Direct Cation Exchange in Monolayer MoS$_2$ via Recombination-Enhanced Migration

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In addition to their unique optical and electronic properties, two-dimensional materials provide opportunities to directly observe atomic-scale defect dynamics. Here we use scanning transmission electron microscopy to observe substitutional Re impurities in monolayer MoS$_2$ undergo direct exchanges with neighboring Mo atoms in the lattice. Density-functional-theory calculations find that the energy barrier for direct exchange, a process that has only been studied as a diffusion mechanism in bulk materials, is too large for either thermal activation or energy directly transferred from the electron beam. The presence of multiple sulfur vacancies next to the exchanged Re-Mo pair, as observed by electron microscopy, does not lower the energy barrier sufficiently to account for the observed atomic exchange. Instead, the calculations find that a Re dopant and surrounding sulfur vacancies introduce an ever-changing set of deep levels in the energy gap. We propose that these levels mediate an "explosive" recombination-enhanced migration via multiple electron-hole recombination events. As a proof of concept, we also show that Re-Mo direct exchange can be triggered via controlled creation of sulfur vacancies. The present experimental and theoretical findings lay a fundamental framework towards manipulating single substitutional dopants in two-dimensional materials.

Two-dimensional materials exhibit unique properties that can be used for novel applications, but just as is the case with semiconductors, it is usually necessary to introduce impurities to achieve desirable functionalization. "Defect engineering" raises many challenges and holds many promises. It has been demonstrated that aberration-corrected scanning transmission electron microscopy (STEM) provides atomic-resolution images [1–6] that can be used to track impurity atoms in both two- and three-dimensional materials and can directly monitor the defect reactions that enable defect engineering. More recently, Lin *et al.* used the electron beam of a STEM to sculpt and simultaneously image nanowires that are only three atoms wide in transition-metal dichalcogenide monolayers [7]. Ishikawa *et al.* reported the direct observation of the migration of Ce and Mn dopant-atoms in a bulk AlN crystal [8]. Han *et al.* reported observations of migrating iridium adatoms and tri-iridium clusters on MgO surfaces [9]. Susi *et al.* reported the observation of silicon dopants in graphene undergoing beam-induced direct interchange with neighboring C atoms [10], a key step towards the control of single dopant atoms [11,12]. All these investigations show that STEM is a powerful tool for studying local atomic movements.

In general, thermal diffusion of substitutional impurities is mediated by native defects such as vacancies and self-interstitials [13]. These processes are well understood and are used widely to model dopant diffusion for engineering applications [14]. The direct exchange between a substitutional impurity and a neighboring host atom has been discussed in the literature going back to the 1940s [15–18], but the energy barrier for such a process is generally believed to be too large. In 1986, Pandey [18] predicted that the energy barrier for direct exchange (he called it concerted exchange) for self-diffusion in Si is comparable to the activation energy for self-diffusion mediated by vacancies or self-interstitials, but verification of such prediction has been lacking. In only one case, namely, boron-doped copper, direct exchange was indirectly established by ruling out defect-mediated mechanisms [19]. So far, the only atomic-scale observation of direct exchange was the inversion of Si-C bonds in graphene, first reported by Susi *et al.*, where they describe a process induced by momentum transferred from the incident electron beam [10]. However, it is likely that other mechanisms also play a role for semiconducting materials.

In this Letter, we report the experimental observation of direct exchange between substitutional Re and Mo host atoms in monolayer MoS_2 by monitoring Re atoms in atomically resolved STEM images. Density-functional theory (DFT) has been employed to investigate several possible pathways for the direct exchange. We find that the exchange barrier is initially very large (~ 11 eV), but it is lowered by surrounding the cation with sulfur vacancies, which create extra space and weaken the local bonding. However, even with six sulfur vacancies surrounding a Re atom, the calculated exchange barrier is only reduced to ~ 2.4 eV. This value is still much higher than the maximum energy, 1.45 eV, transferred to Mo atoms (or 0.75 eV transferred to Re atoms) by the 60 kV electron beam for a single elastic collision and too high to occur efficiently at room temperature. DFT calculations suggest an alternative energy-transfer mechanism as follows. The hydrogenic level of an isolated substitutional Re impurity becomes deeper and deeper with larger and larger displacements of the Re atom. Moreover, when sulfur vacancies are introduced, additional deep levels appear in the energy gap, so that the gap contains several deep levels that constantly move up and down and appear and disappear as sulfur vacancies come and go. These dynamic energy levels provide multiple paths for the recombination of beam-generated electron-hole pairs. The energy released by these explosive recombination events is transferred to local vibrations that ultimately enable the direct exchange of Re dopants as observed in STEM. The required spectator sulfur vacancies make it possible to control the diffusion process through controlled creation of sulfur vacancies as we show in a proof-of-concept experimental demonstration.

