Enhancing Interconnect Reliability and Performance by Converting Tantalum to 2D Layered Tantalum Sulfide at Low Temperature

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Copper (Cu) has been used as the main conductor in interconnects due to its low resistivity. However, because of its high diffusivity, diffusion barriers must be incorporated to surround Cu wires. Otherwise, Cu ions/atoms will drift/diffuse through the intermetal dielectric (IMD) that separates two distinct interconnects, resulting in circuit shorting. Conventionally, tantalum nitride (TaN) has been adopted as the diffusion barrier owing to its superior capability of blocking Cu diffusion.[1,2] However, the adhesion of Cu to TaN is not ideal. To address this issue, tantalum (Ta) has been integrated in-between TaN and Cu to improve the adhesion. The optimized stack consists of a TaN layer deposited on low-k dielectrics, followed by a Ta layer before the Cu deposition, as depicted in Figure 1a. This trench structure is also known as the “damascene structure.” The barrier/liner (TaN/Ta) bilayer must be >4 nm to ensure acceptable liner and diffusion barrier properties. Since TaN/Ta occupy a significant portion of the interconnect cross-section and they are much more resistive than Cu, the effective conductance of an ultrascaled interconnect will be compromised by the thick bilayer. Therefore, 2D layered materials have been explored as diffusion barrier alternatives. However, many of the proposed 2D barriers are prepared at too high temperatures to be compatible with the back-end-of-line (BEOL) technology. In addition, as important as the diffusion barrier properties, the liner properties of 2D materials must be evaluated, which has not yet been pursued. Here, a 2D layered tantalum sulfide (TaS$_x$) with ≈1.5 nm thickness is developed to replace the conventional TaN/Ta bilayer. The TaS$_x$ ultrathin film is industry-friendly, BEOL-compatible, and can be directly prepared on dielectrics. The results show superior barrier/liner properties of TaS$_x$ compared to the TaN/Ta bilayer. This single-stack material, serving as both a liner and a barrier, will enable continued scaling of interconnects beyond 5 nm node.

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The interconnect half-pitch size will reach ≈20 nm in the coming sub-5 nm technology node. Meanwhile, the TaN/Ta (barrier/liner) bilayer stack has to be >4 nm to ensure acceptable liner and diffusion barrier properties. Since TaN/Ta occupy a significant portion of the interconnect cross-section and they are much more resistive than Cu, the effective conductance of an ultrascaled interconnect will be compromised by the thick bilayer.

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bilayer has been demonstrated to fulfill several requirements of the interconnect technology.\cite{1}

With the advent of sub-5 nm technology node, the interconnect half-pitch size will reach \( \approx 20 \) nm and below.\cite{3} Meanwhile, the thickness of the conventional TaN/Ta bilayer cannot be reduced below \( \approx 4-5 \) nm just to maintain its capability of blocking Cu diffusion into the IMDs. However, the TaN/Ta bilayer is much more resistive than Cu. In ultrascaled Cu interconnects, TaN/Ta will occupy a large portion of the cross-section area, which tremendously increases the line resistance, as shown in Figure 1b. The main challenge of scaling conventional TaN/Ta lies in their 3D nature. Ultrathin and continuous TaN/Ta stack will be difficult to achieve by the commonly used sputtering method. Although thinner TaN/Ta films prepared by atomic layer deposition (ALD) have been investigated, the diffusion barrier property was known to be compromised.\cite{4} Given their atomically thin nature, 2D layered materials have been considered as diffusion barrier alternatives.\cite{5-10} Among them, graphene,\cite{5-10} molybdenum disulfide (MoS\(_2\)),\cite{11,13} and hexagonal boron nitride (h-BN)\cite{11} have been demonstrated to have desirable diffusion barrier properties even with sub-nm thicknesses. Although seldomly discussed, it has been discovered experimentally that some 2D materials can suppress inelastic scattering in Cu wires and hence reduce Cu resistivity,\cite{12,14,15} which hints at the possibility that 2D materials may have preferable liner properties. The advantages are summarized in Figure 1c. Nevertheless, most 2D materials are prepared by thermal chemical vapor deposition (CVD) at high-temperature (>800 °C),\cite{5-10} which exceeds the back-end-of-line (BEOL) compatible temperature (<400 °C). Moreover, the transfer process from metal substrates to dielectrics required for some 2D materials\cite{5-9} also hinders the integration to current interconnect technologies. The criteria for evaluating a new barrier/liner are listed in Figure 1d. Not until very recently, has a large-area, transfer-free, and BEOL-compatible MoS\(_2\) barrier been realized.\cite{13}

