Journal Name

Supporting Information

High Carrier Mobility in Monolayer CVD-grown MoS_2 through Phonon Suppression

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Nengjie Huo, †[a] Yujue Yang, †[ab] Yu-Ning Wu, †[cd] Xiao-Guang Zhang, [d] Sokrates T. Pantelides [e] and Gerasimos Konstantatos*[af]

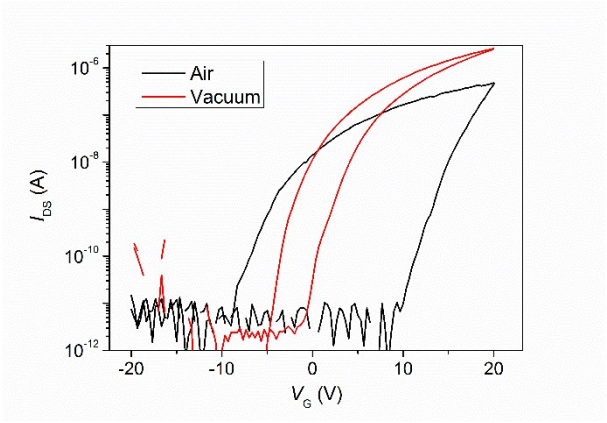

Fig.S1 Transfer curves of pristine MoS_2 transistors without HfO_2 coverage measured in air and vacuum.

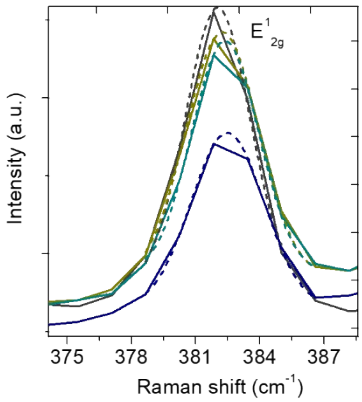

Fig. S2 Raman spectral of E^1_{2g} mode in MoS_2 as a function of HfO_2 thickness, the E^1_{2g} mode almost keep unchanged. The dash lines are the Gauss fitting curves.

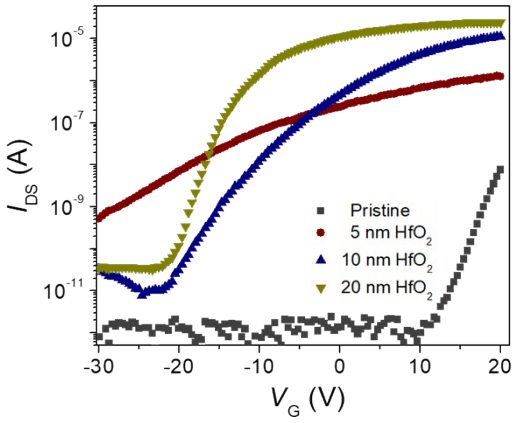

Fig. S3 Transfer characteristics of MoS_2 transistors as a function of HfO_2 thickness, depicting the improved transconductance with increasing HfO_2 thickness. The intrinsic electron density without the gate voltage in each case can be calculated using the formula: $I_{DS} = nq\mu\frac{V_{DS}Wd}{L}$, where I_{DS} is source drain current at V_G of 0V and V_{DS} of 1V, n is the electron density, q is electric charge, μ is the electron mobility, V_{DS} of 1V is applied drain voltage, W, L and d are the width, length and thickness of the channel, respectively.

