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IN HYDROGENATED AMORPHOUS SILICON BY
PHOTOTHERMAL DEFLECTION SPECTROSCOPY

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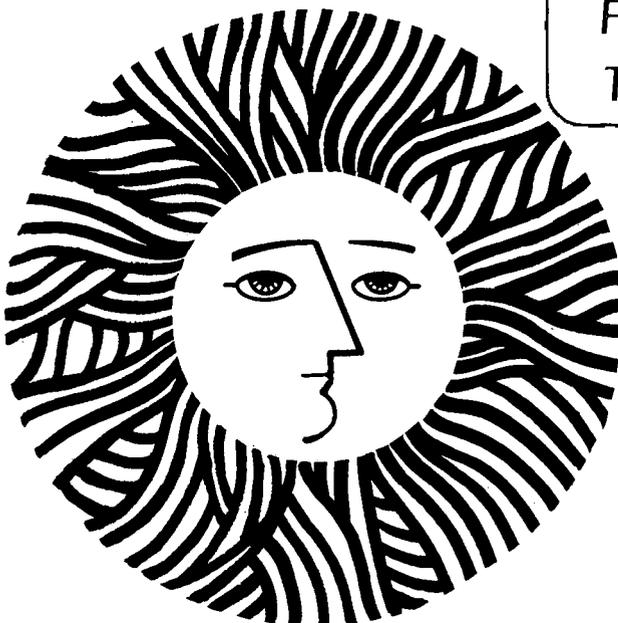
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DIRECT MEASUREMENT OF GAP STATE ABSORPTION IN HYDROGENATED
AMORPHOUS SILICON BY PHOTOTHERMAL DEFLECTION SPECTROSCOPY

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ABSTRACT

We have used the highly sensitive technique of photothermal deflection spectroscopy to directly measure the sub-gap optical absorption of undoped, singly doped, and compensated a-Si:H down to 0.6 eV. We show that the gap state absorption is due to dangling silicon bonds. We also present evidence that while doping creates defects, compensation removes them.

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In amorphous semiconductors, the optical absorption of defects and impurities is most readily observed below the band edge since it is not obscured by the much larger band-to-band absorption. Consequently, sub-gap absorption spectra should provide information about defects in amorphous materials. Although such measurements have been made on chalcogenide glasses,¹ none of the measurements made on hydrogenated amorphous silicon (a-Si:H) have been reliable because of experimental limitations. The films are typically 1 μm thick and are not optically homogeneous, making conventional transmission and reflection measurements of absorption coefficients (α) below 50-100 cm^{-1} unreliable.² Derivation of the absorption from photoconductivity^{3,4} requires reliance upon the experimentally unverified assumption that the $n\mu\tau$ product is independent

of photon energy.⁵ We have recently developed the technique of photothermal deflection spectroscopy (PDS)⁶ which measures low absorption coefficients ($\alpha l \approx 10^{-7} - 10^{-8}$), is highly insensitive to scattering,⁷ and does not rely on the above assumption. Using PDS, we have obtained the first unambiguous and direct measurements of sub-gap optical absorption in undoped, doped, and compensated a-Si:H down to 0.6 eV, and have found evidence that this absorption is due to dangling silicon bonds.

We focussed the monochromatized (0.01 eV bandwidth), intensity-modulated output of a 1 kW HgXe lamp (pump beam) on a sample which was immersed in CCl_4 . Upon absorption of the light, synchronous heating of the sample occurred, causing a periodic index-of-refraction gradient in the CCl_4 . A HeNe laser beam (probe beam) grazing the sample surface experienced a periodic deflection which was detected with a position sensor. The resulting power-normalized deflection signal, for thermally thin samples, is related to the optical absorption by⁶

$$S = A[1 - \exp(-\alpha l)] \quad (1)$$

where A is a constant and l is the film thickness. For $\alpha l \gg 1$, $S = A \cdot l$ was determined by other measurements, and hence α was obtained for $\alpha l < 1$ using Eq. (1). Interference fringes of α were averaged on a logarithmic scale.⁴ Changes in the substrate material or film thickness did not alter the spectra, and the signal did not show phase shifts or the modulation frequency dependence characteristic of non-film absorption.⁶ Therefore, the signal was not due to absorption in CCl_4 or the substrate.

