Experimental observation of moving intrinsic localized modes in Germanium

J. F. R. Archilla,1 S. M. M. Coelho,2 F. D. Auret,2 V. I. Dubinko,3 and V. Hizhnyakov4

1Group of Nonlinear Physics, University of Seville, ETSII, Avda Reina Mercedes s/n, 41012-Sevilla, Spain
2Department of Physics, University of Pretoria, Lynwood Road, Pretoria 0002, South Africa
3NSC Kharkov Institute of Physics and Technology, Kharkov 61108, Ukraine
4Institute of Physics, University of Tartu, Riia 142, EE-51014 Tartu, Estonia

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Ions arriving at a semiconductor surface with very low energy (2 - 8 eV) are annihilating defects deep inside the semiconductor. Several different defects were removed or modified in Sb-doped germanium, of which the E center has the highest concentration. After eliminating other possibilities (electric field, light, heat) we now conclude that moving intrinsic localized modes (ILMs), as a mechanism of long-distance energy transport, are the most likely cause. This would be striking evidence of the importance of ILMs in crystals and opens the way to further experiments to probe ILM properties both in semiconductors and in the metals used for contacts. Although most of the measurements have been done in germanium, similar effects have been found in silicon.

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There is increasing interest in the mechanism and properties of non-linear lattice vibrations in crystals, which may have large lifetimes and propagation distances, and are known as intrinsic localized modes (ILMs), discrete breathers (DBs) [1] and quodons. In recent theoretical works by some of the present authors, the existence of stationary [2] as well as mobile ILMs [3] has been demonstrated in metals by means of molecular dynamics using well-defined MD potentials. This suggests that ILMs are readily produced in low-energy atomic collisions that do not result in permanent atomic displacements. They have also been shown to facilitate various reactions deep in solids [4]. An important peculiarity of this phenomenon is its low energy ranging from fractions of an eV to a few eV. This means that further investigations of low-energy collision events are required.

Deep Level Transient Spectroscopy (DLTS) is an especially useful technique for direct experimental observation of such phenomena in semiconductors, since it allows one to detect microstructural changes deep inside the material produced by low-energy collision events at the surface.

DLTS detects defects that are electrically active, namely that act as electron or hole donors, or traps in the usual terminology. A defect lying in the band gap with energy > 0.1 eV from either band edge is termed deep. See Refs. [2,8] for properties of defects in Ge. For simplicity, we will refer to electron traps, although a similar description is valid for hole traps. When an electron is in the trap level it has some probability of being emitted to the conduction band. The emission rate is given by:

\[ e_n = \sigma_{\text{app}} N_e \nu_{\text{th}} \exp(-E_T/k_B T) \]  

(1)

where \( \sigma_{\text{app}} \) is the apparent capture cross section, \( N_e \) is the effective density of states in the conduction band, \( \nu_{\text{th}} \) is the mean velocity of the electrons and \( E_T \) is the difference in energy from the bottom of the conduction band to the trap level inside the band gap. \( E_T \) is the activation energy for the emission process and it should not be confused with the energy for creating or annealing the defect. The lifetime, \( \tau \), of an electron in the trap is the inverse of the emission rate \( \tau = 1/e_n \).

Deposition of a thin layer of metal on the semiconductor surface produces a Schottky diode or an ohmic contact, a rectifying junction being a prerequisite to perform measurements provided that both contacts are present. Following an injection pulse of carriers the traps are rapidly filled and subsequently release carriers. The capacitance at two different times \( t_1 \) and \( t_2 \) is measured, the change in capacitance \( \Delta C = C(t_2) - C(t_1) \) has a maximum when the emission rate of a defect equals the so-called rate window \( RW = \ln(t_2/t_1)/(t_2 - t_1) \). Rate windows are preset at definite values, typically 80 or 200 s\(^{-1}\).

As the emission rate \( e_n \) of a defect depends strongly on the temperature \( T \), by changing it, it is possible to make \( e_n \) equal to the preset rate window, which appears as a maximum of \( \Delta C \) as a function of \( T \), for a given temperature. Different defects will bring about maxima at different temperatures. Setting two or more different RWs will lead to two different peak temperatures for a given defect and allows one through an Arrhenius plot of \( \ln(e_n/T^2) \) versus \( 1/T \) to determine \( E_T \). Equally \( \sigma_{\text{app}} \) can be obtained and the defect can be fully characterized [3]. For clarity, only the RW 80 s\(^{-1}\) will be presented in this letter.

