**From time-resolved atomic-scale imaging of individual donors to their cooperative dynamics**

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The key elements in the steady miniaturization process of cutting-edge semiconductor devices are the understanding and controlling of charge dynamics on the atomic scale. In detail, we address the study of charging processes of individual doping atoms and, especially, the interaction of those atoms with their surroundings. We use pulsed optical excitation in combination with scanning tunneling microscopy at the n-doped gallium arsenide [GaAs (110)] surface to investigate single donor dynamics within a nanoscaled, localized space charge region. Tuning the tunnel rate can drive the system into nonequilibrium conditions, allowing distinction between the decay of optically induced free charge carriers and the decay of donor charge states. The latter process is atomically resolved and discussed with respect to donor-level binding energies and local donor configurations.

**INTRODUCTION**

Optical excitation of a semiconductor generates electron-hole pairs. Besides simple recombination, the presence of local fields and structural inhomogeneities can result in complex relaxation pathways \(I(t)\). This process includes not only field-driven charge transport but also the interaction with local defects. Up to now, access to the correspondent microscopic processes is usually limited to probing a large volume of the host material \((2, 3)\). On the macroscopic scale, a standard indicator, characterizing dynamic properties of charge processes inside a semiconductor, is the surface photo voltage (SPV). SPV describes the change of local potentials due to the presence of photo-generated charge. Microscopically, the buildup of an SPV is linked to various mechanisms such as the dynamics of dopants and the optically excited, freely movable carriers within the semiconductor. Especially, the controlled charging and discharging of individual dopants is the most elementary process in semiconductor electronics. In state-of-the-art device development, switching is already accomplished by a handful of donors \((4–6)\). In this context, disorder, for example, the specific configuration of doping atoms, is crucial. SPV studies have already reported a significant inhomogeneity of the static properties \((7, 8)\) on the atomic scale. Apart from its relevance in fundamental research, an atomic-level view on charge dynamics is needed for further device miniaturization. In particular, determining the influence of boundaries—for example, surfaces or internal interfaces—will substantially improve our understanding of dynamic properties of semiconductor nanostructures.

Here, we demonstrate the necessity for atomically scaled analysis of locally very inhomogeneous charging dynamics of individual donors, which, up to now, have usually been described by a single decay constant. We have used an optical pump-probe technique combined with scanning tunneling microscopy (STM) \((\text{Fig. 1A; for more details, please see Materials and Methods})\) by applying the shaken-pulse-pair excitation (SPPX) \((9–11)\) procedure. A periodic modulation of the optically induced tunnel current \(dI\) as function of the delay time \(t_d\) between pump and probe pulse represents the time evolution. Our sample system, sketched in \(\text{Fig. 1A, is the STM tip-induced electrostatic potential (color-coded) (12) in silicon-doped GaAs (gallium arsenide, n-type, including the influence of optically excited electron-hole pairs. Comparable to the situation inside a Schottky contact, the electric field separates free charge resulting, at positive bias voltages, in an accumulation layer of holes at the surface. In return, initially ionized donors capture electrons and become neutral. The shift of the surface potential due to the presence of the photo-generated holes, leading to an increase of the tunnel current at the same bias voltage, is called SPV. The relaxation mechanisms of the donors and the electron-hole pairs plus their mutual interaction define the steady state of the charge configuration \((13, 14)\). Additionally, previous studies have shown that tunneling electrons can address and thereby directly annihilate the photo-generated and accumulated holes at the surface \((15, 16)\). Using the tunnel current \(I_0\) as an additional control parameter, we drive the system into different non-equilibrium conditions.

