

Persistent non-equilibrium interface dipoles at quasi-2D organic/inorganic semiconductor interfaces: The effect of gap states



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ABSTRACT

We investigate the role of gap states in the quasi-2D van der Waals crystal SnS₂ and their influence on the electronic structure formed at the hybrid interface between SnS₂ and several different organic semiconductors. We demonstrate that this density of states creates trapped carriers, generating an interfacial electric field that transiently alters the energy level alignment at the hybrid interface. The trapped carriers are extremely long-lived due to the weak interlayer coupling that is characteristic of quasi-2D materials. We suggest that these effects, observed here by photoemission spectroscopy, likely play a role for many different van der Waals materials with moderate screening lengths, with direct impact on optoelectronic and transport properties in the (quasi-)2D limit.

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1. Introduction

Since the introduction of graphene [1], the chemical library of two-dimensional materials has grown rapidly, and new applications of their unique properties continue to be discovered. Metal dichalcogenides are particularly promising due to their finite bandgap, which permits their utilization in a variety of optoelectronic devices [2,3], including ultrathin solar cells [4], photocatalysts [5–7], spintronics [8], and field effect transistors [9–12]. A great deal of progress has been made in understanding the fundamental properties of mono- and few-layer 2D semiconductors, especially regarding the effect of metal contacts [13,14] and simple extrinsic doping [15,16]. However, comparatively little is known about the properties of hybrid interfaces between organic semiconductors and 2D metal dichalcogenides. The electronic asymmetry of such interfaces, coupled with the tunability of molecular properties, promises to yield new physics and opportunities for novel applications.

Many of the key physical properties for 2D systems emerge from the electronic structure of the bulk quasi-2D materials. Hence, as a first step in this direction, the hybrid interface between organic molecules and the bulk van der Waals-layered crystal must be investigated. Indeed, metal dichalcogenide/organic interfaces have already been shown to support highly ordered molecular growth [17], ultrafast interfacial charge transfer with near-unity quantum efficiency [18], and high conductivity [3]. Still missing however is an investigation of the role of gap states at such an organic/inorganic hybrid interface, particularly in the

light of increased emphasis on gap states as a driver for interfacial energy level alignment [19–21].

Here, we report the results of such a study for a broad range of organic semiconductors on quasi-2D multilayer SnS₂. SnS₂ has a bulk indirect bandgap of 2.2 eV, and yields large micron-sized single-crystal domains upon cleavage or micromechanical exfoliation. As a metal dichalcogenide, SnS₂ grows in extended sheets with the Sn atoms sandwiched between two layers of S, illustrated in Fig. 1. Since the individual layers have fully satisfied chemical bonds, the SnS₂ layers are only bonded by van der Waals forces. This yields a surface that is chemically rather inert, atomically abrupt and with little driving force for surface reconstruction, although we show that SnS₂ surfaces can interact strongly with adsorbed molecules.

We use ultraviolet and x-ray photoemission spectroscopies to monitor the evolution of the interfacial energy level alignment as a function of thin film growth of molecular semiconductors on the highly ordered SnS₂ surface. Although we are able to fully describe the interfacial interactions of the as-deposited films, we also observe surprising yet reproducible shifts of the vacuum level as a function of UV illumination. Our results indicate that these shifts arise from interfacial interactions that are enabled by electronic coupling between surface-confined gap states, the bulk electronic structure and molecular states. These effects likely play a role also for charge-transport in organic/(quasi-)2D heterostructures. This interpretation is supported by observations of related behavior for the topologically protected surface states of Bi₂Se₃ [22,23]. This suggests therefore that this phenomenon may also play a role in the 2D limit of metal dichalcogenides, and represents energetic decoupling of surface states in reduced dimensions.

In the following, we present a detailed analysis of the interfacial energy level alignment for thin films of vanadyl naphthalocyanine

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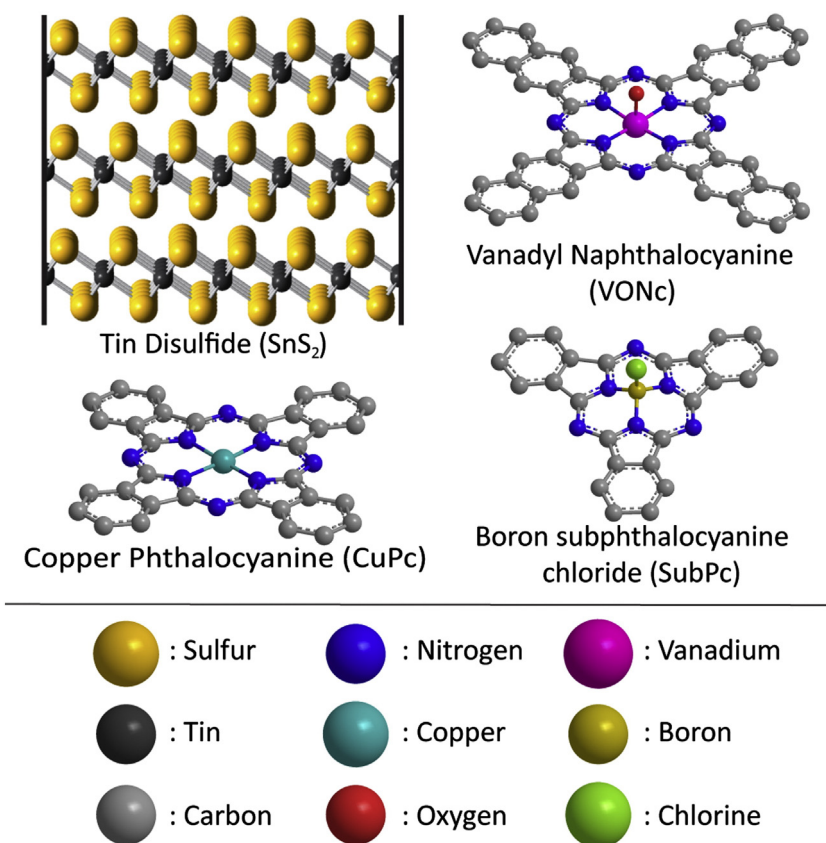


