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XEROGRAPHIC SPECTROSCOPY OF LOCALIZED ELECTRONIC STATES IN AMORPHOUS SEMICONDUCTORS

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Abstract.- Analysis of the temperature dependent decay of surface voltage on an amorphous film after charging but prior to exposure (xerographic dark decay) and of residual decay after exposure can in combination be used to map the density of states and position the Fermi level. The procedure is illustrated for a-Se where both electron and hole residuals can be measured. a-Se is found to be characterized by relatively discrete gap state structure. These measurements readily discern thermostructural and photostructural effects on gap state populations. Thus during structural relaxation of glassy films in the As:Se alloy system systematic variation in number of localized states distributed throughout the mobility gap are observed. This observation is consistent with the view that native defects play a key role in photoelectronic behavior of amorphous chalcogenides.

Introduction.- During a xerographic cycle an amorphous film is charged by corona or contact to voltage, \( V \), then discharged with strongly absorbed light. Light exposure causes a CV (C is film capacitance) of charge to transit the bulk. A fraction of this charge can fall into deep traps (traps whose release time considerably exceeds the transit time. As a consequence the surface potential discharges to some non-zero residual value. For example \( 10^{13} \) electronic charges per \( \text{cm}^{-3} \) uniformly trapped in a 50\( \mu \text{m} \) thick film will give rise to a 40 volt residual (surface potential) which is easily measured. It will be demonstrated that analysis of both the buildup of residual during repeated xerographic cycling of an amorphous film and then the temperature dependent decay of residual after cycling ceases, enables the density of gap states to be mapped. The technique is illustrated for ambipolar a-Se.

Results and Discussion.- Figure 1 is a schematic representation of the essential components in a program of xerographic residual measurements. In a single cycle experiment the surface voltage profile is as shown in Figure 1a. The well rested sample film is first charged to some voltage, \( V_d \), in the dark, then discharged with a pulse of strongly absorbed light (photoinduced discharge, PID).

![Figure 1](http://dx.doi.org/10.1051/jphyscol:1981492)
voltage corresponds to that value of the field for which the carrier range approximates the film thickness. Thus a measurement of first cycle residual can be used to calculate the injected carrier Schubweg \( \mu \tau \). If \( \mu \) is the drift mobility \( \tau \) is the real time lifetime and if \( \mu \) is the microscopic mobility then \( \tau \) is the free carrier lifetime. On repeated cycling residual voltage builds up stepwise as shown in Figure 1b and eventually saturates as illustrated in Figure 1c. If the saturation value of residual does not exhibit strong temperature or cycling rate dependence then it can be taken as proportional to the bulk trap density. For uniformly trapped space charge of density \( N(\text{cm}^{-3}) \) the saturation residual is

\[
1) \quad V_{R}^{S} = \frac{NeL^2}{2\varepsilon}
\]

where \( L \) is the sample thickness and \( \varepsilon \) its dielectric constant. It can be shown that 1) remains correct to within a small multiplicative factor even when the trapped space charge distribution is skewed toward the top (exposed) surface. On termination of cycling the residual decays at a strongly temperature dependent rate as bulk traps thermally depopulate to restore space charge equilibrium (Figure 1d). Analysis of these decays proceeds as follows: The decaying residual voltage is represented phenomenologically by the sum

\[
2) \quad V_{R}(t,T) = \sum_{i} C_{i} \exp \left(-t/\tau_{i}\right)
\]

\[
\tau_{i}^{-1} = \nu_{i}^{*} \exp \left(-\epsilon_{i}/kT\right)
\]

All the temperature dependence is therefore contained in the trap release times \( \tau_{i} \). \( \nu_{i}^{*} \) are "effective" attempt frequencies. In practice it proves possible to consistently fit families of electron and hole residual decay curves parametric in temperature with a relatively small number of exponential terms. The charge releasing from all the traps is in effect partitioned among the energies \( \epsilon_{i} \) according to the temperature independent coefficients \( C_{i} \). This information is conveniently represented in a density of states histogram.

In Figure 2 we combine results of residual measurements with information based on analysis (1) of earlier time of flight studies (drift mobilities) to construct a composite density of states diagram for a-Se. It is assumed that gap states release charges to states near the respective mobility edges. Shallow states which control transport form narrow manifolds respectively located .25eV and .33eV from the valence and conduction band mobility edges.

