

OBSERVATION OF A CONFIGURATIONALLY UNSTABLE DEFECT IN Si

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ABSTRACT

Boron-doped, Czochralski Si Schottky diodes were irradiated *in-situ* at 80K with 1.5 MeV electrons. DLTS studies were concentrated on a defect state at $E_V+0.34\text{eV}$ which exhibits charge-dependent characteristics. It is stronger when quenching the samples under zero bias than under reverse bias prior to beginning the DLTS pulsing. No complementary peaks were detected in these spectra when scanning upwards in the latter case. Surprisingly enough, when the temperature is ramped downwards from $T > 180\text{K}$ a peak H appears irrespective of a previous annealing with or without the application of a reverse bias. When this peak arises the height of the $E_V+0.34\text{eV}$ peak is decreased. A model is suggested invoking metastability to account for our observations. A microscopic picture of the defect is also suggested based on the variation of oxygen clustering around the defect core.

INTRODUCTION

The DLTS technique has been proven very valuable in studying alternate structures of metastable defects. In general, each structure has its own electronic states which give rise to corresponding DLTS peaks. The appearance of a specific defect configuration is achieved by preparing the defect in the proper charge state by electrical or optical excitation following by (a fast) cooling to low temperature¹.

A number of studies of various metastable defects in Si has been reported in the recent years². In this letter we report the detection of a configurationally multistable center in boron-doped Si. It is suggested that entropy changes cause changes in the energy ordering of local minima of Gibbs free energy, leading to spontaneous transformations between the defect configurations at a critical temperature. A microscopic modeling of the phenomenon is attempted.

EXPERIMENTAL DETAILS

Schottky diodes were prepared by evaporation of Aluminum on carefully cleaned, boron-doped, Czochralski-grown prepolished Si wafers. This was done in high - vacuum evaporator at a pressure of 10^{-6} Torr. Irradiation was performed *in-situ* at 80 K with 1.5MeV electrons to a constant dose of about $2 \times 10^{16} \text{ e}^-/\text{cm}^2$. Measurements were taken by using a standard DLTS experimental set - up³, with increasing /decreasing temperature at a constant heating / cooling rate of 0.15K/s, in the range 80-220K.

EXPERIMENTAL RESULTS AND DISCUSSION

Fig.1 presents the DLTS spectrum in the temperature range below 220K. This spectrum was received after annealing out of the vacancies by heating up the specimens at 220K for 30 mins. It contains four traps specified as H(0.13), H(0.29), H(0.34) and H(0.38). In this notation H stands for holes and the number in brackets denotes the energy depths of the traps from the valence band edge respectively. Preliminary discussion on the obtained spectra appeared in reference 4. The solid curve shows the observed peaks after a 5 min anneal at 220K with bias off ($V_R = 0$) quench to 80K and then scanning upwards. The dashed curve is the corresponding of the solid one but with the application of a reverse bias ($V_R = -5V$) during the 5 min anneal. The cooling down procedure in both the above cases was done by keeping the same voltage conditions as during the corresponding anneal. Such a procedure allows us to prepare specific charge states of our samples before applying the DLTS. The variation of the peak amplitude of H(0.34) as seen in figure 1 (solid and dashed curve) indicates that the corresponding center may alternate between two different configurations. The changes in the amplitudes of the H(0.34) peak are observed only for slow enough rate windows which allow the detection of the corresponding peak below 195K. For faster rate windows H(0.34) is always low.

