Manuscript Number:

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Article Type: SI: INFOS 2015

Keywords: Interface barrier, internal photoemission, electron affinity, band offset

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Editor
Special Issue
Microelectronic Engineering
INFOS 2015

19 Februari 2015

Dear Editor,

Please find enclosed our MS entitled

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by

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which we would like to submit for publication in Microelectronic Engineering as proceedings paper of INFOS 2013 conference.

Yours sincerely,

Valeri V. Afanas'ev

Band alignment at interfaces of few-monolayer MoS₂ with SiO₂ and HfO₂

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Abstract

Internal photoemission of electrons from 4- and 2-monolayer thick MoS₂ films prepared by sulphurization of metallic Mo on top of SiO₂ or HfO₂/SiO₂ insulating stacks is detected. This enables determination of the energy position of the MoS₂ valence band which is found to be at 4.1-4.2 eV below the SiO₂ conduction band. At the interface with HfO₂, a barrier height of 3.7 eV is found, corresponding to an increase of the electron affinity of MoS₂ by ≈ 0.5 eV as compared to the SiO₂ case. This suggests the presence of interface charges (or dipoles) in the interfacial HfO₂ 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 MoS₂ has already been shown to deliver significant advantages in terms of transistor channel downscaling and optoelectronic properties [1]. The performance of the MoS₂-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 MoS₂ 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 MoS₂ 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 MoS₂ into an insulating layer. By using 2- and 4-monolayer (ML) thick MoS₂ films on top of SiO₂ layer or HfO₂/SiO₂ 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 SiO₂(50 nm)/ p⁺-Si (B-doped, $n_a \approx 10^{20} \text{ cm}^{-3}$) or HfO₂(2nm)/SiO₂(50 nm)/ p⁺-Si substrates. Next, the Mo/oxide/Si samples were transferred to a furnace and sulfurized in pure H₂S (100 mbar) at 800 °C resulting in the formation of a large-area uniform MoS₂ film with hexagonal crystalline structure and trigonal prismatic coordination geometry. 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 reveals conversion of metallic Mo into MoS_2 . By varying the thickness of the initially deposited Mo, the described sulfurization process allowed the production of samples with 4 or 2 ML thick MoS_2 films. Importantly, this synthesis route allows one to avoid contamination of the MoS_2 /oxide interfaces.

Fig.1. Cross-sectional TEM images and Raman spectra of a 4ML $\text{MoS}_2/\text{SiO}_2/\text{Si}$ sample.

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 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 it possible to detect IPE from the quasi-2D MoS_2 emitter and

infer the corresponding spectral thresholds, suggesting relaxation of the momentum conservation rule.

3. Results and discussion

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 MoS₂/SiO₂/Si sample with Au contact pads. The spectral curves exhibit a clearly visible increasing red-shift with increasing negative voltage applied to the MoS₂ film due to the image-force barrier lowering (the Schottky effect). This observation points to IPE of electrons into the conduction band (CB) of SiO₂ 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 Φ_e between the valence band (VB) of MoS₂ and the oxide CB can be found by extrapolation to zero electric field, giving the value $\Phi_e=4.20\pm0.05$ eV, where the image force dielectric constant ϵ_i is found to be consistent with the value expected for SiO₂: $\epsilon_i \approx n^2=2.1$, where $n=1.46$ is the refractive index of the oxide.

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 MoS₂ 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 E₂ singularity [7]). The quantum yield value of electron IPE from Si is approximately 10 times higher than from a 4ML MoS₂ 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 2ML MoS₂ electrode [cf. Fig. 2(a)] independently indicating that electron IPE from few-ML MoS₂ is observed.

Fig. 2. (a) Quantum yield as a function of photon energy measured on the $(100)\text{Si}/\text{SiO}_2(50 \text{ nm})/\text{MoS}_2(4 \text{ ML})$ 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 ($\bullet$), observed under positive bias, and from a 2-ML MoS_2 film ($\blacksquare$) are also shown for comparison; (b) Determination of the IPE spectral threshold using linear extrapolation of the $Y^{1/3}$ - $h\nu$ plots.

Comparison of the field-dependent spectral thresholds measured in the structures with 4ML 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 ($\approx 150 \text{ meV}$) lower than for the 4ML 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 4ML 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 MoS₂ electrode: Since the density of charge carriers in MoS₂ is insufficient to screen a hole left behind by a photoelectron during IPE, the image-like interaction between these charges causes the observed barrier reduction [7]. However, in the presence of an Au overlayer, the electrostatic potentials of the optically excited carriers will be screened by electrons in the metal, resulting in reduction of their interaction.

Fig. 3. (a) The Schottky plot of spectral thresholds measured on (100)Si/SiO₂(50 nm)/MoS₂ structures using different contact schemes and metallization materials; (b) Schottky plot of spectral thresholds measured on the (100)Si/SiO₂(10 nm)/Mo(10 nm) structures after 30 s annealing in N₂ at different temperatures (after Ref. 7).

It is instructive to compare the energy position of the MoS₂ VB with previous results [7] where the Fermi level of metallic Mo has been measured relative the same reference level of the SiO₂ 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 VB. This observation suggests that Mo might be a viable candidate to provide Ohmic contact to p-type MoS₂ layers.

In the case of IPE from MoS₂ into the HfO₂/SiO₂ stack the spectral threshold is found at 3.70 ± 0.05 eV, with no measurable field dependence as illustrated in Fig. 4. As compared to the IPE into SiO₂, the quantum yield of electron IPE in the presence of a 2-nm thick HfO₂ interlayer is reduced by a factor of $\sim 10^2$, suggesting additional scattering of electrons at charges trapped in the near-interface oxide layer. Furthermore, at the MoS₂/HfO₂/SiO₂ interface it has appeared possible to observe a second threshold at 2.3 ± 0.1 eV, as illustrated in the inset in Fig. 4(b). The difference between these two spectral thresholds coincides (within the indicated accuracy limit) with the 1.4-eV wide bandgap of the 4-ML thin MoS₂ [5]. Therefore, the photocurrent characterized by the 2.3-eV threshold is likely caused by excitation of electrons from acceptor traps in HfO₂ [8] of which the occupancy would be controlled by the Fermi energy in the MoS₂ electrode being close to its CB bottom.

Fig. 4. (a) Quantum yield as a function of photon energy measured on the (100)Si/SiO₂(50 nm)/HfO₂(2 nm)/MoS₂(4 ML) structures under different negative voltages applied to the MoS₂ electrode; (b) Determination of the IPE spectral threshold using extrapolation of the $Y^{1/3}$ - $h\nu$ plots. The inset illustrates the evaluation of the low-energy threshold from the Y - $h\nu$ plot.

Using the above mentioned MoS₂ gap width and the electron affinity of SiO₂ of 0.9 eV [9] the inferred value of Φ_e between MoS₂ and SiO₂ would correspond to an electron affinity for 4-ML MoS₂ of 3.7 eV, which is about 0.3 eV lower than the commonly cited 4 eV value [3,5]. However, at the MoS₂/HfO₂/SiO₂ interface the affinity of MoS₂ appears 0.5 eV larger, suggesting the formation of a charge-containing polarization layer or a dipole.

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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Highlights:

- Internal photoemission of electrons from 4- and 2monolayer thick MoS₂ is observed.
- We found barrier heights for electrons at interfaces between MoS₂ and SiO₂ or HfO₂.
- Sensitivity of the barrier height to oxide composition indicates presence of dipoles.