Determination of the Effective Correlation Energy of Defects in Semiconductors

In a recent Letter,[1] Vardeny and Tauc (VT) report the application of a single-defect model to the analysis of photoinduced absorption experiments [optical-modulation (OM) technique]. This model leads to the possibility of extracting the bare and effective electron-correlation energies of the dominant defects within the gap. In this Comment, we would like both to strengthen their result, and also to describe more systematically the possible values of correlation energies which can be obtained from their experiments, particularly for *a*-Si:H.

In order to determine the value of the effective correlation energy, VT use the sign of the correlation energy suggested by other experiments. However, for a class of systems, which includes both *a*-Si:H and $(CH)_x$, this is not necessary since the OM experiments are consistent with only one sign of the effective electron-correlation energy. From Eqs. (4) and (5) of Ref. 1, we can obtain the following equations for the separate sums of absorption-inducing and bleaching-transition energies:

$$t_1 + t_4 = E_g + 2E_R - U, \tag{1}$$

$$t_2 + t_3 = E_g + U, \tag{2}$$

where E_g is the energy of the gap, U is the bare correlation energy, E_R is the net effective relaxation energy (obtained under the assumption of equal curvatures of energy surfaces), and the transition energies are as defined by VT.[1] If we consider the case of a defect with negative effective correlation energy, the sum of transition energies which enhance absorption is given by $t_2 + t_3$. From Eq. (2), this sum is larger than the size of the gap, whereas for the case of a positive effective correlation energy, the sum of transition energies which enhance absorption is given by $t_1 + t_4$, which [Eq. (1)] can be either larger or smaller than the gap. Thus, if experimentally observed energies of two absorption-enhancing transitions have a sum less than the gap, the defect must have a positive correlation energy. The numbers of VT[1] for *a*-Si:H imply that this is the case, strengthening the tenuous evidence for a positive correlation energy in this system. Since negative correlation energies have been invoked to explain other experimental results,[2] this result is of particular importance.

We emphasize that it is not always possible to determine the sign of the correlation energy from analysis of OM experiments. In particular, for every negative-correlation-energy interpretation there is an equally consistent positive-correlation-energy interpretation. If we denote by a $-$ $(+)$ superscript a consistent interpretation of an OM experiment with negative (positive) correlation energy, they are related as follows:

$$U_{\rm eff}^{+} = -U_{\rm eff}^{-}; \quad E_R^{+} = E_R^{-}; \quad U^{+} = -U^{-} + 2E_R.$$

Selection must therefore be made on the basis of other experiments.

In analyzing further the *a*-Si:H experimental results of VT,[1] we note that there are at least two ways of identifying the transitions, which lead to different numerical results for the correlation energies. The two possibilities are obtained by identifying the onset of bleaching with either t_2 or t_3. In the former case, emphasized in Ref. 1, there is need to invoke an unobserved bleaching transition t_3 at 1.05 eV. This may be reasonable, particularly since t_4 may overlap t_3. In this case the values for U and $U_{\rm eff}$ are 0.6 and 0.5 eV.[1] The other possibility is that the onset of bleaching is t_3, in which case t_2 would be at 1.65 eV. At this energy the larger experimental error bars would make its observation difficult. When we use this alternate identification of the transitions, the values for U and $U_{\rm eff}$ are 1.3 and 0.8 eV. These two sets of values form a reasonable bracket for values consistent with this model for interpretation of the OM experiment.

One problem in interpreting data on *a*-Si:H films is sensitivity to material-preparation techniques. In this regard, it is useful to emphasize that the films used in Ref. 1 were electron irradiated to achieve high defect densities. This may be reflected by the small (~ 0.1 eV) difference between U and $U_{\rm eff}$ suggested in Ref. 1, which is consistent with only minor relaxations accompanying the trapping of charge on neutral dangling bonds. Material with low defect densities may have lower values of $U_{\rm eff}$, consistent with evidence from optical-absorption experiments on doped films.[3]

Finally, band-tail states may complicate the interpretation of such experiments, and different materials may require alternative models for optically induced absorption experiments.[4]

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