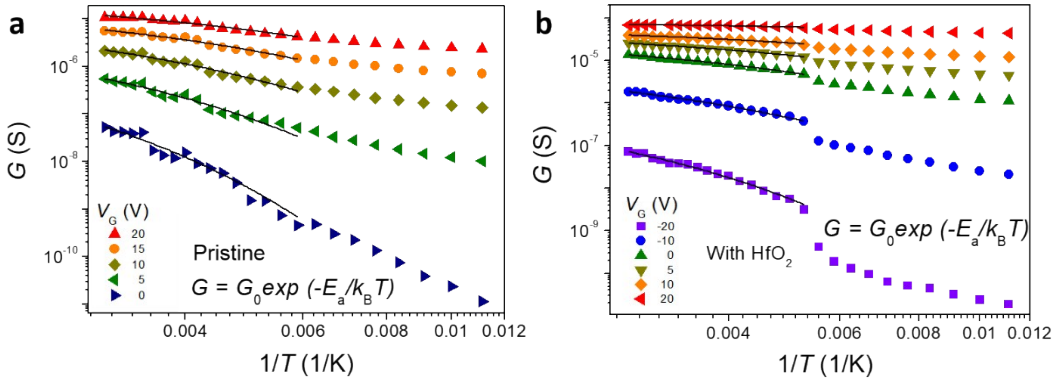

Fig. S4 Temperature dependent electrical transport. (a, b) Arrhenius plot of conductance G for different values of V_G as a function of inverse temperature ($1/T$) of pristine and HfO_2-covered MoS_2, respectively. Solid lines are linear fits to the data using the insert formula, showing thermally activated behaviour at high temperature regime.

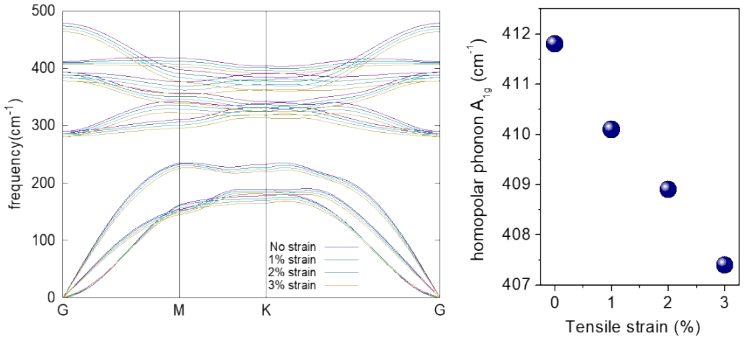

Fig. S5 Calculated phonon dispersions (left panel) and extracted frequency change of homopolar phonon A_{1g} mode (right panel) as a function of tensitle strain.

DFT calculations

The electronic structure calculations are carried out using DFT as implemented in the Quantum-Espresso package,[1] while the complex-wavevector band calculations are performed using PWcond.[2,3] Phonon dispersions are calculated using density-functional perturbation theory (DFPT).[4,5] We used the Perdew-Burke-Ernzerhof (PBE)[6] form of generalized-gradient approximation (GGA) exchange-correlation potential and the ultrasoft pseudopotential[7]. The phonon modes of a 20×20 mesh of q-points in the First-Brillouin zone were calculated with a supercell with 1200 atoms. From this result, we built a supercell of 168 atoms with displacements $u_n(T)$ to calculate the mobility.

Most practical calculations for carrier mobility have relied on the Fermi's Golden Rule and the Born approximation. While the theoretical framework established along this direction is rigorous, first-principles calculations are challenging because of practical and numerical difficulties. Engineers in the microelectronics industry have used the Born approximation but have always employed fitting parameters to reproduce data. Wu. *et al*[8] have recently developed a simple and elegant implementation of the mean-field approximation that allows the calculation to be carried out from first-principles and without the usual Born approximation. Here we adopt the method for two-dimensional materials and apply it to calculate the mobility in MoS_2. A key new result obtained by this method is that mobilities are effectively controlled by the higher-order terms of the Born expansion which amount to fluctuations around the mean phonon occupation numbers. These fluctuations create paths of least resistance for the current-carrying carriers. This parameter-free method was first applied to Si and found to give excellent results, in agreement with experimental data.[8]

According to the Boltzmann transport theory, the carrier mobility in 2D materials is given by

$$\mu = -\frac{2e}{n_c}\sum_j \int \frac{d^2k}{(2\pi)^2} v_{x,j}^2(k)\tau_j(k)\frac{\partial f(\epsilon_{kj})}{\partial \epsilon_{kj}} \qquad (1)$$

where $\tau_j(k)$ is the scattering lifetime of the Bloch state with wave vector k and band index j and $v_{x,j}(k)$ is the group velocity along the direction of the current (chosen as the x direction) given by $v_{x,j}(k) = \frac{1}{\hbar}\frac{\partial \epsilon_{kj}}{\partial k_x}$. The lifetime can be interpreted as an imaginary "self-energy" that is given by $Im\Sigma_j(k) = \frac{\hbar}{2\tau_j(k)}$. Here the factor 2 accounts for the difference between wave function and density lifetimes. The complex self-energy $\Sigma_j(k)$ represents the effect of electron-phonon scattering and depends both on the wave vector k and the band index j.