Our samples were undoped, singly doped, and compensated films deposited by rf glow discharge. The SiH_4 concentration in Ar varied from 5%

to 100%, and the substrates were either 7059 glass, quartz, or sapphire.⁸ The thickness of most films was in the 1-2 μm range. Other deposition parameters are given in Figs. 1 and 2.

The absorption edge of amorphous semiconductors is often divided into three regions:⁹ (a) a power law region; (b) an exponential region or "Urbach edge"; and (c) a sub-gap tail. In Figs. 1 and 2 we show the full absorption edge of a-Si:H in regions (b) and (c). Fig. 1 shows the effect of increasing the rf power density on the absorption edge of undoped material while keeping the substrate temperature fixed.¹⁰ As the rf power increases, the strength of the sub-gap absorption tail increases ($\hbar\omega \approx 1.4$ eV, region (c)). A second effect is the progressive decrease in the slope of the exponential edge as the rf power increases.¹¹

The effects of doping and compensation on the absorption edge are summarized in Fig. 2. In Fig. 2(a) and (b) we give the results for phosphorous and boron doped films. As in the case of undoped a-Si:H, the sub-gap absorption tail rises, and the slope of the exponential edge decreases as the PH_3 or B_2H_6 concentration is increased. However, the slope of the sub-gap region for boron is less than for the phosphorous doped films.

To separate the effects due to dopant incorporation from the effects due to shifts in the Fermi level, we investigated the absorption of a series of compensated films prepared by fixing the PH_3 concentration and gradually increasing the B_2H_6 concentration (Fig. 2(c)). Note that the magnitude of the sub-gap absorption decreases as the boron

content increases. Concurrently, there is a pronounced shift to lower energies and broadening of the exponential region.

Because the sub-gap tail increases as conductivity and luminescence measurements of the defect density also increase, we attribute this absorption to defects. The excess absorption α_{ex} due to sub-gap states can be computed from

$$\alpha_{ex} = \alpha - \alpha_0 \exp [\hbar\omega/E_0] \quad (2)$$

where α_0 and E_0 are determined by a fit to the exponential region. We then can calculate the number of defects, N_s from

$$N_s = \frac{c m}{2\pi^2 \hbar^2} \left[\frac{(1+2n)^2}{e^2 f_{oj} 9n^2} \right] \int \alpha_{ex} (E) dE \quad (3)$$

where c is the speed of light, n (≈ 3.8) is the index of refraction of the material, m is the electron mass, e is the electron charge, and f_{oj} is the oscillator strength of the absorption transition. The expression within the brackets is the inverse square of the defect effective charge adjusted by local field corrections used in interpreting the infrared spectra of a-Si:H.^{12,13} Assuming $f_{oj} = 1$ and recognizing that the local field corrections have been empirically determined to overestimate the correct local field by a factor of 2 in a-Si:H,^{13,14} we then have

$$N_s = 7.9 \times 10^{15} \int \alpha_{ex} dE \quad (4)$$

By plotting the equilibrium spin density data N_s (ESR), versus N_s (ABS),¹⁵ the defect density as deduced by Eq. (4), we obtain an excellent agreement over three orders of magnitude, as shown in Fig. 3 for undoped a-Si:H. Because ESR gives quantitative measurements of defect densities,

the agreement suggests that the sub-gap tail is due to defects with spins. Note that we find no evidence of absorption varying as N_s^2 (ESR), unlike the case of unhydrogenated amorphous silicon.¹⁶

For doped a-Si:H, there is no equilibrium spin density. However, the defect density may be estimated by a light induced ESR, (LESR) signal at $g=2.0055$ or by the quenching of luminescence.¹⁷ If we compare such estimates with those deduced using Eq. (4), again we find excellent correlation between the three types of estimates (see Fig. 4). At high defect densities, however, LESR tends to underestimate the number of defects. Our absorption estimates agree better with the luminescence estimates. The agreement for boron doping is not as good, perhaps (1) because there is a different oscillator strength for this defect or (2) because Eq. (2) overcorrects for the exponential absorption for boron. For compensated a-Si:H, with low boron concentrations, where there is a well defined defect tail, Eq. (4) correctly predicts the number of defect centers, as estimated from luminescence and LESR results.

