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3D Imaging and Manipulation of Subsurface Selenium Vacancies in PdSe$_2$

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Two-dimensional materials such as layered transition-metal dichalcogenides (TMDs) are ideal platforms for studying defect behaviors, an essential step towards defect engineering for novel material functions. Here, we image the 3D lattice locations of selenium-vacancy V$_{Se}$ defects and manipulate them using a scanning tunneling microscope (STM) near the surface of PdSe$_2$, a recently discovered pentagonal layered TMD. The V$_{Se}$ show a characteristic charging ring in a spatially resolved conductance map, based on which we can determine its subsurface location precisely. Using the STM tip, not only can we reversibly switch the defect states between charge neutral and charge negative, but also trigger migrations of V$_{Se}$ defects. This allows a demonstration of direct “writing” and “erasing” of atomic defects and tracing the diffusion pathways. First-principles calculations reveal a small diffusion barrier of V$_{Se}$ in PdSe$_2$, which is much lower than S vacancy in MoS$_2$ or an O vacancy in TiO$_2$. This finding opens an opportunity of defect engineering in PdSe$_2$ for such as controlled phase transformations and resistive-switching memory device application.

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Vacancy defects play a significant role in determining the physical properties of crystalline materials. Most notably, a charge neutral vacancy (V$^0$) can capture an electron (V$^-$) or emit an electron (V$^+$) to become charge states, and each of these states will introduce a different type of dopant in semiconductors. Understanding vacancy behaviors constitutes a significant step in defect engineering that not only modifies the conductance of semiconductors, but also enables novel material functions ranging from high-spin states, such as nitrogen-vacancy centers in diamond [1], ionic diffusion paths enabled by oxygen vacancies in perovskite [2], and catalytic sites introduced by sulfur vacancies in MoS$_2$ [3]. Therefore, controlling vacancy defects, especially the ability of reversibly manipulating vacancies at the atomic level, has become a promising approach to defect engineering and novel material functions [4–8]. As an example, Yang et al. demonstrated a memristor operation by controlling the migration of oxygen vacancy in TiO$_2$ under an applied electric field, but the precision of control was limited to the size of the device on a 50 nm scale [2]. Using a scanning tunneling microscope (STM) tip, Setvín et al. were able to pull oxygen vacancies to the surface with a high bias voltage (∼5 V) to alter the surface properties of TiO$_2$ [9], but a reversible process remains to be demonstrated. Recently, the advent of 2D materials have attracted great research interest on vacancy defects in graphene and transition-metal dichalcogenites (TMDs) [3,10,11]. For example, Sangwan et al. reported a gate-tunable memristive behavior based on control of defect migration at the grain boundary in MoS$_2$ [12]. However, there has been no report on atomic control of the vacancy diffusion process in 2D materials.

PdSe$_2$, a newly discovered pentagonal TMD [13–16], has recently attracted vibrant research interest due to the extraordinary high carrier mobility [13] and air stability [15], which are desirable for 2D electronic applications. In contrast to the frequently reported hexagonal phases in layered TMDs, PdSe$_2$ has an uncommon pentagonal network with a puckered lattice structure. Each PdSe$_2$ slab consists of a Se-Pd-Se trilayer, where each Pd atom is bonded to four Se atoms located on the top and bottom sublayers [15], as illustrated in Fig. 1(a). The two Se atoms located in the top and bottom sublayers form a tilted Se-Se dumbbell crossing the Pd layer, resulting in a lack of rotational symmetry. Such structure is potentially sensitive to defects, as Se vacancy V$_{Se}$ would break the symmetry of the Se-Se dumbbell and induce large structural distortion [14]. This contrasts with the commonly observed layered hexagonal TMDs, where the lattice remains intact even at a relatively high concentration of chalcogen vacancy [17].