Most of the contribution to mobility from electron-phonon scattering is nearly elastic and can be well approximated by the frozen phonon approximation. We calculate the self-energy $\Sigma_j(k)$ by constructing an effective medium that gives the same decay rates of Bloch waves as in frozen-phonon configurations. For each frozen-phonon configuration, the temperature-dependent displacement for each atom (labeled by n) is given by

$$u_n(T) = \frac{1}{\sqrt{m_n}}\sum_{q,i} A_{qi}(T)\hat{n}_{qi} e^{i(q\cdot R_n + \phi_{qi})} \qquad (2)$$

where m_n is the mass of atom n, q and i are mode indices, and $\hat{n}_{qi}$ is the eigenvector for each mode and is normalized over the supercell, $\sum_n |\hat{n}_{qi}|^2 = 1$. A random phase ϕ_{qi} is added to remove correlation between different modes. $A_{qi}(T)$ is a scaled temperature-dependent amplitude that represents the average effect of phonon motion and is estimated from the Bose-Einstein distribution function, $A_{qi}(T) = \sqrt{\frac{\hbar}{\omega_{qi}\left(e^{\hbar\omega_{qi}/k_BT} - 1\right)}}$. For each phonon configuration, a self-consistent DFT calculation is performed to produce a Kohn-Sham potential, which is used to construct the effective medium.

To evaluate the integration for the mobility, further simplification is needed. We first replace the lifetime $\tau_j(k)$ by its value τ_{j0}, at the k point where the rest of the integrand is maximum. We then note that $d^2k = dk_x dk_y = dk_y d\epsilon/\hbar v_{x,j}$ and apply integration by parts over the energy integral to obtain,

$$\mu = -\frac{e}{2\pi^2 \hbar n_c} \sum_j \tau_{j0} \int_{CBM}^{\infty} d\epsilon f(\epsilon) \int dk_y \frac{\partial v_{x,j}(k_y,\epsilon)}{\partial \epsilon} \quad (3)$$

For MoS_2, the band dispersion is $\epsilon = \hbar v_F \sqrt{k_x^2 + k_y^2 + \Delta^2}$, where v_F is the asymptotic group velocity. Finally we get:

$$\mu = \frac{e}{4\pi^2 \hbar n_c} \sum_j \tau_{j0} \int_{\hbar v_F \Delta}^{\infty} d\epsilon \left(1 + \frac{\hbar^2 v_F^2 \Delta^2}{\epsilon^2}\right) f(\epsilon) \quad (4)$$

$$n_c = \frac{1}{2\pi^2} \sum_j \int_{\hbar v_F \Delta}^{\infty} d\epsilon f(\epsilon) \quad (5)$$

Once the lifetime τ_{j0} is computed, it is straightforward to calculate the mobility using the above two equations. In the limit that $\hbar v_F \Delta \gg k_B T$, most of the contribution to the integration is confined to the energy range between $\hbar v_F \Delta$ and $\hbar v_F \Delta + k_B T$. The mobility is reduced to

$$\mu = \frac{e v_F}{N \hbar \Delta} \sum_j \tau_{j0}, \quad (6)$$

where N is the number of valleys at the conduction band minimum (for MoS_2 $N = 2$). From this simplified expression we can separate two factors that can influence the mobility, the ratio v_F/Δ (which is proportional to the inverse effective mass) and the scattering lifetime τ_{j0}.

Supplementary References

1. P. Giannozzi, *et al*., *J. Phys.: Condens. Matter*, 2009, **21,** 395502.
2. H. J. Choi and J. Ihm, *Phys. Rev. B*, 1999, **59,** 2267.
3. A. Smogunov, A. D. Corso and E. Tosatti, *Phys. Rev. B*, 2004, **70,** 045417.
4. S. Baroni, P. Giannozzi and A. Testa, *Phys. Rev. Lett.*, 1987, **58,** 1861.
5. X. Gonze, *Phys. Rev. A*, 1995, **52,** 1086.
6. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77,** 3865.

7. D. Vanderbilt, *Phys. Rev. B*, 1990, **41,** 7892.

8. Y. N. Wu, X.-G. Zhang and S. T. Pantelides, *Semicond. Sci. Tech.*, 2016, **31,** 115016.