Supplementary Information

Experimental Evidence of Exciton Capture by Mid-Gap Defects in CVD Grown Monolayer $MoSe_2$

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1. Extraction of pure $MoSe_2$ signals, reflectivity spectra and calculation of sample absorbance

Reflection and transmission of an optical multilayer thin-film system can be calculated with the transfer matrix method [1], from which the intensity of reflectivity from the $MoSe_2/SiO_2/Si$ structure can be derived [2]:

$$R = \left| \frac{r_1 e^{i(\Phi_1+\Phi_2)} + r_2 e^{-i(\Phi_1-\Phi_2)} + r_3 e^{-i(\Phi_1+\Phi_2)} + r_1 r_2 r_3 e^{i(\Phi_1-\Phi_2)}}{e^{i(\Phi_1+\Phi_2)} + r_1 r_2 e^{-i(\Phi_1-\Phi_2)} + r_1 r_3 e^{-i(\Phi_1+\Phi_2)} + r_2 r_3 e^{i(\Phi_1-\Phi_2)}} \right|^2 \quad (1)$$

where $r_1 = \frac{\tilde{n}_0-\tilde{n}_1}{\tilde{n}_0+\tilde{n}_1}$, $r_2 = \frac{\tilde{n}_1-\tilde{n}_2}{\tilde{n}_1+\tilde{n}_2}$, $r_3 = \frac{\tilde{n}_2-\tilde{n}_3}{\tilde{n}_2+\tilde{n}_3}$ are the complex amplitude of reflection coefficients for air/$MoSe_2$, $MoSe_2/SiO_2$, and SiO_2/Si interfaces, respectively; $\tilde{n}_i = n_i - i\kappa_i$ is the complex refractive index of each material (Note that positive κ stands for absorption), and $\Phi_i = 2\pi\tilde{n}_i d_i/\lambda$ is the complex phase shift due to a change in the optical path and the absorption in $MoSe_2$ or Si. After pump excitation in the $MoSe_2/SiO_2/Si$ structure, the refractive index of both $MoSe_2$ and Si will change (SiO_2 is non-absorbing at 800nm), which results in a reflection change of the whole structure. By exploiting Eq. (1) and the transfer matrix method, we have verified that within a small change of the refractive index, the total reflection change is the linear superposition of the contribution from each material, i.e, $\Delta R_{total}=\Delta R_{MoSe_2}+\Delta R_{Si}$. The verification procedure is shown below.

Using the static values of refractive index for $MoSe_2$ ($\tilde{n}_{MoSe_2,0}$ =5.337-1.218i) [3], SiO_2 ($\tilde{n}_{SiO_2,0}$ =1.453)[4] and Si ($\tilde{n}_{Si,0}$ =3.696-0.0047i) [4], we assume that the pump induced refractive index changes for $MoSe_2$ and Si are

$$\tilde{n}_{MoSe_2}(t) = \tilde{n}_{MoSe_2,0} - 0.002 \times 1.218 \exp(-t/0.5ps) i, \quad (2)$$

and

$$\tilde{n}_{Si}(t) = \tilde{n}_{Si,0} + 0.0002 \times 3.696\exp(-t/0.8ps), \qquad (3)$$

respectively.

