Effects of native defects and molecular adsorption on optical properties of two-dimensional semiconductors

Junqiao Wu, Sefaattin Tongay, Jian Zhou, Wen Fan, Joonki Suh
Department of Materials Science and Engineering, University of California,
Berkeley, CA 94720

Most functionalities of electronic materials are enabled by introduction of selected imperfections such as dopants and native defects. The understanding and database of the behavior of imperfections are relatively established for bulk semiconductors, but much less for two-dimensional (2D) semiconductors, i.e., transition metal dichalcogenides in the monolayer limit. On the other hand, low-dimensional electronic systems are highly susceptible to disorder and imperfections. In 2D semiconductors this propensity is expected to strongly influence electronic and excitonic processes. In this presentation, effects of two types of imperfections, atomic vacancies and adsorbed molecules, will be discussed. It will be shown that these imperfections can be engineered to drastically affect certain materials properties such as improving optical quantum yield and enhancing electron-phonon interaction.

On the effects of atomic vacancies, it is known that they can trap free charge carriers and localize excitons. The interaction between these defects and charge carriers becomes stronger at reduced dimensionalities, and is expected to greatly influence physical properties of the hosting material. We investigated effects of anion vacancies in 2D semiconductors where the vacancies density is controlled by α-particle irradiation or thermal-annealing. We found a new, sub-bandgap emission peak as well as increase in overall photoluminescence intensity as a result of the vacancy generation [1]. Interestingly, these effects are absent when measured in vacuum. We conclude that in opposite to conventional wisdom, optical quality at room temperature cannot be used as criteria to assess crystal quality of the 2D semiconductors.

On the effect of molecular physical adsorption, we observed over 100 times modulation of room-temperature light emission efficiency of 2D semiconductors by physical adsorption of O_2 and/or H_2O molecules [2], while inert gases do not cause such effect. The O_2 and/or H_2O pressure acts quantitatively as an instantaneously reversible “molecular gating” force, providing orders of magnitude broader control of carrier density and light emission than conventional electric field gating. Physi-sorbed O_2 and/or H_2O molecules electronically deplete n-type materials such as MoS_2 and $MoSe_2$, which weakens electrostatic screening that would otherwise destabilize excitons, leading to the drastic enhancement in photoluminescence. In p-type materials such as WSe_2, the molecular physi-sorption results in hole accumulation and thus the opposite optical effect.

Inert gas molecules, on the other hand, strongly affect low-temperature light emission from these 2D semiconductors [3]. We demonstrated reversible control of electron-phonon coupling in 2D semiconductors, monolayer WSe_2 and $MoSe_2$, by interactions with inert gas molecules such as N_2 and He. The interactions induce charge localization regions in the monolayer, where exciton-phonon coupling is much enhanced because of relaxation of the momentum conservation. As a result, excitons recombine by emitting a series of phonon side bands. When the gas is pumped out, the emission spectrum converges to a single peak without the phonon feature, indicating that physical interactions with the gas molecules are responsible for mediating the electron-phonon coupling.

Unique and universal in all 2D semiconductors, these effects shed light on many-body physics in low-dimensional electronic systems, as well as offer new mechanisms for modulating electronic interactions and implementing optical devices.

References

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