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XPS Study of HfO_2 Growth on 2H-MoS_2 Substrate

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Abstract

The growth of high-k HfO_2 on 2H-MoS_2 substrate by plasma sputtering deposition is studied in-situ by x-ray photoelectron spectroscopy (XPS). It is found that plasma sputtering of Hf target in O_2 environment results in interface oxides formation i.e. MoO_3 and SO_x (with $3.5<x<4$). The functionalization of MoS_2 surface via oxide formation leads to pseudo layer-by-layer growth of HfO_2 thin film. The interface band alignment reveals a valence band offset of 1.3 eV and conduction band offset 3.3 eV at the HfO_2 /MoS_2 heterojunction.

1. Introduction

Layered semiconductor MoS_2 has attracted increasing attention in field-effect transistors device application due to its mobility can be enhanced by dielectric engineering. In compared to electron mobility of n-type bulk MoS_2 in the 50-200 $cm^2V^{-1}s^{-1}$ range [1] at room temperature and monolayer MoS_2 of ~1 cm^2 V^{-1} s^{-1} (in air/MoS_2/SiO_2 structures) [2], mobility enhancement is seen when monolayer and multilayers MoS_2 is coupled with high dielectric constant (high-k) materials. For examples, HfO_2/monolayer MoS_2 and PMMA/multilayers MoS_2 register electron mobility of 200$cm^2V^{-1}s^{-1}$ [3] and 470$cm^2V^{-1}s^{-1}$ [4], respectively. To realize the full potential of the high-k/MoS_2 heterojunction, however, demands fundamental understanding of the growth process and the resultant process-dependent heterojunction properties. ALD depositions of HfO_2 on pristine MoS_2 have resulted in island-growth [5-6], which is unfavorable for transistor that demands sharp interface. Interface band alignment of MoS_2 and HfO_2 is also an important aspect of heterojunction performance i.e. barrier height and contact resistance, which affects junction leakage current and charge injection. Most of these studies are also theoretical rather than experimental. To address these research gaps, this work investigates the growth of HfO_2 on pristine, bulk 2H-MoS_2 by using magnetron plasma sputtering. By depositing at various time intervals on a single sample, the interface chemistry, HfO_2 thin film growth mode and HfO_2/MoS_2 band alignment have been elucidated with the aid of XPS.

2. Methodology

X-ray photoemission spectroscopy (XPS) technique has been employed (VG ESCALAB 200i-XL) to study the interface chemistry and band alignment measurement. The XPS is equipped with a monochromatic Al Kα (1486.6eV) x-ray source and the binding energy (BE) is calibrated by using pure nickel (Ni), gold (Au), silver (Ag), and copper (Cu) standard samples by setting the Ni Fermi edge, Au $4f_{7/2}$, Ag $3d_{5/2}$, and Cu $2p_{3/2}$ peaks at BE of 0.00±0.02, 83.98±0.02, 368.26±0.02, and 932.67±0.02 eV, respectively.

Commercially available 2H-MoS_2 (*Burleigh Inst.*) is in-situ annealed to 500°C to remove surface carbon and oxygen contaminations to below XPS detection limits which qualifies the sample surface cleanliness. Deposition of HfO_2 film onto MoS_2 substrate is conducted in-situ by Ar^+ plasma sputtering of Hf metal target which oxidizes in oxygen environment. Different thicknesses of HfO_2 thin film have been grown on MoS_2 up to ~5.5nm. By analyzing the sample surface core-level and valence band photoelectron signals at the pause of each growth interval with XPS, the interface chemical reactions and band alignment are elucidated and resolved in a manner of increasing overlayer thickness.

3. Results and discussions

The deposition of HfO_2 by plasma sputtering has resulted in various interface oxides formation. The analysis of high resolution core-level spectra of Mo 3d, S 2p, Hf 4f and O 1s based on BE positions suggests interface MoO_3 and sulphates/sulphites SO_x (with $3.5<x<4$) formations. XPS quantitative analysis confirms the identified species of HfO_2, MoO_3 and SO_x. The formation of oxides and sulphates/sulphites can be attributed to O radical reaction with the MoS_2 substrate during the deposition.

Composition plot of MoS_2 and MoO_3 with respect to HfO_2 indicate exponential-like signals decay of the substrate and MoO_3. This is indicative of pseudo layer-by-layer growth mode of the HfO_2 thin film. The plot is well fitted with pseudo-layer-by-layer growth model [7] (see Fig. 1). The atomic fractions of substrate MoS_2 (Mo $3d_{5/2}$) is found using the equation (1),

$$C_{Mo}(t) = \frac{100\times exp\left(\frac{-Gt}{\lambda^{Mo}_{3d_{5/2}}}\right)}{exp\left(\frac{-Gt}{\lambda^{Mo}_{3d_{5/2}}}\right)+K\times\left[1-exp\left(\frac{-Gt}{\lambda^{Hf}_{4f_{7/2}}}\right)\right]} \quad (1)$$

and for the atomic fraction of Hf we have

$$C_{Hf}(t) = \frac{100\times\left[1-exp\left(\frac{-Gt}{\lambda^{Hf}_{4f_{7/2}}}\right)\right]}{\frac{1}{K}exp\left(\frac{-Gt}{\lambda^{Mo}_{3d_{5/2}}}\right)+\left[1-exp\left(\frac{-Gt}{\lambda^{Hf}_{4f_{7/2}}}\right)\right]} \quad (2)$$

