

Excited-state spectroscopy of single Pt atoms in SiL. E. Calvet,^{1,*} J. P. Snyder,² and W. Wernsdorfer³¹*Institut d'Electronique Fondamentale–CNRS UMR 8622, Université Paris-Sud, 91405 Orsay, France*²*Independent Consultant, Bloomington, Minnesota 55425, USA*³*Institut Néel, CNRS and Université J. Fourier, BP 166, 38042 Grenoble Cedex 9, France*

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Resonant peaks superimposed on the direct tunneling current in the low-temperature transport of Schottky barrier metal-oxide-semiconductor field-effect transistor inversion layers are investigated. The resonances are attributed to single Pt atoms that have diffused from the metallic contacts into the depletion width near the metal/semiconductor interface. Excited-state spectroscopy and magnetic fields are used to identify different levels. A double donor level in a singlet state and another level that is attributed to a triple donor state are observed.

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I. INTRODUCTION

Impurity spectroscopy in semiconductors has been an important research topic for over 50 years because of the dramatic effects dopants have on electronic and optical properties and the resulting key role they play in practical applications.¹ With the increasingly nanoscopic dimensions of devices, a new demand to understand the electronic properties of single dopants subject to strong electronic fields has emerged. Such impurities can modulate the current in very small scaled transistors² and are of fundamental interest for quantum computing implementations.³ In recent years investigations of impurities in silicon have allowed an unprecedented spectroscopy of single shallow dopants and revealed how the ground state,^{4,5} first charged state, and excited states^{6,7} can be significantly changed from the bulk. In this paper we investigate electronic transport through two different levels of a transition-metal impurity. We show that such multiple-level impurities can be distinguished from shallow-level impurities experimentally by investigating the excitation spectrum and magnetic-field dependence of different charged states. In addition the many-level nature of this impurity allows us to explore the spin filling of an impurity quantum dot with more than two electron states.

A shallow dopant is well described by the effective-mass approximation in which the Schrödinger equation is reduced to hydrogenic form by assuming a (screened) Coulomb perturbation potential.⁸ Here we consider devices in which shallow impurities are not present in our transport window and we thus are able to explore the multilevel impurity atom Pt. Such an atom in Si introduces a large potential that results in the breakdown of the hydrogenic model. Extensive research has shown that structural distortions result in the Pt atom having a filled *d* shell lying deep in the silicon valence band.^{9,10} As a result, this impurity is modeled as a negatively charged lattice vacancy. To predict the energetic spectrum techniques such as empirical tight-binding Green's function calculations¹¹ or *ab initio* (spin-polarized) local-density functional cluster methods¹⁰ have been used. The results reproduce the number of levels and approximate positions in the band gap of the experimental data. Most importantly, predictions about the spin of the single acceptor, in which the nega-

tively charged vacancy becomes charge neutral (denoted as the $-/0$ state) and which is the only state observable by electron spin resonance (ESR), are consistent with experiments. Relative to the conduction and valence band, E_c and E_v , respectively, the levels observed experimentally are at approximately $E_c - 0.243$ eV (single acceptor denoted by $-/0$), $E_v + 0.330$ eV (single donor denoted by $0/+$), and $E_v + 0.1$ eV (double donor denoted by $+/+$).^{10,11}

In addition Pt can form clusters and complexes with hydrogen^{12,13} and oxygen,¹⁴ which result in additional levels mostly around midgap or close to the conduction band. These states have been widely investigated in the bulk because they are used to control the lifetime of minority carriers. While our devices could be susceptible to Pt complexes and clusters due to fabrication processing,^{12–16} the energetic values observed here are in close proximity to the valence band making the double donor state of Pt the most likely candidate. The only other level reported in this energy range was attributed to a single charged state.¹⁴

II. EXPERIMENTAL METHODS

We investigate Pt impurities located in a Schottky barrier metal-oxide-semiconductor field-effect transistor (SBMOS-FET) shown schematically in the inset of Fig. 1. This device, which is a possible solution to engineering the source and drain in ultimate scaled transistors,¹⁷ consists of metallic source and drain contacts here made from PtSi.¹⁸ Devices were fabricated on *n*-type substrates with a 34 Å gate oxide and operated under inversion. We note that this research differs from previous work because there are nominally no shallow acceptor impurities (e.g., no boron impurities) near the valence band. We use a standard lock-in technique in a dilution refrigerator at a bath temperature of 50 mK and investigate resonant impurities in a magnetic field applied parallel to the substrate.

