

Evidence of metastability with athermal ionization from defect clusters in ion-damaged silicon

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We report on the observation of a metastability of defects in heavily damaged silicon. The ion-damaged buried layer is embedded in a Schottky diode and junction capacitance transient measurements are utilized to monitor charge relaxation following trap-filling pulse. The defect energy is observed to deepen progressively on carrier capture, and the emission rate of carrier from any relaxed state is nearly temperature independent. We propose that the phenomena can be understood in terms of large entropy changes acting as the driving force for the relaxation. Our results constitute experimental observation of metastability for small defect clusters in ion-damaged silicon.

At present, there is an intense search for ways and means of studying small defect clusters (interstitial and vacancy related) in silicon since they control many important physical processes such as transient-enhanced diffusion,¹ defect aggregation,² point- to extended-defect evolution,³⁻⁵ etc. Several recent theoretical and experimental studies attempt to understand atomic and electronic structures of extended self-interstitial agglomerates,⁶⁻⁸ and theoretical studies on interstitial clusters predict that small and stable clusters may not have any active states in the band gap due to the absence of dangling bonds in a closed ring structure.⁷ However, electrical signatures of small interstitial clusters have been recently obtained from capacitance based studies of self-ion implanted Si (Refs. 3,9) and in Ar⁺-implanted Si.¹⁰ The associated defect states seem to behave as point defects, and features distinct to clusters are yet to be isolated. Besides the fact that electronic energy levels may be broadened due to associated strain in the clustered defects, one may expect to observe distinguishing features in carrier capture kinetics and relaxation mechanisms of defect clusters, since they are more massive and are likely to possess multiple configurations/states. A systematic study in this direction may shed light on the possible metastable behavior of such defect aggregates due to possible bond rearrangement or other electrostatic interactions.

Metastable deep-level defects in semiconductors have been studied intensively for the last two decades starting with electron irradiation-induced defects in silicon.¹¹ Metastable configurations can be accessed by charge state change, optical excitation, rapid heating and cooling cycles, etc. There exists now a catalog of such defects of which many are very well-known such as the iron-acceptor pair in Si, carbon-related defects in Si, *DX* center in III-V compounds, *EL2* in GaAs, and *M* center in InP.¹² The origin of metastability in most of these cases has been traced to the occurrence of electrostatic interaction, bond reconstruction, large-lattice relaxation, etc., where stable and metastable states are separated by an energetic barrier. The physics of these defects is mostly related to the question of how is the extra energy of the carrier being captured shed during trapping? Most commonly known mechanisms for deep levels have been multiphonon emission, cascades of capture through an

Auger recombination. Much of our knowledge of such metastable states has come from studying electrical and optical transitions to and from these states through principally relaxation transient studies such as deep level transient spectroscopy (DLTS) and related techniques. Though details of the mechanism of relaxation depends on the specifics of a given defect, in many cases metastability is observed to be charge state controlled. Another interesting class of defects has been reported to exhibit metastability attributable to entropic contribution to free energy showing uncommon phenomena such as the disappearance of DLTS signal at a critical temperature.¹³ These reports are sporadic, and not much is known about their systematics.

A perusal of literature, however, shows that many of these metastable defects are of interstitial nature¹² and these kinds of metastabilities (or instabilities) are common in radiation-damaged semiconductors with the indication that the associated defects are complexes produced during radiation damage. There seems to be a possible correlation of the metastability phenomena with interstitial nature of these defects and perhaps disorder in the defect environment. While defect metastability is very common in amorphous semiconductors, the physics of their counterpart in crystalline structure is not analogous. Though several defects in electron-irradiated semiconductors have been found to be metastable, it is expected to be more prominent in heavy ion-damaged semiconductors due to excess interstitials and possible formation of their clusters. Recently, we have reported on the occurrence of a metastable defect with two configurations in heavily damaged silicon.¹⁴

In this paper, we report on the observation of a metastability in an ion-damaged crystalline silicon that is significantly different from those reported earlier in two respects. First, the defect energy is observed to deepen progressively on carrier capture, and second, the emission rate of carrier from any relaxed state is nearly temperature independent. We shall propose that the phenomena can be understood in terms of large entropy changes acting as the driving force for the energy deepening associated with the relaxation.

