Method for Direct Determination of the Effective Correlation Energy of Defects in Semiconductors: Optical Modulation Spectroscopy of Dangling Bonds

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The optical modulation technique is used for direct determination of energy levels and the effective correlation energy U_{eff} of dangling-bond defects. With an accuracy of 0.1 eV we found for the dangling-bond defect in a-Si:H, $U_{\mathrm{eff}}=0.5$ eV; in a-$\mathrm{As_2S_3}$, $U_{\mathrm{eff}}=-1.0$ eV; in $\mathrm{As_2Se_3}$, $U_{\mathrm{eff}}=-0.7$ eV; and in *trans*-$(\mathrm{CH})_x$, $U_{\mathrm{eff}}=0.95$ eV.

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In recent years there has been growing awareness of the role of the effective electron correlation energy U_{eff} in determining the electronic properties of deep defects in semiconductors. For example, Fermi-level pinning in chalcogenide glasses,[1] the Staebler-Wronski effect in hydrogenated amorphous silicon (a-Si:H),[2] and the lack of "mid-gap" absorption for neutral soliton defects in polyacetylene, $(\mathrm{CH})_x$,[3] are thought to be associated with electron correlation. However, there have been no direct measurements of U_{eff} for deep defects. The reason for this is that any currently available experimental technique, either electronic [e.g., deep level transient spectroscopy (DLTS[4])] or optical (e.g., absorption spectrum[5]), can determine the energy levels of *one* defect state (charged or neutral).

In this Letter we describe an optical method, the optical modulation (OM) technique, which can directly measure U_{eff} for deep defects, since all energy levels of *both* defect states are seen in the spectrum. We have applied the OM technique to determine the energy levels and U_{eff} for dangling-bond defects (D) in two important amorphous semiconductors—a tetrahedrally bonded semiconductor, a-Si:H, and a chalcogenide glass, a-$\mathrm{As_2S_3}$—and also in the prototype quasi one-dimensional (1D) semiconductor *trans*-$(\mathrm{CH})_x$.

The effective correlation energy is determined by Coulomb repulsion U ("bare correlation") which is always positive, and the lattice relaxation. For an amphoteric dangling bond one has to consider three states, D^+, D^0, and D^-. If lattice relaxation is not important, there holds[6]

$$2D^0+U\rightarrow D^+ + D^-. \tag{1}$$

When the relaxations of atoms surrounding the charged center are taken into account, the effective correlation energy U_{eff} is defined by the relation

$$2D^0+U_{\mathrm{eff}}\rightarrow (D^+)_r+(D^-)_r, \tag{2}$$

where $(D^{\pm})_r$ represent the fully relaxed $D^{\pm}$ center. If lattice relaxations lower the energies of D^- and D^+ centers by the same amount $\frac{1}{2}E_r$, then according to Eq. (2)

$$U_{\mathrm{eff}}=U-E_r \tag{3}$$

and $U_{\mathrm{eff}}\leq U$. When U_{eff} is negative, the ground state of the defect is a D^+D^- pair.[7,8]

As shown in Fig. 1(a) the energy E_{0r} of $(D^-)_r$ is lower than E_0 of the unrelaxed D^- by $\frac{1}{2}E_r$,[7] but because of the Franck-Condon principle the energy of the optical transition t_4 is larger than the energy difference E_c-E_0 by E_r. With this in mind, we show in Fig. 1(b) all the optical transitions associated with the defect. The two important relations between the optical transitions t_1 to t_4 defined in Fig. 1 are

$$t_3-t_1=t_2-t_4=U-E_r=U_{\mathrm{eff}}, \tag{4}$$

$$t_1+t_2=t_3+t_4=E_g+E_r, \tag{5}$$

where E_g is the optical gap.

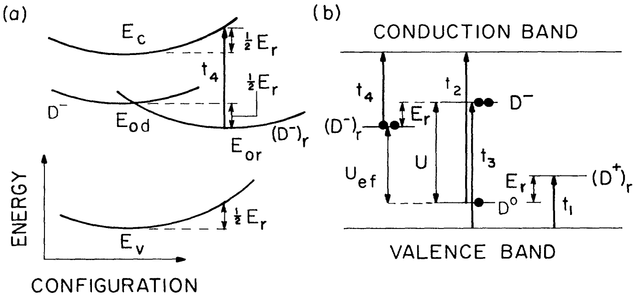

FIG. 1. (a) Configuration-coordinate diagram for D^- and $(D^-)_r$. In the figure and in the text it is assumed that the conduction and valence bands, as well as the defect, have the same curvature. (b) Combined level diagram and optical transitions for the D^0 and $(D^{\pm})_r$ states.