At low temperatures transport is dominated by direct tunneling through the depletion width that forms at the metal/semiconductor interface.¹⁹ As shown in Fig. 1(a) single atoms situated in this region result in resonances superimposed on the current as V_g is made more negative and the electrochemical potential approaches the valence band. We ex-

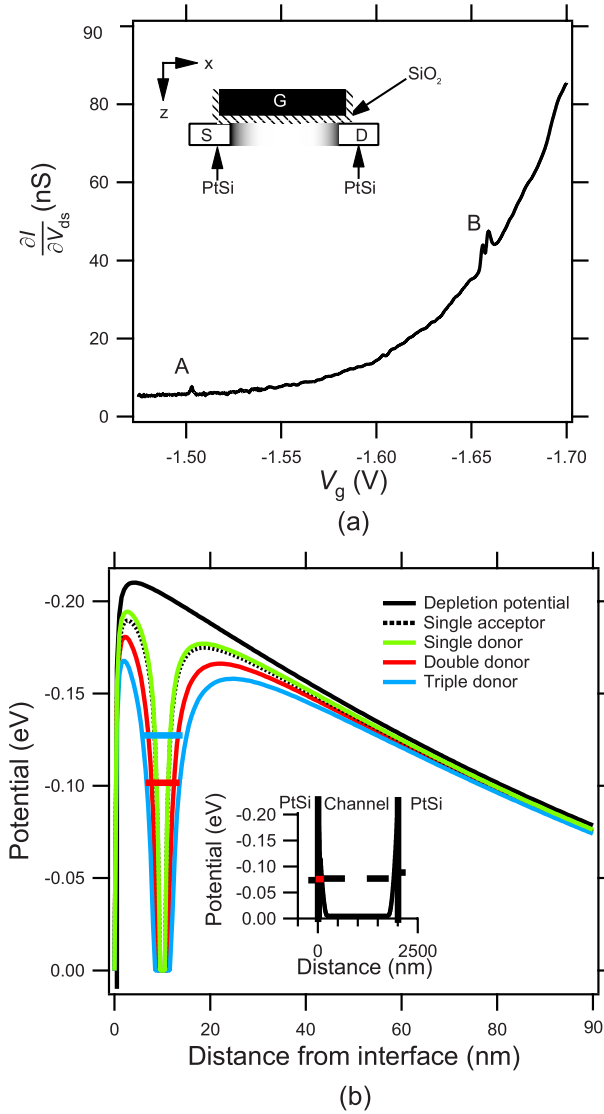


FIG. 1. (Color online) (a) dI/dV_{sd} versus V_g at $V_{sd} = -1$ mV for device 1. The peak at $V_g = -1.5$ V, labeled level A, is attributed to a double donor state and that at $V_g = -1.68$ V, labeled level B, to a triple donor state. The inset shows a schematic of the device with gate (G), source (S), and drain (D). (b) Schematic of the potentials (with substrate doping of $N = 5 \times 10^{21} \text{ m}^{-3}$) with image charge and an impurity located at 10 nm with a model $1/r$ potential and its image charge to depict different states (Ref. 6). The approximate positions of the double donor and triple donor levels are also shown. The inset shows the potential along the entire channel length with the impurity located in the left Schottky barrier, $V_{sd} = 5$ mV, a barrier height of 0.225 eV, and an assumed finite bias magnetic field so that the superconductivity is suppressed. We note that the applied bias is partially dropped across each Schottky barrier as indicated by the quasi-Fermi levels.

explored device 1 with a 20 μm channel width by 2 μm channel length and device 2 with a 20 μm channel width by 5 μm channel length. These devices are part of a larger study that showed that the number of Pt impurities observed in a given device is random and in general does not depend on device size.²⁰ Because the Schottky barrier is ~ 0.2 eV,

we are only able to probe levels that are between E_v and $E_v + 0.2$. We thus expect to observe only the double donor state of Pt. In Fig. 1(b) we schematically depict the different potentials possible. While an acceptor situated close to the Schottky barrier *lowers* the barrier because of the image charge, a donor tends to *raise* the barrier. Here this effect is relatively small compared to the effect of the model $1/r$ impurity potential.

