Entropy-Driven Metastabilities in Defects in Semiconductors

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Several defects are known to have metastable configurations that can be accessed by charge-state change, optical excitation, or heating followed by rapid cooling. Typically, each configuration is stable over a broad temperature range and can be studied by spectroscopic techniques. In this Letter, we report the observation of a novel metastability: A configuration change occurs spontaneously and abruptly at a critical temperature, giving rise to a discontinuous, deep-level transient spectrum. We propose that this phenomenon is a manifestation of entropy variations in the configurational space.

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In recent years, there have been many reports of defects in semiconductors exhibiting metastability. The best known case is the $EL2$ defect in GaAs.[1] In that case, the defect exists in a configuration Q_1, but switches over to a configuration Q_2 upon ionization (a standard Frank-Condon change in configuration). In addition, $EL2$ can be driven into a third configuration Q_3 while remaining neutral during an internal photoexcitation. This third configuration is metastable and is separated from the stable configuration by an energy barrier. Return to the stable configuration is attained by annealing or by carrier injection.

A simpler and more common form of metastability is illustrated in Fig. 1, where we show schematically the form of a defect's total energy as a function of a generalized coordinate Q (configuration-coordinate diagram). A neutral defect may have a stable configuration labeled Q_1 and a higher-energy configuration labeled Q_2. The two configurations are separated by an energy barrier. In each configuration, the defect can be ionized and the ionization energies can be detected by a variety of techniques, including deep-level transient spectroscopy (DLTS). In the ionized state, however, the total-energy curve may look quite different. In Fig. 1(a) we show a case in which Q_1 is the stable configuration for both the neutral and the ionized state of the defect. In Fig. 1(b), we show a case in which Q_1 is the stable configuration for one charge state and Q_2 is the stable configuration for the other charge state. There have been many examples of such defects and their behavior is well documented (Refs. 2-6). Typically, each of the two configurations has a characteristic DLTS peak. If the sample is first heated to some high temperature and then cooled rapidly, the resulting DLTS spectrum contains both peaks, reflecting the quenched-in thermal distribution of the two defects. By applying an external bias or optical pumping before and during cooling, the relative concentrations of the two quenched-in configurations may be altered, allowing one to determine how metastability depends on the charge state. Defects exhibiting such charge-state controlled metastabilities are discussed extensively in Refs. 2-6.

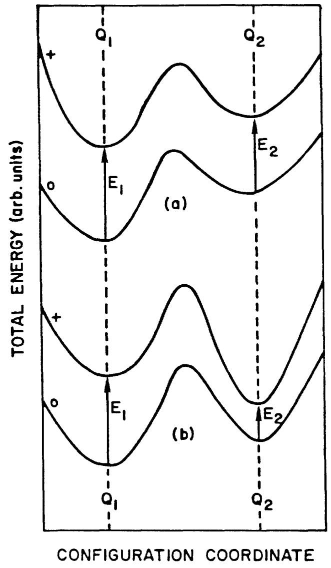

FIG. 1. Schematic illustration of the instability discussed in Refs. 2–4. In case (a) the metastable configuration is the same in both the neutral and ionized states. In case (b) the stable and metastable configurations are reversed in the neutral and ionized states.

In this paper, we report the observation of a novel metastability that is significantly different from those mentioned above: As the temperature is scanned in a cool-down mode, at some critical temperature T_c, the defect changes abruptly to a different configuration. The corresponding DLTS spectrum exhibits a sharp drop in the signal at T_c, implying a sudden "disappearance" of the defect, followed by the appearance of a new peak at lower temperatures. We shall propose an explanation for this phenomenon in terms of *entropy* variations along the path for configuration change. We will show that entropy variations can be such as to totally obliterate the enthalpy barrier at some critical temperature T_c, leading to a barrierless transformation of the defect.

The novel metastability was detected during a study of defects in electron-irradiated float-zone Si. We have seen similar effects in preamorphized, implanted, and rapidly annealed Si. At this point, no chemical or structural identification of the defects that exhibit this metastability could be undertaken. A more extensive report of the experiments will be given elsewhere. In this paper, we concentrate on the observations of the novel metastability and its possible explanation. For convenience, we shall refer to centers exhibiting this kind of metastability as ω centers and designate the specific defect discussed in this paper as ω_{I}.