**RESULTS**

Figure 1B shows a multitude of \(dI(t_d)\) spectra (bias voltage \(U_b = 1.0\) V) for increasing tunnel currents \(I_0\). As a unique feature, and in contrast to previous studies \((10, 11)\), we applied low laser intensities \(P_L\), resulting in a positive optically induced current \(dI\). The correlation between \(P_L\) and \(dI\) and the measuring process of \(dI\) itself are explained in detail in Materials and Methods. \(dI\) under pulsed excitation consists of the increase of conduction band tunneling \(dI_C\) due to the buildup of the SPV and the tunneling into valence band states \(I_v\) due to the presence of the accumulated photo-generated holes at the surface \((\text{Fig. 1C})\). Our study on continuous excitation has shown that the change \(dI_C\) is likely to be the dominant effect \((15)\). However, the percentages of \(dI_C\) and \(I_v\) on \(dI\) depend in detail on parameters such as STM tip shape, bias voltage, tunnel current, and excitation intensity. At \(I_0\) smaller than 250 pA, we observe an exponential decay of \(dI(t_d) = I_0 \exp[-(1/\tau) t_d]\) with a decay constant \(\tau\) decreasing with increasing \(I_0\) \((\text{Fig. 1E, red dots})\). We attribute this \(I_0\) dependency of \(\tau\) to the tunnel process \(I_v\) into photo-generated holes inside the valence band. Note that the size of the space charge region changes when decreasing the tip-sample distance for increasing \(I_0\). However, for a tip movement of 1 to 2 Å (current range in \(\text{Fig. 1B}\) for a usual tunnel barrier height of 4 eV), this effect is negligible \((\text{see fig. S1})\). Consequently, the decay of \(dI(t_d)\) is determined by the annihilation process of the accumulated holes at the surface. By adjusting \(I_0\), we are able to actively control this decay, in the following termed as \(t_{\text{hole}}\).

At \(I_0 = 450\) pA, the line shape of \(dI(t_d)\) changes notably. Although \(dI\) remains positive for a small \(t_d\) and decays fast, it alters its sign for a larger \(t_d\). This effect gets even more pronounced for higher currents \((500\) pA) until a completely negative and exponentially decaying \(dI(t_d)\) is observed \((1000\) and \(1500\) pA). We explain the line shape of \(dI(t_d)\) at
higher currents with a crossover between two relaxation processes. The hole annihilation dominates at low and medium $I_0$ (Fig. 1C). The negative $dI$ can be identified as the signature of donor ionization by electron emission from the donor level into the conduction band (Fig. 1D, green arrow). During the relaxation to the ground state, $dI(t_d) < 0$ reflects a special nonequilibrium condition. For high $I_0$, holes are annihilated rapidly, whereas donors remain neutral (for more details on the nonequilibrium condition, see fig. S2). Consequently, at the surface, nearly no net charge is found, the potential difference between the tip and the surface is almost zero (Fig. 1D). The relaxation of the system (at $t < \tau_{\text{hole}}$) is dominated by the hole annihilation process at the surface via $I_C$. Band tunneling scheme for $t < \tau_{\text{hole}}$. At low tunnel currents, $dI(t_d) \propto I_C$ is dominated by the hole annihilation process at the surface via $I_C$. Band tunneling scheme for $t < \tau_{\text{hole}}$. For high currents, holes at the surface are annihilated fast, whereas surface-near donors still have to emit their electrons into the conduction band to ionize (green arrow). Nearly no net charge at the surface is present, leading to a vanishing $I_C$. Note that in (C) and (D), the same bias voltage is applied. (E) Decay constant $\tau$ plotted against current $I_0$ in case of positive and negative $dI$. The dashed lines are intended as a guide to the eye.