Using the agreement between absorption, ESR, LESR, and luminescence deduced defect densities along with other data, the following picture emerges. For undoped a-Si:H, as the rf power density and the substrate temperature increase, a maximum in the density of states due to dangling silicon bonds appears $\sim 1.3-1.4$ eV below the conduction band. The evidence that the absorption is due to dangling silicon bonds is that the ESR and LESR lines used to calculate N_s (ESR, LESR) have $g = 2.0055$, which is known to be due to dangling silicon bonds,¹⁸ and the dangling Si bond energy has been calculated to be ~ 1.4 eV below the conduction band.²¹ The placement of this maximum below the conduction band is supported by

deep level transient spectroscopy(DLTS),¹⁹ and field effect measurements.²⁰ The number of dangling bonds is 10^{15} - 10^{18} /cc depending upon the preparation conditions. We conclude that these dangling bonds quench the luminescence²² rather than cause it, as previously had been hypothesized,²³ since films with the lowest absorption tails have the highest luminescence.

Doping with phosphorous introduces 10^{17} - 10^{18} defects/cc $\sim 1.3\text{eV}$ below the conduction band, perhaps through an auto-compensation mechanism where the dopant creates a vacancy.¹⁷ The absence of equilibrium ESR and the presence of a $g=2.0055$ LESR line can be explained by the pairing of electrons at the defect center. Strong support for the increase in the number of defects comes from DLTS measurements of the density of states in the gap. For a 3×10^{-4} PH_3 concentration sample, we deduce 3.7×10^{17} defects/cc from Eq. (4) and DLTS has found 3.1×10^{17} states/cc in a density-of-states maximum 1.3eV below the conduction band. Boron doping also introduces defects. While boron induced defects are probably near the valence band, as yet there is no clear evidence to support this hypothesis. Doping with phosphorous or boron introduces defects, but doping with both removes the defects, as evidenced by the decrease in defect absorption. Finally, a general feature of a-Si:H is that defects tend to alter the shape of the band edge.

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Figure Captions

Fig.1 Absorption coefficient vs. energy for undoped a-Si:H for various rf powers, $T_s=230$ °C. The rf powers for the various films are 11:1W, 4:2W, 5:5W, 6:15W, 7:30W; and 8:40W. Sample 3 is a 2W sample doped with 10^{-3} PH_3 in the gas phase.

Fig.2 (a). Absorption coefficient vs. energy for various phosphorous doped films. The doping concentration of the films is 3:1x10⁻³ PH_3 , 16:3x10⁻⁴ PH_3 , and 17:1x10⁻⁵ PH_3 . (b) Absorption coefficient for boron doped films. Doping concentration is 18:10⁻³ B_2H_6 , 19:3x10⁻⁴ B_2H_6 , and 20:10⁻⁴ B_2H_6 . (c) absorption coefficient for compensated samples. All have 10⁻³ PH_3 and the boron concentrations are 3:0 B_2H_6 , 11:2x10⁻⁴ B_2H_6 , 12:4x10⁻⁴ B_2H_6 , 14:2x10⁻³ B_2H_6 , and 15:4x10⁻³ B_2H_6 . All concentrations refer to the relative concentration of the dopant in the gas phase $T_s=230$ °C and rf power is 2W.

Fig.3 Number of defects deduced from absorption by Eq. (4) vs. number of spins measured by ESR.

