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Supplementary information

Chlorine doping of $MoSe_2$ flakes by ion implantation

Slawomir Prucnal[1,*], Arsalan Hashemi[2], Mahdi Ghorbani-Asl[1], René Hübner[1], Juanmei Duan[1,4], Yidan Wei[1], Divanshu Sharma[1,3], Dietrich R. T. Zahn[3], René Ziegenrücker[1], Ulrich Kentsch[1], Arkady V. Krasheninnikov[1,2], Manfred Helm[1,4] and Shengqiang Zhou[1]

[1]Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, P.O. Box 510119, 01314 Dresden, Germany

[2]Department of Applied Physics, Aalto University, P.O. Box 11100, 00076 Aalto, Finland

[3]Semiconductor Physics, Technische Universität Chemnitz, Reichenhainer Straße 70, 09107 Chemnitz, Germany

[4]Technische Universität Dresden, 01062 Dresden, Germany

*Corresponding author: s.prucnal@hzdr.de

Figure S1 shows the Raman spectra obtained from the same $MoSe_2$ flake with and without SiN capping layer. In both spectra, the main A_{1g} phonon mode is located at 240.2 cm^{-2}. The phonon mode at 520.5 cm^{-1} is the Si related transvers optical phonon mode observed from Si substrate. We have investigated the temperature dependent Raman spectra obtained from not-implanted and Cl-implanted few layers $MoSe_2$. With increasing temperature, the first-order Raman active phonon modes show a redshift in the frequency and the linewidth increases. Such behavior can be explained using the anharmonic approximation for phonons, which includes contribution from the thermal expansion.

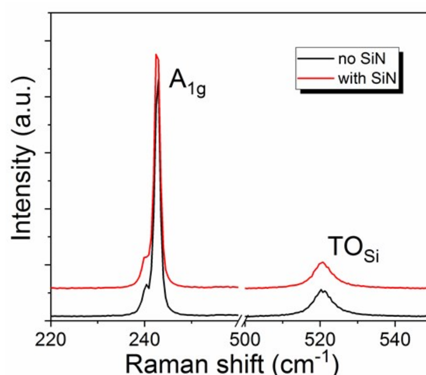

Figure S1. Room-temperature Raman spectra obtained from few-layer thick $MoSe_2$ flake with and without SiN capping layer. The two spectra are essentially identical, therefore we shifted them vertically for clarity. The 6 nm thick SiN capping layer was deposited by PECVD.

Figure S2a shows the shift of the A_{1g} phonon mode in the temperature ranging from 4 to 290 K. The temperature dependent characteristic of the A_{1g} mode can be fitted by the Grüneisen model expressed by $\omega=\omega_0 - \gamma \times T$, where w_0 is the frequency at 0K, γ is the first-order temperature coefficient and T is the measured temperature.[1]

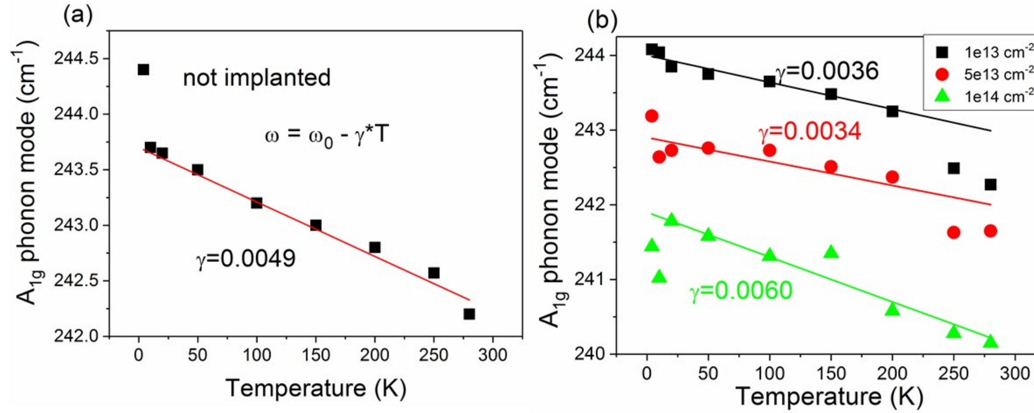

Figure S2. The shift of the A_{1g} phonon mode as a function of temperature obtained from not-implanted sample (a) and from Cl implanted and annealed samples. The absolute values of γ are given in the figures.