![Figure 2](image)

The width of the mobility gap is taken as just slightly larger than the optical gap at 2.1eV. On this basis the relative positions of all localized gap states and \( E_{\text{F}} \) (Fermi Energy) are fixed. The position of \( E_{\text{F}} \) is deduced by simultaneously analyzing dark decay and depletion discharge measurements (2). The deep gap in a-Se is characterized principally by a small integrated trap population of about \( 10^{14} \text{cm}^{-3} \). (It is the low density of deep traps in a-Se which underlies its utility as a xerographic photoreceptor under cyclic
conditions.) This very low trap density near midgap is consistent with time of flight lifetime data and with earlier, though much less precise estimates based on trap limited space charge limited current measurements (3). Secondly, deep trap distributions for both electrons and holes form discrete submanifolds distributed over about .06 - .10eV as shown. Examination of samples prepared from different source materials display some systematic variability. For example, samples exhibiting relatively low first cycle hole residuals are also those with the narrowest energy distribution of deep hole traps. Conversely samples exhibiting particularly high first cycle hole residuals are those for which the respective hole deep trap distributions are broadest. Broadening of the distribution occurs toward the deep gap leaving the shallow end (characterized by its relatively sharp demarcation energy) unchanged. Despite the variability just described the striking feature on examining many a-Se specimens in fact remains the remarkable overall invariance, despite their small integrated number, in the distribution of deep gap states.

It is nevertheless possible to effect changes in deep trapping of both carrier species in a-Se. These changes are easily detected using xerographic techniques. Three mechanisms for inducing change have been identified. They are:

1. Thermostructural
2. Photoinduced
3. Chemically induced.

1. and 2. are transient changes which can be induced in any given film. (The film fully regains its original properties in time.) In 3, a-Se films are prepared from chemically modified source material. Changes in electronic behavior relative to undoped material are permanent. 1. and 3. can be used as tools (4) for probing the origin of the naturally occurring deep traps in a-Se. The following discussion will be restricted principally to the transient induced effects 1. and 2., but chemical effects are presently under active investigation. (In fact the extent to which photoelectric behavior in any amorphous chalcogenide can be modified by doping persists as a major scientific and technological issue.)

1. Structural relaxation is induced in any a-Se film by heating it to above Tg and allowing it to anneal there, then quenching it to room temperature. The effect of this procedure is to simultaneously increase both hole and electron deep trapping and this is manifested in both first cycle and saturation residual potentials. There is no significant accompanying shift in the spectral distribution of the traps involved. Enhanced deep trapping diminishes for both carriers simultaneously as the film anneals at 295K. When the film is fully relaxed at 295K xerographic behavior characteristic of the well annealed film is reproduced again, and the process can be repeated indefinitely. Behavior for the deep traps is thus reminiscent of thermostructurally induced changes in shallow trap controlled transport (1,4). We suggest therefore, that key electronic gap states though widely distributed in energy will vary in number with the structural state of the glass but ultimately achieve an equilibrium population in the fully relaxed film. The latter, we believe, underlies the well established reproducibility of photoelectric behavior in a-Se. Furthermore, population changes in those structurally derived gap states which act as hole and electron traps appear to be correlated as generally suggested by the native defect models proposed for chalcogenides (5,6).

2. Deep trapping of both injected holes (7) and electrons is temporarily enhanced in an a-Se film which has undergone prior photoexcitation with near bandgap light (600-700 nm). The latter is the excitation region identified with low temperature photoluminescence, photoinduced esr and reversible photostructural effects in a-Se (8,9). These effects have been interpreted in terms of photoinduced interconversion of native charged defects. It is to be emphasized that metastable deep trapping occurs in the room temperature range and involves far fewer states than the number presumably implicated in either luminescence behavior, or photo esr.
The decay rate constants for metastable deep trapping (i.e. persistence of the effect) and the time for these metastable traps once filled, to empty (release times), can be distinguished and separately measured by xerographic techniques. Principal results are the following: 1. There are distinct decay times for the excess population of photoinduced hole and electron traps respectively. In fact the metastable electron traps decay away much more slowly than their hole counterparts; 2. However, even the more rapidly decreasing population of metastable hole traps is decaying slowly on a time scale defined by the release of holes from equilibrium deep traps; 3. Dark decay is enhanced. There are two alternative explanations for this behavior. The first is that creation of hole electron pairs in the neighborhood of a pre-existing site activates via a trapping-event the formation of a recombination center or larger cross section trap. The second, that photoexcitation by inducing structural change directly creates new gap states which act as traps. The former if operative might also be expected to induce optical quenching of photoconductivity (10). In addition, eventual saturation of trap photoactivation with increasing light exposure would be consistent with a fixed density of convertible sites. Though a complete discussion of these results is not possible in the present context, we can state that the defect interconversion argument used to interpret luminescence behavior (8) in chalcogenides does not by itself appear sufficient to reconcile results 1. and 2.

Summary -

1. A composite picture of the electronic density of states has been deduced from xerographic measurements on a-Se. Gap states form relatively discrete submanifolds, that is they are separated by regions relatively devoid of states. The integrated number of deep traps is $10^{14} \text{cm}^{-3} (E \geq 0.6 \text{eV})$. The integrated number of traps but not their spectral distribution changes during structural relaxation supporting the view that key gap states are defect derived in chalcogenides.

2. The distribution of deep traps is, despite their small integrated number, a reproducible property of well annealed a-Se films. Deep trapping can, however, be affected by thermostructural (relaxation induced) change, sub-bandgap photoexcitation and chemical modification (doping).

References -


10. VOUTIER, C. and VIGER, C., in Reference 1, p. 222.