The monolayer Re-doped MoS_2 sample used in our experiments was grown on a SiO_2/Si substrate using a chemical vapor deposition method with molybdenum oxide, sulfur, and ammonium perrhenate powders as Mo, S, and Re sources, respectively [20]. The as-grown sample was transferred onto a TEM grid and the STEM imaging was performed with an aberration-corrected scanning transmission electron microscope operated at 60 kV using the medium angle annular dark field (MAADF, inner angle 50 mrad, outer angle 300 mrad) imaging mode with a beam current of about 9 pA.

Electron microscopy characterization reveals that Re dopants are substitutional in the MoS_2 lattice [20]. The intensity in MAADF images is roughly proportional to Z^{2-x}, where Z is the atomic number and x is a fractional number depending on the exact experimental parameters [5]. The STEM images in Fig. 1 show that single Re atoms occupy Mo sites in the hexagonal MoS_2 lattice and they appear as bright spots in the MAADF image. Although double Mo atoms (i.e., a surface Mo adatom on top of a lattice Mo atom) have a similar MAADF image contrast as that from a substituted Re atom, they can be easily
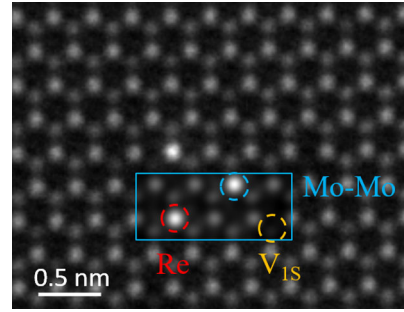

FIG. 1. Comparison between experimental and simulated STEM-MAADF images. The simulated MAADF image (indicated by the blue rectangle) is superimposed on top of the experimental image. Substitutional Re site, double Mo column, and single S vacancy (V_{1S}) are highlighted by red, blue, and orange, respectively, in the simulated image.

identified in experiment, as adsorbed Mo adatoms hop around easily under electron beam irradiation [21]. The stable configurations of the bright cation before and after direct exchange, therefore, rule out the possibility that these features are due to surface Mo adatoms, and the good agreement between the simulated image intensities with the experimental MAADF image verifies that the brightest features in the experimental MAADF images are substitutional Re atoms (Fig. 1).

In addition to the observation of substitutional Re dopants in the MoS_2 lattice, a Re-Mo exchange event is identified by analyzing the recorded sequential MAADF images in areas where Re dopants are isolated. The exchange process is illustrated by the different Re positions in the MAADF images recorded at time t_0 and $t_0 + 3.5$ s as shown in Fig. 2, where the Re atom exchanged positions with a neighboring Mo atom. In the images that document the exchange event [Figs. 2(a) and 2(b)], we observe several sulfur vacancies. The number and arrangements of sulfur vacancies before and after the exchange event are different. It is inferred that sulfur vacancies may play a role in the Re-Mo exchange. The contribution of sulfur vacancies will be further investigated using theoretical calculations as described in the following paragraphs. Mo vacancies were not observed during the cation exchange.