According to the fitting, the γ parameter obtained from not-implanted few layer thick $MoSe_2$ is -0.0049. Late *et al.* have investigated the thermal expansion of mono- and few layers thick $MoSe_2$ in the temperature range from 77 to 700 K.[2] They have estimated the γ for A_{1g} phonon mode of mono- and three layers thick $MoSe_2$ to be -0.0054 and -0.0045. Our estimated value of γ agrees well with that presented in literature for few layer thick $MoSe_2$. After ion implantation the γ first increases to -0.0034 for the Cl fluence of 5×10^{13} cm^{-2} and then decreases to -0.0060 for the Cl fluence of 1×10^{14} cm^{-2} (see Fig. S2b). In order to explain the change of the γ with doping we have to consider different factors which affects the phonon frequencies. The full expression can be written as:

$$\omega=\omega_0+\Delta\omega_{vol}+\Delta\omega_{ph\text{-}ph}+\Delta\omega_{ph\text{-}sp}+\Delta\omega_{ph\text{-}carrier},$$

where first three terms (ω_0, volume expansion and phonon-phonon interaction) should be the same in all samples. Without applying external magnetic field the spin-phonon interaction, $\Delta\omega_{ph\text{-}sp}$, can be neglected. Hence, we attribute the change in the phonon frequency of A_{1g} to the electron-phonon interaction.

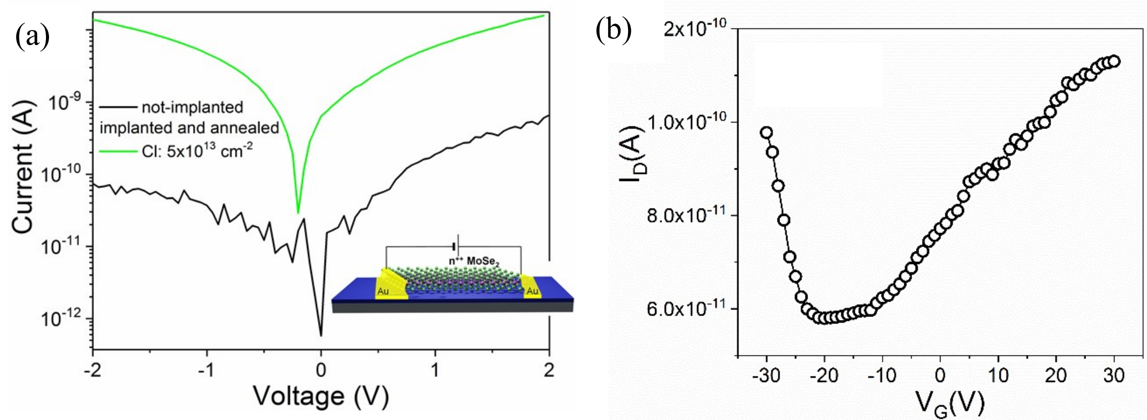

Figure S3. Current-voltage characteristics obtained from not implanted and Cl-implanted $MoSe_2$ flakes (a) and source-drain current I_D as a function of back-gate voltage V_G at $V_d = 1$ V (b). The implanted sample was annealed for 3 ms with an energy density of 51 Jcm^{-2}. The Cl fluence is in the order of 5×10^{13} cm^{-2}. The inset shows schematic representation of the I-V measurements.

The electrical activation of implanted Cl is also proven by current-voltage (I-V) characteristics.

For the electrical measurements the $MoSe_2$ flake was directly transferred on the 50 nm thick gold contacts patterned by optical lithography. The distance between two electrodes was 5 μm. After exfoliation samples were covered with 6 nm thick SiN layer and transferred for the ion implantation and flash lamp annealing. The I-V measurements were performed on the same flake before and after ion implantation and annealing using two-probe station equipped with tungsten needles. The capping layer was not removed before electrical measurements because hard needles can easily penetrate 6 nm thick SiN layer. Figure S3a shows the I-V curves obtained from as-exfoliated $MoSe_2$ flake (black curve) and from $MoSe_2$ doped with Cl (green curve) after FLA for 3 ms with an energy density of 51 Jcm^{-2}. The Cl fluence was 5×10^{13} cm^{-2}. As can be seen after Cl implantation and annealing the current increases by two orders of magnitude. Figure S3b shows the transfer characteristics of control device made at drain voltage of 1V. The calculated field-effect mobility at room temperature is about 1.8 $cm^2V^{-1}s^{-1}$. The μ_F in the reference device is much bigger than in the implanted sample but still not very high. Most probably the electrical contacts and surface passivation should be improved.

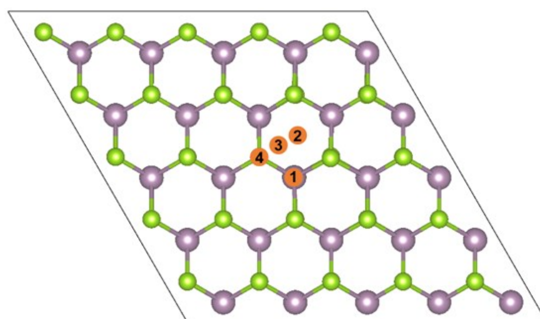

Figure S4. The top view with the Cl adsorption at different sites. Se atoms are marked with green circles.