Fig.4 Number of defects deduced from Eq. (4) vs. number of spins estimated by luminescence (Ref. 17). □ - phosphorous doped samples, Δ - boron doped samples, X - compensated samples.

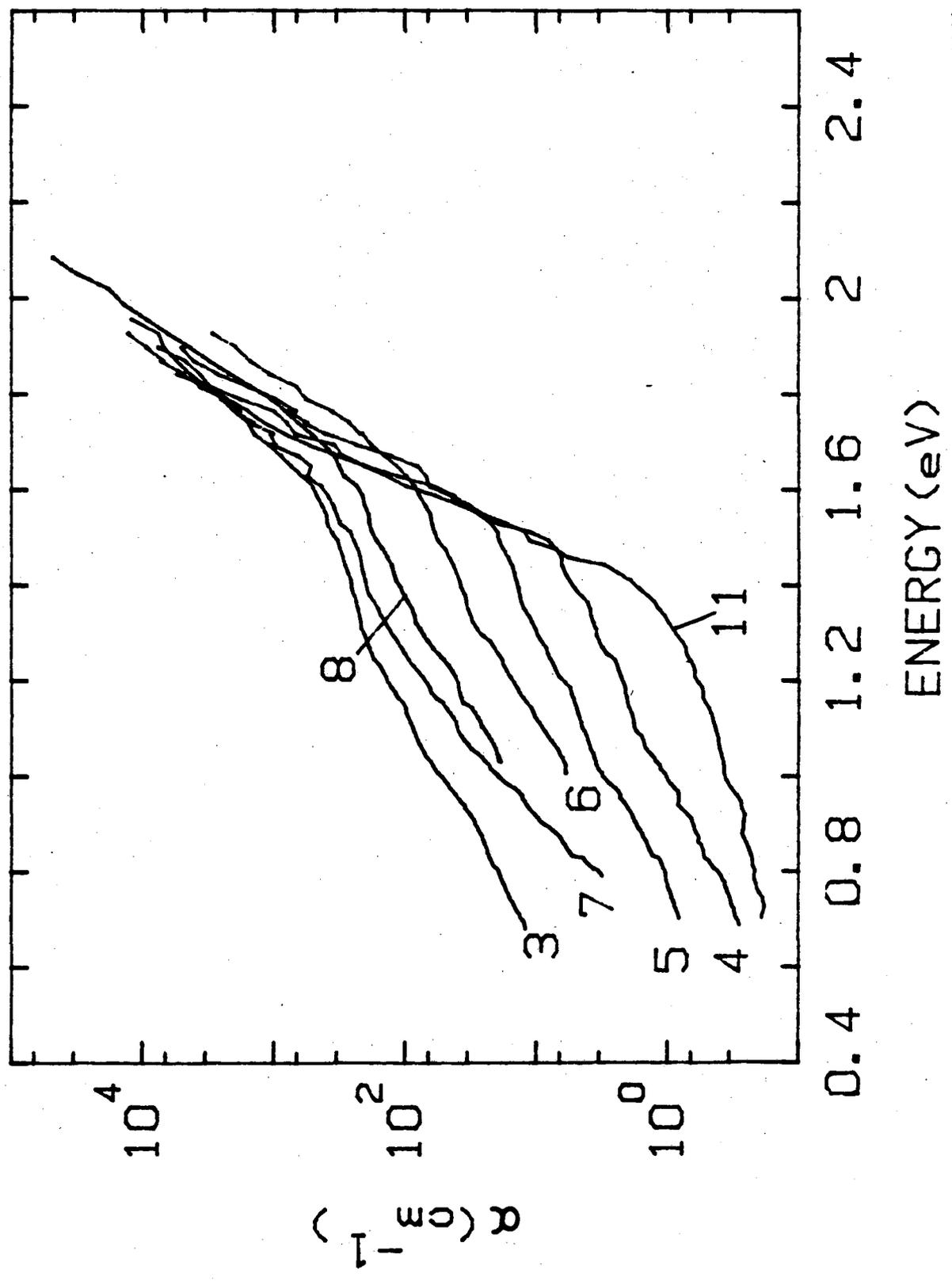
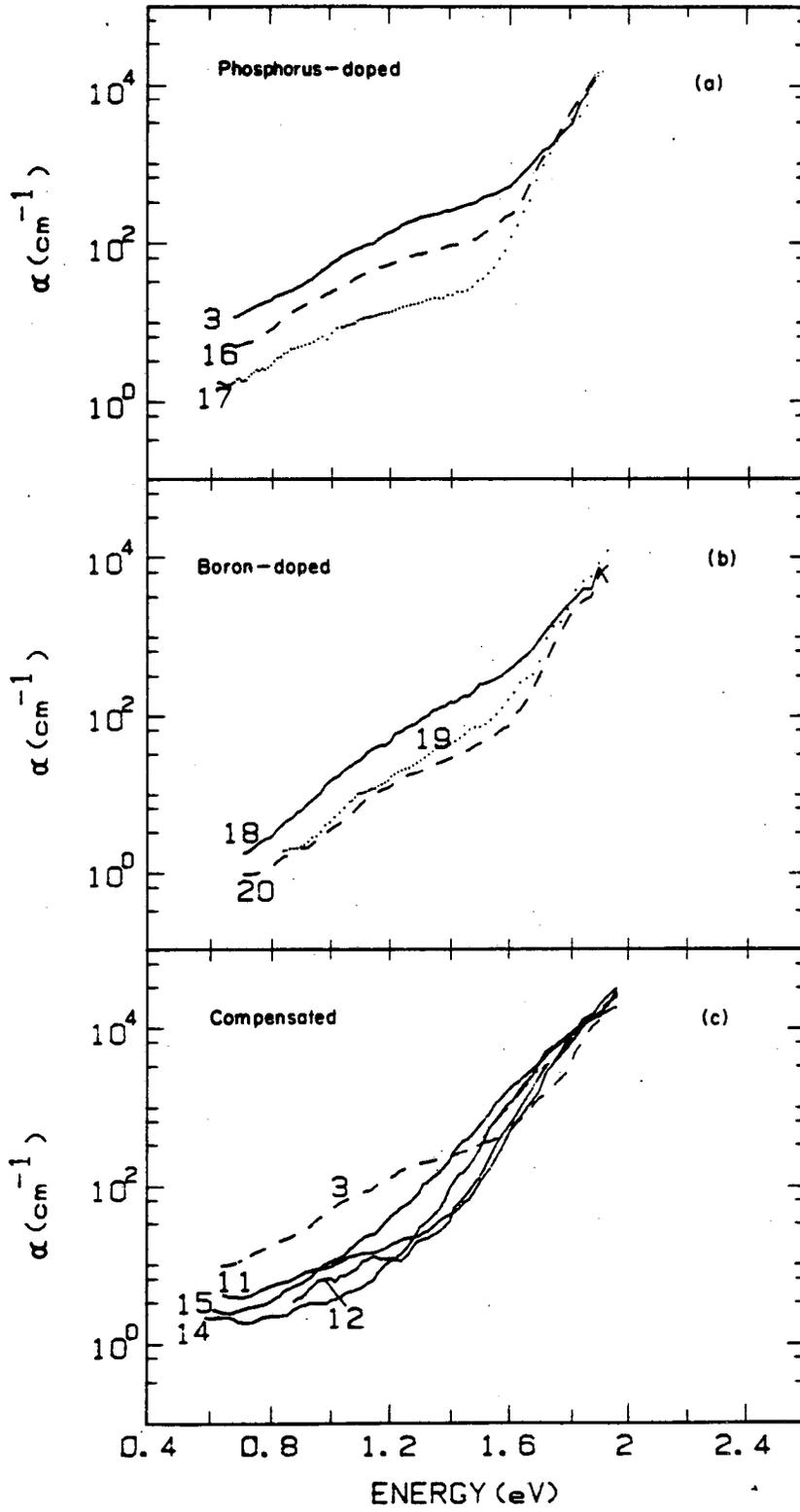


