

Impact of CVD chemistry on band alignment at the MoS₂/SiO₂ interface

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Reliable knowledge of energy alignment of electronic bands at interfaces of few layered Molybdenum Disulfide (MoS₂) is crucial for designing MoS₂ based electronic devices. In this work, we have applied internal photoemission spectroscopy (IPE) to characterize this band alignment. MoS₂ films grown on SiO₂(50nm)/Si using two different methods have been analyzed by IPE to determine the energy position of the semiconductor valence band (VB) relative to the reference level of the insulator conduction band (CB). We found that changing the MoS₂ growth method from Vapor Phase Reaction (VPR) of MoO₃ and sulfur, to Solid Precursor Film (SPF) of sulfurized AHM-NaOH spin coated MoS₂ film, results in significant (≈ 600 meV) enhancement in the electron barrier. Such effects are ascribed to the interaction of hydroxy groups from NaOH and AHM promoters with the SiO₂ surface leading to interface dipole modification.

1. Introduction

Molybdenum disulfide (MoS₂) is one of the most extensively studied 2D material, thanks to its stability, natural abundance, and semiconducting electrical properties.[1][2] In particular, few layered MoS₂ attracts much of interest as a channel material for overcoming the short-channel effects in ultra-scaled field-effect transistors (FETs).[3][4] However, the on-current in such short-channel FETs is severely limited by the contact resistance (R_c) related to energy barrier at the interface between the semiconductor channel and the contact metal. Furthermore, ultrathin MoS₂ can also be used in tunneling stacks to fabricate transistors with very steep sub-threshold slope, mandatory for low voltage electronics.[5] In these devices, the electron band alignment at MoS₂ interfaces directly affects the electrostatics of the stacks such as built-in voltages, transistor thresholds, as well as the tunneling barrier heights.[6]

Motivated by its application potential, a high demand for high quality large area 2D-MoS₂ synthesis techniques becomes obvious. Among several known methods, chemical vapor deposition (CVD) is considered as promising route offering numerous advantages such as large scale growth, high crystal quality and thickness control.[7] Here we address two

different CVD growth methods: (i) the Solid Precursor Film (SPF) approach where pre-deposited thin film of spin-coated ammonium heptamolybdate tetrahydrate (AHM) with sodium hydroxide (NaOH) is sulfurized in a single thermal zone furnace [8] and (ii) the Vapor Phase Reaction (VPR) approach where Mo and S solid powder precursors react in a multiple zones furnace.[9] These two methods were able to produce large area MoS₂ with similar thickness. However, a clear understanding of growth chemistry and its influence on the band alignment of MoS₂/SiO₂ interface in different routes is essential. In addition, it is challenging to accurately measure the band alignments at interfaces of 2D materials due to its atomic sensitivity to environment.

Internal photoemission spectroscopy (IPE) allows one to directly determine the energy barrier height at different interfaces such as metal/insulator and semiconductor/insulator entities. An added advantage of IPE is that it can characterize discontinuous films using high work function metal contact layer, which makes it more relevant to the initial stages of a 2D film formation. Recent works demonstrate successful application of IPE to different 2D layered materials, prepared using the layer transfer or direct growth methods.[11]

In this work, by using the IPE, we report on the influence of the MoS₂ growth chemistry on the band offset at the 3L-MoS₂/SiO₂ interface from the semiconductor VB into the CB of the insulating layer.

2. Experimental Details

Few-layer MoS₂ films were synthesized using ambient pressure CVD (AP-CVD) using two growth methods (i) from powder precursors of molybdenum oxide (MoO₃) and sulfur(S) at 750°C, or (ii) heterogeneous vapor-solid reaction between a pre-deposited film by spin-coated solution containing AHM and NaOH in the presence of sulfur vapor at 850°C, in the Ar carrier gas. Both MoS₂ films were grown on SiO₂(50nm)/p⁺-Si(100) 2 cm x 2cm sized substrates. Atomic force microscopy (AFM, Bruker Dimension Edge) was used to investigate the surface morphology and the thickness of the as-grown MoS₂

nanosheets and Raman spectroscopy (InVia Renishaw, laser wavelength 514.5 nm) analysis on as-grown films confirm the growth of 3 layers MoS₂ as shown in Fig. 1(a-d).

