Band alignment at interfaces of few-monolayer MoS\textsubscript{2} with SiO\textsubscript{2} and HfO\textsubscript{2}

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Internal photoemission of electrons from 4- and 2-monolayer thick MoS\textsubscript{2} films prepared by sulphurization of metallic Mo on top of SiO\textsubscript{2} or HfO\textsubscript{2}/SiO\textsubscript{2} insulating stacks is detected. This enables determination of the energy position of the MoS\textsubscript{2} valence band which is found to be at 4.1–4.2 eV below the SiO\textsubscript{2} characterizing by a hexagonal bandgap edge energies with respect to the SiO\textsubscript{2} valence band. At the interface with HfO\textsubscript{2}, a barrier height of 3.7 eV is found, corresponding to an increase of the electron affinity of MoS\textsubscript{2} by ≈0.5 eV as compared to the SiO\textsubscript{2} case. This suggests the presence of interface charges (or dipoles) in the interfacial HfO\textsubscript{2} layer.

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1. Introduction

Layered transition metal dichalcogenide semiconductors attract considerable interest because of their tunable properties relevant to a broad range of applications. In particular, few-layer MoS\textsubscript{2} has already been shown to deliver significant advantages in terms of transistor channel downscaling and optoelectronic properties [1]. The performance of the MoS\textsubscript{2}-based devices critically depends on the band alignment with other materials since the alignment determines the electrostatics of the stack, height of the tunneling barriers, contact resistance, etc. Therefore, characterization of the barriers at interfaces of few-layer 2D materials generally represents quite an experimental challenge: The electronic transport across the interfaces is strongly affected by hydrocarbon residues of the flake transfer process [2], non-homogeneities (e.g., domain boundaries), and defects in the material itself [3]. For example, it is found that the same metal on MoS\textsubscript{2} may provide both n- and p-type Schottky barriers, pointing to an inhomogeneous work function distribution [3,4].

Therefore, it is important to find a technique allowing one to reliably determine the MoS\textsubscript{2} bandgap edge energies with respect to other materials. In the present work we will show that this goal can be achieved using the spectroscopy of Internal PhotoEmission (IPE) of electrons from MoS\textsubscript{2} into an insulating layer. By using 2- and 4-monolayer (ML) thick MoS\textsubscript{2} films on top of a SiO\textsubscript{2} layer or HfO\textsubscript{2}/SiO\textsubscript{2} stack as the prototype interfaces, we observe IPE from across thin 2D photo-emitter and determine the corresponding energy barriers.

2. Experimental

The studied samples were prepared by thermal evaporation of a thin Mo film on SiO\textsubscript{2}(50 nm)/p\textsuperscript{+}-Si (B-doped, $n_\text{d} \approx 10^{20}$ cm\textsuperscript{-3}) or HfO\textsubscript{2}(2 nm)/SiO\textsubscript{2}(50 nm)/p\textsuperscript{+}-Si substrates. Next, the Mo/oxide/Si samples were transferred to a furnace and sulfurized in pure H\textsubscript{2}S(100 mbar) at 800°C resulting in the formation of a large-area (in the range of cm\textsuperscript{2}) polycrystalline MoS\textsubscript{2} film with crystallites of ≈50 nm size across as revealed by atomic force microscopy. Cross-sectional transmission electron microscopy (TEM) images, such as shown in Fig. 1, reveal the characteristic layered structure of a ~3 nm thick MoS\textsubscript{2} film (~4 molecular planes of 0.65-nm thick each [1]). The Raman spectrum shown in the same figure exhibits two distinct peaks at around 383 cm\textsuperscript{−1} and 408 cm\textsuperscript{−1} corresponding to the in-plane ($E_{2\text{g}}$) and the out-of-plane ($A_{1\text{g}}$) vibrations in MoS\textsubscript{2}, respectively [1]. This observation and electron spectroscopy analysis reveals conversion of metallic Mo into 2H-MoS\textsubscript{2} characterized by a hexagonal crystalline structure and trigonal prismatic coordination geometry, also supported by plane-view TEM images (not shown). By varying the thickness of the initially deposited Mo, it appears possible to produce samples with 4 or 2 ML thick MoS\textsubscript{2} films without contamination of the MoS\textsubscript{2}/oxide interfaces.

