS.

Fig.3 Photoconductivity (primary and secondary) and absorption for a .19% phosphorus doped film. (- - -) SPC 18 Hz (This experiment). (Δ) PPC on a Schottky barrier (Ref. 5). (—) Absorption is measured by PDS.

Fig.4 $\eta \mu \tau$ product vs. photon energy for an undoped film (—) and for a phosphorus doped film (- - -). Error bars indicate maximum relative error. Absolute magnitudes error may be larger.

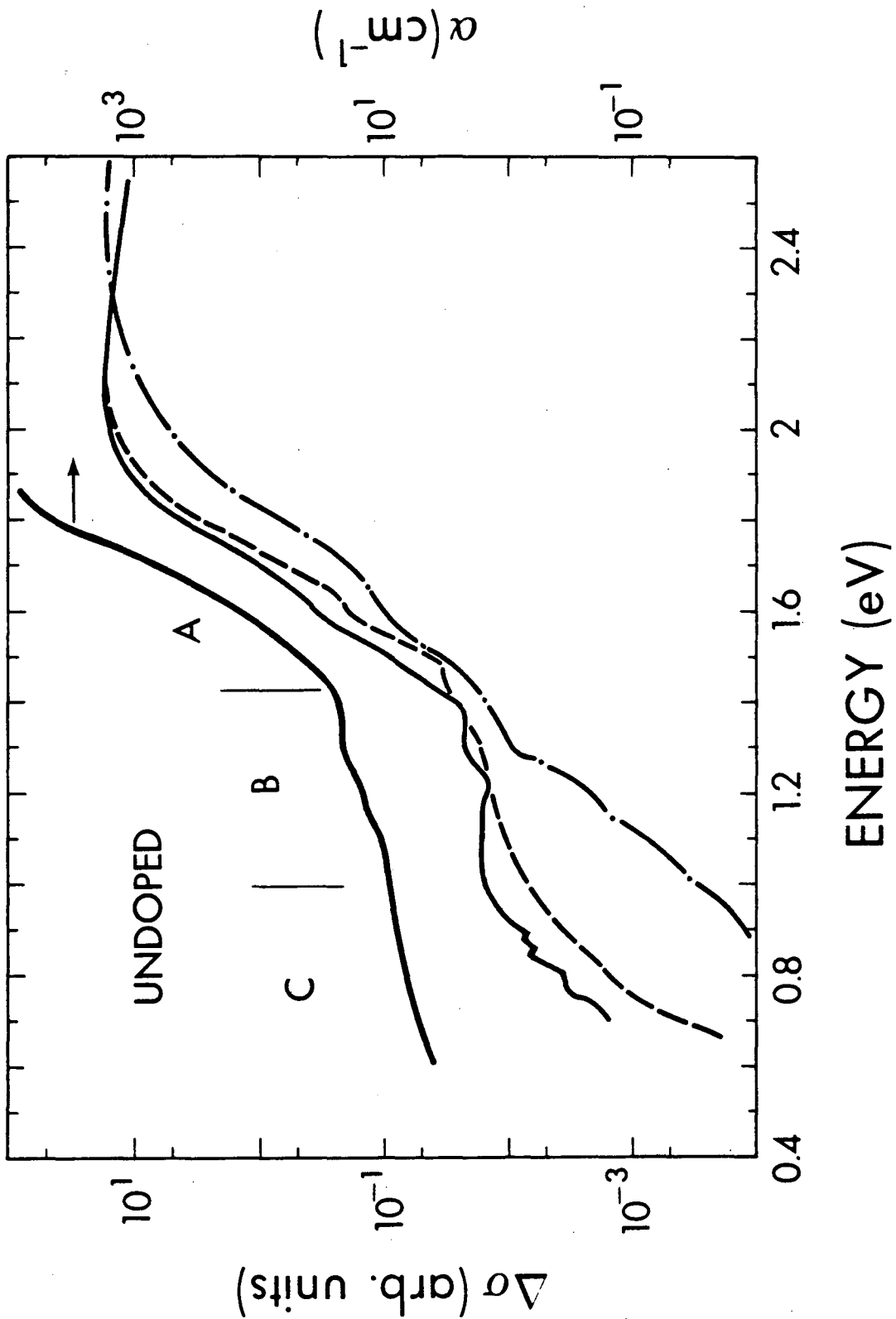
Fig.5 Density of states for undoped and P doped films as measured by DLTS (Ref. 18). As shown are various transitions giving rise to photoconductivity for the different energy regions. States are localized for energies between E_v and E_c .