FIG. (1)

XBL 818-1141



XBL 818 1142

FIG. (2)

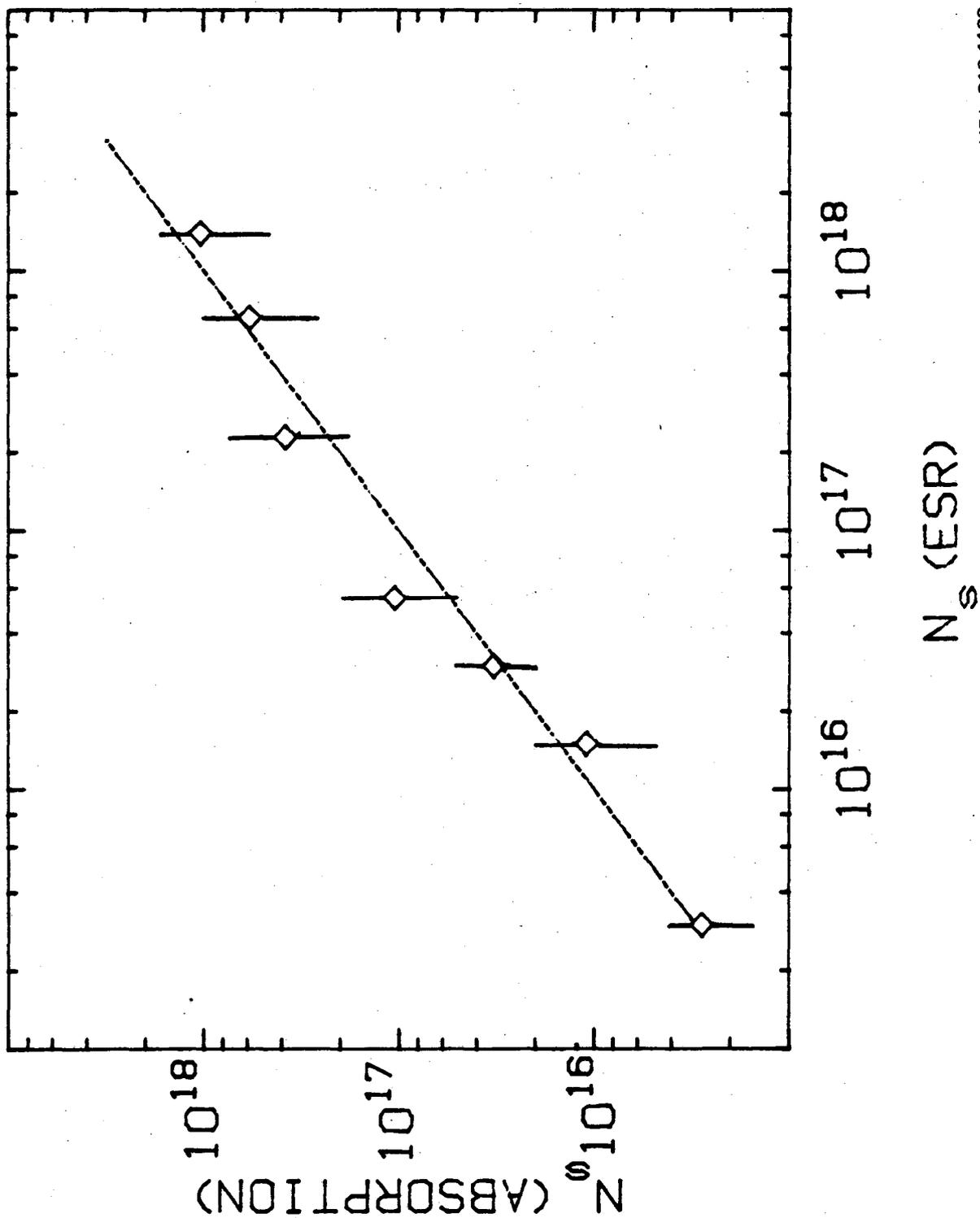


FIG. (3)