According to Fig. 1 and Eqs. (3)-(5), all the important parameters U_{eff}, E_r, and U associated with the defect D can be optically determined if at least three of the above transitions are observed simultaneously; for levels symmetric relative to the middle of the gap only two of them are sufficient. This is achieved by the OM technique.

If $U_{\text{eff}} > 0$, the defect ground state is D^0 and the absorption spectrum α_g contains transitions t_2 and t_3 [Fig. 1(b)]. In OM we measure the change of the absorption coefficient $\Delta\alpha = \alpha_{\text{ex}} - \alpha_g$ produced by illumination of the sample with a chopped laser beam (pump). This illumination transiently transforms some of the D^0's into $(D^{\pm})_r$. Therefore, the $\Delta\alpha$ spectrum contains transitions t_1 and t_4 [Fig. 1(b)] as photoinduced absorption (PA), and also photoinduced bleaching (PB) by transitions t_2 and t_3. Using Eqs. (3)-(5) we can calculate U_{eff}, E_r, and U. If $U_{\text{eff}} < 0$, the defect ground state is $(D^{\pm})_r$, the photoexcited states are D^0,[7,8] and therefore the OM spectrum contains t_2 and t_3 with $\Delta\alpha > 0$ (PA) and t_1 and t_4 with $\Delta\alpha < 0$ (PB). Since D^0 is paramagnetic while $D^{\pm}$ are not, the defect charge state in the ground state and the change produced by illumination can be identified by ESR and light-induced ESR (LESR).

In our OM setup we used an Ar^+ laser at 476 nm with intensity I_L from 1 to 500 mW/cm^2, chopped at 150 s^{-1}. We measured the change ΔT of the transmission T in the range from 0.1 to 2.5 eV using an incandescent light source with a monochromator, semiconductor detectors, and a lock-in amplifier; $\Delta\alpha = -\alpha_L \Delta T/T$ where α_L is the absorption coefficient at 476 nm. The samples were thin films with thickness d such that $\alpha_g d \cong 1$ close to the fundamental absorption which enabled us to use OM in a wide spectral range. We applied this technique to three materials that are known to contain high defect densities.

In a-Si:H the most important defects are neutral dangling bonds $D^0 \equiv T_3^0$ which are paramagnetic with $g = 2.0055$.[9] Our a-Si:H film was a high-quality glow-discharge material which was electron irradiated; the concentration of T_3^0 defects measured by ESR was 2×10^{18} cm^{-3}. Since the density of dangling bonds is so high we expect that transitions involving the defects will dominate the $\Delta\alpha$ spectrum and the contributions associated with the band tails[10] (observed in samples with low defect concentrations) are negligible. In this case, the shape of the $\Delta\alpha$ spectrum associated with transitions involving the defect and one of the band is proportional to the convolution of the density of defect states (DDS) with that of the continuum. If the DDS is a band peaked at E' and the continuum is approximated by a step function at E'', the convolution changes its slope at $|E'' - E'|$ and has a low-energy tail whose width is the DDS width. The OM data shown in Fig. 2 suggest that this may be a useful approximate approach for analyzing the spectrum.

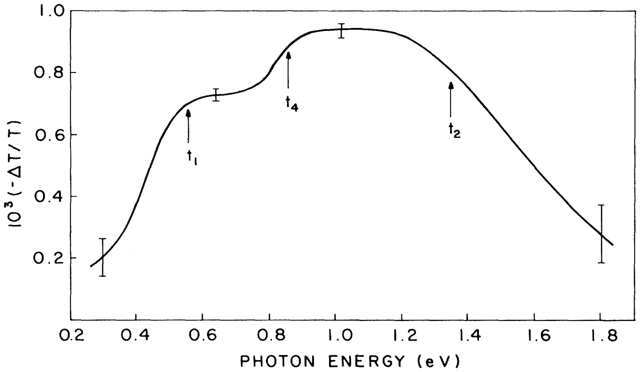

FIG. 2. OM spectrum of a-Si:H at 10 K.