Fig.6 Absorption and PPC (from Ref. 6) for different levels of doping. The absorption curves are (\blacktriangle) - 10^{-3}PH_3 , (-----) - $2 \times 10^{-4}\text{PH}_3$, and (\blacksquare) undoped. The PPC curves are (\triangle) - $2 \times 10^{-3}\text{PH}_3$, (—) - $4 \times 10^{-4}\text{PH}_3$, and (\square) undoped. Concentrations are PH_3 relative to SiH_4 in the gas phase.



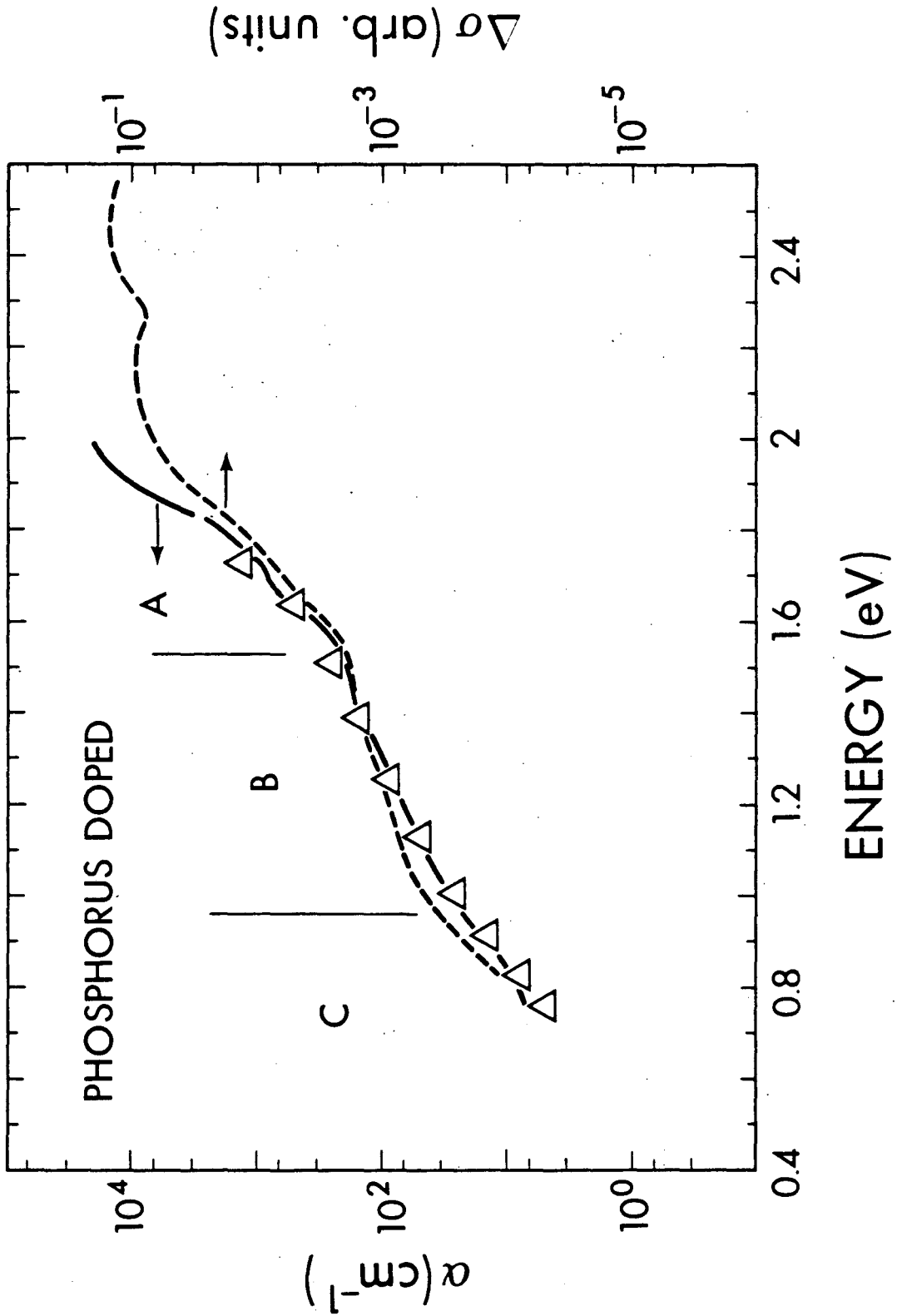
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Fig. (1)