III. RESULTS

Excited-state spectroscopy is used to probe the charge states of different resonances.²¹ We investigate in detail “level A” and “level B” as shown in Fig. 1(a), which exhibit different magnetic-field dependencies. As the source-drain bias V_{sd} is increased excited states of the resonances can be observed as they come into the transport window. As shown in Fig. 2, plots of dI/dV_{sd} for many values of V_g and V_{sd} allow an investigation of the excited states of the impurity. In the simplest case of a shallow donor impurity state the resonance is due to the transition from a neutral to positively charged impurity ($0/+$) denoted by E_{res}^0 . The only excited states possible are those of the neutral state because once the donor has donated its electron it becomes electrically inactive. A deep level impurity such as Pt has a double donor resonance, corresponding to the transition between a single charged and a double charged impurity state, denoted by $+/+$, at position in energy E_{res}^+ . In the transport window of such a resonant impurity level, one can observe excited states of both the single and the double donor. Specifically, excitations located at $E < E_{res}^+$, called “down-going” excitations, correspond to excitations of the single donor and/or those with $E > E_{res}^+$, called “up-going” excitations, correspond to the double donor. In some instances, we can distinguish levels belonging to a deep-level impurity versus shallow-level impurity based on its excitation spectrum.

To further differentiate between different charged states we consider the spin filling of the level that is apparent in a finite magnetic field.²¹ The spin of an additional charge on an impurity atom depends on its coupling to previous charges and its environment. In the simplest case, the spin filling should follow a simple Pauli law, with an additional electron having the opposite spin orientation of the previous one. Such effects have been observed in few electron semiconductor quantum dots,²² in molecular quantum dots,²³ and in shallow single impurities containing two charge states.^{6,7} However, for some deep-level impurities the competition between the Jahn-Teller effect and spin orbit interactions can lead to alternative filling.²⁴ We note that if the barriers are very asymmetric, as might be expected from the schematic of the potentials in Fig. 1(b), an investigation of the rate equations²⁵ implies that Zeeman splitting may only be observed in one bias direction.

In Fig. 2 we plot the differential conductance dI/dV_{sd} as a function of V_g and V_{sd} at 0 T and 4.82 T for level A and level B from Fig. 1(b). We note that the PtSi electrodes become superconducting below ≈ 1 K and thus a superconducting gap is observed around zero bias in Figs. 2(a) and 2(d). In a finite parallel field, the current around zero bias is suppressed

