Influence of substrates on photocarrier dynamics in monolayer TMDs

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Abstract: We demonstrate that dielectric screening from substrates has a strong influence on photocarrier dynamics in monolayer TMDs. In particular, the interband recombination time is found dramatically shortened with the increase of substrate dielectric constants.

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1. Introduction:

The unique electronic and optical properties of two-dimension (2d) materials make it an ideal material platform to construct highly integrated devices. In particular, transition metal dichalcogenides (TMDs) have received significant attention and have been used to enable many functional devices such as FETs, LEDs, and photodetectors [1]. Effective control of the optical properties of TMDs is the key for further improvement of device characteristics, but is hindered by the ultra-thin feature of monolayer TMDs, where photocarriers' behaviors are found highly sensitive to environmental factors [2]. Some previous work has focused on resolving the dielectric screening effect on electrical properties of 2d materials. For example, a thin layer of Al_2O_3 is found to significantly improve the mobility of WS_2 FETs by reducing the density of charge traps and Coulomb impurities [3]. Although photoluminescence of MoS_2 on different substrates have been studied [4], the impact of environmental factors on photocarrier dynamics in monolayer TMDs is yet to be investigated.

Here we address this issue by studying the photocarrier dynamics of monolayer $MoSe_2$ on substrates with wildly different dielectric constants (SiO_2 κ=3.9, Al_2O_3 κ=10, and HfO_2 κ=16.5). It is found that using different substrates can effectively modulate the relaxation time constants of photocarriers in monolayer $MoSe_2$. In particular, the interband recombination time exhibits the most salient dependence on the substrate dielectric constants. We attribute such phenomenon to dielectric screening effect from substrates. Our results provide updated design guidelines for tuning the optical properties of 2d materials.

2. Results and discussion

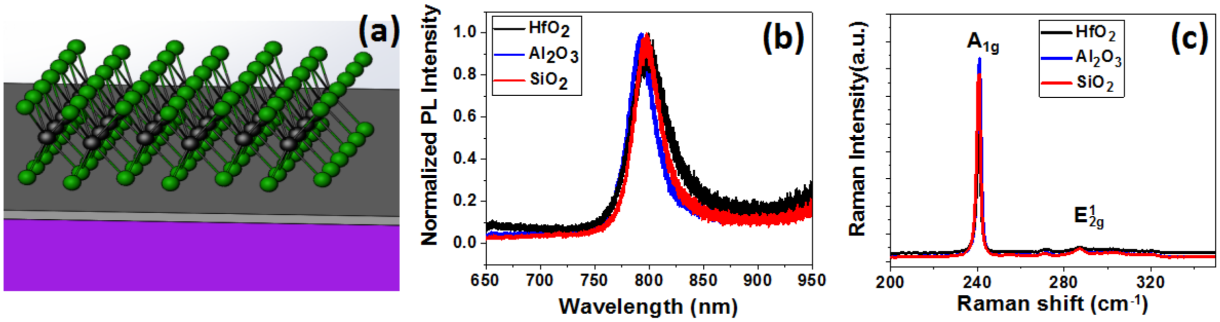

Fig.1 (a) Schematic of monolayer $MoSe_2$ on different substrates. (The gray part denotes the oxide layer and the purple part is p-type Si) (b) Raman spectra, and (c) normalized photoluminescence spectra of samples on different substrates.

The single crystal monolayer $MoSe_2$ is grown on SiO_2/Si substrate by chemical vapor deposition (CVD) method. After growth, the monolayer $MoSe_2$ is transferred onto new substrates, where different oxide layers are grown onto p-doping Si substrate by atomic layer deposition (ALD), as illustrated in Fig.1a. For the transfer process, the chip was firstly coated with a water-soluble polymer, polyvinylpyrrolidone (PVP), which served as the adhesive layer [5]. After heating the chip for 1 min at 75℃, another water-soluble support layer, poly (vinyl alcohol) (PVA), was dropped onto the PVP film and heated for drying. Then the film was peeled off from the chip and pasted onto other substrates. Finally, the film was removed by soaking in water at 80° C for ~20 min. Fig.1b and Fig.1c show the normalized photoluminescence (PL) and Raman spectra of the sample. PL peaks of different samples are located at ~800 nm, although there is an error about few nm between samples. Two distinct peaks in Raman spectra at 240 cm^{-1} and 287 cm^{-1} correspond to the A_{1g} and E^1_{2g} vibration modes. These spectra prove that transferring onto different substrates has little impact on the intrinsic optical properties of the samples.