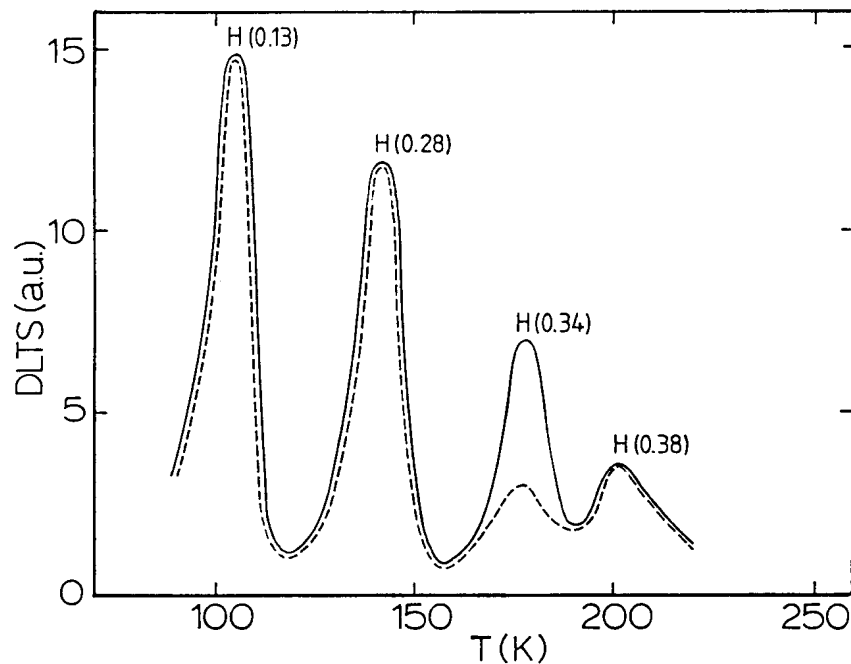


Fig.1 The DLTS spectrum of Si:B irradiated with electrons at 80K. The solid curve was received after cooling down from 220K with bias off and the dashed curve with bias on. The spectra were recorded with the temperature ramped upwards.

Surprisingly enough, when the temperature is ramped downwards from values above $T=180K$ an additional feature H appears in the spectra (Fig. 2) irrespective of the previous annealing with or without the application of a reverse bias. Peak H exhibits the following systematic behaviour. Initially it appears on the left side of peak

H(0.13). After a couple of days, while measurements were always restricted below T-220K, H suddenly emerges on the right side of H(0.13) where it finally remains. In this position it appears always in the temperature range just below 120K no matter what rate window is operated. It appears always in the downwards scanning mode when beginning from T>180 K and it has the appearance of a peak which is abruptly interrupted during its tracing. For temperatures lower than 120K, peak H disappears but peak H(0.34) is still low. These changes indicate that a specific relationship exists between the appearance/ disappearance of the H peak and the H(0.34) one. When H emerges the amplitude of H (0.34) is low and remains low having an intermediate value between that of the solid and that of the dashed curve in Fig. 1. It is worth noticing that detailed studies and analyses of the data have shown that the two peaks emerge and anneal out simultaneously from the spectra. These facts strongly indicate that the two peaks should be considered as alternative manifestations of the same metastable defect. Finally it is noted that the appearance of the additional DLTS peak in the downward scanning as compared to the upward scanning, was not observed using float zone Si instead the pulled Si.

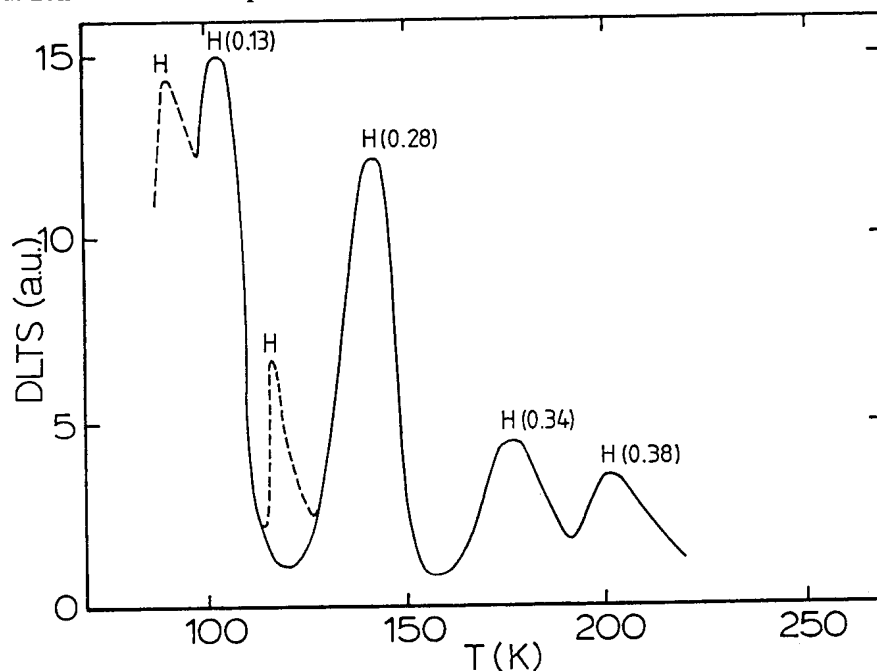


Fig. 2 The DLTS spectrum obtained with the downwards scanning mode from 220K. The additional feature H initially emerges on the left side of H (0.13) peak and finally on its right side.