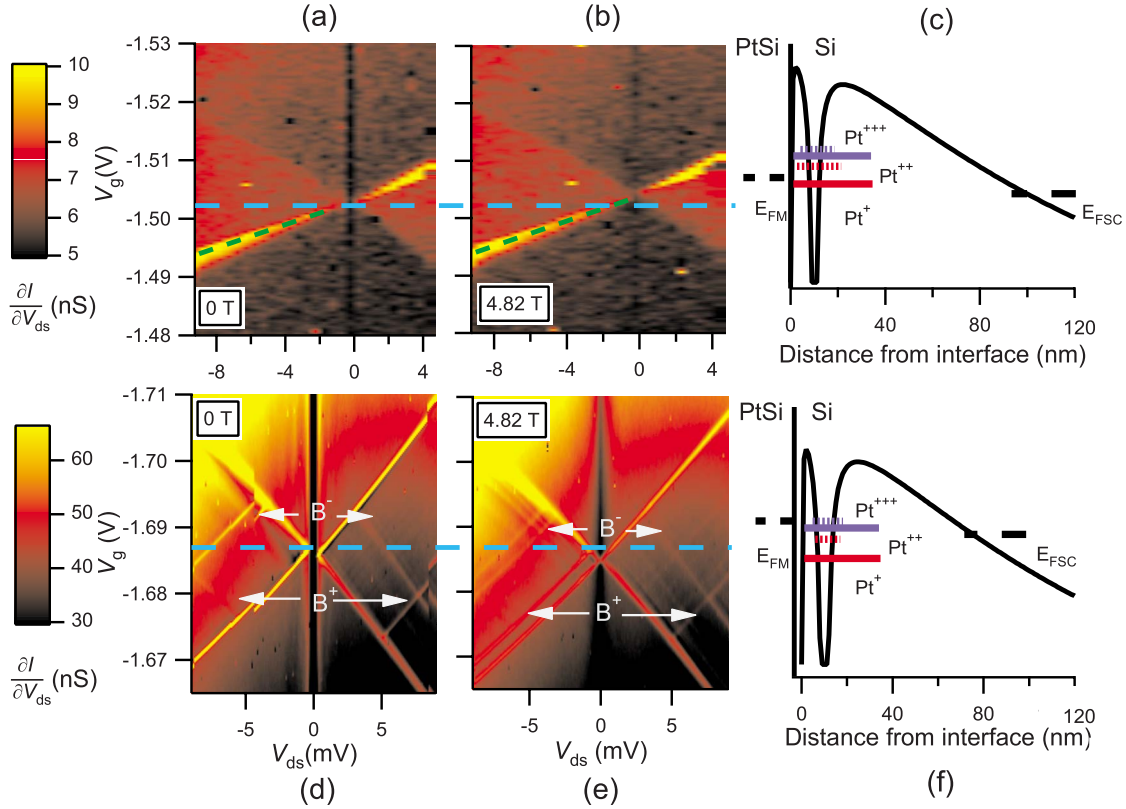


FIG. 2. (Color online) $\partial I / \partial V_{sd}$ versus V_g for many values of V_{sd} is shown for the peaks at $V_g = -1.5$ V and $V_g = -1.68$ V at 0 T (a), (d) and 5 T (b), (e), respectively, for device 1. We have also included band diagrams that depict when V_g aligns the electrochemical potential with the double donor (c) and triple donor (f) at $V_{sd} = 5$ mV. To emphasize the motion of the resonances at zero bias in an applied magnetic field we have drawn a dashed line through the zero bias 0 T resonant peaks. The down-going and up-going excited states of level B are labeled B^- and B^+ , respectively, and are estimated to be approximately 3.73 ± 0.21 meV below and 2.5 ± 0.023 meV above the ground state, respectively. The dashed lines in (c) and (f) correspond to excited states. In (c) and (f) we have indicated the quasi-Fermi levels in the metal (E_{FM}) and semiconductor (E_{Fsm}) and the attributed state of the Pt impurity at different energies.

due to the electron-electron interactions in the semiconducting density of states.²⁶ From an investigation of the zero-bias suppression we estimate the electron temperature to be ≈ 100 mK. For clarity we have drawn dashed lines corre-

sponding to the zero bias, 0 T peak position in the four graphs. It is clearly observed that in an applied field level A moves to more negative values of V_g , thus toward the valence band, and level B moves to less negative values of V_g ,

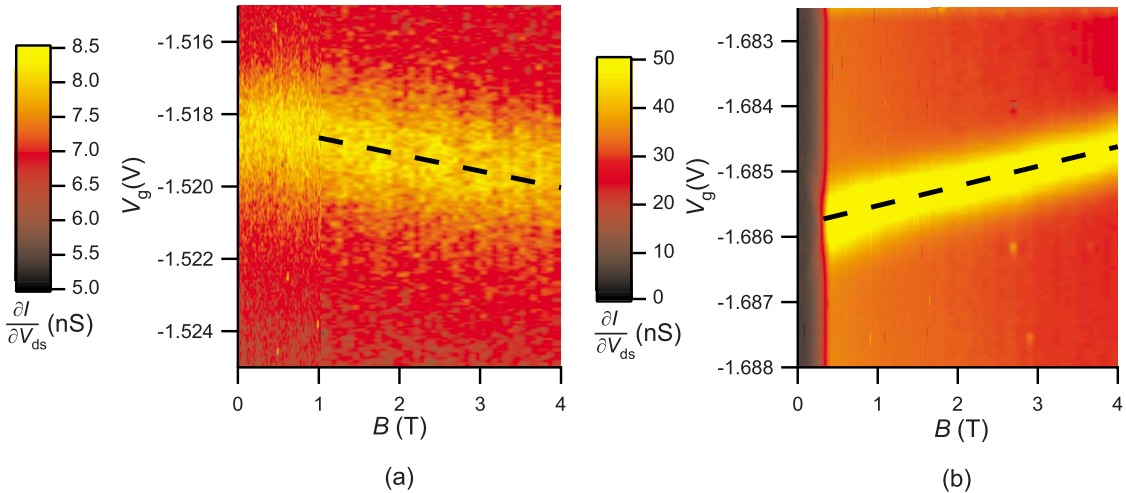


FIG. 3. (Color online) (a) The magnetic-field dependence at $V_{sd} = 0$ V for a level B resonance for device 2. (b) The magnetic-field dependence of the triple donor from Figs. 2(d) and 2(e).

