Electronic and Vibrational Properties of 2D Materials from Monolayer to Bulk

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Introduction and Motivation

The placement of two dimensional (2D) materials such as hexagonal boron nitride (h-BN) and transition metal dichalcogenide (TMDC) at the forefront of materials and device research was pioneered by the discovery of graphene, an atomically thin 2D allotrope of carbon obtained through mechanical exfoliation [1]. These 2D materials possess a wide range of electronic behaviors from insulator to metallic, resulting from their in-plane strong covalent bonds and their weaker out-of-plane coupling [2]. The intrinsic bandgap of the semiconducting TMDCs makes them materials of choice for next-generation low-dimensional optical and electronic devices for defense and civilian applications. These *2D* van der Waal (vdW) materials hold promise for a range of electronic, thermoelectric and optoelectronic devices such as field effect transistor (FET), light emitting device (LED), energy harvesting devices and ultrafast optical devices [3].

The in-plane geometry exhibited particularly in TMDC materials is governed by the location of the transition metal atom sandwiched between the two dichalcogenide atoms which govern the phase of the materials from metallic (1T) to semiconducting (2H) [4]. The out-of-plane geometry between the vdW layers, however, can be changed in various ways such as by misalignment (sliding), misorientation, and formation of heterostructures [5]. Misorientation between the layers originates from the weak interlayer coupling or vdW interaction between the layers. Similarly, when different layers of materials are stacked on one another their physical and quantum properties can, in effect, combine, interfere or cancel one another, to varying degrees depending on the materials, leading to the new properties [5]. The overall properties of these heterostructures rely on interlayer coupling between the layers. In addition, modifying the interlayer coupling through chemical and physical treatments can also lead to new out-of-plane topology between the layers.

Motivated by this and a growing interest in 2D vdW materials, in this talk I will give an overview of the theoretical and experimental synergetic efforts in exploring the effect of in-plane and out-of-plane geometries of 2D materials and their heterostructures on their electronic and vibrational properties.

Results and Discussion

An atomistic representation of the experimentally observed single layer (1T) and bulk (4H) phase of tin disulfide (SnS_2) is shown in Fig. 1 (a). In this study, band structure measurements in conjunction with *ab-initio* calculations and photoluminescence (PL) spectroscopy show that SnS_2 is an indirect bandgap semiconductor over the entire thickness range from bulk to monolayer which is different from other TMDC materials such as molybdenum disulfide (MoS_2). The difference arises because of the different orbital compositions of the valence band at Γ.

Misorientation between the layers was also shown to affect the thermophysical properties of graphene/graphene. Since the commensurate bilayer system size grows exponentially with decreasing misorientation angle, large scale molecular dynamics simulations, which include the anharmonic effects, are used to analyze the angle-dependent, experimentally observed low-energy vibrational modes [7]. The results are verified against the Raman signatures, as shown in Fig. 2. Experimental observation, along with the theoretical validation, suggests that the low-energy vibrational modes are insensitive to the misorientation angle in the bilayer misoriented graphene system.

Modulation of the vdW gap and bandstructure in few-layer MoS_2 was achieved via partial intercalation of oxygen [8]. Changes in the film thickness and PL spectra due to partial intercalation are analyzed using *ab-initio* simulations. Calculations employing hybrid functionals combined with semi-empirical corrections to account for vdW interactions are used to quantitatively compare to experimental results. It was found that, as the layer thickness increases from 2 layers to 4 layers, the indirect to direct transition vdW gap distance

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increases by 45%. An increase of the vdW gap distance by 30% with respect to the equilibrium distance between each monolayer, is sufficient to observe the indirect to direct crossover in the bandgap, as shown in Fig. 3 (a, b). This observation is consistent with our recent experimental optical measurements [9]. The intercalated MoS_2 bilayers exhibited circularly polarized PL consistent with the spin-valley-layer selection rules predicted theoretically. This vdW-gap dependent indirect-direct bandgap transition was also observed in the MoS_2-WS_2 heterostructures [10]. Finally, some of the existing opportunities for combining 2D materials with organic polymers will be identified and discussed. Combining these materials, a new device-design, TMDC-based Excitonic Field Effect Transistor (TexFET) is conceptualized. The working principle of this device which exhibits low-power and ultra-fast switching mechanism will be presented.