Recently, Hamilton, Peaker and Pantelides⁵ (HPP) reported defect metastabilities detected in electron-irradiated float-zone Si. As the metastabilities they observed did not indicate any changes in their charge-state, they proposed according to earlier theoretical developments⁶ that these phenomena manifest entropy variations in the configuration space and they were able to give a macroscopic explanation of their DLTS spectra.

In this letter, we will show that our DLTS spectra can be equally well explained according to the arguments of the HPP theory. Based on the macroscopic explanation

of the HPP theory we will discuss a possible microscopic description based on short range order and randomness.

The HPP theory anticipates that stable defect configurations imply a minimum in the Gibbs free energy of formation, G , of the defect. The variation of G with a configuration parameter, as shown in fig.3, indicates regions where stable or metastable defect configurations may exist. This implies that it is not only the formation enthalpies, H , (formation energies) of the defects which will determine the kind of the defect stability but it is also the formation entropies, S , which play a dominant role. Thus according to the HPP theory, critical temperatures T_c exist at which the changes in the formation entropy and the formation enthalpy determine transition regions between various metastable configurations of the defect.

In the present case, like in the HPP theory, we can associate our experimental findings with variations of the Gibbs free energy of formation along a configuration parameter. Thus, we can argue that, annealing the sample with bias-off, it results in free hole capturing into the level leaving the defect in its more positive charge state (C^+). In this charge state the defect can exist in three configurations :A stable, B1 and B2 metastable (curve C^+ in Fig.3). Cooling down the sample, the defects freeze in configuration A which gives rise to a strong peak H(0.34) in the spectra. Annealing the sample with bias on leaves the level empty of holes setting the defect in the less

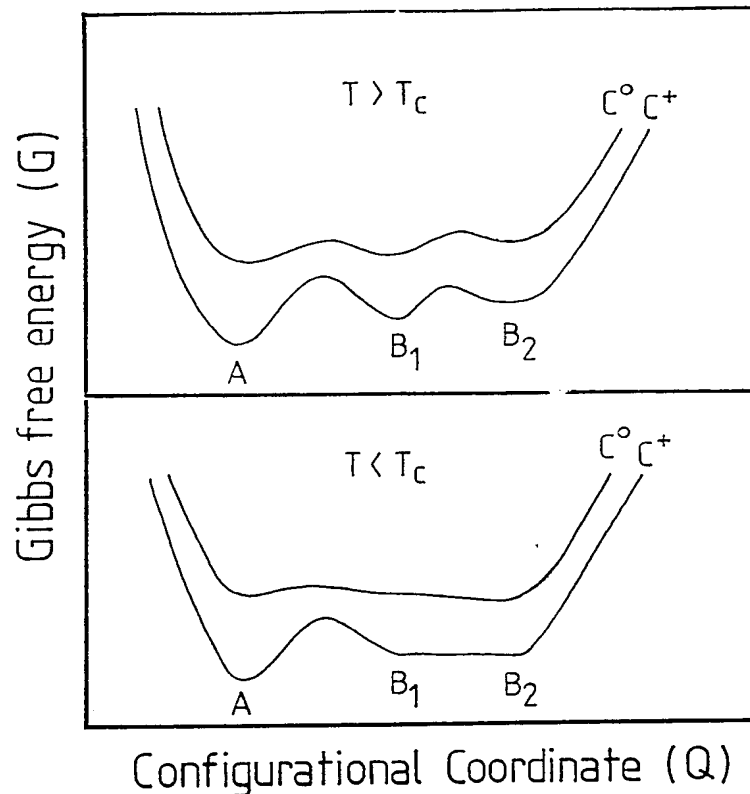


Fig.3 A rough configurational coordinate diagram for the defect system.

positive charge state (C^0), (curve C^0 in Fig.3). In this charge state, configurations A and B₁ have similar values of Gibbs free energy and therefore both of them could be populated. This explains why H(0.34) still remains in the spectra but with low amplitudes. B₂ is assigned to the defect configuration which is not observed in DLTS, and to which the defect is transformed when the temperature becomes less than $T=120K$. Its presence is justified from the fact that H(0.34) peak remains low after the disappearance of the H peak. Thus annealing with bias-on sets the defect in B₁ but quenching to 80K transforms it to B₂.

