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Investigating interface states and oxide traps in the MoS₂/oxide/Si system

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ABSTRACT

This paper reports on the study of inverted metal-oxide semiconductor (MOS) structures formed through mechanical exfoliation of MoS₂ flakes onto Al₂O₃ or SiO₂ layers grown on degenerately doped *p* type silicon substrates. Using Au/Ni metal top contacts, multi-frequency capacitance and conductance characterisation were performed to investigate electrically active defects in the MoS₂/oxide structures. This data has been paired with physics-based ac simulations which indicate close to ideal interfacial properties.

1. Introduction

In recent years 2D materials have featured prominently in research, as they exhibit energy gaps which span from semi-metals through to wide band gap semiconductors with potential applications including sensors, electronics, and flexible display technologies [1,2]. In the area of insulating gate electron devices, the 2D structure of the semiconductor has the potential to result in near ideal semiconductor/oxide interface [3] properties, which is one of the main factors motivating research into MOSFET and tunnel FET devices based on 2D semiconductors. The application of multi-frequency capacitance and conductance measurements to investigate electrically active defects in MoS₂/oxide structures is a research area which has emerged in recent years [4–8], covering back-gated MoS₂ transistors [4] and top-gated [5–8] MoS₂ MOSFETs. The aim of this contribution is to extend the study of back gated metal/MoS₂/oxide/Si MOS structures, where the MoS₂ layer is thicker than the maximum depletion width. The results from three separate processes, combining experimental data and physics-based ac simulations, all indicate close to ideal interfacial properties.

2. Experimental methods and analysis

Fig. 1a shows an optical image of an inverted AuNi/MoS₂/Al₂O₃/p⁺Si MOS capacitor, along a schematic of the structure (Fig. 1b) and cross sectional TEM images of the experimental devices (Fig. 1c). The structure was formed based on mechanical exfoliation of highly crystalline MoS₂ and subsequent transfer to the Al₂O₃ (23 nm)/p⁺Si substrate. This process requires the flakes to have a large and flat surface area to allow for metal contact formation. In addition, the MoS₂ flake thickness should exceed the maximum depletion width. Hall measurements on the starting MoS₂ crystals provide an indication for the required flake thickness. [9] The Ni (5 nm)/Au (160 nm) metal contact was aligned with the 728 nm MoS₂ flake by optical inspection, with no subsequent processing prior to electrical measurements.

The multi-frequency (100 Hz to 1 MHz) CV response of the structure from approximately −9V to +5 V is shown in Fig. 2a. The CV response in the depletion region shows negligible/no dispersion suggesting a very low density of electrically active interface defects (*D*_{it}). The negative shift in the CV response yields a net fixed oxide charge density of $8.3 \times 10^{12} \text{ cm}^{-2}$ (+ve), assuming all the fixed oxide charge is located at the MoS₂/Al₂O₃ interface. The fixed oxide charge density is determined based on the shift of the flat band voltage from the ideal value. This positive charge is typically observed for ALD grown Al₂O₃ prior to H₂/

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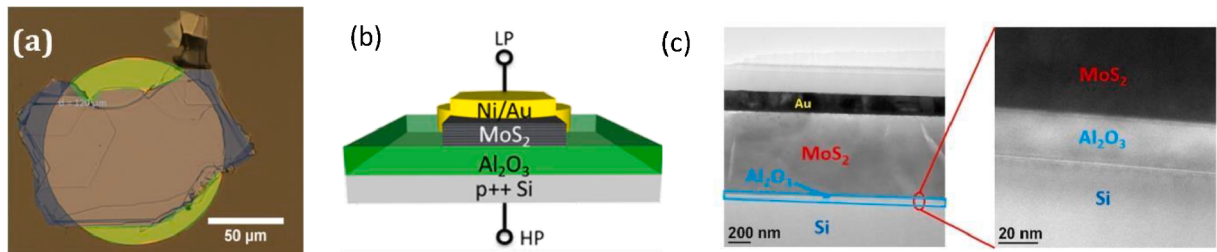