To ensure reliable electrical contacts, optically nontransparent (100-nm thick) Au or Al pads (0.01 mm\textsuperscript{2} area) were evaporated on top of the MoS\textsubscript{2} film. For the sake of comparison, one 4 ML MoS\textsubscript{2} sample was metalized by evaporating semitransparent...
The IPE quantum yield $Y$ measured as a function of the photon energy $h\nu$ and the $Y^{1/3}$-$h\nu$ plots used to extract the spectral thresholds are shown in Fig. 2 (open symbols) for a 4 ML MoS$_2$/SiO$_2$/Si sample with Au contact pads. The spectral curves exhibit a clearly visible red-shift with increasing negative voltage applied to the MoS$_2$ film due to the image-force barrier lowering (the Schottky effect). This observation points to IPE of electrons into the conduction band (CB) of SiO$_2$ since the barrier lowering becomes visible only in the case of ballistic photo-electron transport across the interface barrier. The corresponding spectral thresholds extracted from the $Y^{1/3}$-$h\nu$ plots [6] shown in Fig. 2(b) obey the image-force model as evidenced by the Schottky plot shown in Fig. 3(a). The barrier height $\Phi_b$ between the valence band (VB) of MoS$_2$ and the oxide CB can be found by extrapolation to zero electric field, giving the value $\Phi_b(MoS_2) = 4.20 \pm 0.05$ eV, where the image force dielectric constant $\varepsilon_i$ is found to be consistent with the value expected for SiO$_2$: $\varepsilon_i \approx n^2 = 2.1$, where $n = 1.46$ is the refractive index of SiO$_2$.

For the sake of comparison, in Fig. 2(a) are also shown IPE yield spectra corresponding to electron emission from the p$^+$-Si substrate (●, positive bias) and from the 2-ML MoS$_2$ film (■). Electron IPE from Si can be identified on the basis of the yield drop observed at $h\nu \approx 4.3$ eV corresponding to the excitation of direct optical transitions in the Si substrate crystal (the $E_2$ singularity [7]). The quantum yield value of the electron IPE from Si is approximately 10 times higher than from a 4 ML MoS$_2$ photomitter (cf. the range $h\nu > 5$ eV), reflecting the small volume available for the optical excitation in the last case. This explanation is also consistent with even lower yield observed in the case of IPE from a 2 ML MoS$_2$ electrode [cf. Fig. 2(a)] independently, indicating electron IPE from few-ML MoS$_2$.

Comparison of the field-dependent spectral thresholds measured in the structures with 4 ML MoS$_2$ electrodes and Au or Al contact pads [Fig. 3(a)] reveals that the metal work function has no significant influence on the results, further supporting the identification of the IPE as constituting electron emission from MoS$_2$. In the case 2 ML MoS$_2$, the spectral thresholds are slightly ($\approx 150$ meV) lower than for the 4 ML MoS$_2$ layer but still obey the same image-force law. By contrast, as evident from Fig. 3(a), the sample with the Au blanket contact on top of 4 ML MoS$_2$ shows no measurable barrier lowering while the spectral threshold value exactly corresponds to the zero-field barrier value found in the case of IPE from an unmetallized MoS$_2$ layer. This effect can also...
Since the density of charge carriers in the MoS2 interlayer is reduced by Mo in-diffusion or defect formation into the HfO2 film [5]. Since the direct interlayer electron injection (IPE) from the MoS2 layers into the conduction band (CB) of SiO2 is insufficient to screen a hole left behind by a photoelectron excited from the VB, this has appeared possible to observe an electron IPE barrier in the SiO2/MoS2 interface with Mo/SiO2/C stacked structures [6], where the Schottky plots shown in Fig. 3(b) indicate that no Fermi level pinning is found at the interface with SiO2/C interfaces [7]. The zero of the energy scale is at the top of the valence band of the Si substrate.