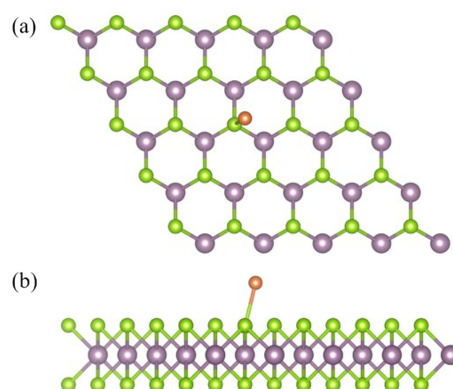

Figure S5. The (a) top and (b) side views of Cl@$MoSe_2$.

Table S1. Energy differences correspond to Cl adsorption at different sites. The values are given as compared to the most stable configuration.

site	1	2	3	4
Cl@$MoSe_2$	0.33	0.15	0	0.01

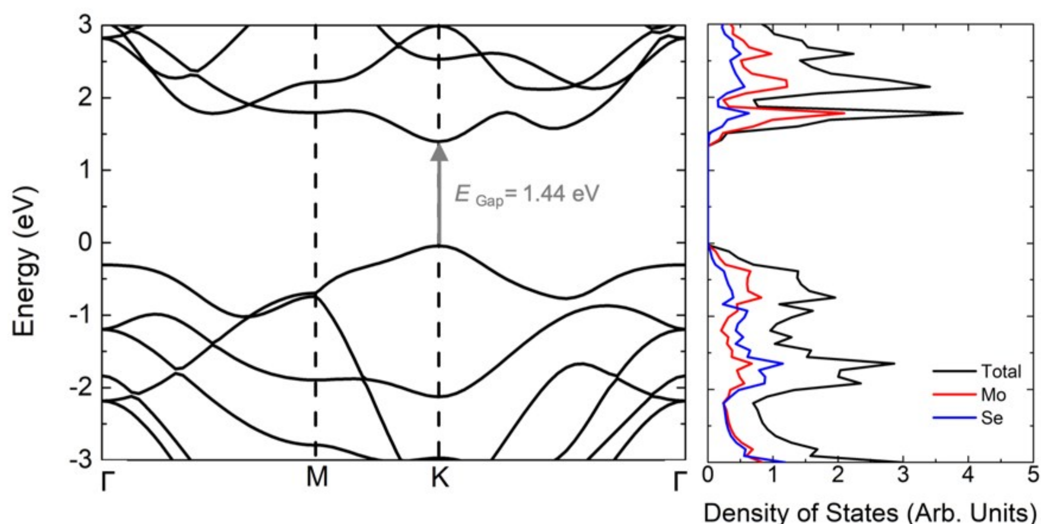

Figure S6. Electronic band structure and the projected density of states of $MoSe_2$. The Fermi level is shifted to zero.

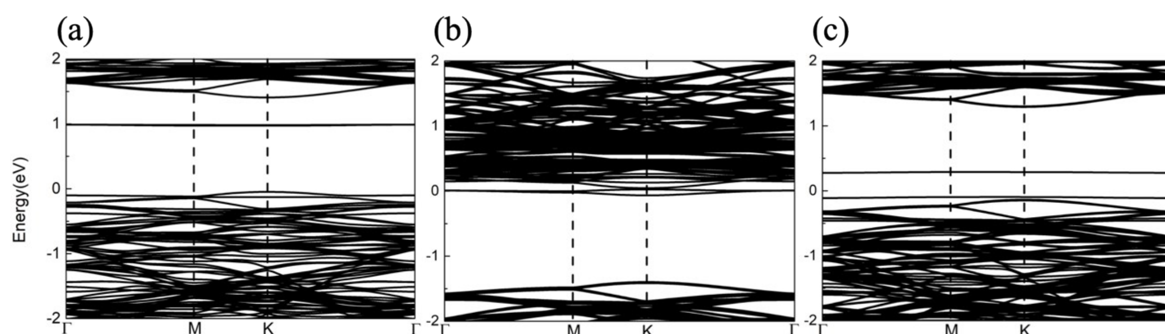

Figure S7. The band structures of (a) $MoSe_{2-x}$, (b) $MoSe_{2-x}Cl_x$ and (c) Cl@$MoSe_2$. The Fermi level is shifted to zero. Case b clearly shows the shallow donor state.

REFERENCES

1. E. S. Zouboulis and M. Grimsditch, Raman scattering in diamond up to 1900 K, *Phys. Rev. B* 1991, **43**, 12490 –12493.
2. J. Late, S. N. Shirodkar, U. V. Waghmare, V. P. Dravid and C. N. R. Rao, Thermal Expansion, Anharmonicity and Temperature-Dependent Raman Spectra of Single- and Few-Layer $MoSe_2$ and WSe_2, *Chem. Phys. Chem*. 2014, **15**, 1592-1598.