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Contribution of Dipole Defects to DLTS Spectrum

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Deep Level Transient Spectra (DLTS) have previously been analyzed assuming that the only contributions to the variations in junction capacitance recorded come from detrapping of carriers singly from monopolar defects. The concentration of defects deduced in this way is too small to account for measured carrier lifetimes. It is also smaller than is deduced from theory and from TEM. We argue that many deep level defects are clusters of point defects whose electrical activity results in dipole, and higher multipole charge states. Transitions among these states can also contribute to the DLTS signal but much more weakly. Consequently, conventional analysis grossly underestimates the number of defects present.

I. Motivation

DLTS spectra have generally been analyzed [1] as if the deep level defects being observed were simple point defects, although it has been widely recognized that this is not true[2-4]. In samples that have seen room temperature or above, one may expect to find complexes of point defects formed from the supersaturations of defects introduced by high temperature processing, e.g., by crystal growth, or by irradiation. This is because simple point defects are generally ionized and rather mobile at room temperature and readily form coulombically or elastically bound clusters. Nevertheless, in DLTS analysis it has been assumed that the observed variation in junction capacitance comes only from the trapping and detrapping of single carriers at the various defect centers. Some justification for the simple form of analysis has come from the fact that experiments have been designed with the intent to trap only holes, h_v^+, or only electrons, e_c^-. Experimentalists have assumed that by limiting minority carrier densities, they succeeded in preventing possible contributions to the DLTS signal through recombination, reorientation, or de-excitation of dipolar and higher multipolar charge distributions at the defects.

There is much reason to believe that the conventional analysis of DLTS spectra has significantly underestimated the concentrations of deep defects present. Although the analysis supposedly gives defect concentrations, cross sections and activation energies, attempts to calculate carrier lifetimes from DLTS measurements generally overestimate these lifetimes rather badly when proper account is taken of the expected saturation of the traps [5,6]. A generally successful theory of the thermochemistry of semiconductor defects[4] predicts substantially higher concentrations of defect clusters than have been inferred from DLTS. For example, in compound semiconductors like GaP and GaAs, it is predicted that the cluster consisting of one antisite defect, e.g., a P on a Ga site, P_{Ga}, bounded by two vacancies, e.g., V_{Ga}, to form a (110) oriented complex, e.g., $V^-_{Ga}P^{+2}_{Ga}V^-_{Ga}$, one atom in diameter and 3 lattice sites long should typically occur in mid $10^{17}/cm^3$ concentrations even in the best quality material[7,8]. DLTS workers have not reported any spectra they could associate with such a defect at anywhere near that high a concentration. On the other hand, ultrahigh resolution, direct lattice imaging TEM does find defect clusters having this size, shape, orientation and concentration in the best quality GaAs and it has been shown that they are active in infrared absorption[9]. It can also be argued that such concentrations of defects are necessary to account for the degradation of electrooptic devices[8,10].

Thus, the motivation of this paper is to understand why DLTS studies have not reported as many deep level defects as have been predicted from theory or inferred from electrical measurements, TEM, and observations of degradation phenomena. In Sec. II we make introductory remarks about experiments, defects, and defect interactions. In Sec. III we discuss what processes the defect clusters that one should expect to be present might exhibit which would produce a DLTS signal much weaker than that produced by simple detrapping. In Sec. IV we explain why the experimental design failed to count all the defects that were there by detecting detrapping and failed to prevent the operation of the weaker

processes. Thus, one defect may produce more than one DLTS signature and the concentration deduced from each may be much too small.