Fig. 1. Inverted MOS capacitor based on mechanically exfoliated MoS₂ (728 nm) transferred to 23 nm of ALD grown Al₂O₃ on degenerately doped p⁺ type silicon (1×10^{-2} to $2 \times 10^{-3} \Omega\text{cm}$). The top metal is 5 nm Ni and 160 nm Au. a) Optical picture of the device showing the metal in contact with (green) the Si/Al₂O₃ substrate and (blue) the MoS₂. b) Schematic cross section of the device. c) Cross sectional TEM of the structure, with a zoomed in image of the MoS₂/Al₂O₃/p⁺Si region. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

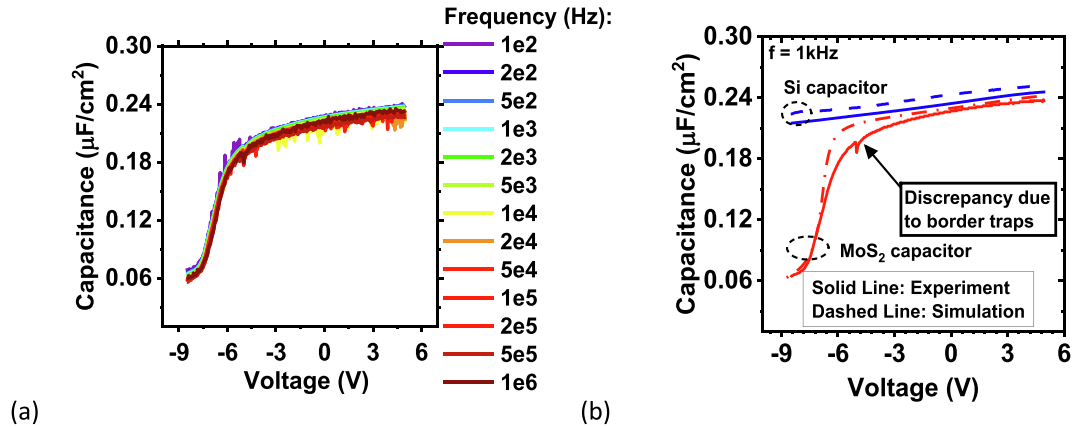


Fig. 2. (a) Experimental multi-frequency CV response of the NiAu/MoS₂/Al₂O₃/p⁺Si described in Fig. 1. CV was recorded at room temperature. (b) 1 kHz CV responses of AuNi/MoS₂/Al₂O₃/p⁺Si structure and the reference AuNi/MoS₂/Al₂O₃/p⁺Si structure. The dashed lines are the physics based ac simulations of the structure.

N₂ annealing, and the density value obtained is consistent with other ALD grown films with a thickness around 24 nm [10].

In conjunction with the experimental data, physics-based ac simulations of the CV response based on TCAD software [11] are also presented. Fig. 2b shows the 1 kHz CV response for the case of the reference AuNi/Al₂O₃/p⁺Si structure (blue) and the 1 kHz CV plot of the AuNi/MoS₂/Al₂O₃/p⁺Si structure (red). The dashed lines are physics-based ac simulations of the CV response. The availability of the reference structure, with no MoS₂, allows a determination of the doping concentration in the p⁺ silicon, which can subsequently be used in the simulation of the full AuNi/MoS₂/Al₂O₃/p⁺Si structure. From the reference structure (AuNi/Al₂O₃/p⁺Si), a boron doping concentration in the Si of 3×10^{19}

cm⁻³ is obtained, consistent with the p⁺ wafer resistivity range of 1×10^{-2} to $2 \times 10^{-3} \Omega\text{cm}$. For these simulations of the reference structure, the Al₂O₃ thickness is 23 nm (from TEM), with a dielectric constant of 6.5.

In the case of the simulations for the AuNi/MoS₂/Al₂O₃/p⁺Si structure, TCAD models for MoS₂ are not yet available. The MoS₂ parameters used in the simulations are: energy gap = 1.20 eV, electron affinity = 4.5 eV, electron effective mass = 0.57, hole effective mass = 0.8. The carrier density versus Fermi energy is taken from [12,13]. Fitting of the simulated CV response to the experimental response yields an *n*-type doping concentration in the MoS₂ of $1.75 \times 10^{17} \text{ cm}^{-3}$. The effective fixed positive charge in the Al₂O₃, has an equivalent value of 8.3×10^{12}