In this Letter, we report on imaging and manipulation of individual Se vacancies V$_{Se}$ in PdSe$_2$ using a STM. By imaging the characteristic charge rings of defects arising from a tip-induced band bending (TIBB) effect...
controlled phase transformations [14,23] or new material manipulate substrate the use of a STM tip as a movable electrostatic gate to square network with lattice constants of \( a \approx 0.575 \text{ nm} \) and \( b \approx 0.587 \text{ nm} \) [28], and its in-plane unit cell is very close to the square network shown in Fig. 1(b) after considering experimental uncertainty. Figure 1(c) shows the measured \( dI/dV \) spectrum on PdSe\(_2\) at 0.9 V, \( I = 3 \text{ nA} \), \( V_{\text{dc}} = 10 \text{ mV} \), \( f = 1000 \text{ Hz} \), \( T = 120 \text{ K} \).

Here, we study the behaviors of individual defects by visualizing and manipulating \( V_{\text{Se}} \) defects in bulk PdSe\(_2\) with a STM. PdSe\(_2\) single crystals were synthesized by a self-flux method as previously reported [15]. A bulk crystal of PdSe\(_2\) was cleaved along the [001] direction in situ in ultrahigh vacuum at room temperature. Figure 1(b) shows a typical STM image of a cleaved PdSe\(_2\) surface. The atomically resolved STM image [upper inset of Fig. 1(b)] shows a square network with lattice constants of \( 0.58 \pm 0.01 \text{ nm} \) and bright spots visualizing the Se atoms on the topmost sublayer. A simulated image [lower inset of Fig. 1(b)] is in excellent agreement with the STM image, corroborating this interpretation. PdSe\(_2\) has an orthorhombic unit cell with in-plane lattice constants of \( a \approx 0.575 \text{ nm} \) and \( b \approx 0.587 \text{ nm} \) [28], and its in-plane unit cell is very close to the square network shown in Fig. 1(b) after considering experimental uncertainty. Figure 1(c) shows the measured \( dI/dV \) spectrum (red curve) with a band gap of 0.06 ± 0.02 eV (see Supplemental Material, Fig. S1 for more details [29], with Refs. [30–32]). This measured band gap is corroborated by calculated density of states (DOS) [black curve in Fig. 1(c)] using density-functional theory with the many-body GW approximation. Individual \( V_{\text{Se}} \) defects on PdSe\(_2\) can be visualized by STM images. Defects on the top surface are shown as dark holes, which indicates the missing of Se surface atoms [blue circles in Fig. 1(b)]. This observation confirms the existence of \( V_{\text{Se}} \) in PdSe\(_2\) as reported previously [14]. The \( V_{\text{Se}} \) introduces unoccupied in-gap states (Fig. S2), which can be revealed as alternative dark and bright contrast when varying sample bias from positive to negative values (see Fig. S3 for more details [29]).

We now examine \( V_{\text{Se}} \) defect behaviors. Figure 2(a) shows a STM topographic image on an area with 11 \( V_{\text{Se}} \) defects labeled numerically. In the spatially resolved differential conductance \( dI/dV \) maps [Figs. 2(b)–2(f)], these defects appear as a ringlike feature in the sample bias range of 0.9–0.4 V. At a constant bias voltage below

![Image of STM image showing Se vacancies in PdSe_2](image)

**FIG. 1.** Probing the structure and band gap on PdSe\(_2\) surface. (a) Sketch of the crystallographic structure of PdSe\(_2\) with the purple and yellow spheres representing the Pd and Se atoms, respectively. \( L1_a, L1_b, \ldots \) define Se sublayers along the [001] direction where the Se top surface layer is counted as layer \( L1_a \). (b) A typical STM topographic image of PdSe\(_2\), blue circles indicate some \( V_{\text{Se}} \) defects (sample bias \( V_s = -1.0 \text{ V} \), tunneling current \( I = 50 \text{ pA} \), temperature \( T = 120 \text{ K} \)). The inset in (b) shows the atomically resolved STM image (top right corner, Fourier filtering was applied to enhance the contrast) and simulated image (bottom right corner) of PdSe\(_2\) at 0.3 V. (c) \( dI/dV \) spectrum on PdSe\(_2\) in comparison with theoretical DOS of PdSe\(_2\) ( \( V_s = -0.9 \text{ V} \), \( I = 3 \text{ nA} \), \( V_{\text{dc}} = 10 \text{ mV} \), \( f = 1000 \text{ Hz} \), \( T = 120 \text{ K} \)).