Figures 1a,b show the AFM topography image and the height profile (below) of the MoS₂ on the substrate, respectively. From the height profile, the thicknesses of the MoS₂ grown by using two CVD routes were found to be about 2 nm, suggesting that there are about 3 monolayers (MLs) MoS₂. A slight increase in the surface roughness was observed in AHM+NaOH assisted MoS₂ growth as shown in Figure 1b. The Raman spectrum of MoS₂ exhibits two characteristic modes, the in-plane E_{2g}¹ mode at 383.8, 384.1 cm⁻¹ and the out-of-plane A_{1g} mode at 406.5, 406.3 cm⁻¹ at room temperature, respectively. The separation between A_{1g} and E_{2g}¹ modes is 22.7 cm⁻¹ (MoS₂ from MoO₃ and S powders) and 22.2 cm⁻¹ (MoS₂ from sulfurized AHM-NaOH), which is consistent with 3-layer film thickness as shown in figure 1c, d respectively. Further details of the growth and structural characterization on the MoS₂ films grown by different CVD methods have already been reported elsewhere [9][10].

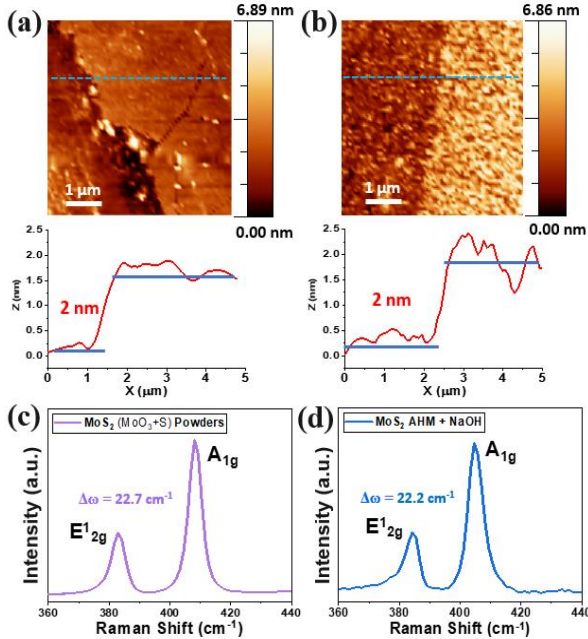


Fig. 1: AFM topographies of the MoS₂ films grown on SiO₂/Si (a) from MoO₃ and sulfur powder precursors and (b) from sulfurized AHM and NaOH; height profiles (below) where solid lines are traced to retrieve film thickness. Raman spectra indicating the presence of the typical 2 main phonon modes in MoS₂. Their frequency difference $\Delta\omega$ corresponds to 3 layers: (c) from MoO₃ and S powders (d) from sulfurized AHM and NaOH spin-coated solution.

Fig 2 shows the schematic adopted for IPE measurements. It consist of a capacitor structure with top semi-transparent (15-nm thin) Au contacts of 0.5 mm² area thermo-resistively evaporated on top of the MoS₂ film through a shadow mask, and the Al back contact layer. When illuminating the sample with light of known photon energy, $h\nu$, and intensity, electrons excited from the VB of MoS₂ can be injected into the CB of SiO₂. Under applied negative bias the injected electrons drift towards Si substrate resulting in

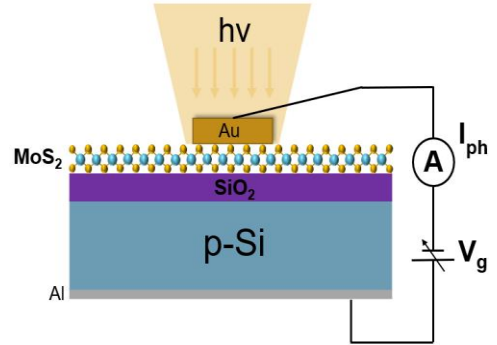


Fig 2: Schematic of IPE measurements on a MoS₂/SiO₂(50nm)/p-Si capacitor with a top metal semitransparent contact. The negative bias voltage (V_g) is applied between the top Au film and the back Al contact.

photocurrent measured using a Keithley 6517a electrometer. The photocurrent, defined as the difference between the current measured under illumination (I_{light}) and the dark current (I_{dark}), was normalized to the incident photon flux to calculate the IPE quantum yield (Y) [11].