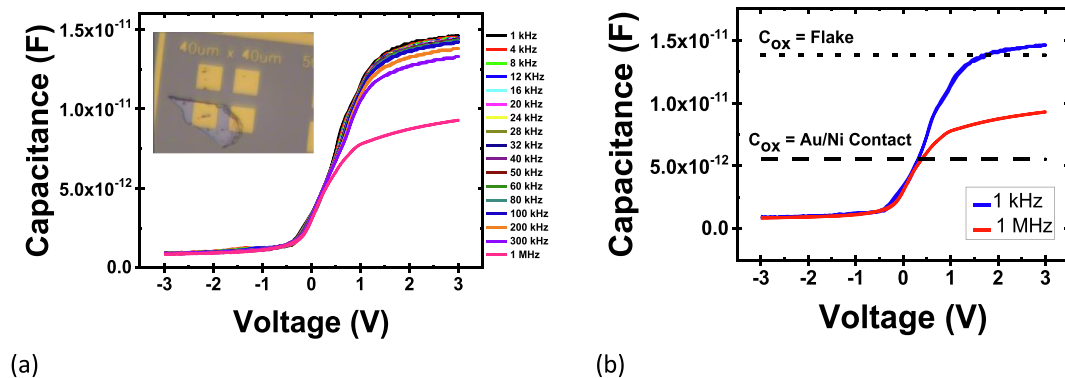


Fig. 3. (a) Experimental multi-frequency CV double sweep response at room temperature. The voltage range is between -3V and +3 V and the frequencies vary between 1 kHz and 1MHz. The inset shows an optical image of the AuNi/MoS₂/SiO₂/p⁺Si structure. (b) The CV response at 1 kHz and 1 MHz with the expected maximum capacitance shown as a dotted line for the cases where the area is defined by the Ni/Au contact and where the area is defined by the MoS₂ flake.

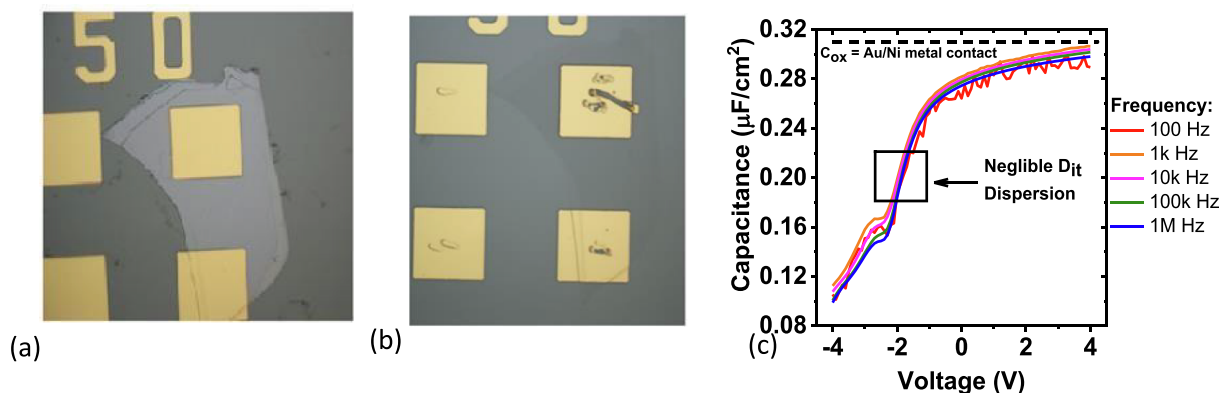


Fig. 4. a) Top view optical image of the AuNi/MoS₂/Al₂O₃/p⁺Si structure where the Ni(5 nm)/Au(160 nm) contacts and the MoS₂ flake are both visible, (b) the same structure after reactive ion etching of the MoS₂ layer using the Ni/Au as a hard mask. Note that an impression remains of the original flake position due to the height differences during the reactive ion etching. The marks on the Ni/Au pads are probing marks. c) Corresponding experimental multi-frequency CV response of the AuNi/MoS₂/Al₂O₃/p⁺Si shown in Fig b) (top right square). CV was recorded at room temperature and the sweeps were performed from -4V to +4 V. The CV response demonstrates negligible CV dispersion in depletion.