where $K = \left[\frac{I^{\infty}_{Hf}}{I^{0}_{Mo}} \frac{S^{Mo}_{3d_{5/2}} \cdot T^{Mo}_{3d_{5/2}}}{S^{Hf}_{4f_{7/2}} \cdot T^{Hf}_{4f_{7/2}}}\right]$ is a constant since $S^{Mo}_{3d_{5/2}}, T^{Mo}_{3d_{5/2}}, S^{Hf}_{4f_{7/2}}$ and $T^{Hf}_{4f_{7/2}}$ are the sensitivity factors and instrumental transmission factor associated with detecting Mo $3d_{5/2}$ and Hf $4f_{7/2}$ XPS peaks, respectively, while I^{0}_{Mo} and I^{∞}_{Hf} are the XPS intensities of the clean MoS_2 substrate (before deposition) and HfO_2 bulk layers, respectively. These values are determined experimentally.

The band alignment of bulk MoS_2 and bulk HfO_2 is obtained from direct measurements of the valence band edges (see Fig. 2). We obtained valence band offset (VBO) of 1.3eV and conduction band offset (CBO) of 3.3eV between MoS_2 and HfO_2. During the growth, we observe a 0.4eV shift in MoS_2 core-levels which is explained as internal built-in field at the junctions of $HfSO_x/MoS_2$ and/or MoO_3/MoS_2. As no further shift is observed after initial deposition, we conclude that no interface band bending has taken place.

4. Conclusions

In conclusion, plasma sputter deposition is a viable method to grow sharp HfO_2/MoS_2 interface. It is a single-step functionalization-and-growth of HfO_2 on MoS_2 using plasma sputtering. We elucidate the deposition mechanisms from the interface interactions and found O_2 to be reacting with the MoS_2 substrate, resulting in MoO_3 and SO_x formation which helps to support layer-by-layer growth of HfO_2, as evidenced by curve-fitting XPS composition plot with pseudo-layer-by-layer growth model. Valence band structure probed by XPS suggest the HfO_2/MoS_2 VBO and CBO are 1.3 and 3.3eV, respectively. No band bending has been observed near the overlayer/MoS_2 interface during the deposition process.

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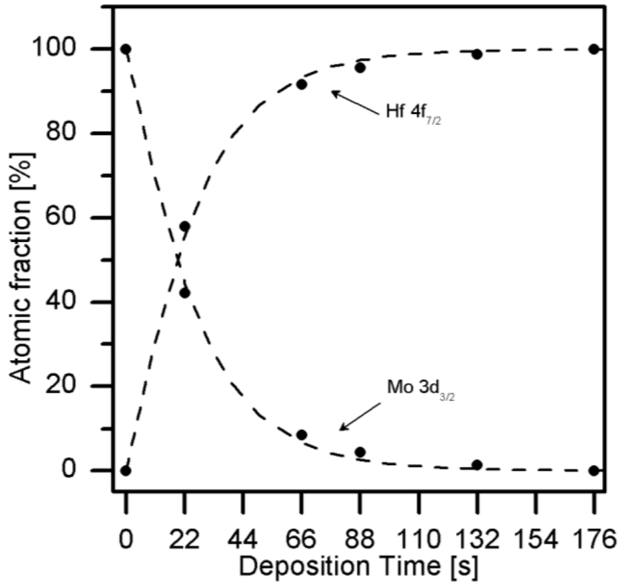

Fig. 1 Exponential-like XPS composition evolution of Mo $3d_{3/2}$ (MoS_2) and Hf $4f_{7/2}$ (HfO_2) suggest layer-by-layer growth of HfO_2 thin film.

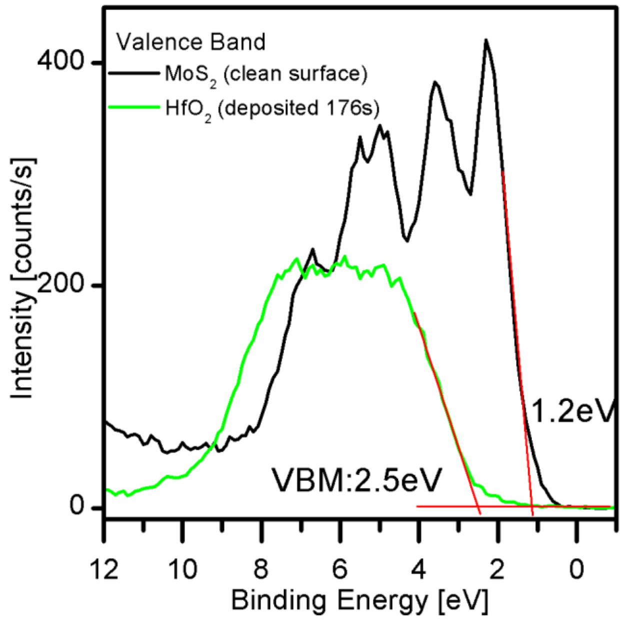

Fig. 2 Bulk MoS_2 and HfO_2 valence band structure and edges at 1.2eV and 2.5eV, respectively, result in valence band offset of 2.5-1.2=1.3eV at HfO_2/MoS_2 interface.