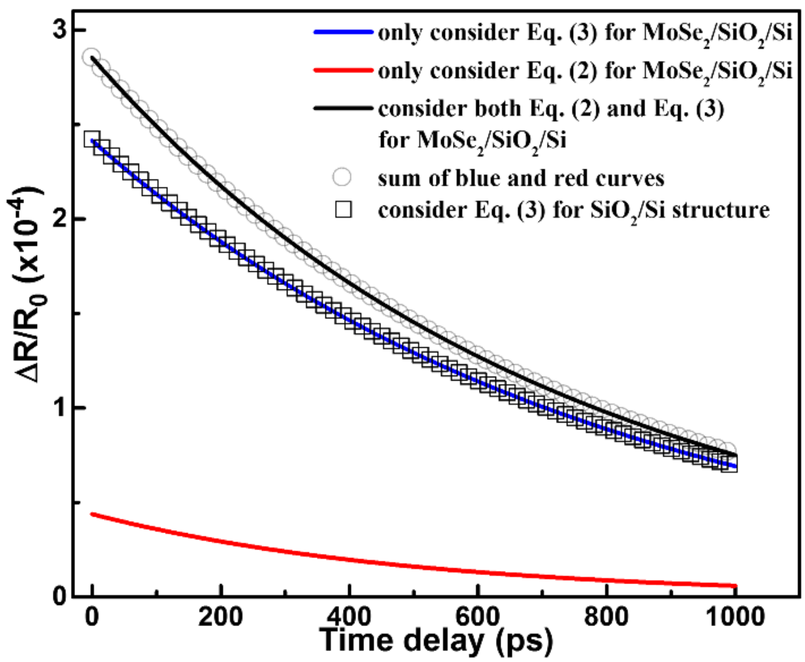

Fig. S1. Differential reflection signals of $MoSe_2/SiO_2/Si$ structures, simulated for the cases where only $\tilde{n}_{Si}(t)$ takes effect, only $\tilde{n}_{MoSe_2}(t)$ takes effect, and both $\tilde{n}_{Si}(t)$ and $\tilde{n}_{MoSe_2}(t)$ take effect, respectively. Differential reflection of SiO_2/Si structure is also simulated assuming the same $\tilde{n}_{Si}(t)$ taking effect.

Simulations based on Eq. (1)-(3) are performed to calculate the differential reflection signals, as shown in Fig. 1S. It can be seen that in the $MoSe_2/SiO_2/Si$ structure the total differential reflection signal (the black curve) for the case where both $MoSe_2$ and Si are taken into account is identical to the summation (the circles) of the signals from pure $MoSe_2$ (the red curve) and pure Si (the blue curve). This means the pure optical response of the $MoSe_2$ layer, $\Delta R_{MoSe_2}/R_0$, can be obtained by directly subtracting the Si response, $\Delta R_{Si}/R_0$, from the total signal, $\Delta R_{total}/R_0$, provided that $\Delta R_{Si}/R_0$ is already known.

However, we still cannot extract $\Delta R_{MoSe_2}/R_0$ by subtracting the Si data, $\Delta R_{Si}/R_0$, from the total data in Fig. 1 (a) in the main text, because the Si data in Fig. 1 (a) is measured in the SiO_2/Si structure while the total data is measured in $MoSe_2/SiO_2$/Si. To continue the extracting process, we need to know the relation between $(\Delta R_{Si}/R_0)_{SiO_2/Si}$, the differential reflection measured in the SiO_2/Si structure, and $(\Delta R_{Si}/R_0)_{MoSe_2/SiO_2/Si}$, the desired pure Si response component in the $MoSe_2/SiO_2$/Si structure. From the transfer matrix method [1] and the cited refractive indexes of $MoSe_2$, SiO_2 and Si, we calculate reflectivity R_0 and transmissivity T_0 at the SiO_2/Si interface in the $MoSe_2/SiO_2$/Si structure and the SiO_2/Si structure, and absorbance A_0 (A_0=1-R_0-T_0) of the $MoSe_2$ layer in the $MoSe_2/SiO_2$/Si structure at 800 nm. The results are: $R_{0,MoSe2/SiO2/Si}$=0.3019, $R_{0,SiO2/Si}$= 0.3149, $T_{0,MoSe2/SiO2/Si}$=0.6807, $T_{0,SiO2/Si}$=0.6851, $A_{0,MoSe2}$=0.0174. The calculated static reflectivities are consistent with our measured static reflectivity spectra at 800 nm (0.3020 for $MoSe_2/SiO_2$/Si and 0.3182 for SiO_2/Si), as shown in Fig. S2, confirming the validity of the transfer matrix method and the correctness of the cited refractive index. Obviously, the pump induced refractive index change of Si is determined by the pump intensity incident from SiO_2 into Si at the SiO_2/Si interface. It is found that the transmissivities at the SiO_2/Si interface T_0 are quite close for the $MoSe_2/SiO_2$/Si(0.6807) and SiO_2/Si(0.6851) structures, so it can be expected that the pump intensities in the Si layer and, hence, the pump-induced refractive index changes in Si are very close when the incident intensity is the same, as the case of our experiment. Moreover, the reflectivities R_0 are also very close for the two structures (0.3019 and 0.3149). Therefore, it can be concluded that with the same incident intensity, $\Delta R_{Si}/R_0$ in the two structures are almost identical. To further verify this conclusion, we assume the same optical response in Si: $\tilde{n}_{Si}(t) = \tilde{n}_{Si0} + 0.0002 \times 3.696\exp(-t/0.8ps)$ and simulate the differential reflection signal in the SiO_2/Si structure, which is shown in Fig. 1S by the squares. The result is almost totally overlapping with the one simulated for the case when only $\tilde{n}_{Si}(t)$ takes effect in the $MoSe_2/SiO_2$/Si structure, which confirms the above conclusion. Therefore, we have proven that the pure $MoSe_2$ signal component in the $MoSe_2/SiO_2$/Si structure can be obtained by directly subtracting the Si signal $\Delta R_{Si}/R_0$ measured in the SiO_2/Si structure from the total differential reflection signal measured in the $MoSe_2/SiO_2$/Si structure.