This metastability has been found in heavy-ion-damaged silicon, where damage is induced by irradiation of MeV (Ar⁺ and Au⁺) ions. Ar⁺ ions with energies 1.45 MeV from

a van de Graaff accelerator with doses $5 \times 10^{13} \text{ cm}^{-2}$ were used to create damage just below amorphization threshold, and these samples were partially annealed at 400°C for 30 min in vacuum. For the heavier Au^+ ions, an energy of 4.5 MeV at a much lower dose ($5 \times 10^9 \text{ cm}^{-2}$) could create damage with defects showing similar phenomena. The Au^+ -implanted samples were not subjected to any post-irradiation annealing. The defect spectrum in the damaged layer is studied by embedding it in the depletion layer of a Schottky contact. The Schottky contacts were made by vacuum evaporation of gold dots on properly cleaned Si wafers. The back Ohmic contacts were made by alloying vacuum deposited Al at 480°C for 30 min prior to implantation. The capacitance measurements were done using a Boonton capacitance meter operated at 1 MHz.

The relaxation of defects in semiconductors has been most widely studied using transient capacitance spectroscopic techniques such as DLTS. However, DLTS, being a temperature scanning technique, cannot be used to monitor processes where the rate of relaxation does not show thermal activation. Hence, the phenomena being reported here has been studied using isothermal transient spectroscopy. The technique called time analyzed transient spectroscopy¹⁵ (TATS) is based on sweeping rate window in the time domain, which is in contrast to DLTS where rate window is kept fixed and the temperature is varied. The TATS signal is given by

$$S(t) = V(t) - V(t + \gamma t), \quad (1)$$

where $V(t)$ is the relaxation transient to be analyzed at a fixed temperature and γ is a selectable experimental constant. Analogous to DLTS signal, $S(t)$ has a maximum at time t_m when plotted against $\ln(t)$. For an exponential transient of time constant τ_e , t_m and τ_e are related by

$$\tau_e = \frac{\gamma t_m}{\ln(1 + \gamma)}. \quad (2)$$

The power and advantages of using time domain spectroscopies such as TATS in a defect study have been illustrated previously.^{15,16,14} In our transient experiment, the depletion layer containing the defects is widened to a fixed value under constant capacitance condition using a feedback circuit. Subsequent to trap-filling pulse (with $V=0$), the voltage changes occurring due to carrier emission from the defects are monitored as bias transient $V(t)$ that is analyzed using TATS formalism to obtain emission signature of the defect.

Our previous studies on as-implanted and low-temperature annealed samples showed that the dominant defect in as-implanted Si is a midgap compensating center, and defect energy is found to be sensitive to low-temperature annealing, indicating relaxation of the defect structure.¹⁷ The origin of the dominant defect seems to lie in the formation of interstitial clusters.¹⁰ Figure 1 shows CC-TATS spectra at room temperature for a series of filling times (t_f) varying from 20 ms to 59 s. The well-formed peak shown in the figure is due to a new distinct peak whose time constant (τ) is strongly dependent on the filling time, becoming slower for longer duration of filling pulses. Note that the time constant of emission changes by 3–4 orders of magnitude, as

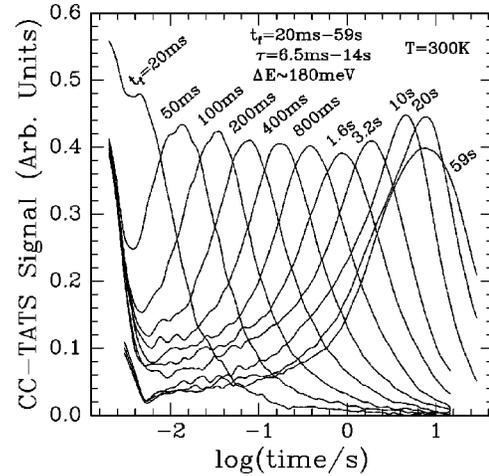


FIG. 1. CC-TATS spectra for different filling-time duration (t_f) at a fixed temperature (300 K) showing evolution of a defect level whose time constant of emission increases with increasing filling times.