CONCLUDING REMARKS

To conclude, I will review some of the limitations and challenges associated with the application of 2D materials for real device applications. I will summarize my talk by providing an overview of ongoing and planned 2D materials based research activities at Army Research Laboratory (ARL) which is mainly focused on designing lighter, faster and robust optoelectronic devices for future army applications.

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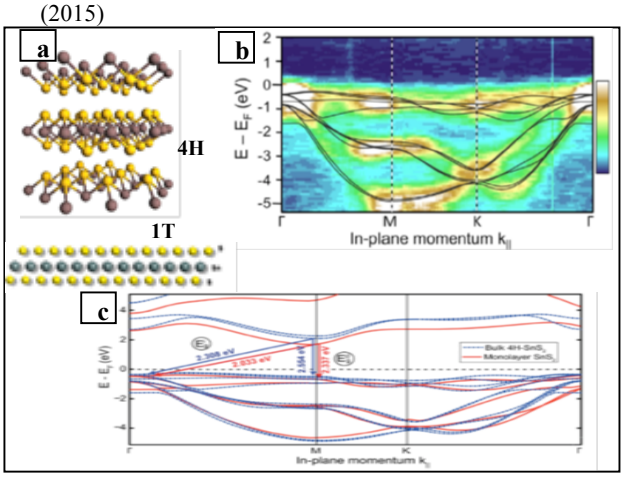

Fig. 1. (a) 1T and 4H SnS_2 atomistic structure, (b) ARPES mapped bandstructure of bulk 4H SnS_2, and (c) *Ab-initio* (HSE-level) bandstructure for monolayer (1T) and bulk (4H) SnS_2. Reprinted with permission from { Ref. 6 } Copyright 2014, Americal Chemical Society.

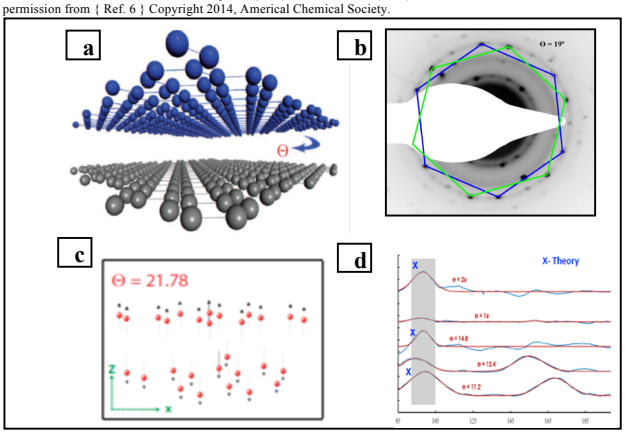

Fig. 2. (a) Misoriented bilayer graphene atomistic structure, (b) SAED image of misoriented bilayer graphene, (c) Force directions for misoriented bilayer graphene with angle 21.78°, and (d) Calculated l low frequency modes (X) overlaid on the Raman spectrum of the misoriented graphene samples.

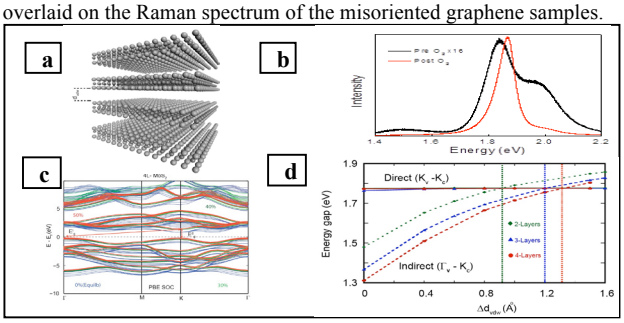

Fig. 3. (a) Multilayer MoS_2 atomistic structure, (b) PL-spectra of pre-O_2 treatment (black) and post-O_2 treatment (red) for multilayer MoS_2, (c) Illustration of vdW-gap modulated indirect to direct transition in bandstructure, and d) vdW gap dependent indirect to direct bandgap transition for 2L,3L and 4L (bulk-like) MoS_2. Reprinted with permission from { Ref.8} Copyright 2015, John Wiley and Sons.