II Distinctions among Experiments and among Defects; Interaction among Defect Ionization Levels

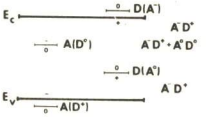
There are two kinds of donors and acceptors. There are those, which we call coulombic, which are neutral when filled by free carriers, like S_P and Zn_{Ga} in GaP, and there are those, which we call isoelectronic, which are ionized when filled by free carriers, like Bi_P and N_P in GaP. Vacancies and interstitials are important examples of isoelectronic defects. In recognition of this fact DLTS experimentalists report "h_V^+-traps" and "e_C^--traps". The defect clusters that form during cooling from crystal growth/processing temperatures will probably contain combinations of both types. The $V_{Ga}P_{Ga}V_{Ga}$ center is an example. Such combinations are likely because coulombic defects, like dopants, usually migrate via vacancy or interstitial mechanisms. Also the clusters can accumulate several point defects during extended periods of atomic migration. Thus, the larger clusters are apt to be able to both trap and emit carriers of both type in transitions between states which may or may not have the same net charge.

We distinguish two kinds of DLTS experiment: ACDLTS, in which the AC capacitance is measured[1], and DIDLTS, in which the total displacement current integrated through the rate window interval, RWI, is measured[11]. Suppose that an e_C^- h_V^+ pair is bound at a defect site giving it a dipole moment and contributing to its polarizability. When the recombination of such a pair is thermally activated, as is usual for non-radiative deep levels, it will produce an ACDLTS signal due to the change in the polarizability of the center in the junction field and a DIDLTS signal due to the change in dipole moment. However, the magnitude of this signal per defect will be weaker by a factor of order 10^{-4} than that which would occur if there were simple detrapping of a carrier. Using the expression for the dipole contribution to the polarization of the dielectric, $\Delta\epsilon/\epsilon = N\mu^2/3kT$ and the relation $\Delta C/C = \Delta\epsilon/2\epsilon$, it is possible to calculate that 10^{18} dipoles having unit electron charges separated by 0.3 nm will produce the same magnitude DIDLTS signal as only 10^{14} detrapping defects. The ACDLTS signal would depend upon the spring constants at the dipole. The concentration of defects ascribed to this DLTS signature would be underestimated by a factor of order 10^4; the relative magnitude of the signal will be different for ACDLTS and DIDLTS. If instead the pair dissociates releasing both carriers from the defect and both are swept entirely out of the depletion region, DIDLTS will see a full detrapping signal from pair emission, but ACDLTS will record only the weak signal because the net charge in the depletion region does not change. For the case when both carriers are captured at other defect sites before they can be swept out, DIDLTS will also record only a weak signal. If one carrier is swept out and one is retrapped, both methods will record a strong signature due to the one that got out and a weak signature due the subsequent behavior of the one retrapped.

Ionization levels of defects in close association are not independent of the proximity and ionization state of other nearby defects. We denote a two defect complex in some semiconductor host AD, where A and D are point defects which singly would have acceptor or donor ionization levels, ${}^{-}_{0}A$ and ${}^{0}_{+}D$, in the gap respectively. (Of course, many defects, such as V_{Si}, have both donor and acceptor levels.) The proximity of a neutral donor, D^0, generally lowers ${}^{-}_{0}A$ and vice versa. The proximity of an ionized donor, D^+, greatly lowers ${}^{-}_{0}A$ and vice versa. We denote the ionization levels ${}^{-}_{0}A(D^0)$ and ${}^{-}_{0}A(D^+)$ for the acceptor and ${}^{+}_{0}D(A^0)$ and ${}^{+}_{0}D(A^-)$ in the accompanying figure. The magnitude of this spread for ionized point defects is $e^2/\epsilon R + L_A(D^+)$, where ϵ is the effective dielectric constant, R the spacing, and $L_A(D^+)$ is the lattice relaxation at the ionized acceptor in the presence of the ionized donor. For nearest neighbor pairs the coulombic, first term alone would be about 0.5 eV. Lattice relaxation contributions may sometimes be even larger[12].