In order to elucidate the mechanism for the Re-Mo exchange process and the pertinent activation energy, we performed systematic DFT calculations using the projector augmented wave method [22,23], as implemented in the Vienna *ab initio* simulation package (VASP) [24–26]. Total energies were obtained in the generalized gradient approximation using the PBE functional formulated by Perdew, Burke, and Ernzerhof [27]. For Mo, S, and Re atoms, Mo-$4p$, $4d$, and $5s$, S-$3s$, and $3p$, and Re-$5p$, $5d$, and $5s$ states were treated as valence states. A cutoff energy of 500 eV was used in all calculations. We used a 7×7 supercell with a $2 \times 2 \times 1$ Monkhorst-Pack k-point mesh.
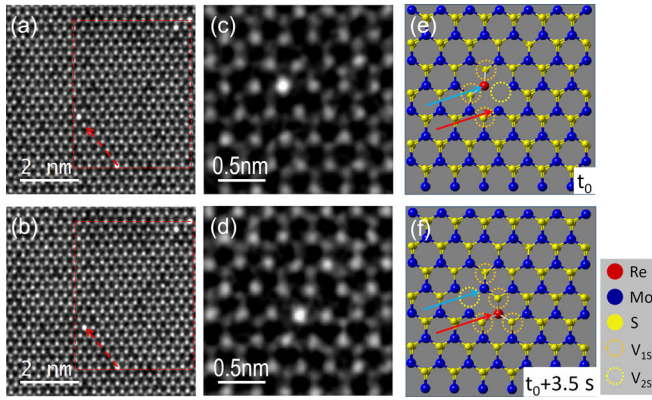
FIG. 2.   Direct Re-Mo exchange in Re-doped monolayer MoS_2. (a),(c) STEM-MAADF images showing the position of the Re relative to other Re atoms (a) and (c) the local area of Re-doped MoS_2 with the corresponding structural model (e), recorded at time t_0 before the exchange event. (b),(d) STEM-MAADF images showing the position of the Re relative to other Re atoms (b) and (d) the local MAADF image with the corresponding structural model (f) recorded after the exchange event at $t_0 + 3.5$ s. The exchange of Re and Mo atoms is highlighted by blue and red arrows, while sulfur monovacancies are indicated by orange dashed circles and sulfur double vacancies are indicated by yellow dashed circles. Re atoms are in red, Mo in blue, and sulfur in yellow.

The Re-Mo exchange barrier was calculated in the presence of different numbers of sulfur vacancies.

To determine migration barriers, we used the nudged elastic band method implemented within density-functional theory. In the calculations, three migration pathways (see Fig. S1 [20]) were considered, with the initial and final cation configurations derived from the experimental MAADF images. The Re-Mo direct-exchange barrier as a function of the number of sulfur vacancies (V_S) is shown in Fig. 3(a). The Re-Mo exchange barrier is calculated to be

~11 eV when there are no neighboring sulfur vacancies. The barrier drops significantly with increasing numbers of vacancies, but even with six sulfur vacancies, the exchange barrier is still 2.4 eV, which is larger than the possible energy transfer from the 60 keV electron beam to Mo and Re atoms (1.45 and 0.75 eV, respectively; see Fig. S2 [28]). Obviously, the sulfur vacancies surrounding the Re and Mo sites provide more space for the exchange and weaken the binding with surrounding Re and Mo atoms.