Fig. 1. Crystal structure of tin disulfide (SnS_2), illustrating three vertically stacked layers of extended 2D sheets, along with molecular structures of three organic semiconductor molecules that were deposited on SnS_2 .

(VONc) on SnS_2 . We then describe slow changes in this alignment that are caused by UV illumination and demonstrate that such shifts are independent of film morphology and molecular structure and are not caused by sample charging or degradation. Finally, by comparing a range of different organic semiconductors on SnS_2 we establish that these shifts are caused by the lack of resonance between the molecular highest occupied molecular orbital (HOMO) and the bulk substrate bands. We explain these shifts in terms of coupling and charge-trapping between the organic molecules and SnS_2 gap states, enabled by the unique properties of the quasi-2D surface.

2. Experimental

UPS spectra were collected at room temperature in a VG EscaLab MK II photoelectron spectrometer, base pressure 5×10^{-10} Torr. The excitation source was a He(I) lamp (Spec UVS 10/35, 30° angle of incidence from normal), and maximum sample emission currents of $10 \mu\text{A}$ were used. Spectra were referenced to the known position of the analyzer Fermi level, which was calibrated using a sputter-cleaned Au foil. The work function was measured from the baseline intercept with the spectral slope at the inflection point in the low kinetic energy region (secondary electron cutoff, SECO). Full spectra were recorded with a takeoff angle of 0° with respect to normal, $\pm 12.5^\circ$ acceptance angle, -5 V sample bias, and 5 eV pass energy. In the valence band/highest occupied molecular orbital (HOMO) region, no sample bias was used. In order to measure spectra as close as possible to equilibrium conditions, fast scan rates keeping acquisition time to a few minutes were used.

Core level photoemission spectroscopy of SnS_2 was performed in a Kratos Axis Ultra DLD XPS/UPS system using a monochromatized Al $K\alpha$ anode with a pass energy of 20 eV. For the variable power XPS

measurements, a constant anode voltage of 15 kV was used, while the emission current was varied from 1 mA to 20 mA.

Bridgman-grown SnS_2 samples were prepared according to previously published methods [24]. The carrier concentration of the doped crystal was determined to be $2.3(1) \times 10^{17} \text{ cm}^{-3}$ by the van der Pauw method [24]. The SnS_2 sample was cleaved in air immediately before introduction into an ultrahigh vacuum loadlock with a base pressure of 1×10^{-9} Torr. After pumping down, the sample was transferred to the photoelectron spectrometer, equipped with an integrated sample heater. The sample was degassed and cleaned by holding the sample at $\sim 250^\circ \text{C}$ for approximately 12 h. Sample stability at this temperature was confirmed by comparison to an SnS_2 crystal that was intentionally heated to its degradation point ($>300^\circ \text{C}$). At this point S begins to sublime, creating an Sn-enriched sample that has a distinctive optical appearance and causing new features to appear in both ultraviolet and x-ray photoelectron spectra.

VONc was purchased from Sigma-Aldrich and used without further purification. Prior to sublimation from a home-built Knudsen cell, the cell was ramped from 100°C to 450°C over three hours in order to degas the sample. The cell was then maintained at 450°C for approximately 30 min to establish a steady deposition rate. Copper phthalocyanine (CuPc), boron subphthalocyanine chloride (SubPc), and fullerene (C_{60}) were purified by gradient sublimation and deposited in a similar fashion to VONc, with the temperatures tailored to the particular molecule.

Sample deposition occurred at around $0.4 \text{ \AA}/\text{min}$ in a custom-built deposition chamber with a base pressure of 1×10^{-9} Torr. Film thicknesses were determined using a quartz crystal microbalance that was calibrated against known thicknesses of VONc on highly ordered pyrolytic graphite (HOPG) [25,26]. 4 \AA VONc was determined to be 1 monolayer equivalent (MLE).

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