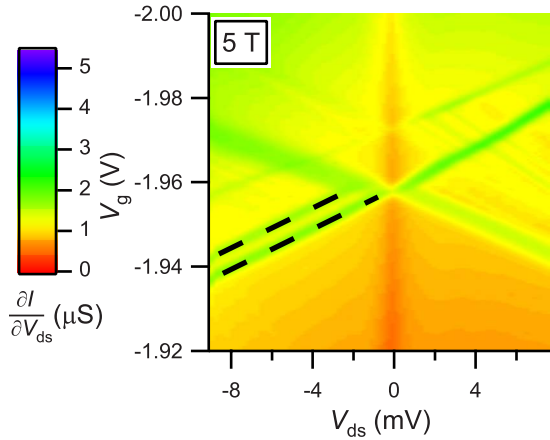


FIG. 4. (Color online) $\partial I / \partial V_{sd}$ versus V_g for many values of V_{sd} at 4.82 T for the peak at $V_g = -1.96$ V. The dotted lines are fits to the maximum peak position and yielded intercepts of $a = -1.9634 \pm 4.18\text{e-}005$ V and $a = -1.9585 \pm 3.87\text{e-}005$ V.

thus away from the valence band. Out of 12 resonances investigated in two devices we have observed five that resemble level A and the remaining resemble level B. In Fig. 3 we plot the zero-bias magnetic-field dependence for a level A and a level B resonance and obtain slopes of $-458 \pm 77 \mu\text{V/T}$ and $306 \pm 6 \mu\text{V/T}$, respectively.

IV. DETAILED ANALYSIS

We have used two methods to carry out a detailed analysis of the magnetic-field dependence of different resonant peaks and their excited states. The simplest and by far the most accurate technique is to plot the peak position versus magnetic field as shown in Fig. 3; however, such data were not taken for all of the peaks and excited states. We therefore describe how the slope was obtained from the three-dimensional (3D) plots of $\partial I / \partial V_{sd}$ versus V_g and V_{sd} at 0 T and 4.82 T.

Finding the peak position at 0 T or at 4.82 T is complicated by the density of states of the superconducting elec-

trode or the semiconducting electrode, respectively.²⁶ The simplest case is when the resonance exhibits a Zeeman splitting, as for the peaks at $V_g = -1.96$ V and $V_g = -2.1051$ V. We then determine the peak position of the two Zeeman split peaks as a function of V_{sd} , extrapolate to zero bias, and determine the spin splitting. This method is depicted in Fig. 4 for the peak at $V_g = -1.96$ V. To check for consistency, we reconsidered the peak located at $V_g = -1.68$ V. As shown in Fig. 7(a), the ground state of this peak shows a clear Zeeman splitting. The method described above results in a slope of $300 \pm 6 \mu\text{V/T}$ consistent with the value obtained in Fig. 3.

When the peak does not exhibit a Zeeman splitting we determine the zero-bias peak position by finding the maximum peak at different values of V_{sd} separately for negative and positive bias directions and at 0 T and 4.82 T. We then average the two intercepts and compare their difference. This technique can lead to a large standard error if the grid of V_{sd} values is sparse. This method was used for the resonances at $V_g = -1.83083$ V, $V_g = -1.8909$ V, and $V_g = -1.9741$ V. One example is shown in Fig. 5 for the $V_g = -1.5$ V peak of device 1.

Excited states of level B are clearly visible in Figs. 2(c) and 2(d) and those that are the easiest to discern are labeled B^- and B^+ indicating that one belongs to an impurity level with one less charge (B^-) or to level B (B^+). To determine the magnetic-field slope of excited state B^- we considered the magnetic-field dependence at $V_{sd} = 6$ mV shown in Fig. 6. We observed a clear Zeeman splitting (ii) that revealed a slope of $333 \pm 23 \mu\text{V/T}$. To determine the magnetic-field slope of the excited state B^+ , we consider the Zeeman splitting at 4.82 T as shown in Fig. 7. Fitting the two peak positions as a function of V_{sd} and extrapolating to zero bias we find a slope of $270 \pm 41 \mu\text{V/T}$.

We report level A like states in 5 out of 12 resonances in two devices and in Table I report the seven resonances observed from device 1. Although Fig. 3(a) shows one of the resonances from device 2, the procedure described here used for determining the slopes of the peak position in magnetic field led to large standard deviations and are thus not reported. We note that the “level B” corresponding to the “level A” peak at $V_g = -1.5$ V in Fig. 3(a) was at $V_g = -1.74$ V.