[4–8,18–22], we first determine the 3D lattice locations of \( V_{\text{Se}} \) precisely in the subsurface region. We then demonstrate the use of a STM tip as a movable electrostatic gate to manipulate \( V_{\text{Se}} \) by reversibly switching the charge states of defects between neutral \( V^0 \) and negative \( V^- \) states. We find a relatively small bias voltage (~2.0 V) at the STM tip can be used to trigger vacancy migrations, which allows us to demonstrate both direct writing and erasing of atomic defects in PdSe\(_2\) while tracing their diffusion pathways. The results are corroborated by first-principles calculations that reveal the formation energies and diffusion barriers of Se vacancies in PdSe\(_2\). This work opens an opportunity for defect engineering in PdSe\(_2\) at the atomic level to achieve controlled phase transformations [14,23] or new material functions such as resistive-switching memory [12,24–27].

Here, we study the behaviors of individual defects by visualizing and manipulating \( V_{\text{Se}} \) in bulk PdSe\(_2\) with a STM. PdSe\(_2\) single crystals were synthesized by a self-flux method as previously reported [15]. A bulk crystal of PdSe\(_2\) was cleaved along the [001] direction in situ in ultrahigh vacuum at room temperature. Figure 1(b) shows a typical STM image of a cleaved PdSe\(_2\) surface. The atomically resolved STM image [upper inset of Fig. 1(b)] shows a square network with lattice constants of \( 0.58 \pm 0.01 \text{ nm} \) and bright spots visualizing the Se atoms on the topmost sublayer. A simulated image [lower inset of Fig. 1(b)] is in excellent agreement with the STM image, corroborating this interpretation. PdSe\(_2\) has an orthorhombic unit cell with in-plane lattice constants of \( a \approx 0.575 \text{ nm} \) and \( b \approx 0.587 \text{ nm} \) [28], and its in-plane unit cell is very close to the square network shown in Fig. 1(b) after considering experimental uncertainty. Figure 1(c) shows the measured \( dI/dV \) spectrum (red curve) with a band gap of 0.06 ± 0.02 eV (see Supplemental Material, Fig. S1 for more details [29], with Refs. [30–32]). This measured band gap is corroborated by calculated density of states (DOS) [black curve in Fig. 1(c)] using density-functional theory with the many-body GW approximation. Individual \( V_{\text{Se}} \) defects on PdSe\(_2\) can be visualized by STM images. Defects on the top surface are shown as dark holes, which indicates the missing of Se surface atoms [blue circles in Fig. 1(b)]. This observation confirms the existence of \( V_{\text{Se}} \) in PdSe\(_2\) as reported previously [14]. The \( V_{\text{Se}} \) introduces unoccupied in-gap states (Fig. S2), which can be revealed as alternative dark and bright contrast when varying sample bias from positive to negative values (see Fig. S3 for more details [29]).

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**FIG. 2.** Imaging Se-vacancy defects and switching charge state of the defects in PdSe\(_2\). (a) STM topographic image showing \( V_{\text{Se}} \) defects as dark disks and labeled as \( V1 \) to \( V11 \) (\( V_s = 0.5 \text{ V} \), \( I = 50 \text{ pA} \), \( T = 120 \text{ K} \)). (b)–(f) The evolution of measured differential conductance \( dI/dV \) map as a function of sample bias, showing defects located on different lattice layers as rings of different diameters. (g) The dependence of ring diameter as a function of sample bias for 11 defects. (h) A sketch of the lateral tip-induced band bending on the sample below the STM tip showing the switch of charge neutral \( V^0 \) to negative state \( V^- \). (i) A sketch of depth-dependent band bending of conduction band (CB), valence band (VB), and defect state (\( E_D \)) below the tip position.
the threshold, a higher tunneling current leads to a larger ring (Fig. S4 [29]). This result indicates that the ring size actually varies with the tip-sample distance in which a farther separation results in a smaller ring [Fig. S4(i)]. These observations suggest that the ring features in $dI/dV$ maps do not correlate with the local DOS; instead, they can be explained as defect charge states due to the TIBB effect [33]. Similar features were previously observed in doped semiconductors GaAs [34] and InAs [18], Co-adatoms in graphene [35], vacancies in black phosphorous [22], and Fe dopants in Bi$_2$Se$_3$ [36]. The switch of charge state gives rise to the ring feature in $dI/dV$ maps, which occurs at a specific voltage when the dopant level crosses the bulk Fermi level [Fig. 2(b)] [18,22,34]. In such a process, larger rings are expected for a smaller sample bias and smaller tip-sample separation (larger TIBB). Therefore, depending on the sample bias, the STM tip can switch reversibly the charge states of an individual $V_{\text{Se}}$ defect in PdSe$_2$ between $V^0$ and $V^-$ (Fig. S5 [29]).