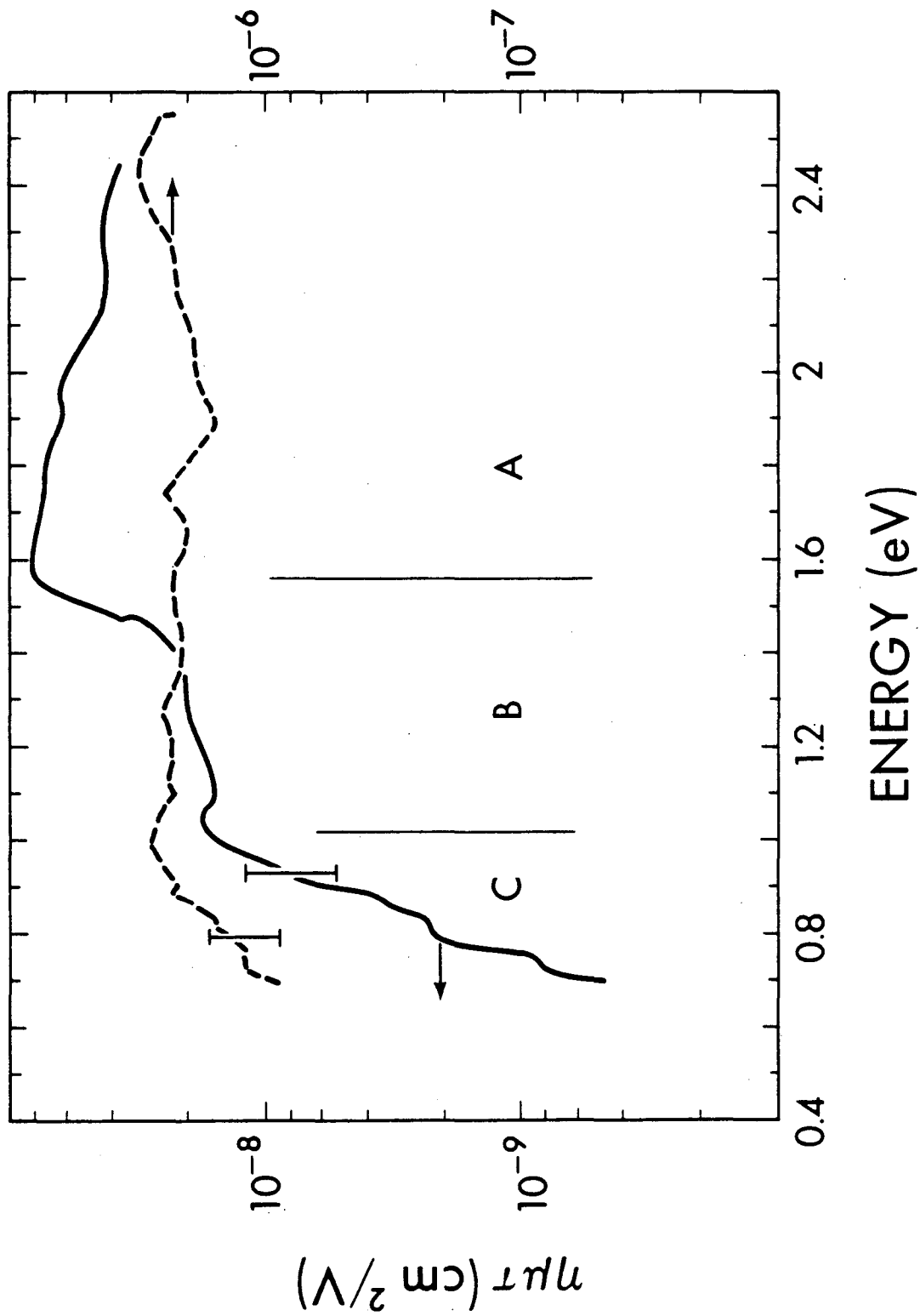
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Fig. (2)