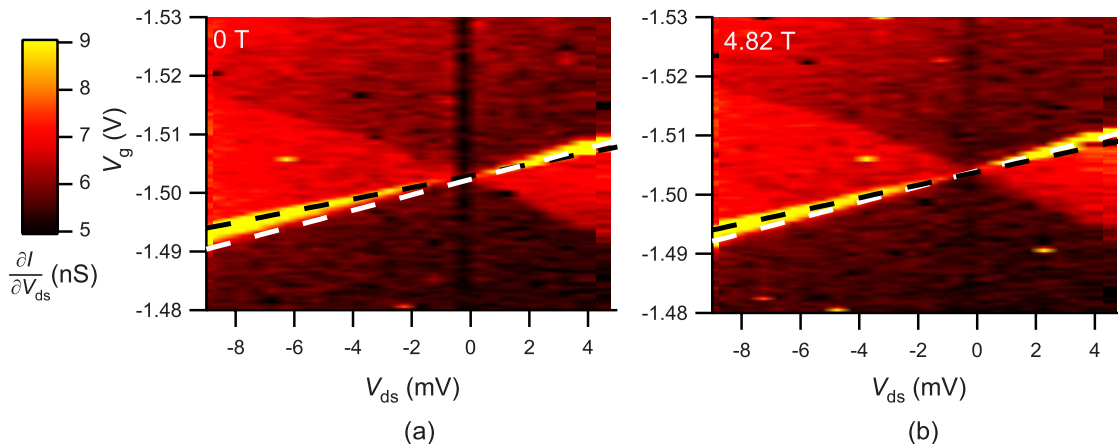


FIG. 5. (Color online) $\partial I / \partial V_{sd}$ versus V_g for many values of V_{sd} at 0 T and 4.82 T of the resonance at $V_g = -1.5026$ V in device 1. The light dashed lines are the fits to the peak position versus positive V_{sd} values and the black lines at negative V_{sd} .

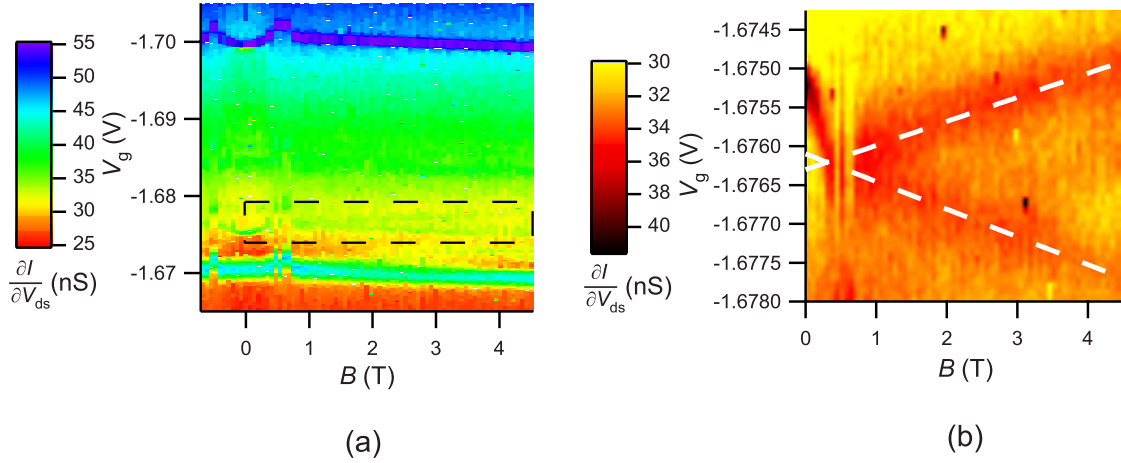


FIG. 6. (Color online) Excited state B^- as a function of magnetic field at $V_{sd}=6$ mV. (a) shows the magnetic-field dependence of the entire bias window and (b) shows a detail of the region indicated in the dotted box in (a), where a Zeeman splitting is observed.