Here, we provide an approach that converts Ta, the current industry liner material, to a 2D layered material, namely tantalum sulfide (TaS\(_x\)), to serve as an ultrathin barrier and a liner at the same time. The \( \approx 1.5 \) nm thick polycrystalline TaS\(_x\) film is obtained on dielectrics (to demonstrate that it can be deposited on IMDs) at a BEOL-compatible temperature. The BEOL-compatible TaS\(_x\) directly deposited on dielectrics in this work meets all the requirements.
The results show that TaS$_x$ possesses superior liner and barrier properties simultaneously. By contrast, conventional TaN/Ta bilayer requires two types of thicker films to meet the requirements for both barrier and liner. By replacing the TaN/Ta bilayer with a 2D TaS$_x$ layer, the percentage of Cu volume in an ultrascaled interconnect can be significantly increased to achieve low line resistance. Showing the promising barrier/liner properties of TaS$_x$, our work may encourage future development of high quality, single-layer tantalum sulfide films for BEOL applications.

2D materials are normally grown at high temperatures (>800 °C), which does not satisfy the requirement of BEOL-compatibility. Therefore, in this work, plasma enhanced chemical vapor deposition (PECVD)\cite{16-18} was chosen to lower the growth temperature by utilizing the energy of the remote plasma. Centimeter-scale, uniform TaS$_x$ was prepared by converting a polycrystalline Ta film in a hot-zone furnace illustrated in Figure 2a. The Ta film was predeposited on a Si/SiO$_2$ substrate by an e-beam evaporator. Hydrogen sulfide (H$_2$S) was used as the precursor while Ar was used as the carrier gas. The flow rates for both gases were 10 sccm. The growth temperature, time, and the plasma power were set at 400 °C, 20 min, and 70–80 W, respectively. During the growth, the remote plasma dissociated H$_2$S into H and S radicals. The S radicals react with Ta and convert the Ta to TaS$_x$. The mechanism of conversion is illustrated in Figure 2b, by using 1T-tantalum...
disulfide (TaS₂) as an example. This method was modified from the method for low-temperature MoS₂ growth.\[17,18\]

In addition to the BEOL-compatible growth temperature, preparation of large-area films is also crucial to the integration with the interconnect technology. However, some of the 2D material synthesis recipes can only produce 2D flakes with micrometer-scale areas. Figure 2c confirms that a large-scale, uniform polycrystalline Ta to TaS₄ conversion was realized using our PECVD method. As a demonstration, an ≈3 nm Ta film was deposited on SiO₂(90 nm) grown on a Si(100) surface. After the conversion process through PECVD, an ≈8 nm TaS₄ film was formed at growth temperature of either 400 or 800 °C, as confirmed by the cross-section transmission electron microscopy (TEM) image in Figure 2d. The increased film thickness is consistent with the previously reported MoS₂ conversion.\[17\] The different colors between 400 and 800 °C conversion shown in the optical microscope images of Figure 2c may imply different material properties, as will be discussed further.

A layered structure can be observed in the TEM images. Some oxidized TaS₄ can be observed on the top of the film from the TEM image due to surface oxidation, as confirmed by energy dispersive X-ray spectroscopy (EDS) mapping in Figure S1 (Supporting Information). This has also been reported in other studies of TaS₂.\[19,20\] Oxidized Ta could also be one of the origins of the oxidized TaS₄, as confirm by X-ray photoelectron spectroscopy (XPS) analysis in Figure S2 (Supporting Information). Unreacted Ta can also be found at the bottom (from TEM) of the TaS₄ film grown at 400 °C, which can be attributed to the insufficient energy at the lower process temperature. These thick (≈8 nm) TaS₄ films were intentionally selected for better imaging of the layered structures. For all electrical tests that will be discussed, TaS₄ with the thickness of interest (≈1.5 nm) will be used.