Because of the limited energy transfer from electron beam bombardment in elastic collisions (Fig. S2 [20]), other energy transfer mechanisms for triggering the exchange need to be explored. It has long been known that, in semiconductors under nonequilibrium conditions, defect migration can be enhanced by electronic processes [30]. More specifically, under electron or laser irradiation, large concentrations of electron-hole pairs are present. If a defect has localized energy levels in the gap, these levels can mediate electron-hole recombination: an electron in the conduction band is first captured at the defect level and subsequently annihilates a hole in the valence bands. In each of the two steps, the energy is dissipated to local vibrations that enhance the migration rate. Each recombination event transfers an amount of energy that is equal to or larger than the band gap. The transfer of the electron-hole recombination energy to defect-atom vibrations is instantaneous (electronic-transition timescale), while its effect on the defect, i.e., the exchange process, occurs in phonon timescales. The phenomenon is extremely fast, as documented by experimental observations of boron and silicon-interstitial migration in Si at 20 K [31]. In the 1980s, several cases of such recombination-enhanced defect migration (REDM) processes were explained in detail by theoretical calculations [32–39]. The most intriguing one is the case of the Si self-interstitial, which, in the presence of electron-hole pairs, migrates with an
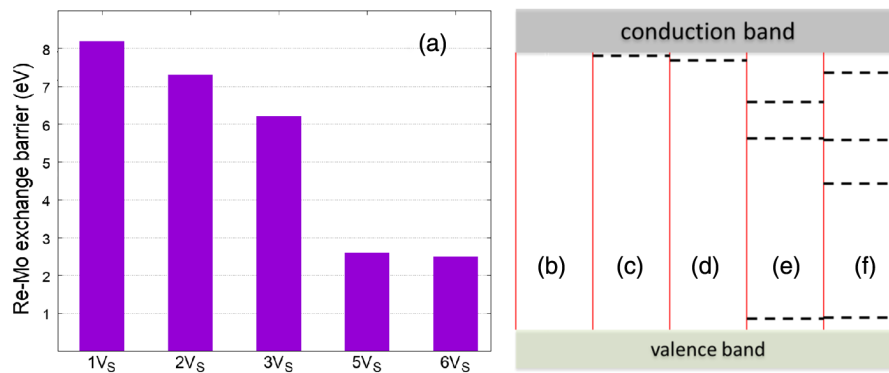

FIG. 3.   Energy barriers for Re-Mo exchange in the presence of sulfur vacancies and defect energy levels of Re-doped MoS_2. (a) The calculated Re-Mo exchange migration barriers in the presence of different numbers of sulfur vacancies. (b)–(f) defect energy levels (at Γ) in the gap region of Re-doped monolayer MoS_2. (b) The energy gap of perfect MoS_2. (c) The defect energy level of a single substitutional Re in MoS_2. (d) The defect energy level of a Re dopant atom when the atom is displaced by 0.2 Å. (e) Defect energy levels of a Re atom displaced by 0.2 Å with a nearby sulfur vacancy. (f) Defect energy levels of Re atom displaced by 0.6 Å with two nearby sulfur vacancies.
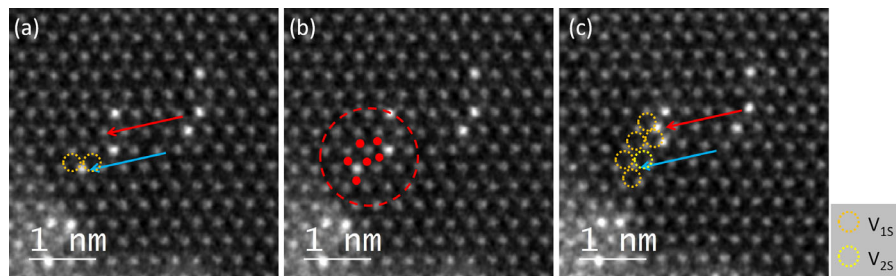
FIG. 4. Controllable Re-Mo exchange triggered by controlled creation of sulfur vacancies around the selected Re and Mo atoms. (a), (c) The STEM-MAADF images before and after the controlled scanning. The atomic positions in exchange are highlighted by the yellow and red arrows. (b) Illustrates the region scanned by the electron beam and the sulfur sites where the electron beam was parked. Related sulfur vacancies are highlighted by orange (V_{1S}) and yellow (V_{2S}) dashed circles in (c).

effective zero barrier (athermal migration) [17,39]. The combination of those reports with our observations motivated us to propose the dynamically changing defect levels to mediate direct exchange.

In order to explore the REDM mechanism for the Re-Mo direct exchange in MoS_2, we performed a series of calculations of defect energy levels. Typical results are shown in Fig. 3. In Fig. 3(b), a clean band gap for the pure MoS_2 is shown. When one Re substitutional impurity is included, one shallow donor level is found below the conduction band minimum as shown in Fig. 3(c). If the Re atom is displaced by 0.2 Å (these are representative small displacements that may be induced by the transfer of energy from the electron beam [10]), the shallow donor level moves deeper in the gap as shown in Fig. 3(d). In Fig. 3(e), when a sulfur vacancy is placed near the Re impurity, two split donor levels are present together with an acceptor level emerging above the valence band minimum. If we further impose a larger displacement of 0.6 Å and place two sulfur vacancies near the Re atom, the defect levels move even deeper in the gap, as shown in Fig. 2(f). Clearly, as more vacancies are added, even more defect levels appear in the band gap.

