Selective hydrogenation improves interface properties of high-\(k\) dielectrics on 2D semiconductors

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ABSTRACT

The integration of high-\(k\) dielectrics with two-dimensional (2D) semiconductors is a critical step towards high-performance nanoelectronics, which however remains challenging due to the high density of interface states and the damage to the monolayer 2D semiconductors. In this study, we propose a selective hydrogenation strategy to improve the interface properties while the 2D semiconductors are not affected. Using the interface of monolayer molybdenum disulfide (MoS\(_2\)) and silicon nitride as an example, we show substantially improved interface properties for electronic applications after the interfacial hydrogenation, as evidenced by reduced inhomogeneous charge redistribution, increased band offset, and nearly intact electronic properties of MoS\(_2\). Importantly, this hydrogenation process selectively occurs only at the silicon nitride surface and is compatible with the current semiconductor fabrication process. We further show that this strategy is general and applicable to other interfaces between high-\(k\) dielectrics and 2D semiconductors such as hafnium dioxide (HfO\(_2\)) on the monolayer MoS\(_2\). Our results demonstrate a simple yet viable way to improve the integration of high-\(k\) dielectrics on a broad range of 2D transition metal disulfide semiconductors, shedding light on practical electronic and optoelectronic applications.

KEYWORDS
two-dimensional (2D) materials, high-\(k\) dielectrics, molybdenum disulfide, interfacial properties, transition metal disulfide (TMD)

1 Introduction

Two-dimensional (2D) semiconducting materials are appealing for nanoelectronic applications in the post-Moore era as their ultrathin thickness can help to minimize the short channel effect confronted with current Si based technologies [1, 2]. Among them, monolayer transition metal disulfides (TMDs) such as MoS\(_2\) and WS\(_2\) have attracted tremendous interest as promising channel materials for electronic or optoelectronic devices due to their stability, direct band gaps, tunable electronic and optical properties, and many other excellent physical properties [3–13]. The monolayer MoS\(_2\) based nanotransistors have shown encouraging device performance such as a high on/off ratio [14–16]. However, to utilize monolayer TMDs in practical electronic applications, there remain many challenges [17], which include the large-scale growth of high-quality TMDs layers [18–22], metal contact with low resistance [23–28], and the integration of high-\(k\) dielectrics [29–32].

In particular, for electronic applications, the integration of high-\(k\) dielectrics is highly desired as their large dielectric constants can effectively screen the scattering from charge impurities, and thus improve the device performance [33, 34]. However, it is found difficult to achieve high-quality interfaces between high-\(k\) dielectrics and monolayer TMDs due to high interface state density [31, 32]. Currently, a high-quality interface can be realized by van der Waals (vdW) integration of h-BN or CaF\(_2\) layers on TMDs semiconductors [35–37]. However, recent studies show a high leakage current in the 2D electronic devices using h-BN as the dielectric, impeding its practical application as the gate dielectric in ultrascaled nanoelectronics [38]. Besides, the integration strongly relies on the transfer process, which is challenging to be scaled up for practical applications. While various attempts have been made to directly deposit high-\(k\) oxides such as HfO\(_2\) [39], Al\(_2\)O\(_3\) [40, 41], and ZrO\(_2\) [42] on TMDs layers using atomic layer deposition (ALD) or sputtering technique, their interfacial properties are still much inferior to those of HfO\(_2\)/Si and need further improvement [32, 43].

One such endeavor is interface engineering, which includes interface passivation by annealing [44, 45] and utilization of interface seeding or buffer layers [31, 32, 46]. These strategies have
brought some improvement from their respective effects, but may also raise new problems such as the damage of the 2D TMDs semiconductors and accordingly deteriorated electronic properties \cite{31, 32}. Thus, it is highly desirable to develop a holistic strategy that not only can effectively passivate the interfacial dangling bonds of high-k dielectrics, but also protect the 2D semiconductors. In this study, we propose selective hydrogenation as such an ideal strategy, due to the fact that the hydrogen atoms are prone to be adsorbed on the surface of high-k dielectrics but inert to the basal planes of 2D TMDs. We use the interface between monolayer MoS₂ and $\beta$-Si₃N₄ (0001) as an example to deliver the concept, and apply this strategy to another interface between MoS₂ and HfO₂ to demonstrate its generality.