It is instructive to compare the energy position of the MoS2 CB with previous results [7] where the Fermi level of metallic Mo has been measured relative to the same reference level, namely that of the MoS2/CB. The Schottky plots shown in Fig. 3(b) indicate that after annealing of the Mo/SiO2/Si entities at a temperature above 700 °C, the barrier for electron IPE from metallic Mo nearly coincides with that inferred above for IPE from the MoS2/CB. This observation suggests that Mo might be a viable candidate to provide an Ohmic contact to p-type MoS2 layers.

In the case of IPE from MoS2 into the HfO2/SiO2 stack we found an energy threshold at $\Phi_e(MoS_2) = 3.7 \pm 0.05$ eV, with no measurable field dependence as illustrated in Fig. 4. The latter suggests that electron injection from the CB of HfO2 into the CB of SiO2 does not constitute the rate-limiting step of electron injection, pointing to trap-assisted electron transport across the HfO2/SiO2 interface. As compared to the IPE into SiO2, the quantum yield of electron IPE in the presence of a 2-nm thick HfO2 layer is reduced by a factor of $\sim 10^2$, suggesting additional scattering of electrons at charges located in the near-interface oxide layer. Furthermore, at the MoS2/HfO2/SiO2 interface it has appeared possible to observe a second threshold at $\Phi_e = 2.3 \pm 0.1$ eV, as illustrated in the inset in Fig. 4(b). This threshold is caused by excitation of electrons from acceptor traps known to be abundant in SiO2 [8]. The electron occupancy of these traps would be controlled by the Fermi energy in the electrode [9] which is expected to be near the CB bottom of MoS2 under negative bias. This is illustrated in Fig. 5 which shows schematic band diagrams of the studied interfaces constructed using the electron IPE barrier values, the above mentioned MoS2 gap width, and the electron affinity of SiO2, 0.9 eV [10]. The drop of the photo-yield in the spectral range 3.7–3.9 eV (cf. Fig. 4) is caused by photocurrent in the opposite direction. This signal is probably trap-related and originates in the sample area outside of the biased capacitor, leading to a quasi-stationary current due to emitter-to-trap [11] or trap-to-electrode charge carrier transfer [8].

Fig. 5 also indicates electron affinities for 4-ML MoS2 inferred by referencing the CB minimum energies [12–14] to the vacuum level, $E_{\text{vac}}$, defined as the energy of the electron at rest at infinity, i.e., in a region without electric fields [15,16]. For the MoS2 grown directly on SiO2, an affinity of 3.7 eV is found that is about 0.3 eV lower than the commonly cited 4 eV value [3,5]. However, at the MoS2/HfO2/SiO2 interface the MoS2 affinity appears to increase by 0.5 eV larger, suggesting the formation of a polarization layer containing negative charges or a dipole. The increase of the affinity and the earlier mentioned disappearance of the barrier field dependence closely resemble the effect of electron trapping by impurities or defects in the insulator earlier observed in the case of Eu-doped SrF2 [17]. Therefore, we hypothesize that electron traps are introduced into near-interface HfO2 layers during MoS2 synthesis due to Mo in-diffusion or, else, defect generation during the sulfuration anneal. These negatively charged defects “pin” the top of the potential barrier close to the MoS2 surface, making the field dependence of its height undetectable.
4. Conclusions

Observation of IPE from quasi-2D few-ML MoS₂ photoemitters is shown to enable determination of the band alignment with oxide insulators. In addition to providing the relevant band offsets with good accuracy, an effect of the HfO₂ interlayer on the barrier is revealed, suggesting an influence of interface charges or dipoles.

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References