cm⁻² (+ve) located at the MoS₂/Al₂O₃ interface. It is noted that while the MoS₂ crystal used for the mechanical exfoliation was not intentionally doped, Hall analysis performed on the starting bulk crystal [9] yielded an *n* type semiconductor with a doping concentration of $\sim 10^{17}$ cm⁻³ consistent with the value extracted from fitting the experimental CV response. The CV simulations, with no interface states included, fit the CV response in depletion. There is a small discrepancy at approximately -5V, when the Fermi level at the surface reaches the MoS₂ conduction band edge, which is likely due to oxide traps in the Al₂O₃ (also referred to as border traps) [14]. However, the overall results demonstrate a close link between the theoretical and experimental data, without the inclusion of electrically active interface defects.

Further studies were performed using different deposition and fabrication facilities, where MoS₂ was exfoliated on heavily doped SiO₂ (10 nm)/p⁺Si and capacitor structures were formed using Ni(5 nm)/Au (160 nm) metallisation. In this case, the MoS₂ flake was not etched, and the resulting multi frequency CV responses of the structure highlight an effect which is evident when the dimensions of the flake exceed the dimensions of the metal contact. The multi-frequency (1 kHz to 1 MHz) CV sweeps performed between -3V and +3 V are shown in Fig. 3a. In this case, the CV responses are double sweep hysteresis curves with no hold time in the accumulation region (+3V) of the SiO₂/Si and the MoS₂/SiO₂ interfaces. In Fig. 3a the capacitance is plotted as the measured value, and not normalised to μF/cm², as the effective area of the sample is not a unique value for all ac signal frequencies. The expected maximum capacitance, based on the metal contact area of the 40 μm × 40 μm square, is 5.52×10^{-12} F and is shown as a dashed line in Fig. 3b. At ac signal frequencies from 1 kHz to approximately 100 kHz, electrons can follow the ac signal throughout the MoS₂ layer, beyond the metal contact, and therefore the area of the sample for the conditions of maximum capacitance is defined by the flake area as opposed of the metal contact area. Based on an estimated flake area of 4×10^{-9} m², the expected maximum capacitance value is 1.38×10^{-11} F and the experimental data showed the maximum capacitance to be 1.46×10^{-11} F. A significant observation from the CV response is that negligible hysteresis in the CV is present.

A repeat of the process is shown in Fig. 4. In this case the Ni(5 nm)/Au(160 nm) metal was used as a hard mask during reactive ion etching of the MoS₂ (the MoS₂ flake averaging ~ 350 nm in height) on doped Al₂O₃ (20 nm)/p⁺Si. This approach allows a well-defined area of MoS₂ in the capacitor structure. The gas used during etching was SF₆ (5sccm)/Ar (45sccm) for 30 s at 100 W and 6mT. An image of the initial flake outline is still visible in Fig. 4. b due to the height difference (MoS₂ and Al₂O₃) during the etch process. Following the etching process, Fig. 4c demonstrates a good agreement between the theoretical maximum

oxide capacitance of 0.31 μF/cm² (dashed line) and the experimental values. This sample also shows negligible frequency dispersion in depletion from 0 to -2 V. The origin of the ledge in the CV response at ~ 2.5 V could be a consequence of deep depletion in the MoS₂ substrate or an interface defects response, and requires further study.

The observation of a negligible interface state density and negligible hysteresis from the multi-frequency CV response is technologically advantageous, but also somewhat unexpected, as the surface of exfoliated MoS₂ is known to contain a high density of structural defects on the surface when imaged by STM [15], where density values can exceed 10^{12} cm⁻². In addition, it is reasonable to expect single or multiple atomic steps in the MoS₂ surface which is placed in contact with the Al₂O₃ or SiO₂ surface. Our results indicate that these defects are either: not electrically active or are passivated between exfoliation and subsequent transfer to the SiO₂/Si substrate.

3. Conclusion

In conclusion, these results demonstrate that interface state density values below the detection limit can be achieved between crystalline MoS₂ and amorphous Al₂O₃ or SiO₂, supporting one of the main motivations for using 2D semiconductors in MOSFETs and Tunnel FETs. More studies are currently underway to investigate the structural, chemical, and electronic properties of this interface and to understand why we observed negligible densities of electrical active interface defects as well as negligible CV hysteresis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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