The main effect is shown in Fig. 2(a) in the DLTS spectrum labeled (2): As the temperature is scanned in a cool-down mode, the DLTS signal abruptly drops to zero (solid line), instead of the normal expectation of a fairly symmetric peak (dashed curve). In order to appreciate the physical origin of this effect it is useful to first describe briefly what is being measured. Data are collected in samples that have been fabricated as *pn* junctions. At each temperature, voltage pulses are used to alternately fill (zero bias) and empty (reverse bias) the deep level in the energy gap. The emptying process takes place by thermal emission in the depletion region of the diode and gives rise to a transient increase of the diode capacitance. In the present experiments, electron emission is measured from defects in the *n* side of the *pn* junction so that the capacitance shows a transient increase. The transient is monitored on an oscilloscope and its values were recorded at two times, t_1 and t_2. The DLTS signal plotted in Fig. 2 is simply the quantity $\Delta C = C(t_2) - C(t_1)$, where C denotes the diode capacitance and the average is taken over a number of pulses at each temperature. An illustration of the procedure is given in Fig. 3. At high temperatures, electron emission is fast, the capacitance reaches its maximum very quickly, and ΔC is zero. At lower temperatures, ΔC becomes nonzero, reaches a maximum, and finally falls off to zero when the electron emission becomes so slow that no appreciable capacitance increase occurs in the chosen time interval. Clearly, the position and width of the DLTS peak depend on the choice of the window $t_2 - t_1$.

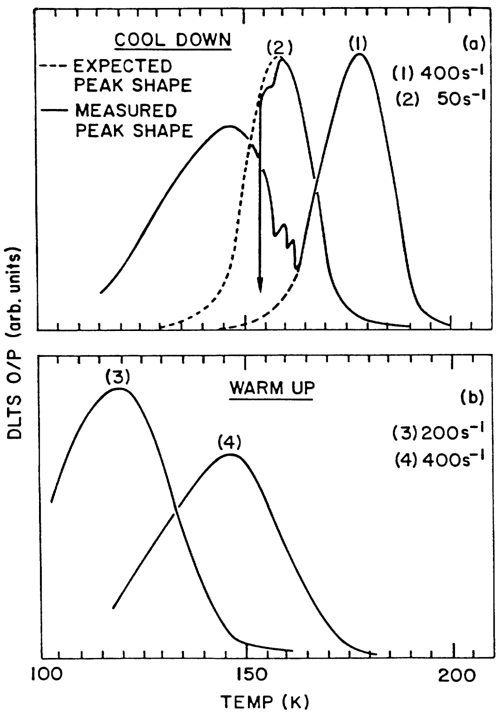

FIG. 2. DLTS spectra for the ω_{I} center (a) in the cool-down mode and (b) in the warm-up mode. Two rate windows are shown in each case.

Let us now go back to Fig. 2(a). Spectrum (1) measured at a rate window of 400 s^{-1} shows a well-defined peak near 180 K. In the low-temperature tail of this peak, however, near 160 K, there is a burst of noise in an otherwise noise-free spectrum. After the measurement recovers, a broad peak is detected near 145 K. The noise feature in isolation would not be particularly remarkable. However, it occurs at the same temperature as the catastrophic loss of the signal observed in spectrum (2) and is reproducible. It clearly signifies an abrupt change in the emission transient.

The significance of the event near 160 K is more palpable in spectrum (2) of Fig. 2(a) which is measured at a rate window of 50 s^{-1}. Now, the DLTS peak is very close to this temperature. As the temperature is scanned in a cool-down mode, the signal shows an anomalous drop. At 155 K, the signal drops essentially vertically, within the response capability of the electronics. The effect is reproducible when we scan from room temperature toward lower temperatures. Again, the abrupt drop in the signal is caused by an abrupt change in the electron emission transient. In Fig. 3 we show the actual transients as well as the transients that would correspond to normal behavior. The peak that would correspond to normal behavior is shown as a dotted line.