As mentioned before, the calculated static reflectivity (0.3019 for $MoSe_2/SiO_2$/Si and 0.3149 for SiO_2/Si) from the transfer matrix method are consistent with our measured static reflectivity spectra at 800 nm (0.3020 for $MoSe_2/SiO_2$/Si and 0.3182 for SiO_2/Si), as shown in Fig. S2, confirming the validity of the transfer matrix method and the correctness of the cited refractive index.

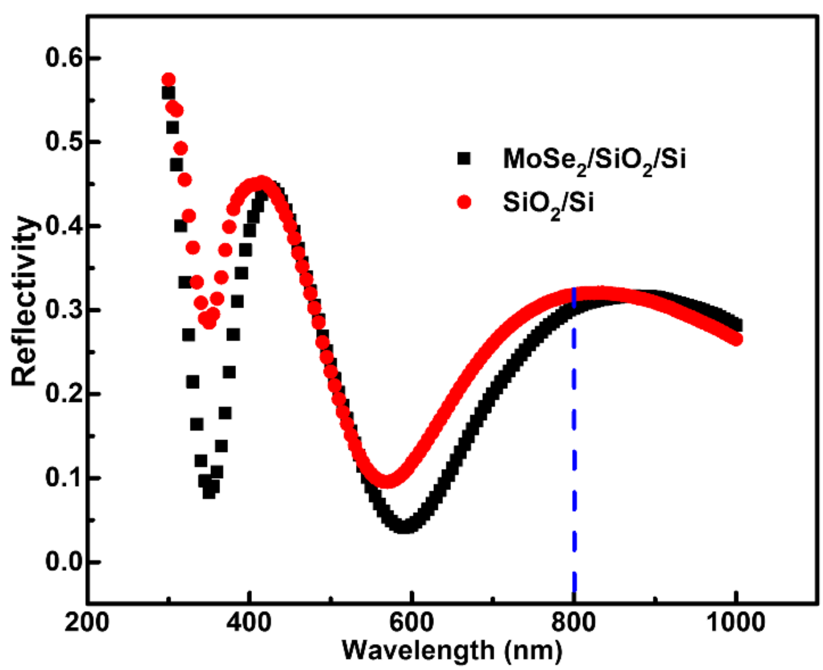

Fig. S2. Reflectivity spectra of MoSe2/SiO2/Si and SiO2/Si structures.

For CVD 10-layer sample, the absorbance can also be calculated in the same way as monlayer sample with transfer matrix method. We calculate reflectivity R_0 and transmissivity T_0 at the SiO2/Si interface for the 10layer-MoSe2/SiO2/Si structure at 800nm. The results are: $R_{0,10layer\text{-}MoSe2/SiO2/Si}$=0.2549, $T_{0,10layer\text{-}MoSe2/SiO2/Si}$=0.6009. Therefore, $A_{0,10layer\text{-}MoSe2}$=0.1442.