The spectrum in Fig. 2 consists of two PA bands followed by a reduction of absorption. The changes of slope occur at 0.55 and 0.85 eV, and the onset of bleaching is at 1.2 eV; assuming the same bandwidth of 0.15 eV, we evaluate the PB energy level at 1.35 eV. We identify the energies 0.55, 0.85, and 1.35 eV as transitions t_1, t_4, and t_2, respectively [Fig. 1(b)], involving the dangling bonds, for the following reasons. Transition t_2 is seen in the absorption spectrum[5] of a-Si:H; this transition is bleached upon illumination as T_3^0 become charged and T_3^- and T_3^+ are formed. This is confirmed by LESR results in a-Si:H with high density of dangling bonds in which the $g = 2.0055$ line is quenched upon illumination.[9] The three bands in the OM spectrum share a common origin as confirmed by their dependence on I_L; all of them follow the $I_L^{1/2}$ dependence.

Our results show that the T_3^+ level (t_1) peaks at 0.55 eV above the valence band and the T_3^- level (t_4) peaks at 0.85 eV below the conduction band, in agreement with the DLTS data.[4] Using Eq. (4) we obtain $U_{\text{eff}} = 0.5$ eV which is within the range of values for U_{eff} determined by other less direct methods.[5,11] Since $E_g = 1.75$ eV at low temperature, we conclude from Eq. (5) and our values of t_1 and t_2 that E_r of $T_3^{\pm}$ is 0.1 eV.

Important defects in a-As_2S_3 are the D^+D^- pairs[12,13] which are called intimately related valence-alternation pairs (IVAP)[8] with $U_{\text{eff}} < 0$. Upon illumination, IVAP can capture[12] either an electron or a hole, inducing paramagnetism and absorption in the gap, by the reactions $D^+D^- + e \rightarrow D^0D^-$ or $D^+D^- + h \rightarrow D^+D^0$. There are four optical transitions related to each pair, similar to what is shown in Fig. 1, except that E_r is very large so that $(D^+)_r$ (which is D^+D^- acting as an acceptor) is very close to the conduction band, and $(D^-)_r$ (which is a D^+D^- acting as a donor) is very close to the valence band.[7,8] If the recombination of two oppositely charged IVAP is faster than our modulation frequency (150 Hz), then OM gives the spectrum associated with transitions from D^0D^- into the conduction band (t_2) and from the valence band into D^+D^0 (t_3) and bleaching of the transitions associated with the D^+D^- pair (t_1 and t_4). Such fast recombination has been identified in photoluminescence by optically detected magnetic resonance,[13] excited above E_g, as due to (D^+D^0)-(D^0D^-) pair emission.

The OM spectrum of a-As$_2$S$_3$ ($d \cong 100\ \mu$m) at 10 K is shown in Fig. 3. Only one PA band is observed with onsets of 1.3 eV for absorption and 2.3 eV for bleaching. This indicates that either one charged defect (D^+ or D^-) is optically active, or charge conjugation symmetry exists in As$_2$S$_3$. We adopt the latter explanation[7,8] and assign the optical transitions for absorption $t_2 = t_3 = 1.3$ eV and for bleaching $t_1 = t_4 = 2.3$ eV within 0.1 eV. Using $E_g = 2.5$ eV at 10 K and Eqs. (4)–(6) we calculate $E_r = 1.1$ eV, $U = 0.1$ eV, and $U_{\text{eff}} = -1.0$ eV. Our results also give the energy of shallow donor and acceptor levels[7,8] from the nearest band edges (0.2 eV).

Bishop, Strom, and Taylor[14] were the first to observe the photoinduced absorption in a-As$_2$S$_3$ and a-As$_2$Se$_3$. In their cw experiments, the decays of PA were very long and the results were interpreted as due to isolated native defects. With our chopping frequency of 150 Hz we believe that it is not possible to detect the isolated defects and that therefore we observe defect pairs with much shorter recombination times as described above. Bishop, Strom, and Taylor[14] found the onsets of the PA bands at 1.3 eV in a-As$_2$S$_3$ and at 0.9 eV in a-As$_2$Se$_3$.

