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Band alignment at interfaces of few-monolayer MoS_2 with SiO_2 and HfO_2

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ABSTRACT

Internal photoemission of electrons from 4- and 2-monolayer thick MoS_2 films prepared by sulphurization of metallic Mo on top of SiO_2 or HfO_2/SiO_2 insulating stacks is detected. This enables determination of the energy position of the MoS_2 valence band which is found to be at 4.1–4.2 eV below the SiO_2 conduction band. At the interface with HfO_2, a barrier height of 3.7 eV is found, corresponding to an increase of the electron affinity of MoS_2 by ≈0.5 eV as compared to the SiO_2 case. This suggests the presence of interface charges (or dipoles) in the interfacial HfO_2 layer.

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_2 has already been shown to deliver significant advantages in terms of transistor channel downscaling and optoelectronic properties [1]. The performance of the MoS_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. However, 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_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_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_2 into an insulating layer. By using 2- and 4-monolayer (ML) thick MoS_2 films on top of SiO_2 layer or HfO_2/SiO_2 stack as the prototype interfaces, we observe IPE from a 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_2(50 nm)/p^+-Si (B-doped, $n_a \approx 10^{20}$ cm^{-3}) or HfO_2(2 nm)/SiO_2(50 nm)/p^+-Si substrates. Next, the Mo/oxide/Si samples were transferred to a furnace and sulfurized in pure H_2S(100 mbar) at 800 °C resulting in the formation of a large-area (in the range of cm^2) polycrystalline MoS_2 film with crystallites of ≈50 nm size 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_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^{-1} and 408 cm^{-1} corresponding to the in-plane (E_{2g}) and the out-of-plane (A_{1g}) vibrations in MoS_2, respectively [1]. This observation and electron spectroscopy analysis reveals conversion of metallic Mo into 2H-MoS_2 characterized by 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_2 films without contamination of the MoS_2/oxide interfaces.

To ensure reliable electrical contacts, optically nontransparent (100-nm thick) Au or Al pads (0.01 mm^2 area) were evaporated on top of the MoS_2 film. For the sake of comparison, one 4 ML MoS_2 sample was metalized by evaporating semitransparent (13-nm thick) blanket Au electrodes of 0.5 mm^2 area. The steady-state

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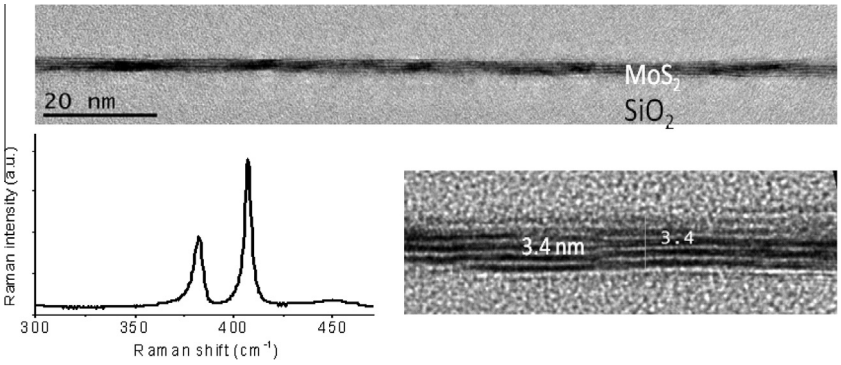

Fig. 1. Cross-sectional TEM images and Raman spectra of a 4 ML $MoS_2/SiO_2/Si$ sample.

value of the IPE current was measured between the Si substrate and the MoS_2 layer by applying a negative bias to MoS_2 to enable electron photoinjection. Generally, the major challenge in the realization of IPE from a 2D material is related to the fact that direct optical transitions result in electrons with predominantly in-plane momentum orientation [1,5] which would not allow them to surmount the interface barrier. Nevertheless, the present study indicates that IPE from the quasi-2D MoS_2 emitter can be detected, suggesting relaxation of the momentum conservation rule.

3. Results and discussion

The IPE quantum yield (Y) measured as a function of the photon energy (hν) and the $Y^{1/3}$-hν 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 increasing 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 $Y^{1/3}$-hν 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 Φ_e between the valence band (VB) of MoS_2 and the oxide CB can be found by extrapolation to zero electric field, giving the value $\Phi_e(MoS_2) = 4.20 \pm 0.05$ eV, where the image force dielectric constant ε_i is found to be

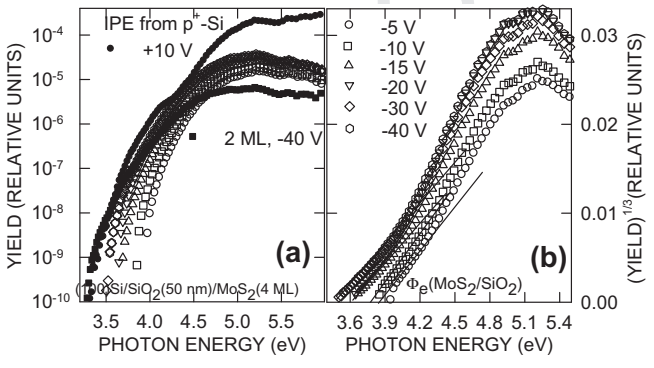

Fig. 2. (a) Quantum yield as a function of photon energy measured on the (100)Si/SiO_2(50 nm)/MoS_2(4 ML) structures under different negative bias voltages applied to the MoS_2 electrode (open symbols). The IPE yield spectra corresponding to electron emission from the p^+-Si substrate (●), observed under positive bias, and from a 2-ML MoS_2 film (■) are also shown for comparison; (b) Determination of the IPE spectral threshold using linear extrapolation of the $Y^{1/3}$-hν plots.

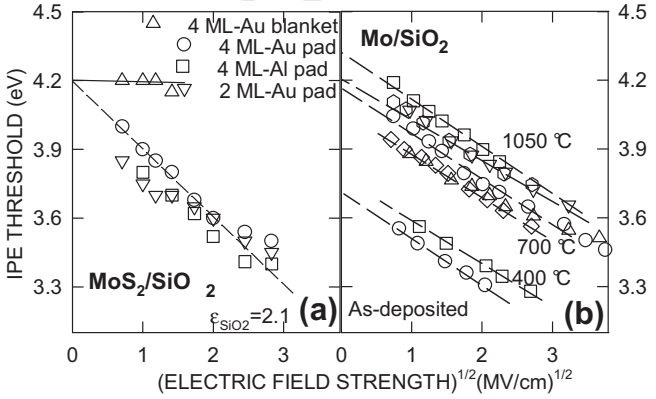

Fig. 3. (a) The Schottky plot of spectral thresholds measured on (100)Si/SiO_2(50 nm)/MoS_2 structures using different contact schemes and metallization materials; (b) Schottky plot of spectral thresholds measured on the (100)Si/SiO_2(10 nm)/Mo(10 nm) structures after 30 s annealing in N_2 at different temperatures (after Ref. [7]).

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 electron IPE from Si is approximately 10 times higher than from a 4 ML MoS_2 photoemitter (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 (≈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 be seen as indication that the IPE occurs by excitation of electrons from the MoS_2 electrode: Since the density of charge carriers in MoS_2 is insufficient to screen a hole left behind by a photoelectron