2. Differential reflection signal at wavelength around A exciton resonance

We have tested that probing from 820 nm to 790 nm, the differential reflection signals keep the firstly-negative-peak-then-a-positive-peak shape. No one-sign decay signal is observed. This result shows that what our signal reflects is indeed the formation of the A exciton and then its fast vanishing, but not a result from spectral broadening effect.

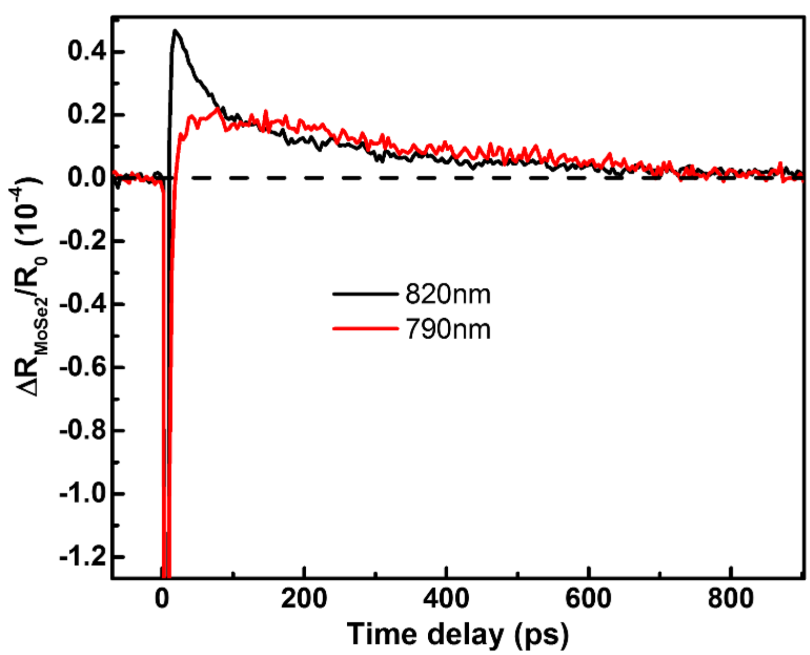

Fig. S3. Differential reflection signal of CVD monolayer MoSe2 on SiO2/Si measured with degenerate pump/probe with 820nm and 790nm wavelength.

3. AFM data of the thick exfoliated MoSe2 sample

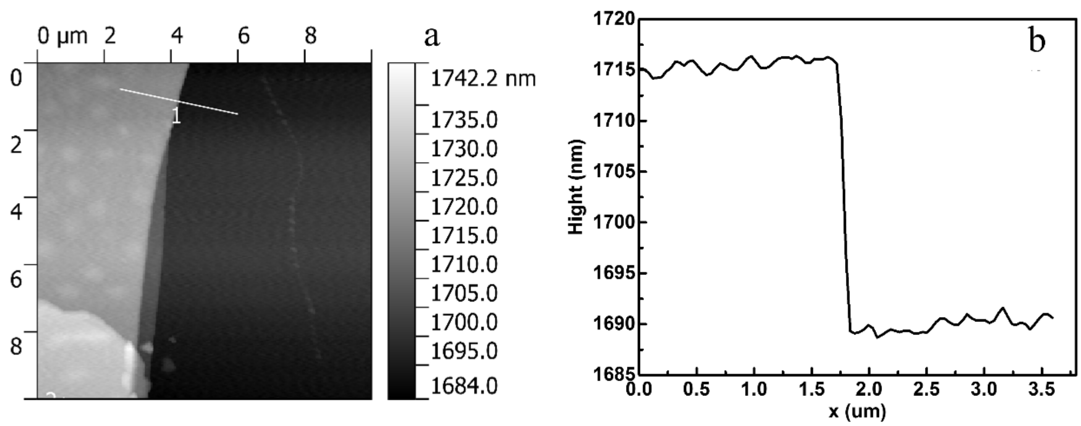

Fig. S4. a. AFM figure of the thick exfoliated MoSe2 sample. b. Height value along bar 1 across the sample boundary shown in Figure S4 **a**. A 26 nm height difference indicates a layer number of 40.