does the filling time. Also note that the height of the new peak is approximately similar for all different filling times showing that the corresponding defect is located in the same region of damage and has nearly the same degree of occupancy irrespective of duration of pulse. Though the figure shows only a selection of curves, the time constant was observed to be continuously changing even when monitoring with small changes in filling time. In other words, the emission time constant of carriers from the defect progressively increased with filling time, and hence, this is not a case of a defect relaxing through discrete states in energy. At the same time, the line-shape analysis shows that the peaks correspond to nearly exponential transients for lower filling times, becoming slightly broad for the largest filling time. This shows that for any particular filling time, carrier emission takes place from a discrete defect level. Had it been from a part of broad density of states in energy, we would still have observed broadening in line shape for all the filling times. Hence, the effect of charge redistribution from shallower to deeper states cannot be responsible for the observed behavior. The peak evolves from a time constant of 6.5 ms to 14 s for filling times of 20 ms to 59 s, at a particular temperature. These three orders of change in time constant at fixed temperature would translate to about 180-meV change in terms of activation energy. This is indicative of occurrence of hierarchical relaxation through continuously evolving metastable states. This gradual slowing down (with τ and t_f obeying a power law) of emission or deepening of energy is typical of hierarchically constrained dynamics.¹⁸ The emission time constant is dependent on the resident time of the electron in the defect site. This dependence on history is a signature of a possible *non-Markovian* process possessing a memory of the duration that the electron spends at the occupied defect.¹⁹

Another intriguing feature of this phenomena is that the time constant is nearly temperature independent for any particular filling time t_f . This is illustrated in Fig. 2 where TATS spectra for a filling time of 1 s are shown for different temperatures varying over 30 K. The time constant of the major peak on the left of the figure does indeed change, as

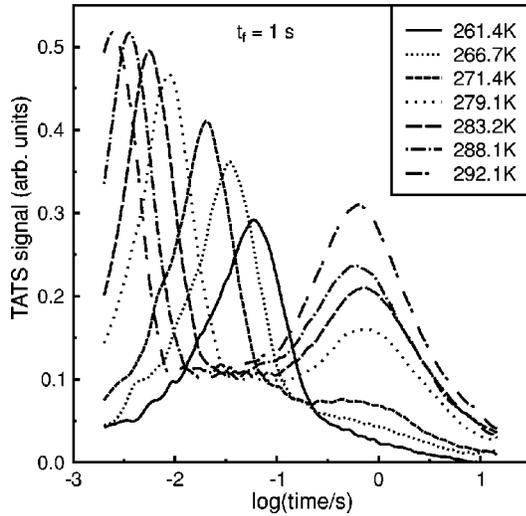


FIG. 2. CC-TATS spectra at different temperatures for a fixed filling time ($t_f=1s$) showing temperature independence of the evolved-peak position.

would be expected of a normal thermally activated process. However, the evolved peak corresponding to Fig. 1 does not show shift in time constant with temperature. This shows that the process associated with the relaxation is nearly athermal.

From the observed athermal nature, we suggest that the part of the free energy changing with defect relaxation can be considered to be proportional to temperature T . Incorporating the power-law dependence of the filling time (t_f) and emission time constant (τ), the effective energy associated with the relaxation can be written as

$$U_{eff} \sim k_b T \ln[(1 + t_f/t_{eff})^\alpha], \quad (3)$$

where it is characterized by an effective time constant of relaxation t_{eff} and exponent α . In Fig. 3, we show such a dependence of τ and t_f where the linear portion of the plot can be fitted with $t_{eff}=0.15$ ms and $\alpha=1.2$. The nature of this energy term also suggests that it can be viewed as an