Figure 2(b) shows the result of scanning of the DLTS spectrum from low to high temperatures. If the sample is cooled to below 160 K, the broad peak at low temperatures was observed, but the high-temperature peak is ab-

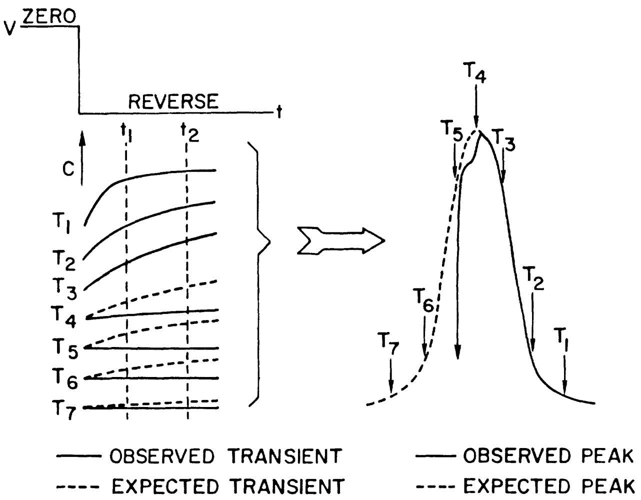

FIG. 3. Illustration of the transient evolution with temperature and the resulting DLTS spectrum for the ω_1 center (solid lines) and the corresponding expected behavior for a normal defect (dashed lines).

sent. A short anneal at about 250 K leads to recovery of the high-temperature peak. This result implies that the change of configuration in the heating mode encounters an energy barrier. In contrast, the abrupt changes observed in the cool-down mode implies no energy barrier.

All the above observations were based on the "boxcar" version of DLTS[7] which is well suited to detect abrupt changes in the electron emission transients. The full transients were, of course, monitored on an oscilloscope and they were as shown in Fig. 3. We found that the high-temperature peak arises from an exponential transient whereas the low-temperature peak arises from a nonexponential transient. Additional information contained in these transients can be extracted by detailed fits of the data, as was done for example in the automated version of DLTS reported in Ref. 8. None of our conclusions above regarding the abrupt disappearance of the DLTS signal would be affected by such analysis.

We now wish to discuss possible causes for the novel metastability. As we already remarked, configuration-coordinate diagrams such as those of Fig. 1 cannot explain the phenomena we observed. Carrier injection and rapid cooling under variable bias conditions were used to search for a charge-state effect as in the metastable defects discussed in Refs. 2–4, but none was detected. The DLTS signals remained independent of such perturbations, demonstrating that the metastability at hand has a different origin.

In their general use, configuration-coordinate diagrams represent the total energy as a function of some generalized coordinate Q. The total energy is usually not specified further, but is treated as an enthalpy. Entropy changes that might accompany changes in configuration have not so far been addressed in the context of metastable defects that have been observed by spectroscopic techniques. The role of entropy in transformations of intrinsic defects that mediate diffusion has, on the other hand, been discussed at length beginning with the 1968 paper by Seeger and Chik.[9] The entropy of intrinsic defects has also been discussed by Van Vechten and Thurmond.[10] The effect of entropy on defect migration was examined more recently by one of us (S.T.P.).[11] In particular, it was shown that if the migration energy of a defect is small and the migration entropy is large, after some critical temperature T_c, the saddle point becomes the stable configuration, whereupon an entirely different path with higher activation enthalpy becomes the dominant path. It was shown that the vacancy and self-interstitial in Si are likely to exhibit such phenomena. We believe that entropy variations in the configuration space are also responsible for the experimental observations reported here.

The stable configuration of a defect at temperature T corresponds to the absolute minimum of its *Gibbs free energy* of formation G, which can be written as

$$G = H - TS, \qquad (1)$$

where H is the formation enthalpy and S is the formation entropy. Let us now consider a defect whose configuration enthalpy is given by a curve such as that marked $T=0$ in Fig. 4. In other words, at $T=0$, the lowest-energy configuration of the defect is Q_2. Another configuration Q_1 lies at a higher energy and may not even be a true minimum. If the entropy of the defect is constant as a function of Q, the Gibbs free energy has precisely the same shape as the enthalpy at all T. The behavior of such a defect would be as described in Refs. 2–4 and illustrated in Fig. 1. If, however, $S(Q)$ varies between Q_1 and Q_2, different interesting phenomena can occur. For example if $S(1) > S(2)$, then, at some criti-