Expecting a great influence of different atomically scaled donor configurations at the GaAs surface, we studied locally resolved $\tau_{\text{don}}$. The constant current topography in Fig. 2A shows the signatures of three donors positioned at different depths beneath the surface. To suppress the contribution of the hole dynamics, we used high tunnel currents ($I_0 = 1$ nA) while recording $dI(t_d)$ spectra at each raster scan point of the topography in Fig. 2A. Additionally, we chose a sample voltage ($V_0 = 1.3$ V) where lateral interaction between donors can be neglected (17). Single, time-resolved spectra, taken directly at the marked dots, show significantly different decay constants for each donor (for logarithmic scale analysis of Fig. 2B, see fig. S5). Although it has already been shown that local defects have an impact on the relaxation process (10, 11), the considerable variation in the dynamics of individual defects has not yet been resolved. To explore these dynamics, we plot $\tau_{\text{don}}$ spatially resolved in Fig. 2C [the supplementary material includes a movie showing the spatiotemporally resolved decay of $dI(t_d)$]. A local enhancement of $\tau_{\text{don}}$ clearly visible at the donor position. Moreover, $\tau_{\text{don}}$ changes from donor to donor with the highest $\tau_{\text{don}}$ for donors closest to the surface. Compared to the free surface (that is, far away from a visible donor) showing a $\tau_{\text{don}}$ $\sim$100 ns, a donor in layer 1 below the surface (for depth evaluation, see fig. S6) exhibits a $\tau_{\text{don}}$ of 530 ns. Obviously, the surrounding of the defects plays a crucial role, for example, the presence of the surface and/or the influence of other donors. In this sense, the absolute values of $\tau_{\text{don}}$ will depend on the local dopant configuration. To elucidate the variation in $\tau_{\text{don}}$ in Fig. 2C, we analyzed the emission mechanism of the ionization process in detail. By performing a temperature-dependent study, thermal emission can be ruled out (fig. S7). Previous results by Wijnheijmer et al. (18) have shown that $E_B$ monotonically increases with decreasing depth of the donor (Fig. 2D and fig. S6). On the basis of these findings, we propose a field-driven tunneling process of electrons from the donor level to the conduction band (Fig. 2E) to explain the correlation between $E_B$ and $\tau_{\text{don}}$ (Fig. 2D).
The binding energy $E_B$ and the local field $E$ at the donor position determine the electron emission rate for this tunneling process. To cross-check this $E_B$ dependency, we compare the experimental $\tau_{\text{don}}$ quantitatively with the ionization times $\tau_{\text{hydro}}$ calculated for hydrogen atoms in an electric field (19) with adapted parameters for silicon donors in bulk GaAs (Fig. 3A and fig. S8). For comparison, the found pairs of $E_B$ and $\tau_{\text{don}}$ for the three different dopant depths below the surface in Fig. 2A are included in Fig. 3A. Nearly no charge and hence a weak electric field at the surface characterize the relaxation from the nonequilibrium conditions at high currents $I_0$ (Fig. 1D). Charge fluctuations of donors and thereby field fluctuations take place (17, 20), triggering further field-driven ionizations. We model an electrostatic potential in a cross section at the GaAs surface (Fig. 3, B and C), including random donor positions in charged (blue dots) or neutral (green dots) state, according to the doping density of our sample ($3 \times 10^{18}$ cm$^{-3}$, 7 nm average distance between two donors). To estimate the probability of charging events, we calculated exemplary Coulomb potentials of ionized donors in this half-space geometry.

Regarding the ionization process of donors with a binding energy $E_B$ of 10 meV and a $\tau_{\text{don}}$ of 237 ns (Fig. 3B, blue/white dot), the required field $E$ of 0.2 mV/nm will already be given if any of the donors in a spherical volume marked by the white contour line in Fig. 3B ionizes. In contrast, to charge a donor with a binding energy $E_B$ of 45 meV and a $\tau_{\text{don}}$ of 530 ns (Fig. 3C, red/white dot), a field $E$ of 2.5 mV/nm is needed. The radius of the correspondent volume reduces to 8 nm (Fig. 3C, white contour line), and consequently, the number of possible donor candidates decreases, making the ionization process unlikely. We deduce that the variation in $E_B$ cannot be the only reason for the variation of $\tau_{\text{don}}$. In fact, we expect a considerable increase of the ionization probability when more than one donor is involved. From this deduction, we propose a relaxation to the ground state as a stepwise buildup of the electric field, starting with the ionization of donors positioned in the bulk material and continuing to donors near the surface. Hence, the donor dynamics cannot be treated as individual charging and discharging processes connected to a dedicated decay constant $\tau_{\text{don}}$. Instead, they have to be regarded as a stochastically distributed ensemble of linked subsequent charging events.

**Fig. 2.** Spatially resolved charging dynamics of donors at different depths below the GaAs surface. (A) Topography of the GaAs(110) surface with three donors (marked as red, green, and blue dots) positioned at different depths below the surface (bias voltage, 1.3 V; tunnel current, 1 nA). (B) Locally resolved time spectra (bias voltage, 1.3 V; tunnel current, 1 nA; excitation parameters: repetition cycle, 8 µs; pulse width, 40 ns; average power, 16 µW) recorded at the positions marked in (A). (C) Spatially resolved decay time $\tau_{\text{don}}$. (D) Donor binding energies $E_B$ plotted versus depths. Adapted from Wijnheijmer et al. (18). $\tau_{\text{don}}$ of the corresponding donors in (B) is assigned respectively. (E) Model of field ionization. In this case, electrons tunnel from the donor level into the conduction band.
triggered by random charge fluctuations. Thus, the actual relaxation dynamics will vary from one local donor configuration to another.

**DISCUSSION**

We are convinced that this coupled charging dynamics of individual donors, including the influence of surfaces and interfaces, can have a massive impact on the functionality of semiconductor devices. Bistabilities in the charge state of coupled donors have already been observed in the millisecond time regime \(^{(17)}\). The map for the relaxation time of individual donors in Fig. 2C shows nonisotropic local enhancements of \(t_{don}\), indicating the interaction among themselves. Continuous charging and discharging events are responsible for shot noise in semiconductor devices \(^{(21)}\), but are not yet experimentally resolved on the local scale. Even quantum computer approaches discuss single donors as isolated qubits \(^{(22–24)}\). Ultimately, in all these subjects, only an atomic-scale characterization can provide a detailed understanding.