4. Differential reflection signal of monolayer CVD $MoSe_2$ before and after surface cleaning

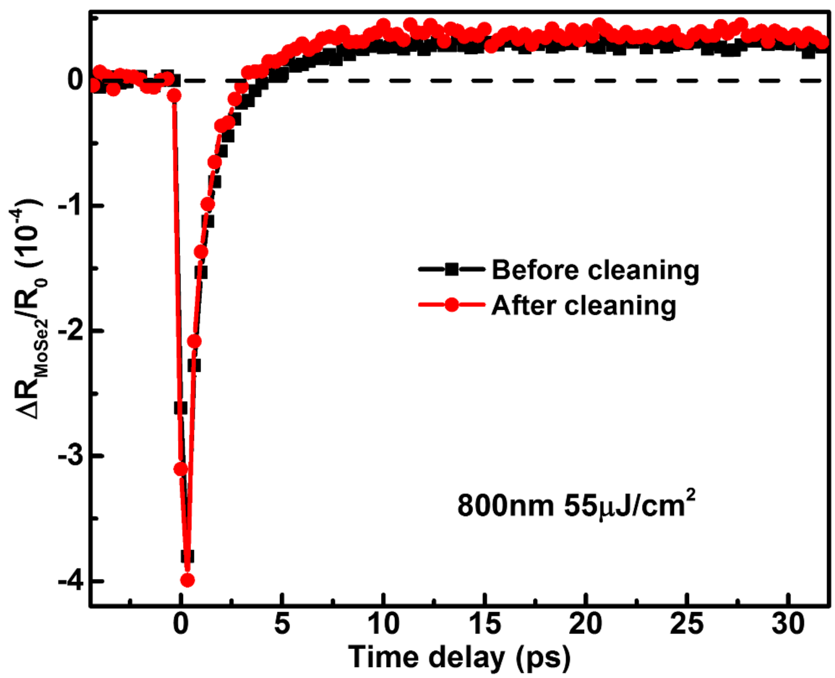

Fig. S5. Comparison of differential reflection signal of CVD monolayer $MoSe_2$ sample before (black) and after (red) surface cleaning, at 800 nm central wavelength and 55 μJ/cm^2 pump fluence.

In order to investigate the effect of the possible physical adsorbates (such as gas molecules, particles, and organic contaminant) on the exciton dynamics, we cleaned the CVD monolayer sample surface and compared the differential reflection signals before and after cleaning to see whether the sign-change still exists. The clean method is described here: we firstly placed the sample into acetone solvent, ultrasonically cleaned it for one minute; then we placed the sample into Isopropyl alcohol (IPA) solvent, ultrasonically cleaned it for another minute; after that we placed the sample in a vacuum oven working at 100°C for one hour to dry it. After this cleaning procedure, we re-did the pump-probe experiment immediately. The measured transient differential reflection signals, $\Delta R/R_0$, before and after cleaning are shown in Figure S5. It can be seen that the signal has shown almost no change after the surface cleaning treatment. Moreover, during the pump-probe measurement, femtosecond laser pulse can also give a surface cleaning effect that removes the physical adsorbates [5]. In conclusion, the sign-changing feature in $\Delta R/R_0$ observed in CVD sample does not come from the physical adsorbates.

However, for the chemical impurity that was introduced during the CVD growth process, which usually has strong covalence bond to the atoms of the sample, we cannot completely rule out its role for the sign-changing signals, because it is difficult to remove these chemical impurities by ordinary surface cleaning or with femtosecond laser pulses. Because CVD TMDs has lots of chalcogen vacancies and grain boundaries, it is very likely that during the growth some active atom like oxygen from the precursor will form bond to the transition metal atoms, taking up the chalcogen vacancies and the boundary edge sites as chemical impurities. From X-ray Photoelectron Spectroscopy (XPS) measurements shown in Fig. 6 in the manuscript, we have found strong evidence of a large amount of oxygen-associated impurity defects only in the CVD $MoSe_2$ sample, but not in the exfoliated sample, which supports the hypothesis that the impurity defect of CVD sample can be responsible as the exciton/carrier trapper.

References:

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