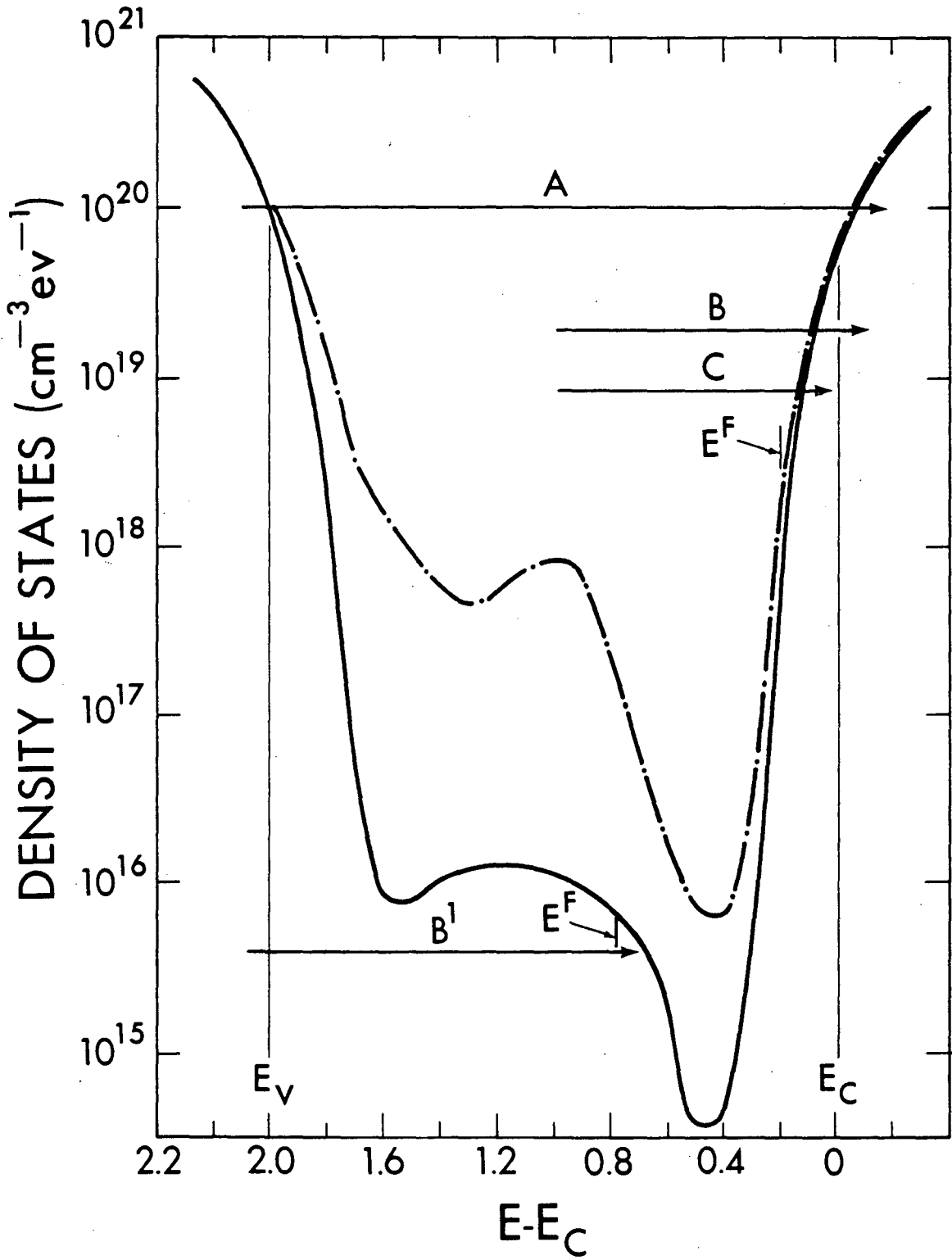
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Fig. (3)