The height of the DLTS peak is proportional to the de-
Defect concentration as $N_T = 2N_D(\Delta C/C)_{\text{Peak}}$, $N_D$ being the concentration of donor atoms.

An important property of the technique is that the reverse bias of the diode determines the size of the depletion layer and allows for the detection of how deep inside the semiconductor the defects are and even to obtain the dependence of the concentration with depth.

The semiconductor used is Ge doped with Sb with a concentration $n_{SB} = 1.3 \times 10^{15}$ cm$^{-3}$. The typical size of the Ge wafer is $3 \times 5 \times 0.6$ mm.

Defects are created by damaging the semiconductor with 5 MeV alpha particles (Americium foil). Subsequently a thin layer of metal, with typical thickness of about 25 nm, is deposited using resistive evaporation (RE), a technique which is known not to introduce defects in semiconductors. Up to a depth exceeding 2600 nm, the defect concentration in the sample was almost uniform. AuSb was evaporated previously onto the back surface to form the ohmic contact.

The observed process of non-thermal annealing is obtained when the semiconductors are treated with an inductively coupled plasma (ICP) of Ar. As can be seen in Fig. 1 several defects are annealed or transformed. Here we will focus on the most abundant corresponding to the highest peak at 185 K. A complication is that there is another defect with almost the same emission rate but with much faster kinetics than the $E$ center. This unidentified defect has sometimes been confused with the $E$ center in the literature. Research on it is underway and will be published elsewhere. After 6 hours at room temperature it is completely annealed out and only the $E$ center remains.

To summarize the experimental procedure: 1) Damage material with 5 MeV alpha particles. 2) Rest 24 hours at room temperature to anneal out the unknown defect. 3) Evaporate Au diodes (25 nm) on half the sample (diode A) and measure defects. 4) ICP-treat sample (4 eV Ar ions) for 30 minutes at room temperature in intervals of 10 minutes to prevent heating. 5) Evaporate Au diodes on 2nd half of sample (diode B). 6) DLTS on diode A. 7) DLTS on diode B.

Therefore, three DLTS spectra were obtained, as seen in Fig. 1 with the following results:

1) $E$ center concentration, initially at $N_T = 1.07 \times 10^{14}$ cm$^{-3}$, fell 29% after ICP on germanium. When the ICP was done through the Au contact, the reduction in concentration was only 8% but still evident.

2) Resistive evaporation of metals onto Ge also reduced the defect concentration. These changes in defect concentration were metal dependent and did not increase when the contact was more that 25 nm thick.

3) The sample heats up a bit to about 40°C, although the ICP is done in 10 minute steps to allow cooling. If the ICP treatment is done continuously the sample heats up more ($\simeq 65^\circ C$) and the effect of ICP annealing diminishes dramatically showing that heating is not the cause.

4) The defects were annealed up to a depth exceeding 2600 nm below the Ge surface. With 5.66 Å lattice constant, it means that the effect of the Ar plasma is felt more than 4500 lattice units deep.

5) The maximum reduction is observed with a 4 eV plasma, being somewhat weaker at 8 eV and very small at 2 eV.

6) The temperature to achieve similar rate of annealing is about 150°C [2, 3].

Our proposed explanation is that Ar ions impacting with the Ge surface produced moving ILMs. The reasons for this hypothesis are the following:

1) ILMs obtained in solids with molecular dynamics have energies of about 0.5-5 eV [2, 3] depending on the material. The maximum energy transfer from a 4 eV Ar ion to a Ge atom is about 3.6 eV.

2) The perturbation has to be localized, because if not it will spread into the semiconductor transforming into phonons, with much less annealing capability.

3) The energy for annealing a defect is of the order of 1 eV and can be obtained from annealing curves in Ref. [2], and density functional theory [10]. A specific value of 1.36 eV is given in Ref. [4]. Therefore, a large part of the ILM energy has to survive several thousand lattice units.