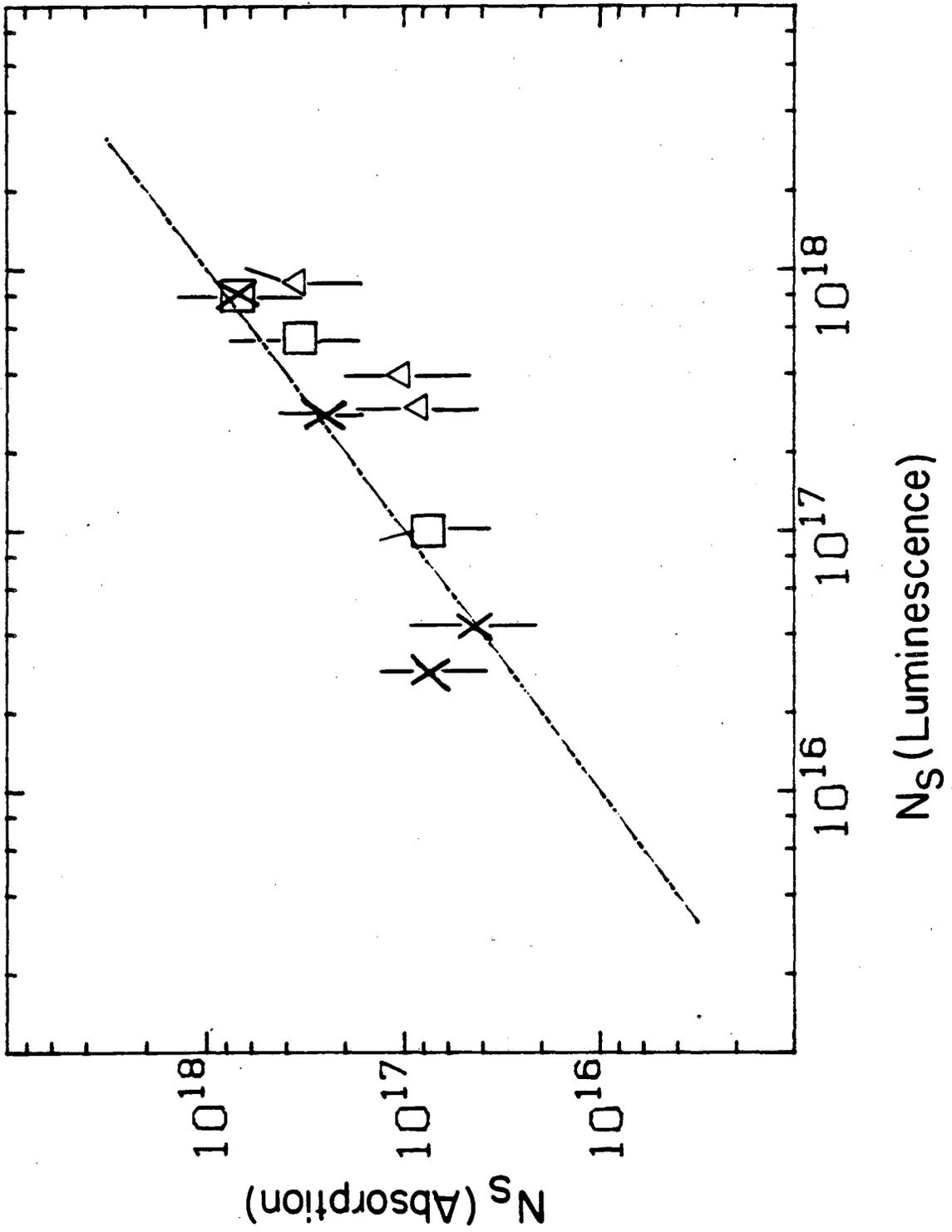


FIG. (4)

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