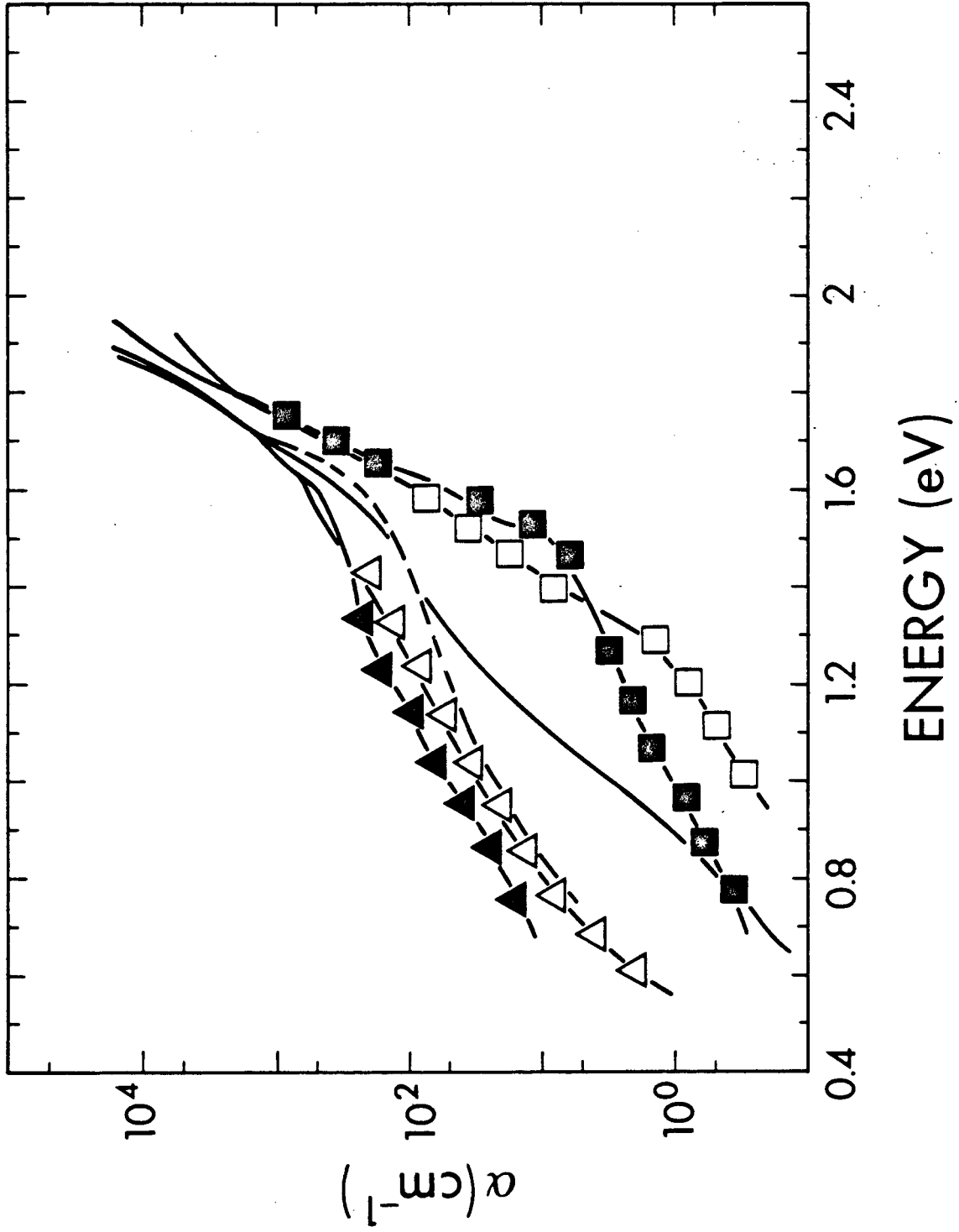
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Fig. (4)



XBL 8110-1415

Fig. (5)



XBL 8110-1419

Fig. (6)

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