In order to convert V to eV, we use the superconducting gap of PtSi. In semiconductor quantum dots, one typically assumes that one electrode is at ground potential and the other is at V_{sd} . By fitting the slopes in the stability diagrams, one obtains the capacitance between the dot and the electrodes. Here, the main difficulty encountered in converting from V in gate voltage units to eV is that the source-drain voltage is not necessarily dropped only across the Schottky barrier containing the impurity. We are fortunate in that we have another technique based on the superconductivity of the Pt electrode. As shown in Fig. 8, resonances are shifted as the magnetic field is increased. This shift is due to the closing of the superconducting gap. Using the well-known relation $2\Delta(0)=3.5kT_c$, which connects the superconducting gap with the critical temperature (~ 1 K in our samples), the motion of the resonance in V_g units can be directly converted into eV. We find that $\alpha=0.155$ eV/V, which is consistent with the conversion obtained via the temperature dependence of the resonance from earlier research.^{4,5} We observed approximately the same shift for each impurity.

V. DISCUSSION

We have observed both up-going and down-going excited states for both level B and level A resonances implying that these levels are unlikely due to shallow dopants. For level A, the excited states have the same magnetic-field dependence as the ground state and thus cannot be due to a triplet state. We believe that level A is due to the double donor of Pt in a singlet state mainly because of its motion in magnetic field. The large variation in the slope of the peak position versus magnetic field may be due to the position (and distortion) of the impurity in the silicon lattice relative to the magnetic field⁹ and/or to the variation of the electric field from the nearby metal/semiconductor interface.⁷

The magnetic-field dependence and the observation of up-going and down-going excited states indicate that level B may either be due to a triple donor state or a double donor in a *triplet* ground state. In order to explore whether this is a generic trait of impurities observed in PtSi Schottky barrier metal-oxide-semiconductor field-effect transistor (SBMOS-

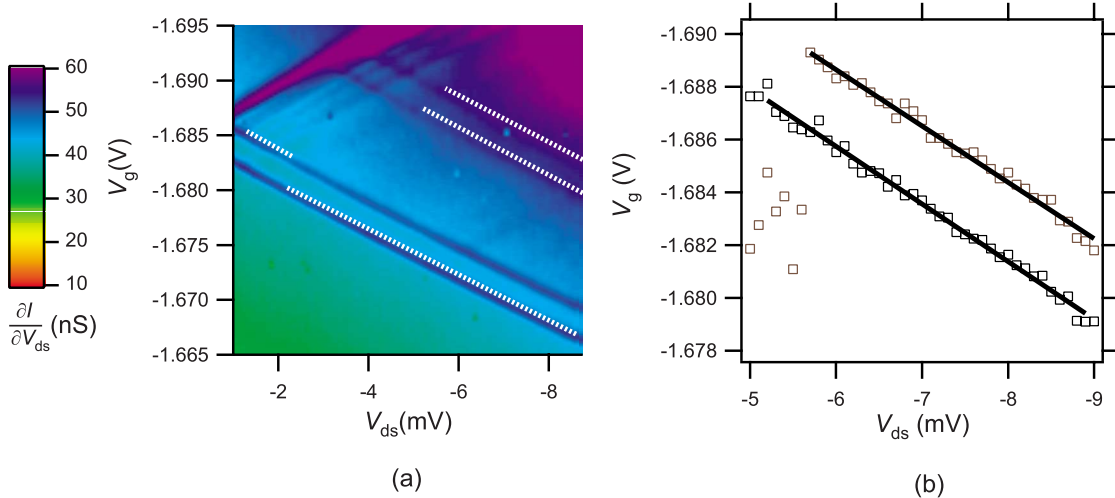


FIG. 7. (Color online) (a) $\partial I/\partial V_{sd}$ versus V_g for many values of V_{sd} at 4.82 T indicating the Zeeman splitting of both the ground state and the excited state B^+ . To check our fit we first found the Zeeman splitting of the ground state, $300 \mu\text{V}/\text{T} \pm 6$ mV, consistent with the dependence at zero-bias voltage. We then considered the splitting of the excited state as shown in greater detail in (b).

TABLE I. Summary of the resonances observed in device 1. We report the peak position, the slope of the peak position/magnetic field and the state we attribute to the impurity. For triple donor states the value in parenthesis is the distance between the double donor and triple donor. While the peak at $V_g = -1.68$ V was obtained by fitting the zero-bias magnetic-field dependence, the other slopes were obtained by extrapolating the peak position versus $\pm V_{sd}$ to 0 V from the 3D plots of the $\partial I / \partial V_{sd}$ as a function of V_{sd} and V_g at 0 T and 4.82 T.