Cooling down from 220K while the DLTS system is operating, the defect is partly in configuration B₁ and partly in configuration A. The defect has the tendency to be in A during the application of the filling pulse and in B₁ when the filling pulse is removed⁷. The conversion from A to B₁ during the cool down scanning does not take place in the same extension as in the case leading to the dashed curve of fig.1. This explains the intermediate height of the H(0.34) peak of Fig.2. It is evident from the proposed configurational coordinate diagram of Fig.3 that the defect could convert to the B₂ configuration only in the C^0 charge state for $T < T_c$.

In the following we will attempt a microscopic explanation of our results based on the macroscopic concepts discussed above. The microscopic picture we propose is based on the additional observation that float-zone Si does not exhibit the above described behaviour in the cool down scanning mode. This allows us to assume that the H peak and the associated changes in H(0.34) are due to the excess oxygen in pulled Si⁴.

Irrespective of the charge state of the defect, temperature changes allow either oxygen concentration to vary around the defect or the number of atoms/ions participating in the defect to undergo substantial structural changes. These introduce local electrostatic and strain field changes at the defect as well as changes in the configurational entropy, σ , of the defect. An estimation of the configurational entropy of the defect may be found by considering the defect as a cluster of a Bethe lattice whose central atom has a (temperature dependent in general) coordination number Z. If we assume that all species except oxygen participating in the defect act as A-type and oxygen acts as B-type constituent of the defect, we can find the configuration entropy, σ , of such a defect from the equation^{8,9}

$$\sigma = kZ \left(\sum_{i=A,B} x_i \ln x_i - \frac{1}{2} \sum_{i,j=A,B} P_{ij} \ln \left(\frac{1}{2} P_{ij} \right) \right) \quad (1)$$

where k is Boltzmann's constant, x_A is the concentration of the A-species, $x_B = 1 - x_A$ and P_{ij} denotes the probability a lattice site to be occupied by species i when the neighbouring one is of j-type. The entropy σ , represents the number of possible ways one can populate the sites of a cluster (with the conditions $\sum_{i=A,B} x_i = 1$ and $\sum_{i,j=A,B} P_{ij} = 1$)⁸. To the entropy σ one can add entropy changes due to any other structural changes of the defect. The various P_{ij} , $i, j = A$ or B are explicitly known by giving $P_{A/B}$ and x_A (see for example reference 9). The variation of entropy σ for various values of x_A , $P_{A/B}$ and given Z are not so large compared to variations due to changes in Z. For Z values between 6 and 12 and for various x_A and $P_{A/B}$ the values of σ predicted by eqn.(1) may vary in the range of 2k - 9k justifying the

assumptions of the HPP theory.

According to the above description the change in the entropy which results from the variation of the oxygen concentration of the defect is assumed to be much greater than that due only to structural changes of a defect whose oxygen concentration is not changing with the variation of temperature. On the other hand the observed relationship between the H(0.34) and the H peak supports our assumption of oxygen induced changes in the entropy of the defects because it reflects the creation of one type of a defect configuration at the expense of some other one (of the same or different charge state), a condition that can be justified by oxygen movement.

It is therefore the short range order correlation ($P_{A/B}$) and the coordination number Z (for certain concentration value x_A) that specify the conditions for a defect configuration. The temperature may specify the local changes in the coordination number Z . Such changes may be the result of structural changes of/and the capturing of (unbound) oxygen atoms¹⁰.

According to the above discussion the variation of G is due to the changes of both the formation entropy of the defect as predicted by eqn.(1), and the changes in the formation enthalpy. It is understood that at this stage we cannot go beyond the present model assumptions. We cannot, for example, separate the effect of the electronic changes which accompany the structural changes of the defect from the effect of the entropy changes. Also we cannot exclude possibilities where Si self-interstitials may play a dominant role in capturing oxygen and promote or not its diffusion parameters¹⁰. Nevertheless the arguments of the present microscopic description indicate that entropy changes should not be underestimated in the consideration of the stability of the defects in Si. At the same time we propose a possible microscopic process which, when engaged in extensive numerical work, may justify the present and the HPP description.

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