We applied the same analysis to the transient OM spectrum of As$_2$Se$_3$ at 20 K published by Orenstein and Kastner.[15] From the onset of PA and PB we find $t_2 = t_3 = 1$ eV, $t_1 = t_4 = 1.7$ eV and since $E_g = 1.9$ eV, we calculate $E_r = 0.8$ eV, $U = 0.1$ eV and $U_{\text{eff}} = -0.7$ eV, in good agreement with U_{eff} recently determined from transient photoconductivity.[16] These results show that although U (0.1 eV) and the shallow donor and acceptor energies (0.2 eV) are equal in As$_2$Se$_3$ and As$_2$S$_3$, U_{eff} is different because of different lattice relaxations.[17]

The main difference between the amphoteric dangling bonds in *trans*-(CH)$_x$, usually called neutral solitons $D^0 \equiv S^0$, and T_3^0 in a-Si:H or $D^\pm$ in As$_2$S$_3$ is the small kinetic mass of the solitons.[18] This is manifested in a narrow ESR line for S^0,[18] in conductivity thought to be mediated by S^0,[19] in the appearance of strong ir-active vibrations (IRAV) seen in PA spectra,[20] and in the absorption spectrum of doped (CH)$_x$.[18] With photoexcitation the process $2S^0 \rightarrow S^+ + S^-$ was identified as the main mechanism to produce $S^\pm$ in undoped (CH)$_x$.[21] Usually *trans*-(CH)$_x$ films contain about 10^{19} cm^{-3} of S^0,[18] so that it is easy to observe the soliton defect transitions by OM.

The *trans*-(CH)$_x$ film with $d \cong 2000$ Å was polymerized on KBr substrate. The OM spectrum at 210 K is shown in Fig. 4, where well defined PA and PB bands are seen; the better resolution than in the previous materials is due to the quasi-1D character[18] of (CH)$_x$. The additional modulation around the PB peak is caused by vibronic sidebands or electroabsorption; we identify the zero-phonon transition at 1.45 eV. Associated with the PA band, which peaks at 0.5 eV, is a narrow photoinduced IRAV at 0.17 eV which shows that the PA band is due to a photoinduced charged defect ($S^\pm$).[20] No bleaching of IRAV associated with the PB band is observed and therefore the PB band is due to the bleaching of S^0 transitions. Charge conjugation is evident from the OM spectrum since we observed only two transitions. We therefore identify $t_1 = t_4 = 0.5$ eV and $t_2 = t_3 = 1.45$ eV. Using the 1D energy gap at[22] 1.7 eV and Eqs. (4)–(6) we calculate $U_{\text{eff}} = 0.95$ eV, $E_r = 0.25$ eV, and $U = 1.2$ eV. The large Coulomb repulsion energy may be due to the quasi-1D character of (CH)$_x$ and fits the semiempirical approach[23] that U is large for a half-filled 1D solid.

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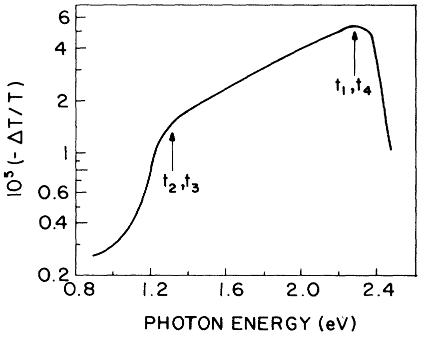

FIG. 3. OM spectrum of a-As$_2$S$_3$ at 10 K.

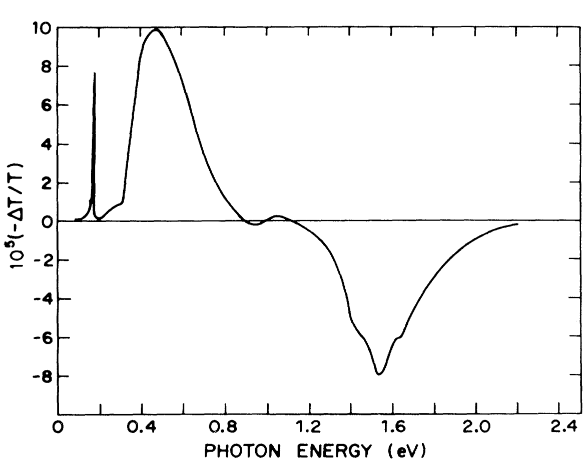

FIG. 4. OM spectrum of *trans*-(CH)$_x$ at 210 K.

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