In this context, pulsed optical excitation combined with STM opens up an exciting research field with a myriad of applications.

**MATERIALS AND METHODS**

**Experimental setup and sample system**

All data were recorded in a home-built low-temperature, ultrahigh vacuum STM at a base pressure of \(1 \times 10^{-10}\) mbar and at base temperatures of 77 and 6 K. The bias voltage was defined as the sample voltage. The silicon n-doped GaAs \((3 \times 10^{18}/\text{cm}^3)\) crystals were chemically thinned down to 100 \(\mu\)m and cleaved inside the vacuum chamber exposing the (110) surface. The optical setup, implemented in the STM, is shown in Fig. 4. The laser beam of a continuous-wave laser diode \((785\text{ nm})\) was processed into a pulsed shape by a fiber-coupled EOM \((\text{EOSpace})\). We used the SPPX \(^{(10)}\), conceived by Terada et al. at the University of Tsukuba. A high-frequency arbitrary waveform generator \((\text{AWG};\ \text{Keysight A81160})\) produced the SPPX in an all-electronic method. The shortness of the pulses is restricted by the bandwidth of the AWG to \(\approx 1\) ns. The pulsed laser beam was focused into the tunnel junction with a focus diameter of less than 20 \(\mu\)m. The periodically modulated, laser-induced tunnel signal \(dI(t_d)\) was measured by a lock-in amplification.

**Excitation state–dependent sign of the optically induced current \(dI(t_d)\)**

The quantity \(dI(t_d)\) is the difference in the tunnel current induced by a sequence of two shortly separated pulses compared to the current induced by a train of two well-separated pulses. In comparison to other pump-probe experiments, the pump and the probe pulse have identical intensities and both trigger the same mechanism: a change in the tunnel current. In contrast to our studies, \(dI\) in previous optical pump-probe SPV measurements had a negative sign \(^{(9–11)}\). We show that different excitation states after the pump pulse \((t = t_{PW})\) determine the sign of \(dI\).

Figure 5 schematically shows two shortly separated optical pulses (Fig. 5A, green), discusses a saturated (Fig. 5B, blue) and a nonsaturated excitation case (Fig. 5C, red), and compares this with the excitation induced by two well-separated double pulses (Fig. 5D).
At low optical excitation intensity ($P_1$, 10 μW average power), saturation of the SPV during the pump pulse is not obtained, resulting in a positive $dI$. Blue curves: At high $P_1$ (70 μW average power), saturation of the SPV is obtained after the pump pulse. Consequently, the $dI$ becomes negative. (B) Decay constant $t_d$ plotted against the set point current for high (blue) and low (red) excitation densities. The current dependency of $t_d$ in both cases is identical.

If the pump pulse has induced the maximum change in the tunnel current $I_1$ (Fig. 5B), the effect of the probe pulse on the tunnel current will be at maximum of the same order. Because of the overlap in the decay (deep blue shading), the average current was less than the average current (black dashed lines) induced by two well-separated pulses (Fig. 5D). As per definition, this leads to a negative $dI$. If the first pulse does not induce the maximum effect, the shape of the system response, triggered by the second pulse, can change considerably. Figure 5C shows the configuration for which the excitation by the probe pulse leads to more tunnel current (light red shading) in comparison to one single, isolated pulse. In the differential measuring method of the averaged signal (black dashed line), this may lead to a positive $dI$.

Experimentally, saturation (Fig. 5B) or nonsaturation (Fig. 5C) in the excitation state can be investigated by applying different laser intensities $P_1$ [Fig. 6A, red (low excitation intensity) and blue (high excitation intensity)]. The time to obtain saturation for the charge configuration at the surface is connected to the time it takes for a donor to capture one of the photo-generated electrons and to become neutral subsequently. At higher $P_1$, the electron density at the surface is denser and, consequently, the SPV builds up faster during the pump pulse. The current dependency of the decay constants extracted from $dI(t_d)$ spectra is identical for high and low excitation intensity (Fig. 6B). This is a clear indication that in each case, the same relaxation mechanism is probed, namely, the annihilation of the holes via tunneling. The only difference in both cases is the excitation state of the charge configuration at the surface after the pump pulse, resulting in the sign alteration of $dI$.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/3/e1601552/DC1

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