To determine the IPE energy threshold (Φ_{MoS_2}), which corresponds to the energy barrier for the electron transitions between the upper occupied electron states in the VB top of MoS₂ and unoccupied states at the CB bottom of SiO₂, we use the following equation [12]:

$$Y(h\nu) = A \cdot (h\nu - \Phi_{\text{MoS}_2})^p,$$

where A depends on the optical properties of the sample and is assumed to be constant in the near-threshold spectral range. The p value is taken equal to 3 for IPE from MoS₂ and corresponds to the linear increase with energy in the VB density of electron states below the VB top edge [12][13].

3. Results and Discussion

The IPE yield spectra of MoS₂ grown by two different synthesis routes, shown in Fig 3(a, b), clearly reveal different spectral thresholds in the $Y^{1/3}$ - $h\nu$ plot (the Powell coordinates) [12]. The spectral thresholds extracted by linear fitting of these $Y^{1/3}$ - $h\nu$ plots at

different applied voltages are combined in the Schottky plot shown in Fig. 4(a) yielding the zero-field energy barriers of 4.2 ± 0.1 eV (black symbols) and 3.6 ± 0.1 eV (red symbols) for AHM-NaOH sulfurized MoS_2 and MoS_2 grown from MoO_3 and S powders, respectively. Such a significant variation of interface barrier values reveals strong impact of the CVD chemistry on the $\text{MoS}_2/\text{SiO}_2$ band alignment. This sensitivity indicates the change of energy position of the VB top edge of MoS_2 below the SiO_2 CB bottom edge due to the extrinsic factors related to the semiconductor synthesis route.

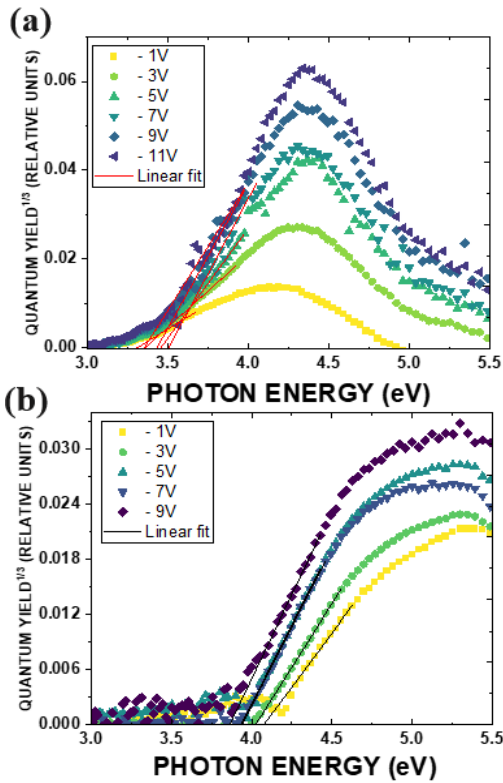


Fig 3: Powell plots of electron IPE quantum yield from (a) MoS_2 films grown by MoO_3 and S powders [3L $\text{MoS}_2/\text{SiO}_2$ (50 nm)/Si] and (b) by AHM-NaOH after sulfurization [3L $\text{MoS}_2/\text{SiO}_2$ (50 nm)/Si], measured under the indicated negative bias (from -1V to -11V).