Figure 2(g) shows the change of ring diameter as a function of the sample bias voltage for the 11 defects labeled in Fig. 2(a). The charging rings become smaller as bias voltage approaches the threshold, corroborating a TIBB process. At the same bias voltage, different ring sizes indicate the different depths of these defects from the surface of PdSe$_2$. The defects located at a deeper layer have smaller TIBB [Fig. 2(i)], and thus their rings are smaller. Moreover, defects deeper below the surface have a lower charging threshold, which is clearly seen in the $dI/dV$ maps shown in Figs. 2(b)–2(f). Based on this information, we can assign $V_{\text{Se}}$ defects to individual Se sublayers, as shown in Figs. 2(b)–2(g), although the assignment for deeper than the third layer (L3) is less accurate due to the limit of statistical data. The onset voltage of charging ring of defects in the two sublayers at two PdSe$_2$ slabs is almost the same, e.g., 0.9 V for L1$_a$ and L1$_b$, 0.7 V for L2$_a$ and L2$_b$, and 0.6 V for L3$_a$ and L3$_b$. This is simply because the distance between two Se sublayers in one PdSe$_2$ slab is smaller compared to the distance between two adjacent Se sublayers at two PdSe$_2$ slabs [15]. Therefore, the STM tip not only allows us to reversibly switch the charge state of a $V_{\text{Se}}$ defect, but also enables us to identify the location of the defects in the subsurface atomic lattice. It provides us a capability for precise 3D imaging of individual defects in a crystalline lattice, especially in 2D layered materials where their atomic layers are well separated.

We now try to manipulate $V_{\text{Se}}$ by changing its lattice locations with the STM tip. Figure 3(a) shows three $V_{\text{Se}}$ located, respectively, on lattice layers L1$_a$, L2$_b$, and L3$_d$ according to the sizes of their charge rings and voltage thresholds (the complete set of $dI/dV$ maps at different biases is shown in Fig. S6). A new $V_{\text{Se}}$ defect emerges on layer L2$_a$, as shown in Fig. 3(b), after scanning the area with a high negative sample bias ($-1$ V with a tunneling current of 50 pA). We believe that the STM tip at negative sample bias triggers $V_{\text{Se}}$ migration to underneath the tip during scanning, as illustrated in Fig. 3(c). This hypothesis is corroborated with a controlled experiment. Figure 3(d) is a STM image acquired at a normal condition of $V_s = 0.5$ V, $I = 50$ pA, showing $V_{\text{Se}}$ defects as dark spots. The same area of the PdSe$_2$ surface is then treated by STM scanning with a high negative bias at $-2$ V, 50 pA. Figure 3(e) is then acquired with the normal condition, which contains new $V_{\text{Se}}$ defects in the sample area, as marked by dashed blue circles. Most of these defects disappear after a reverse treatment with a high positive sample bias (1 V, 50 pA), as marked by dashed black circles in Fig. 3(f). This kind of tip-induced vacancy “writing and erasing” process is similar to that observed recently in oxygen vacancies $V_{\text{O}}$ in TiO$_2$ [9,37], although a significantly higher bias (5.2 V) was required for moving $V_{\text{O}}$ and only the writing process was demonstrated in TiO$_2$ with the STM tip. It is noted that the field-induced migration of $V_{\text{O}}$ in metal oxides is already applied in novel resistive memory device applications [2,27]. Our result shows that 2D materials like PdSe$_2$ can be next generation materials for the memory device with much lower energy consumption and higher efficiency.