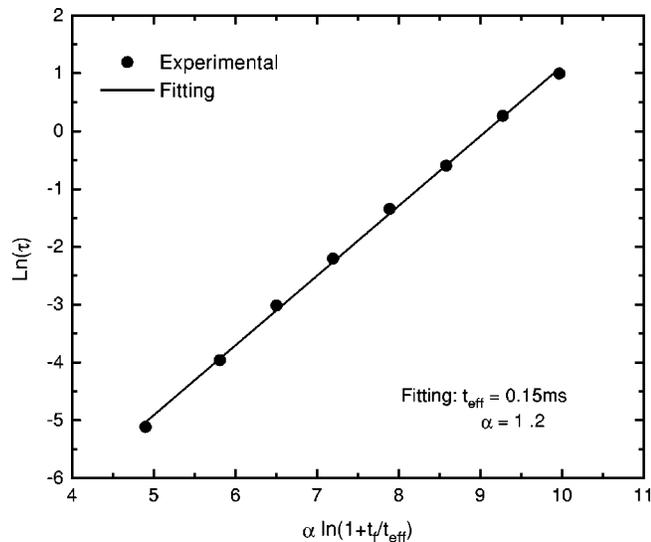


FIG. 3. Power-law dependence of τ and t_f for spectra shown in Fig. 1. Solid line refers to a best fit to relation: $\tau \sim (1 + t_f/t_{eff})^\alpha$.

entropic contribution to the measured enthalpy. Physically it would mean that traps undergoing relaxation during electron occupation have a distinct entropy.

The driving force, in fact, can be due to entropic variations in configurational space. The energy measured through these experiments is change in free energy $\Delta G = \Delta H - T\Delta S$. If the free-energy change of the defect in question has entropic contribution dominating over the enthalpic part, the corresponding carrier emission rate would be nearly temperature independent. Further, our experiments show that the entropy changes are dependent on filling time, since the defect basically relaxes during the carrier capture process, progressively decreasing its entropy as the number of capture events occurring at defect sites keep increasing. Incorporating the entropic and enthalpic part in free energy, trap emission rate can be expressed as

$$e_n = \sigma_n v_{th} N_c \exp\left(\frac{\Delta S}{k_b}\right) \exp\left(-\frac{\Delta H}{k_b T}\right). \quad (4)$$

There are two factors that contribute to entropy, namely, (i) electronic degeneracy (ΔS_e) and (ii) atomic vibrational change (ΔS_a). The temperature dependence of electronic ionization energy has, in the past, been conveniently represented by associating an ionization entropy resulting from electron-phonon interaction.²⁰ The estimates of entropy change on ionization from deep level defect due to electron-phonon interaction varies between $3 - 4k_b$ in the temperature range of our observations.²¹ Hence, the lattice vibration-related entropic contribution to ionization can be well in the range of 100 meV at room temperature. The contribution due to degeneracy factors cannot be exactly estimated due to lack of knowledge about degeneracy factors for deep levels. However, using the values known for shallow levels, it comes out to be of the order of $few k_b$.²² Therefore, the net free-energy change of 180 meV is, in our case, in good agreement with theoretical estimates assuming entropic contribution to free energy, and it strongly supports our proposition that, in the present case, the defect relaxation is driven by entropic variation in configurational space.

Entropy driven metastabilities have been invoked by Hamilton *et al.*¹³ to explain the existence of a critical temperature at which certain configuration becomes unstable giving rise to a discontinuous DLTS spectrum. This has been discussed in the context of large migration entropy of intrinsic defects as well as self-diffusion at high temperature.²³ Though the earlier case is distinct from the ones described here, the significance of entropic terms in determining relaxation is to be noted. Further, it is also significant that most of these observations have been reported in electron- or ion-irradiated semiconductors. This is to be attributed to occurrence of multiple or continuously varying configuration for an electrically active point defect in the environment of irradiation-induced damage. In view of our previous investigations on the nature of electrically defects in heavily damaged Si, we believe that small interstitial clusters are giving rise to such multistable behavior, perhaps related to configurational relaxation of the multiatom cluster. In this sense, a metastable atom is best thought of as a ‘‘defect molecule’’ with highly localized electronic charge.¹² Among the stable clusters, the four-interstitial cluster model of Arai *et al.*⁷ was

shown to introduce large change in bond angle and bond length, which was argued to result in electronic levels in the band gap of silicon. Note that the energy level would critically depend on the details of the processing conditions¹⁷ and the dynamics of the local potential variation during relaxation of the structure.