2 Method

All the calculations were performed using density-functional theory (DFT) based the Vienna \textit{ab initio} simulation package (VASP.5.4.4.14) with the Perdew–Burke–Ernzerhof (PBE) functional and the projector-augmented wave (PAW) potentials \cite{47–49}. The cutoff energy for the plane wave expansion was set to 500 eV. T-centered $9 \times 9 \times 4$, $12 \times 12 \times 1$, $6 \times 6 \times 1$, and $9 \times 9 \times 1$ k-point meshes were used to sample the first Brillouin zone of bulk $\beta$-Si₃N₄, monolayer MoS₂, the interface of monolayer MoS₂ on $\beta$-Si₃N₄ (0001), and $\beta$-Si₃N₄ (111), respectively. A vacuum layer with a thickness of 15 Å was used for all slab structures to minimize the artificial Coulomb interaction between two adjacent surfaces. For the interface structures, the vdW correction has been included by Grimme’s DFT-D3 method \cite{50}. For all calculations, the electronic and ionic convergence criteria were set to 10⁻⁵ eV and 0.01 eV/Å, respectively. The lattice constants are calibrated to be $a = b = 7.659$ Å and $c = 2.925$ Å for $\beta$-Si₃N₄, $a = b = 3.184$ Å for monolayer MoS₂, and the corresponding PBE band gaps are 4.24 and 1.66 eV, respectively. All these results were well consistent with the previous studies \cite{51–55}.

The interface structures were constructed by placing the (4 × 4 × 1) monolayer MoS₂ supercell on the (\(\sqrt{3} \times \sqrt{3} \times 1\)) $\beta$-Si₃N₄ (0001) surface without/with surface hydrogen passivation, in which a 3.97% compressive strain was applied to Si₃N₄. This strain yields a reduced PBE band gap by ~0.2 eV in the Si₃N₄ (see Fig. S1 in the Electronic Supplementary Material (ESM)), while the main electronic structure did not change much compared with that of the pristine bulk Si₃N₄. The thickness of the $\beta$-Si₃N₄ (0001) surface was set to 7 atomic layers, the bottom layer of which was passivated using hydrogen atoms. In the interface structures, dipole correction was applied \cite{56}. To examine interfacial stability of monolayer MoS₂/hydrogen passivated $\beta$-Si₃N₄ (0001), \textit{ab initio} molecular dynamics simulations were performed on the interface supercell, where the canonical ensemble (NVT) and the Nosé heat bath were adopted with a time step of 1 fs and a time length of 6 ps, respectively.

The interfacial interaction strength between monolayer MoS₂ and dielectrics (D, Si₃N₄, or HfO₂) could be estimated from the adsorption energy ($E_a$) as defined below:

\[
E_a = \frac{E_{\text{MoS}_2+D} - E_{\text{MoS}_2} - E_D}{A}
\]

where $E_{\text{MoS}_2+D}$ is the total energy of the hybrid interface structure for MoS₂ on the dielectric, $E_{\text{MoS}_2}$ and $E_D$ are the total energy of the isolated MoS₂ monolayer and the dielectric (Si₃N₄ or HfO₂) surface, respectively, and $A$ is the interface area. Similarly, the charge redistribution $\Delta \rho$ for MoS₂ monolayer on the dielectric surface is defined as:

\[
\Delta \rho = \rho_{\text{MoS}_2+D} - \rho_{\text{MoS}_2} - \rho_D
\]

where $\rho_{\text{MoS}_2+D}$ is the charge density of the hybrid interface structure for MoS₂ on the dielectric, and $\rho_{\text{MoS}_2}$ and $\rho_D$ are the charge density of the isolated MoS₂ monolayer and the dielectric (Si₃N₄ or HfO₂) surface, respectively.

3 Results and discussions

Silicon nitride ($\text{Si}_3\text{N}_4$) has a large band gap and high thermal stability, which has been widely applied in current Si based electronic devices \cite{53, 54, 57}. It was reported that high-quality Si₃N₄ thin films could be deposited on graphene \cite{52, 58, 59}, while the electronic properties of the latter did not change much \cite{58}. Furthermore, Si₃N₄ might be a better choice than the metal oxides as a high-k dielectric, because it does not contain metallic ions which tend to interact strongly with 2D TMDs \cite{51, 60, 61}. Thus, in this study, we use the interface between monolayer MoS₂ and $\beta$-Si₃N₄ as a model example to study the hydrogenation effect on the interface properties.