The results shown in Figs. 3(e) and 3(f) and similar results for other defect configurations make it clear that, as a Re atom initiates a displacement and sulfur vacancies appear and disappear, an array of defect levels move up and down in the band gap, appear and disappear, and provide a plethora of electron-hole recombination paths in a dynamical fashion. The fact that we captured snapshots of sulfur vacancy motion in Fig. 2 and Video S1 [20] is strong evidence that the number of sulfur vacancies around the targeted Re atom and thus the levels in the gap are in a constant flux. Therefore, several recombination events can occur during a single Re-Mo exchange, providing energy equal to several times the band gap. This explosive recombination-enhanced defect migration or multivacancy-assisted REDM is the most likely mechanism that makes possible the observed Re-Mo exchange in MoS_2 lattice. Since Re-Mo exchanges are induced by the electron beam via the explosive recombination mechanism rather than a

thermally activated process, the activation barriers cannot be determined by Arrhenius plots.

Having established that sulfur vacancies are essential for the Re migration process, we performed experiments to explore the possibility of controlling the sulfur vacancy generation process, aiming to steer Re migration. We found that the number of electron-beam-induced sulfur vacancies follows a linear relationship with the total electron dose (Fig. S3 [20]). This suggests that the creation of sulfur vacancies at designated positions could be achieved by precise control of the position of the electron beam in STEM, as already demonstrated in Refs. [10,11], and the electron dose. As a proof-of-concept experiment, we further demonstrated that the direct exchange of Re and Mo atoms in the MoS_2 lattice can be triggered by controllably creating sulfur vacancies at specific sites surrounding the designated Re-Mo pair (Figs. 4 and S4 [20]). As shown in Fig. 4(b), during the controlled scanning, the electron beam was scanned over a small region within the red dashed circle and was then intentionally parked at specific sulfur sites, as indicated by the red dots, to create sulfur vacancies around the selected Re-Mo pair [highlighted by the yellow and red arrows in Fig. 4(a)]. Figure 4(c) shows the structure after this controlled scanning experiment, where the designated Re-Mo pair exchanged positions.

In summary, we report atomic-scale observations of direct Re-Mo exchange events in a monolayer MoS_2 lattice. The high diffusion barrier for exchange diffusion is effectively lowered by the presence of multiple spectator sulfur vacancies. However, energy transfer from the electron beam is still not sufficient to drive the direct exchange. Electron-hole recombination via dynamically changing deep levels in the gap is proposed to explain the observed phenomenon. Overall, we have demonstrated that, in addition to the direct energy transfer from the electron beam to atoms, energy can also be transferred indirectly; i.e., the beam generates electron-hole pairs, which then undergo defect-mediated recombination and transfer the energy to local phonons, causing or enhancing defect migration. We also demonstrate that, by controllably creating sulfur vacancies around a selected Re-Mo pair,

this Re-Mo direct exchange can be triggered in a controlled manner. The present Letter has clarified the exchange mechanism of cations in monolayer MoS_2, which lays the foundation for future work towards manipulating single atoms using an electron beam.

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[1] P. E. Batson, N. Dellby, and O. L. Krivanek, Nature (London) **418**, 617 (2002).

[2] P. D. Nellist et al., Science **305**, 1741 (2004).

[3] D. A. Muller, L. F. Kourkoutis, M. Murfitt, J. H. Song, H. Y. Hwang, J. Silcox, N. Dellby, and O. L. Krivanek, Science **319**, 1073 (2008).

[4] O. L. Krivanek et al., Nature (London) **464**, 571 (2010).

[5] W. Zhou, M. P. Oxley, A. R. Lupini, O. L. Krivanek, S. J. Pennycook, and J.-C. Idrobo, Microsc. Microanal. **18**, 1342 (2012).