If the isolated defects are shallow, e.g., Zn - S pairs in GaP [13], close association drives the ionization levels into the bands, i.e., ${}^{0}_{+}D(A^-)$ touches the conduction band edge, E_c, and ${}^{-}_{0}A(D^+)$ touches the valence band edge, E_v. Then the neutral states of A and D become metastable. For any position of E_f, the equilibrium state of the center, A^-D^+ has a dipole, but no monopole, moment. It would never be seen detrapping in DLTS although it would scatter carriers. If the ionization levels of the isolated point defects are deeper, then the spread of individual ionization levels, i.e., ${}^{-}_{0}A(D^0)$ - ${}^{-}_{0}A(D^+)$ and ${}^{0}_{+}D(A^-)$ - ${}^{0}_{+}D(A^0)$ may not touch either E_v or E_c. For Cd - O close pairs in GaP the acceptor spread touches E_v but the donor spread does not touch E_c[14]. Thus, the complex can stablely bind an e_C^- and maintain a negative state, A^-D^0, when E_f is sufficiently high. Otherwise, it is neutral with a dipole moment, A^-D^+. It will scatter carriers and have some activity as a recombination center. It would be seen detrapping in DLTS for n-type material, but not for p-type material.

Suppose now that $^{-}_{0}A(D^0)$ lies above $^{+}_{0}D(A^0)$ as is common for pairs of isoelectronic point defect. (It is true for V_{Si}.) Because the spread between $^{-}_{0}A(D^0)$ and $^{-}_{0}A(D^+)$ and between $^{0}_{+}D(A^-)$ and $^{0}_{+}D(A^0)$ is so large for close pairs, greater than 0.5 eV, they may overlap and together span a large fraction of the band gap. When this occurs, then there is a large range of E_f over which the clusters are stable either as A^0D^0 or as A^-D^+, but not as A^-D^0 or as A^0D^+. The relative proportion of these two neutral states (for larger clusters there would be several) depends upon E_f as well degeneracy factors. In the accompanying figure we show the case that the overlapping ionization levels touch both band edges. Such a defect could only be stable when neutral, binds carriers only in pairs, and may or may not have a dipole moment. It could be a very active recombination center.



III Alternative Mechanisms Changing Junction Capacitance

We discussed the recombination of e^-_c h^+_v pairs above. Deep level defects are particularly important precisely because many of these act as recombination centers. High recombination activity suggests that both e^-_c and h^+_v are trapped at the defect so that their wave functions overlap strongly. This in itself implies that the relevant defects have a dipole rather than a monopolar charge distribution. When it is thermally activated, internal rearrangement of charge within a cluster will produce a DLTS signature. The three neutral states of $V_{Ga}P_{Ga}V_{Ga}$, $V^-_{Ga}P^{+2}_{Ga}V^-_{Ga}$, $V^0_{Ga}P^{+}_{Ga}V^-_{Ga}$, and $V^0_{Ga}P^{0}_{Ga}V^0_{Ga}$, each have different polarizabilities and ranges of E_f for which they will be stable. Note the first and last have no dipole moment while the middle does and that all bind 2 e^-_c's; no trapping or detrapping of free carriers is involved in these transitions. However, any of the neutral states would be an effective nonradiative recombination center for h^+_v's.

Many deep levels exhibit recombination enhanced diffusion[15], RED. Recombination may alter either the magnitude or the orientation of a cluster's dipole moment. Even if it does not alter the field free dipole moment, atomic reconfiguration of the cluster will likely change its polarizability. The pair recombination event in RED is apt to leave the cluster in a distorted, nonequilibrium configuration. Then thermally activated atomic migration would be expected to return the defect to its equilibrium configuration. Any such reconfiguration will change its polarizability and produce an ACDLTS signal. Reorientation of a dipole would also produce an additional contribution to the DIDLTS signal unless the dipole moments were randomly oriented and their rate of reconfiguration were independent of orientation.