We have constructed various interface structures by sliding the MoS₂ on the Si₃N₄ surface. The energy difference among these configurations is within 12 meV (see Fig. S2(a) in the ESM), inferring a weak interfacial interaction. The top and side views of the most stable interface configuration are shown in Fig. S2(b) in the ESM and Fig. I(a), respectively, in which the interfacial S atoms of MoS₂ tend to arrange near the interface Si atoms of Si₃N₄ to maximize the potential bonding. Similar trend has been reported at the MoS₂/HfO₂ and high-k dielectrics/graphene interfaces \cite{51, 62, 63}. The interface spacing between monolayer MoS₂ and $\beta$-Si₃N₄ (0001) is about 2.9 Å at the lower bound of the vdW interaction range, further indicating the weak interface interaction. The interface interaction strength can also be measured from the adsorption energy ($\sim$23.2 meV/Å). This value is slightly higher than that of bi-layer MoS₂ ($\sim$22.4 meV/Å), but it is much smaller than those of other high-k dielectric/TMDs interfaces such as MoS₂/HfO₂ and MoS₂/SiO₂ \cite{51, 61, 64}.

The projected density of states (PDOSs) of monolayer MoS₂ on $\beta$-Si₃N₄ (0001) is shown in Figs. 1c)–1e). One important observation is that the electronic structure of monolayer MoS₂ is nearly intact in the presence of the Si₃N₄ due to relatively weak interaction between them. As the PDOS shown in Fig. 1c), the monolayer MoS₂ remains semiconducting with a PBE gap of ~1.6 eV. This is highly desired because a sizable band gap in semiconductors enables a stable device operation with a large on/off ratio. However, due to the dangling bonds in $\beta$-Si₃N₄ (0001) (see Fig. S3 in the ESM), orbital hybridization is seen between MoS₂ and Si₃N₄. As shown in Figs. 1b)–1d), the Mo $e_g$ orbitals couple with the p orbitals of Si and N ions near the valence band edge, while at the conduction edge, the hybridization among Mo $e_g$, S $p_z$, and Si p orbitals is more noticeable. This orbital hybridization leads to insignificant band offsets between MoS₂ and Si₃N₄, which is unfavorable for device applications. To minimize the tunneling current in semiconductor devices, the valence and conduction band offset between the semiconductor (e.g., MoS₂ in this study) and the gate dielectric (e.g., Si₃N₄ here) should be larger than 1 eV \cite{33}. In addition, the interfacial interaction causes charge redistribution at the interface (see Fig. 1a)), where the accumulated charges are closer to Si₃N₄ surface while the depleted charges are more pronounced near the MoS₂ side. The charge redistribution induces electron–hole puddles in monolayer MoS₂, as shown in Fig. 1b). This is another detrimental effect for electronic device applications as the electron–hole puddles can be charge scattering centers which reduce the carrier mobility \cite{65}.

Since the degraded interface properties are mainly due to the

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dangling bonds at the β-Si₃N₄ (001) surface, one natural attempt for improving the interface properties is to passivate them. We note that the hydrogenation process has been widely used in semiconductor technologies to passivate the intrinsic defects [66]. Such a process may also be applied to passivate the dangling bonds of the β-Si₃N₄ (001) surface considered in this study. After passivation (see the atomic structures in Fig. S4(a) in the ESM), the dangling bonds induced states nearly vanish, as confirmed by the PDOSs in Fig. S4(b) in the ESM. Consequently, the interfacial interaction between monolayer MoS₂ and hydrogen passivated β-Si₃N₄ (001) surface is further weakened. The calculated adsorption energy (see Fig. 2(a)) decreases slightly to −18.2 meV/Å². The charge redistribution is shown in Figs. 2(b) and 2(c), which clearly suggests that the weaker interfacial interaction results in much less pronounced interfacial charge redistribution, as well as the suppressed electron−hole puddles in the Mo atomic plane.