Further, the spectral thresholds exhibit a linear dependence on the square root of electric field in the oxide as can be seen from the Schottky plot in Fig. 4(a) but with different slopes. The latter indicates that change in the MoS_2 growth method affects distribution of electric field at the $\text{MoS}_2/\text{SiO}_2$ interface resulting in different field-induced barrier lowering. The barrier difference indicates that the VB top value in 3L MoS_2 grown from VPR method (in hydrogen-free conditions) lies ≈ 600 meV above the VB top

value in the 3L MoS_2 film synthesized with SPF method from the H-containing AHM-NaOH-S precursors as measured relative to the common reference level of the SiO_2 CB bottom. This behavior appears to be consistent with the previously reported impact of hydrogen presence in the synthesis ambient on the $\text{MoS}_2/\text{SiO}_2$ interface barrier despite physically and chemically different routes of the MoS_2 synthesis used in these two studies.[13] It is worth noticing that these process-dependent IPE behavior of MoS_2 suggests a chemical modification at the interface of MoS_2 with SiO_2 probably occurring at the oxide side of the interface because structural analysis shows the 3L- MoS_2 films to be nearly identical.

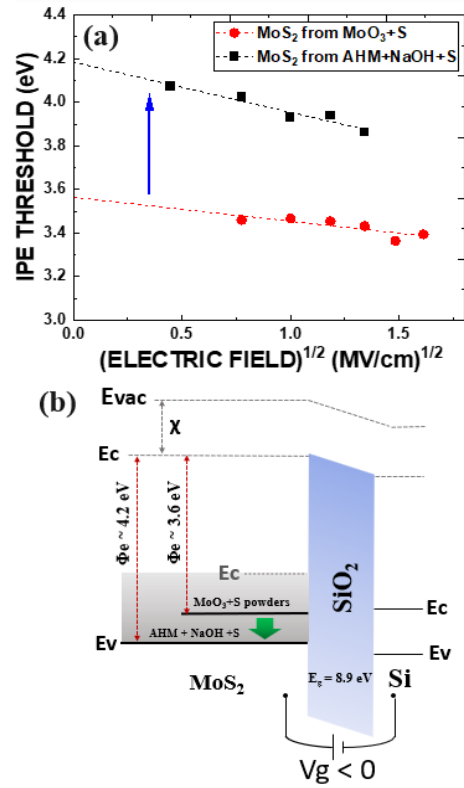


Fig 4: (a) Field dependence of IPE thresholds as measured at 3L- $\text{MoS}_2/\text{SiO}_2$ (50nm)/Si capacitors (red symbols for MoS_2 from powders; black symbols for MoS_2 from AHM + NaOH). Dashed lines illustrate linear extrapolation to zero field in SiO_2 . (b) Schematic of the energy band diagram of the 3L- $\text{MoS}_2/\text{SiO}_2/\text{Si}$ stack measured under negative bias.

It is possible that interaction of hydroxide ions from NaOH promoter with the SiO_2 surface layer leads to the formation of an interface dipole and negative charges. It was hypothesized [13] that the presence of hydrogen during MoS_2 sulfurization process affects the density of silanol groups at the oxide side of the interface which is sensitive to temperature and chemical environment. Our findings seem to support this model. Figure 4b shows the scheme of the energy

band lineups measured at the two interfaces used in this work, i.e., the 3L MoS₂/SiO₂ from MoO₃ and sulfur and 3L-MoS₂/SiO₂ from AHM-NaOH and sulfur. Hypothetically, this dipole layer formation can be seen as an array of polar O-H bonds in silanol (SiOH) groups from AHM + NaOH seed layer as has been previously reported for the MoS₂/SiO₂ interfaces.[13,14]

4. Conclusion

Our IPE spectroscopy study reveals that the VB top of 3L-MoS₂ synthesized from sulfurization of AHM and NaOH spin-coated solution on top of SiO₂ insulator is positioned \approx 0.6 eV lower in energy than the VB of MoS₂ film of the same thickness grown from MoO₃ and sulfur powders. Such variation indicates the considerable impact of the synthesis method on the band alignment. This effect is probably related to the formation of interface charges or dipoles due to the formation of hydroxy groups or trapped charges from NaOH and AHM promoters. This factor needs to be taken into account when CVD-grown MoS₂ films is considered as channel material in low-voltage devices as it may lead to significant device variability.

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