It is to be noted that samples used in this work provide a convenient laboratory for further studies on details of this relaxation mechanism. In a group of samples implanted with Au⁺ ions at a lower dose, studied in this context we observe qualitatively similar behavior, as described here, but with the difference that multiple traps evolve with larger filling time. These show that relaxations may be dependent on the nature of damage that may allow multiple final configurations for long-term filling of the trap. In the case of cluster of interstitial defects, lattice relaxation around the defect causes lowering of the symmetry that may aid the defect relaxation. Furthermore, the energy minimization requires bond reconstruction and lattice relaxation at the defect site. Therefore, charge trapping-induced deepening of emission energies in clusters may be treated as a manifestation of its local configurational change in microscopic scale.

In the literature, there has been intensive but inconclusive discussions on similar relaxation of defects corresponding to gap states in amorphous silicon by Cohen *et al.*,¹⁹ Han *et al.*,²⁴ Branz and Schiff,²⁵ and Jackson and Johnson.^{26,27} Cohen *et al.* proposed a hierarchical defect relaxation mechanism in which polarization around negatively charged defects causes relaxation and drives the average energy deeper into the gap. An alternative explanation of the phenomena was proposed by Farmer and Su²⁸ who invoked charge redistribution from shallower to deeper levels through multiple trapping at gap states distributed exponentially with energy. However, Jackson and Johnson later demonstrated that the entire effect in *a*-Si:H is an artifact due to non-Ohmic back contact in the Schottky diode. They argued that as the effect is absent in a device with Ohmic back contact, the anomalous filling time result in Ref. 19 could be due to a time-dependent charge injection phenomenon at the back contact. However, how the emission rate is affected by a slow capture during trap filling has not been clarified. Nevertheless, in the case of amorphous Si, the observed transients were highly nonexponential. Further, since a broad density of states is clearly involved in the case of amorphous silicon, the corresponding transients are highly nonexponential¹⁹ in contrast to our case. The defect spectra in preamorphized damage Si is dominated by discrete density of states making observation and analysis simpler. In our case, we have eliminated the broad density of states by choosing the fluence to be below amorphization threshold and further, have observed near exponential decay from spectroscopic analysis. As we

have used a Ohmic back contact in our Schottky devices, the observed relaxation effect cannot be related to contact related properties. In fact, *C-V* and *I-V* characteristics of our annealed samples gradually approach those of the virgin sample,¹⁰ and DLTS spectra show large concentration of defects up to 400 °C annealing. Contrary to the case of *a*-Si:H with non-Ohmic back contact, where Jackson and Johnson observe a time-dependent charge injection phenomena, we observe a fast filling of traps as reflected by a fast capacitance response reaching saturation within a few microseconds (of filling time duration) in the temperature range of observation. Hence, the observed effect is related to bulk property of the material under study, rather than contact related.

In the context of amorphous Si, Branz and Schiff²⁵ proposed that relaxation energies are primarily determined by local bonding in the amorphous network and similar energy deepening observed in capacitance transient measurement could be calculated assuming a crystalline model. The energy deepening observed in *a*-Si could be explained assuming dangling bond relaxation towards a pyramidal bonding configuration. However, the remarkably slow dynamics of relaxation could be accounted for by assuming a many-atom relaxation, in a hierarchical way, in disorder environment. We believe that the many-body nature of the defect clusters embedded in a partially disordered environment of otherwise crystalline Si, relaxes upon capture of electron in the present case and gives rise to slow dynamics.

A plausible physical scenario for this energy deepening could be that, with the capture of a carrier, a positive polarization cloud in the vicinity of the defect deepens the potential well and emission is monitored from this deepened state in the absence of capture. During the capture pulse, successive emission and capture events can drive the defect to relax continuously to more stable states if the polarization cloud is unable to follow this process rapidly. In other words, a relaxation process much slower than emission or capture processes would have the memory of net duration of occupation.

In summary, in ion-damaged deep buried layers of silicon we have presented evidence for a defect relaxation process where defect energy progressively deepens with trap-filling time and this process is found to be nearly athermal. The possible role of leaky contact and charge redistribution effects in the observed characteristics was systematically ruled out. Entropic contribution to ionization energy is believed to be responsible for the relaxation of the defect under study. Anticipated defect metastability from interstitial clusters opens up avenues for studying details of the kinetics of such relaxations.

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