After the hydrogen passivation on the β-Si₃N₄ (001) surface, the orbitals near Fermi level between monolayer MoS₂ and Si₃N₄ are well separated. From Fig. 2(d), we can see that the valence band edge now is contributed by p orbital from Si₃N₄, while the states contributed by Mo d orbital are located at ~0.98 eV below the Fermi level. In contrast, the conduction band edge is mainly derived from Mo d orbital, and the contribution from p orbital of Si₃N₄ starts from ~ 4.04 eV and above. This leads to a type-II band offset between monolayer MoS₂ and Si₃N₄, in which the valence band (VBO) and conduction band offset (CBO) can be estimated to be 0.98 and 3.36 eV at the PBE level (see Fig. S5 in the ESM), respectively. It should be noted that these band offset values might be underestimated, which could be larger if the quasiparticle corrections or hybrid functionals were used. With the hydrogen passivation, we also find improvement on the electronic properties of monolayer MoS₂. As shown in Fig. 2(e), the electronic structure of monolayer MoS₂ on the hydrogen passivated Si₃N₄ is nearly identical to that of free-standing monolayer MoS₂. Thus, we can see that using this simple hydrogenation process, the interface properties of MoS₂/Si₃N₄ are improved remarkably, as evidenced by the large band offsets, suppressed electron–hole puddles, and intact electronic properties of MoS₂.

More importantly, the hydrogenation process is energetically selective to β-Si₃N₄ (0001) surface. As shown in Fig. 3(a), the adsorption energy for hydrogen atom on top of Si site at the Si₃N₄ surface is −0.23 eV, and the lowest adsorption energy on the top of the N sites is −1.11 eV due to the dangling bonds of N ions at the surface. The negative adsorption energy indicates that the hydrogen adsorption is energetically favorable, and the hydrogenation can occur spontaneously even at a low temperature. In contrast, the energy for hydrogen atoms adsorbed on the monolayer MoS₂ is calculated to be 1.84 eV, consistent with previous studies [67]. The large positive adsorption energy suggests that the hydrogenation on the monolayer MoS₂ is energetically unfavorable, which is less likely to happen even at a high processing temperature. Further quantum mechanical molecular dynamics simulation shows that the hydrogen passivated MoS₂/Si₃N₄ interface is thermodynamically stable at the high temperature of 800 K. From Fig. 3(b) and Fig. S6 in the ESM, it is noted that the variation of interfacial Si−H and N−H bond lengths is within 0.2 Å during the MD simulation, suggesting that the Si₃N₄ surface adsorbs hydrogen atoms so strongly that they are unlikely to diffuse to monolayer MoS₂ even at the temperature of 800 K (see Fig. 3(c)). This implies that the spontaneously selective hydrogenation process is compatible and stable with current semiconductor device fabrication processes, as most of them are conducted below 800 K [68].

Next, we show that the hydrogenation process is also applicable for improving interface properties of other high-k dielectrics and monolayer MoS₂. Since HFO₂ has been widely used in current electronic devices, we use it as a model example to further
Figure 2  Interface properties of monolayer MoS$_2$ on hydrogenated β-Si$_3$N$_4$ (0001). (a) Adsorption energy of monolayer MoS$_2$ on β-Si$_3$N$_4$ (0001) with or w/o surface hydrogenation. (b) The side view of interface structure for monolayer MoS$_2$ on hydrogenated β-Si$_3$N$_4$ (0001) superimposed with visualized charge density redistribution using an iso-surface value of 1.5 × 10$^{-6}$ e/Å$^3$, in which the red and green dots denote the depleted and accumulated charge density, respectively. (c) The charge puddles distributed on the Mo plane (top view). (d) The PDOSs on Mo d and p orbitals of central Si$_3$N$_4$ layer. (e) LDOSs of MoS$_2$ monolayer on hydrogenated β-Si$_3$N$_4$ (0001) and the pristine monolayer MoS$_2$ (p-MoS$_2$).