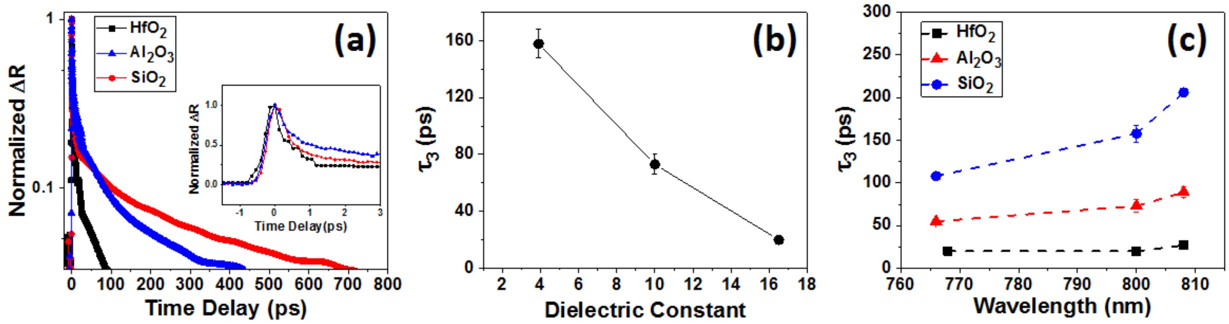

Fig. 2(a) Photocarrier dynamics of the three samples (b) The third relaxation time as a function of substrates' dielectric constant when the probe wavelength is 800nm. (c) The third relaxation time as a function of probe wavelengths.

Photocarrier dynamics are carried out using a 76 MHz repetition rate Ti:sapphire laser, with a pulse duration of ~150 fs. In our setup, one port of the laser is focused on a beta barium borate (BBO) crystal to generate the high photon-energy pump beam, which can excite carriers to conduction band. The rest of the laser works as a probe for detecting carrier dynamics by measuring the relative change of probe reflection. A 10X objective is used to focus the pump and probe beams on the samples.

The photocarrier dynamics at the A-exciton resonance are summarized in Fig.2a (pump 400 nm/probe 800 nm). All curves exhibit an instantaneous rise within 400 fs (see inset of Fig. 2a). The transient relaxation curves exhibit multi-exponential decays, and can be fitted using a triple exponential decay function: the resulting relaxation time constants of samples on SiO_2 are 0.49 ps (τ_1), 10.9 ps (τ_2), 171 ps (τ_3); time constants of samples on Al_2O_3 are 0.5 ps, 6.2 ps, 71 ps; and time constants of samples on HfO_2: 0.36 ps, 3 ps, 23 ps. While the first (and fastest) relaxation process stays almost constant for all samples (~ 400-500 fs), it is apparent that the third relaxation time (interband recombination) becomes dramatically shortened as the dielectric constant of the substrates increases, as shown in Fig. 2b. This makes sense as substrates with high dielectric constants can reduce the density of charge traps, Coulomb impurities and defects through dielectric screening effect. We also change probe wavelengths and find that the influence of dielectric screening effect on carrier recombination exists robustly, as illustrated in Fig.2c. The almost one order of magnitude tuning of the recombination dynamics highlights the importance of considering substrate effects in interpreting the transient spectroscopy data and are particular relevant for the design of TMD based saturable absorbers and photodetectors.

3. Conclusion

In summary, we investigated the influence of substrate dielectric screening effect on photocarrier dynamics for CVD-grown monolayer $MoSe_2$. Our experimental results show that the interband recombination time is dramatically shortened on substrates with high dielectric constant. Such an effect is observed over a broad spectral range and may provide an effective way to control the relaxation time constants of two-dimensional TMDs.

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