To understand the tip-induced $V_{\text{Se}}$ migration in PdSe$_2$, we calculated the energy barriers for $V_{\text{Se}}$ diffusion between two layers (interlayer) or within the same layer (intralayer) using the climbing image nudged elastic band method [38]. The nudged elastic band method finds saddle points and minimum energy paths between the initial and final states, by optimizing a number of intermediate images along the reaction path (see more details in the Supplemental Material [29], with additional Refs. [38–43]). The four possible configurations for $V_{\text{Se}}$ positions (marked with red
circles) are sketched and labeled as A, B, C, and D in Fig. 4(a). The corresponding energy barriers for the diffusion of a $V_{\text{Se}}$ between these configurations are shown in Fig. 4(b). The relaxed atomic structures for these four configurations and the corresponding transition states are shown in Fig. S7 [29]. The energy barrier is 1.59 eV for the interlayer $V_{\text{Se}}$ diffusion from configuration A to B. In comparison, we performed a similar calculation for S vacancy $V_{\text{S}}$ in MoS$_2$ and find a much higher barrier of 4.44 eV for the similar interlayer $V_{\text{Se}}$ diffusion in MoS$_2$. This significant difference can be attributed to the fact that the interlayer binding energy in PdSe$_2$ is notably larger than that in MoS$_2$, and the average interlayer distance in PdSe$_2$ is much shorter than that in MoS$_2$ [15,44,45]. Furthermore, for the intralayer $V_{\text{Se}}$ diffusion in PdSe$_2$ from configuration C to D, the energy barrier is computed to be around 1 eV, which is also much lower than the barrier (2.30 eV) for the corresponding intralayer $V_{\text{S}}$ diffusion in MoS$_2$ [46]. Compared to hexagonal MoS$_2$, the unique pentagonal network with relatively weaker covalent bond strength in PdSe$_2$ facilitates the $V_{\text{Se}}$ migration. Finally, almost no barrier (0.03 eV) exists for the intralayer $V_{\text{Se}}$ diffusion from configuration B to C, i.e., from the bottom Se sublayer to the top Se sublayer [Fig. 4(a)], due to the covalent bond between these two Se atoms (also see Fig. S7 [29]). In short, unlike the well-known MoS$_2$, the $V_{\text{Se}}$ diffusion in PdSe$_2$ is considerably easier. This is consistent with an additional experiment where we find that $V_{\text{Se}}$ can easily diffuse both vertically and laterally in the PdSe$_2$ at room temperature, even when scanning at relatively low sample bias of 0.4 V (Fig. S8). Thus, a STM tip can be used both to trigger vacancy migration and to trace the pathways of vacancy diffusion. However, in our experiment, we often observed the diffusion of a Se vacancy in about 10 nm. It must consist of multiple movement steps.

In conclusion, we have shown how a STM can be used for 3D imaging and manipulation of individual $V_{\text{Se}}$ defects in PdSe$_2$. The $V_{\text{Se}}$ is shown as a circular ring feature in a spatially resolved conductance map whose diameter changes in response to a TIBB effect. Based on the behaviors of this charging ring, the subsurface lattice location of $V_{\text{Se}}$ can be precisely determined. The TIBB can be further utilized to reversibly switch the defect from charge neutral to charge negative states. Moreover, the electrical field from a STM tip can induce migrations of vacancies, which allows direct writing and erasing of atomic defects and tracing the diffusion pathways of $V_{\text{Se}}$. The diffusion kinetic barrier of $V_{\text{Se}}$ in PdSe$_2$ is much lower than $V_{\text{O}}$ in TiO$_2$ or $V_{\text{S}}$ in MoS$_2$, paving the way for manipulating the $V_{\text{Se}}$ in PdSe$_2$ in defect engineering for novel functionalities, such as controlled phase transformations [14,23] and memory device application [12,24–27].

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