![Graph](attachment:image.png)
This is impossible with wave packets and phonons, while large amplitude ILMs have been shown to decay slowly through a two-phonon process [11].

4) Increasing the energy of the Ar plasma to 8 eV does not result in an enhanced effect. This is typical of ILMs, which usually have a range of amplitudes and energies for their existence.

5) At least stationary ILMs have been constructed for Si and Ge [12] using molecular dynamics.

This hypothesis also has implications for the metals used as contacts, as they are also able to transmit localized perturbations to the semiconductor with an efficiency of about 30% for a thickness of 25 nm. Perturbation in metals can be focusions which are known to have a range of the order of tens of lattice sites at room temperature or ILMs which appear in MD in metals [2, 3]. The properties of localized energy transmission by different metals is a subject of future research.

The plasma beam source (COPRA DN-160) accelerates ions towards an extraction grid from which the beam propagates towards the germanium wafer situated at a distance $x = 10$ cm. This source is described in Ref. [13]. The ion energy distribution function (IEDF) consists of two peaks, a high energy peak due to the ions in the beam attenuated through charge exchange collisions with the neutrals, and a low energy peak due to thermalized ions. The high energy peak diminishes rapidly with pressure, according to $I_{lep} = I_{hep} \exp(-x/l_x)$, being $l_x$ the mean free path due to the charge exchange collisions and $x$ the distance to the source. At the present experiment’s values $p=0.1$ mb, $x=10$ cm and $l_x \approx 1$ mm it has completely disappeared. Therefore, the ion flux arriving at the Ge wafer is due to the thermalized second peak, i.e., the ions being accelerated in a collisional sheath [14]. Both the ions’ energy and the current density $J$ diminish with pressure. The current density $J$ at our working pressures was not provided by the manufacturer and we have measured it with a Faraday cup. The corresponding ion flux $\Phi_i = J/e$ obtained within the range of accuracy (ion energy above 6 eV) are shown in Fig. 2. It can be seen that $\ln(\Phi_i) \propto \exp(-\alpha p)$, with $\alpha \approx 91$ mb$^{-1}$, which allows us to obtain the flux at $p = 0.1$ mb as $\Phi_i = 5.6 \times 10^{10}$ cm$^{-2}$s$^{-1}$. Note that due to charge exchange collisions there is also a flux of energetic neutrals which could increase the bombardment frequency by a factor of the order of the unity.

Note that for the more usual operational pressures of 10$^{-3}$ mb, the mean free path for charge exchange is about 1 cm, and most of the beam arrives at the wafer with much larger ion current density.

In the following we try to obtain an estimate of the efficiency of ILM creation by $Ar^+$ hits and subsequent ILM annealing of defects.

The number of defects annealed can be obtained easily. There are initially $N_T = 1.07 \times 10^{14}$ cm$^{-3}$ defects and 29% of them are annealed in $t = 30$ minutes of ICP up to a depth exceeding 2600 nm.

The number of defects annealed per unit time and unit area is:

$$\dot{N}_{ann} = \frac{0.29N_Td}{t} \approx 4.5 \times 10^6 \text{cm}^{-2}\text{s}^{-1}, \quad (2)$$

meaning that approximately $10^4$ Ar$^+$ hits are needed to anneal a defect.

Let us introduce the parameter $\gamma$, the efficiency of ILM creation, defined by:

$$\Phi = \gamma \Phi_i. \quad (3)$$

In principle, we can suppose that $\gamma \leq 1$, as it seems unlikely that an Ar hit will produce more than one ILM.

The rate of annealing by ILMs is given by

$$\frac{\dot{N}_{ann}}{N_T} = -\sigma_{ILM} \Phi_i. \quad (4)$$

where $\sigma_{ILM}$ is the scattering cross section of ILMs by defects. Let us write $\sigma_{ILM} = \alpha \sigma_0$ with $\alpha \geq 1$ and $\sigma_0$ equal to the area occupied at the surface by a Ge atom $\sigma_0 = (n_{Ge})^{-2/3} \approx 8 \times 10^{-16}$ cm$^2$.