[6] H. Sawada, T. Sasaki, F. Hosokawa, and K. Suenaga, Phys. Rev. Lett. **114**, 166102 (2015).

[7] J. Lin et al., Nat. Nanotechnol. **9**, 436 (2014).

[8] R. Ishikawa, R. Mishra, A. R. Lupini, S. D. Findlay, T. Taniguchi, S. T. Pantelides, and S. J. Pennycook, Phys. Rev. Lett. **113**, 155501 (2014).

[9] C. W. Han, H. Iddir, A. Uzun, L. A. Curtiss, N. D. Browning, B. C. Gates, and V. Ortalan, J. Phys. Chem. Lett. **6**, 4675 (2015).

[10] T. Susi et al., Phys. Rev. Lett. **113**, 115501 (2014).

[11] M. Tripathi, A. Mittelberger, N. A. Pike, C. Mangler, J. C. Meyer, M. J. Verstraete, J. Kotakoski, and T. Susi, Nano Lett. **18**, 5319 (2018).

[12] O. Dyck, S. Kim, S. V. Kalinin, and S. Jesse, Appl. Phys. Lett. **111**, 113104 (2017).

[13] C. S. Nichols, C. G. Van de Walle, and S. T. Pantelides, Phys. Rev. B **40**, 5484 (1989).

[14] P. M. Fahey, P. Griffin, and J. Plummer, Rev. Mod. Phys. **61**, 289 (1989).

[15] H. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).

[16] F. Seitz, Acta Crystallogr. **3**, 355 (1950).

[17] E. Kaxiras and K. C. Pandey, Phys. Rev. B **47**, 1659 (1993).

[18] K. C. Pandey, Phys. Rev. Lett. **57**, 2287 (1986).

[19] B. Ittermann, H. Ackermann, H. J. Stockmann, K. H. Ergezinger, M. Heemeier, F. Kroll, F. Mai, K. Marbach, D. Peters, and G. Sulzer, Phys. Rev. Lett. **77**, 4784 (1996).

[20] S.-Z. Yang et al., Adv. Mater. **30**, 1803477 (2018).

[21] J. Hong, Y. Pan, Z. Hu, D. Lv, C. Jin, W. Ji, J. Yuan, and Z. Zhang, Nano Lett. **17**, 3383 (2017).

[22] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[23] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[24] G. Kresse and J. Hafner, Phys. Rev. B **48**, 13115 (1993).

[25] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).

[26] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[27] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[28] See Supplemental Material http://link.aps.org/supplemental/10.1103/PhysRevLett.122.106101 for calculation of maximum transferrable energy from the electron beam, which includes Ref. [29].

[29] F. Banhart, Rep. Prog. Phys. **62**, 1181 (1999).

[30] S. T. Pantelides, Deep Centers in Semiconductors (CRC Press, Boca Raton, FL, 1992).

[31] G. D. Watkins, Phys. Rev. B **12**, 5824 (1975).

[32] J. R. Troxell, A. P. Chatterjee, G. D. Watkins, and L. C. Kimerling, Phys. Rev. B **19**, 5336 (1979).

[33] K. Maeda, M. Sato, A. Kubo, and S. Takeuchi, J. Appl. Phys. **54**, 161 (1983).

[34] G. A. Baraff, M. Schluter, and G. Allan, Phys. Rev. Lett. **50**, 739 (1983).

[35] S. T. Pantelides, A. Oshiyama, R. Car, and P. J. Kelly, Phys. Rev. B **30**, 2260 (1984).

[36] H. Sumi, J. Phys. C **17**, 6071 (1984).

[37] K. H. Chow and G. D. Watkins, Phys. Rev. Lett. **81**, 2084 (1998).

[38] J. W. Steeds, W. Sullivan, A. Wotherspoon, and J. M. Hayes, J. Phys. Condens. Matter **21**, 364219 (2009).

[39] R. Car, P. J. Kelly, A. Oshiyama, and S. T. Pantelides, Phys. Rev. Lett. **52**, 1814 (1984).