Peak position (V)	Slope ($\mu\text{eV/T}$)	Assignment
-1.5026	-40.5 ± 12.5	DD
-1.68	45.9 ± 0.9	TD (27 meV)
-1.83083	103.1 ± 9.5	
-1.8909	-79.4 ± 2.6	DD
-1.9575	76.2 ± 0.9	TD (10 meV)
-1.9741	51.3 ± 4.4	
-2.1051	72.5 ± 1.2	

FET) inversion layers we consider the trends observed in Table I. We find that level A resonances are often followed by level B resonances. We observe most often sharp resonant peaks for level B, but when level A is well resolved, level B was difficult to distinguish over the background current. As demonstrated in Table I we observe more level B resonances than level A. As V_g is made more negative, resonant peaks are more common and tend to overlap as V_{sd} is increased. It is not clear whether these levels indicate additional charged states of the same impurity or different impurities. Typically a device exhibits either several levels or none at all.

These results indicate that level A and level B correspond to two different levels and are likely related to the same impurity. First, the observation that the two levels are often observed relatively close together and that only one will exhibit a sharp resonance is consistent with the two levels be-

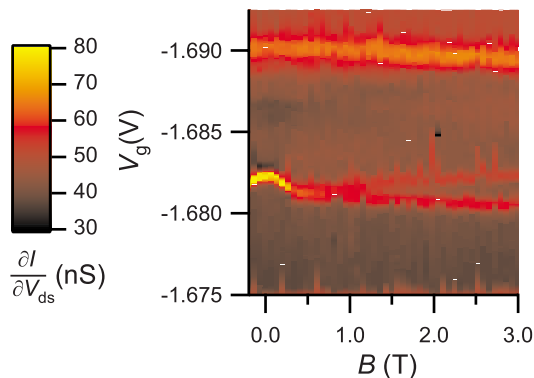


FIG. 8. (Color online) Magnetic-field dependence at $V_{sd} = -3$ mV. The shift in the peak position in electrochemical split peak at $V_g = -1.687$ V is due to the closing of the electrochemical gap. This shift is used to convert from gate voltage to electron voltage.

ing situated at the same distance from the metallic contact. As shown schematically in Fig. 1(b), such levels will experience very different potentials and leak rates. Next, the change in the peak position versus magnetic field indicates that these two levels typically have similar dependencies, even though there is a large variation among different pairs. Further, we note that the magnetic-field dependence of the excited state B^+ cannot correspond to a singlet state. The field dependence of B^- , however, is consistent with it being a high lying triplet state of a double donor with a singlet ground state.

A triple donor state of Pt has never been observed and has not been predicted to exist. The origin of the triple donor state observed here thus requires further theoretical consideration. It could arise from the presence of another impurity atom nearby or from the strong electric fields due to the metal/semiconductor interface or gate electrode.

VI. CONCLUDING REMARKS

We have investigated transport spectroscopy through a nonhydrogenic impurity and shown that excited-state spectroscopy combined with magnetic-field dependence is a powerful tool to identify and explore the energy spectrum of multilevel impurities that contain states not too far from the valence or conduction band. Such levels can be difficult to detect using standard techniques like deep-level transient spectroscopy. We have shown how one can distinguish shallow hydrogeniclike impurities from multilevel ones and observed simple Pauli spin filling in a transition-metal atom containing three electrons. The transport observed here might be correlated with room-temperature measurements to further understand how sources of defects²⁷ or how inhomogeneous Schottky barriers can affect device behavior at room temperature.²⁸

More importantly, these results suggest a possible new pathway for quantum computing. In particular, we expect that in rare-earth silicide SBMOSFETs (Ref. 29) rare-earth atoms may introduce similar multilevel resonances near the metal/semiconductor contact and should be distinguishable from shallow impurities. Rare-earth impurities are typically found in a similar +3 oxidation state in many host materials.^{30–34} In this configuration the $4f$ electrons can be considered either completely screened³² or strongly localized³³ by the $5s$ and $5p$ orbitals so that their atomiclike properties are often maintained. The secondary effects of the crystal field lower the symmetry of the multifold degenerate states and give rise to the possibility of creating rare-earth qubits.³⁴ Such levels may provide the possibility of realizing rare-earth solid-state qubits in silicon devices that can be manufactured using current silicon technology.

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