Now we consider a mechanism which requires only majority carriers and a change in charge state of at least one member of the defect cluster, as would be caused by the flow of current or the shift in E_f between the trap filling and measurement phases of the DLTS experiment. As many deep defects have different equilibrium configurations in different charge states, a change in charge state can cause atomic motion. When the original charge state is regained, atoms may go to different but formally equivalent lattice locations. This is known as the Bourgoin-Corbett, B-C, mechanism and produces rapid, athermal migration[16]. This, too, may reconfigure the defect cluster in a way that changes its dipole moment. As it regains its equilibrium configuration by thermally activated atomic motion during the measurement phase, a DLTS signal is produced.

If the junction field is strong enough at the measurement temperature to align defects which normally have a dipole moment, then athermal migration caused either by the B-C mechanism or by RED during the trap filling stage would randomize their orientation. One would see a DLTS signal due to the thermally activated motion of reorientation. As the junction fields are of order 10^4 eV/cm and dipole lengths are of order 10^{-7} cm, the relative fraction of such centers aligned would normally be small, e.g., 4 % at room temperature. Thus, the relative magnitude of this contribution to that which would have resulted from thermally activated detrapping is even smaller by that factor. The underestimate of the number of such centers present would be correspondingly greater.

IV How might Monopolar Contributions be Missed; How Limited is Minority Carrier Concentration?

The existence of the mechanisms just described is not in doubt. On the other hand, in order to show that they may have produced a significant error in the estimate of the number of deep level defects present, we must show why an experiment designed to affect and detect the detrapping of carriers singly from the expected defect clusters should have failed to do so. If the monopolar effect were seen, it would be so much larger than the dipolar that we would merely have reported a few too many defects.

Of course, we bear in mind that any athermal process, such as recombination by tunneling, will go undetected in DLTS.

As was noted above, if the level scheme indicated in the figure occurs, then the center will only bind carriers in pairs, pulling an electron out of the valence band if necessary to fill the $\bar{0}A(D^+)$ level after D has attained the D^+ by either emitting an e_c^- or trapping a h_v^+. Changes in net charge state would always be over before the RWI opens and the center would be undercounted by the factor 10^{-4}.

For B-C migration we would need to suppose that the center has returned to its original charge state before the rate window opens during the measurement phase. This would occur only if the carrier is trapped in a state that is metastable and therefore likely to be occupied only when current is flowing during the trap filling and transient stages or if the filled state is so shallow that it empties so soon after E_f passes through it that the detrapping is not recorded. If Cd exhibited B-C migration in GaP, the Cd-O pair in n-type GaP would be an example of this. Point defects known to exhibit B-C migration are rather deep[16], but in forming clusters their levels could spread to the band edge.

In addition to the minority carriers running free in their band, which the experimentalist controls with bias voltage (or optical pumping), one must also consider those bound in the defect complexes. When raising E_f to inject e_c^-'s to be trapped, one will also release some concentration of h_v^+'s, that may be comparable with the total number of point defects present. These can bind at the same sites which just trapped the e_c^-'s to neutralize the center again. Recombination and all the effects associated with it above may follow. Another important point is that some defects, in particular the single vacancy[17] in Si, V_{Si}, exhibit a "negative U" for certain ionization states. That is $V^0{}_{Si}$ and $V^{+2}{}_{Si}$ are stable, but $V^+{}_{Si}$ is not stable. This means that the trapping of a hole at a $V^0{}_{Si}$ will be followed by an athermal process in which an e_c^- is emitted and $V^{+2}{}_{Si}$ results. Thus, one minority carrier is generated for each majority carrier trapped in such "negative U" defects. These effects would cause under counting by some statistical factor less severe than 10^{-4}.

Impact ionization at defect centers by carriers accelerated by the transient fields of the experiment is possible. Since fields as high as 10^4 V/cm exist over regions as wide as 1 μm, carriers may be excited to energies reaching 1 eV. During injection a fast majority carrier might knock a minority carrier free. It also might knock a majority carrier out of a deep trap that would normally be filled during the measurement phase. This could shift the level of a minority trap to its band edge. Thus, impact ionization could provide minority carriers to be trapped in the region under test at concentrations a significant fraction of the total number of carriers swept through, which would be comparable with the background doping level.

V References

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