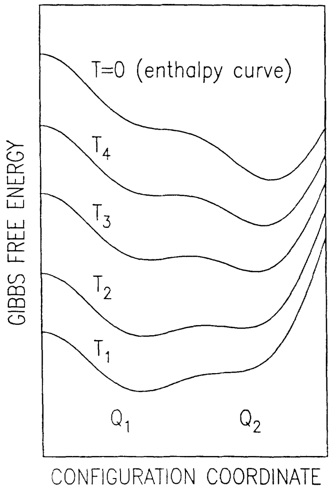

FIG. 4. The Gibbs free energy of formation as a function of a generalized coordinate Q illustrating the behavior of the ω_1 center as described in the text.

cal temperature T_c the equality

$$\Delta H = T_c \Delta S \tag{2}$$

is satisfied. Here ΔH is the maximum enthalpy change along the path from Q_2 to Q_1 and ΔS is the corresponding entropy change. As a result, at temperatures $T > T_c$, configuration Q_1 becomes the stable configuration. All of that would, of course, depend on the shape of S between Q_1 and Q_2. If the entropy is largest in the vicinity of the saddle point, which is quite likely, after some critical temperature the saddle-point configuration becomes the stable configuration. A wealth of possibilities exist. In Fig. 4 we show a set of curves that we believe can account for our observations. We have chosen a continuous variation of $S(Q)$ from Q_1 to Q_2 that yields the particular shapes of curves shown. In addition to $T=0$, the Gibbs free energy for four other temperatures at equal intervals are shown. In this figure, $S(Q)$ was treated as independent of temperature. It is clear, however, that a temperature dependence can be added (as needed, for example, to satisfy the third law of thermodynamics) and still produce curves that exhibit a similar qualitative behavior.

The data can now be understood as follows. If we start at high temperatures, the defect is in configuration Q_1. As the temperature is decreased, at some temperature near $\sim T_4$ the defect spontaneously and abruptly transforms to configuration Q_2. Thus, though at high temperatures the experiment is sensing the ionization energy of the defect in configuration Q_1, after the critical temperature the experiment begins to sense the ionization energy of the defect in configuration Q_2. Hence the abrupt drop in the DLTS signal and the simultaneous appearance of a new signal corresponding to a different ionization energy. If, on the other hand, the defect is cooled to very low temperatures and then the experiment is done in reverse, Fig. 4 indicates that the defect will remain in configuration Q_2 because of the barrier it has to overcome in order to switch to configuration Q_1. Thermal annealing at temperatures higher than T_c can achieve the switch.

It is clear that Fig. 4 was constructed so as to reproduce the data. It is probably not unique. In addition, it is clear that many other possibilities exist. For example, for some defects a barrier remains in both directions. Overall, we believe that entropy considerations provide a new dimension in efforts to understand defect metastabilities. A number of defects whose metastable properties, e.g., the $EL2$ defect in GaAs, should be revisited in view of the concepts discussed in this paper.

Finally, we note that though entropy-driven phase transformations in condensed matter have been known for some time, the work of Ref. 11 and this paper represent the first time that entropy-driven changes in defect configurations and defect migration paths have been discussed. This paper has presented experimental evidence of a defect that exhibits entropy-driven metastabilities. In the case of the vacancy and the self-interstitial, the critical temperature T_c is likely to lie in a range in which these defects are difficult to study experimentally (vacancies created by electron irradiation anneal out by room temperature and, because the migration energy is ~ 0.3 eV, T_c is likely to be several hundred degrees higher, but still lower than the range of temperatures at which a substantial concentration of vacancies is present; self-interstitials created by irradiation are believed to anneal out at cryogenic temperatures). The defects we studied in this paper, though their identification is unknown, must have two configurations such that the ratio $k\Delta H/\Delta S = 0.013$ eV, which corresponds to a critical temperature of about 160 K. Values such as $\Delta H = 0.1$ eV and ΔS in the range $8k-10k$ and would satisfy the requirement. Since the ω defects result from radiation damage, they may very well be quite extended, as would be required for such large entropies at such low temperatures.

After completion of this work, a paper by Londos[12] reported "anomalous" DLTS signals observed in irradiated pulled Si. A DLTS peak labeled H was described to exhibit "a bizarre behavior," "as if a structural rearrangement happens during the thermal emission of the trapped carriers." No explanation of what might cause such a behavior was proposed, but it was suggested that the defect involves oxygen on the grounds that the same DLTS feature is not observed in float-zone Si. We suggest that the H defect, which may indeed contain oxygen, is another example of the class of defects that manifest entropy-driven metastabilities as discussed in this paper.

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