Therefore

$$\frac{\dot{N}_{ann}}{N_T} = -\alpha \gamma \sigma_0 \Phi_i. \quad (5)$$

The value of the product $\alpha \gamma$ is approximately 3.6. Given the diamond structure of germanium, where there are no nearest neighbor straight lines of atoms, at least three atoms in a surface perpendicular to the ILM direction will form part of it. Therefore, if we choose...
\[ \sigma_{\text{ILM}} = 6^2 \sigma_0 \text{ or } \alpha \simeq 36, \text{ then } \gamma \simeq 0.1, \text{ meaning that about 10 Ar}^+ \text{ hits produce an ILM.} \]

We can try different combinations of numbers, whose exact value we do not know at this stage, but what is clear is the extremely high efficiency of these three processes, ILM creation by Ar ion hits, ILM transmission through germanium, and the annealing of defects by ILMs.

It is interesting to see that the annealing effect is not simply produced by more energy delivered to the defects. For that we can compare the density of energy for ILMs and for phonons at the temperature where the latter have a similar rate of annealing, which is \( T_{\text{ann}} = 423 \text{ K} \). [7, 8].

If we estimate the speed of ILMs as \( v_{\text{ILM}} \simeq 5400 \text{ m/s}, \) the sound velocity in germanium, their energy density is up to a depth exceeding 2600 nm. When the ion energy is about 10 Ar, 

\[ \rho_{\text{ILM}} = n_{\text{ILM}} E_{\text{ILM}} = \frac{\Phi_{\text{ILM}} E_{\text{ILM}}}{v_{\text{ILM}}}, \quad (6) \]

with \( E_{\text{ILM}} \simeq 3 \text{ eV}. \)

For phonons, we construct a simple model. The density of states of phonons in Ge shows a strong peak of overlapping optical bands between 8 and 9 THz or 33 and 37 meV at the top of the phonon band [15]. So, let us use an Einstein model of phonons with the same energy \( E_{\text{ph}} = 35 \text{ meV} \). The energy density of phonons at the temperature of annealing \( T_{\text{ann}} = 423 \text{ K} \) is given by:

\[ \rho_{\text{ph}, \text{ann}} = \frac{3n_{\text{Ge}} E_{\text{ph}}}{\exp(E_{\text{ph}}/k_B T_{\text{ann}}) - 1}. \quad (7) \]

Supposing \( \gamma = 1, \) the ratio between these two energy densities that brings about the same rate of annealing is \( \rho_{\text{ILM}}/\rho_{\text{ph}, \text{ann}} \simeq 10^{-16}, \) which shows very clearly that the effect produced by ILMs is not a thermal one.

The other point of view is that low energy, low flux plasmas seem an ideal source to produce ILMs in materials. The energy of each individual ion is of the order of magnitude of what is necessary to produce an ILM, the direction perpendicular to the surface is appropriate for an efficient energy transfer of momentum towards the interior of the semiconductor. The low density and flux of the plasma means that each ion impact is almost isolated. In 0.5 ns an ILM traverses the 2600 nm tested depth of the germanium wafer. During that time, no other Ar hit is produced in a circle of radius \( 10^6 \) lattice units, thus there is no possibility of a wavefront being produced or of an ILM being perturbed by another ILM. Of course, a technique as precise and sensitive as DLTS is necessary to appreciate the effect. We should also note that ILMs can not only anneal defects but they can also create or transform them as described in the experiment reported here but also in Ref. [10], where a new defect, known as \( E_{\text{O}, \text{31}} \) was created deep into Ge by 8-60 eV ICP plasma.

In conclusion, it was observed that the interaction of a low energy (4 eV) Ar plasma with the surface of Sb-doped germanium brings about the annealing of defects up to a depth exceeding 2600 nm. When the ion energy increases to 8 eV or decreases to 2 eV the annealing efficiency decreases. This suggests that the transmission of localized energy in the form of moving intrinsic localized modes takes place. If this hypothesis is correct, ILMs have an amazing capability of annealing defects and of travelling long distances in Ge. On the other hand, low energy plasmas seem an ideal source to produce nonlinear vibrational excitations in crystal, due to its low density, direction of ion impact and energy of the ions similar to that expected for ILMs. Our experiment opens an extended area of experimentation involving nonlinear excitations in semiconductors and metals.

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* Electronic address: archilla@us.es

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