Figure 3  Hydrogenation selectivity and stability. (a) The hydrogen adsorption energy on β-Si$_3$N$_4$ (0001) and monolayer MoS$_2$. (b) The interface Si–H bond variation during the molecular dynamic (MD) simulation at the temperature of 800 K. (c) The final atomic structure (side view) of MoS$_2$ monolayer on the hydrogenated β-Si$_3$N$_4$ (0001) surface after the 6 ps MD simulation.

examine the hydrogenation effects. It has been reported that Hf-terminated HfO$_2$ interacts strongly with MoS$_2$, leading to inferior electronic properties, while the interface between O-terminated HfO$_2$ and MoS$_2$ shows improved interface performance [51]. Thus, we focus on the interface of Hf-terminated HfO$_2$ and monolayer MoS$_2$ without/with the interfacial hydrogenation. As shown in Figs. 4(a) and 4(c), the interfacial covalent Hf–S bonds form at the interface of Hf-terminated HfO$_2$ and monolayer MoS$_2$. This
induces noticeable charge transfer from HfO$_2$ into MoS$_2$, making the MoS$_2$ metallic. Similarly, the interface properties can be improved using the hydrogenation process. Figures 4(b) and 4(d) are the local density of states (LDOS) and charge redistribution for monolayer MoS$_2$ on the hydrogen passivated Hf-HfO$_2$ (0001) surface, respectively. The reduced interfacial charge redistribution and the suppressed mid-gap metallic states in MoS$_2$ clearly suggest that better interface properties are reached by the selective hydrogen passivation.

It has been noted that 2D materials with HfO$_2$ thin films grown by ALD technique show better device performance than those using sputtering or physical vapor deposition (PVD) [69]. We argue that the underlying mechanisms, in addition to the film uniformity and quality, could be partially ascribed to unintended hydrogen passivation on the high-k oxide film. In ALD process, the Hf metal-based precursor and water vapor are used for the deposition of HfO$_2$ [70], in which residual hydrogen source [71] might evolve to passivate the dangling bonds, whereas the high vacuum required in sputtering or PVD process leads to negligible residual hydrogen sources. Thus, we expect that the interface between high-k dielectrics and MoS$_2$ can be further improved by intentionally depositing the high-k dielectric films in the hydrogen environment in the first few cycles. Please note that the effectiveness of this interfacial hydrogenation strategy is strongly dependent on the difference in the hydrogen adsorption on 2D materials and high-k dielectrics. If hydrogen interacts strongly on the 2D materials such as graphene [72] or phosphorene [73], the hydrogenation process would result in undesired hydrogen adsorption on the 2D materials, leading to considerable changes in the electronic properties of 2D materials. On the contrary, as long as a 2D material is unfavorable to bind hydrogen, the hydrogenation process proposed here is beneficial to its integration with high-k dielectrics. The beneficial effects of this hydrogenation strategy on the interface integration are two-fold: One is to passivate the dangling bonds in the high-k dielectrics, resulting in reduced interface state density; the other is to passivate the native defects in 2D TMDs, which improves electronic properties of the 2D semiconductors, as supported by the electronic structure (see Fig. S7 in the ESM) of monolayer MoS$_2$ with/without the hydrogen passivation on the S vacancies.

4 Conclusions

In conclusion, we report a simple yet effective strategy to improve the interfacial properties of high-k dielectrics and 2D semiconductors, as supported by the substantially improved electronic properties at the interface between Si$_3$N$_4$ and monolayer MoS$_2$ using the proposed selective hydrogenation process. This hydrogenation process spontaneously occurs on Si$_3$N$_4$, leaving the monolayer MoS$_2$ nearly intact. We reveal that the hydrogenated MoS$_2$/Si$_3$N$_4$ interface is stable at high temperatures, which is compatible with the current semiconductor fabrication process. We further show that the interfacial hydrogenation strategy can be applied for the integration of other high-k dielectrics on MoS$_2$ monolayer. Given similar surface chemistry among TMD semiconductors, this hydrogenation process can be extended to the interfaces of many high-k dielectrics and a broad range of transition metal disulfides such as MoS$_2$, WS$_2$, or HfS$_2$, as well as some transition metal dichalcogenides such as MoSe$_2$ or WSe$_2$, or other 2D materials that are inert to hydrogen adsorption, enabling us to boost the development of 2D semiconductors based nanoelectronic devices.

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Electronic Supplementary Material: Supplementary material (DOEs of Si$_3$N$_4$: energy difference of MoS$_2$/Si$_3$N$_4$ interface structures; PDOSs of Si$_3$N$_4$ surface without/with hydrogen passivation; band offset diagram; N-H bond variation during MD simulation; atomic and electronic structures of MoS$_2$ with S vacancy and the passivated vacancy) is available in the online version of this article at https://doi.org/10.1007/s12274-021-4025-4.

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