Raman spectra in Figure 2e reveal that the 800 °C TaS₄ is 1T-TaS₄\[19,20\] as the related peak at around 100 cm⁻¹ was observed. The peak can only be resolved into multiple TaS₂ peaks at low temperatures.\[19\] However, this peak was not observed in the 400 °C TaS₄. The material was further investigated by XPS. Figure 2f shows the Ta 4f and S 2p core level spectra of the 400 °C TaS₄ film obtained by XPS using a monochromatic Al Kα radiation (hv = 1486.7 eV). Spectral features associated with Ta-S bond are detected at 23.5 and 161.3 eV in the Ta 4f₁/₂ and S 2p₃/₂ core levels, respectively. Based on XPS analyses, the S:Ta ratio was estimated to be ≈2.5 (Ta₂S₃). An additional chemical state is detected at higher binding energy in the Ta 4f (26.2 eV) and S 2p (162.5 eV) core levels aside from that of the Ta-S bond. The binding energy of the new chemical state is lower than the reported value\[20,21\] for Ta₂O₅, but higher than the Ta-S chemical state, which is assigned to the formation of Ta-O-S compound with a stoichiometry of TaO₁.₅S₂.₅. The Ta 4f core level shows also a chemical state at lower binding energy (22.9 eV). The binding energy of this chemical state in the Ta 4f core level, in conjunction with the additional chemical state detected in the N 1s core level at 396.4 eV, suggests the formation of a covalent Ta-N bond (labeled in orange).\[22\] The intensity ratio of Ta-N to Ta-S features is 0.14. We presume that Ta-N does not play a significant role in blocking Cu diffusion, based on its relative concentration and the nonstoichiometry (TaN₁.₁). The small amount of N could originate from the nitrogen purging procedure, as described in the “Experimental Section.” It is also important to note that the Ta 4f core level region is convoluted with O 2s core level at 24.0 eV. Based on the physical characterization, the composition of the converted film appears to consist of TaS₆.₅ layers mixed with naturally oxidized TaS₇.₅O₂.₁ region. It is noted that not only TaS₄ is well-known to exhibit layered structures, but TaS₃ has also been reported to exhibit such structures.\[23\] In addition, the phase diagram\[24\] shows that TaS₃ tends to be formed at lower temperatures with H₂S as the precursor, while TaS₂ can be formed at higher temperatures. Based on these observations, we denote this film as “TaS₄,” to avoid any misinterpretation. Our main purpose here is to study the liner and diffusion barrier properties of this “TaS₄” film.

Although the TaS₄ film shown in the cross-section TEM image (Figure 2d) was around 8 nm, for the electrical test structures for the barrier and liner properties, TaS₄ thin films with thickness of interest were adopted. The thickness is ≈1.5 nm, close to the thickness of a two-layer (2L) TaS₄, as confirmed by atomic force microscopy (AFM) in Figure 3a. Three-layer (3L) regions were also found occasionally, with the thickness of ≈2 nm. A precise thickness control can be achieved by using other Ta deposition methods. For the simplicity, this film will be denoted as “1.5 nm TaS₄” throughout the rest of the paper.

Ta has been used as the “liner layer” to provide good Cu adhesion enabling survival after multiple damascene process steps.\[11-13\] However, it is also well known that theinelastic scattering at the Ta/Cu interface\[25,26\] can increase Cu resistivity, especially when Cu wire dimensions are extremely scaled. Since the reason of utilizing an ultrathin 2D layered TaS₄ barrier/liner is to address the issue of conductivity degradation in extremely scaled interconnects, it is important to understand the impact of TaS₄ on the surface scattering of Cu interconnects. Here, such surface scattering at the SiO₂/Cu, Ta/Cu, and TaS₄/Cu interfaces was studied. To facilitate the analysis, ultrathin Cu films with thicknesses of ≈15 nm were deposited on the abovementioned three different surfaces to enhance the contribution from the interface. Cu thin films were patterned into Kelvin structures for accurate resistance measurements, as illustrated in Figure 3c. Details of the fabrication are described in the “Experimental Section.” Figure 3d shows the measured Cu resistivity of multiple devices on the three surfaces. Despite the fact that Cu resistivity increases as its dimension decreases,\[27\] the thinnest Cu (13 nm) on TaS₄ has the lowest resistivity among the three groups, indicating a more specular/elastic interface scattering. The enhancement of Cu conductivity by inserting/capping with a 2D layered material has also been observed and studied in other works.\[14,15,28,29\] It is believed that the inferior conductivity of Ta/Cu and SiO₂/Cu can be attributed to the perturbing localized interfacial states.\[15,28\] By contrast, the weaker interaction between 2D layered materials and Cu\[30] is expected to result in a less perturbed interface and hence preserve the pristine Cu surface states more effectively.\[30\]

In addition to the surface scattering effect of a liner on Cu resistivity, the wettability and adhesion of Cu to liners are also of great importance. The former is essential to provide a good surface for the Cu seeding layer and for the subsequent
electroplating of Cu, while the latter is crucial for Cu to survive chemical-mechanical polishing (CMP) processes and directly impacts the electromigration lifetime of Cu wires.[31] To investigate the wettability, much thinner Cu films (≈10 nm) were deposited on different surfaces. The left panel of Figure 3e reveals lots of cracks on the Cu film deposited on SiO₂, indicating a poor wettability. By contrast, TaSₓ provides a good wettability as Ta does, as can be observed in the middle and right panels of Figure 3e. The adhesion of Cu on TaSₓ was verified by a tape test method.[32] After the preparation of TaSₓ, ≈80 nm Cu was deposited on TaSₓ followed by the attachment of a 3M Scotch Tape for a simple adhesion test.[32] After detaching the tape, only the regions with TaSₓ had Cu left; Cu on SiO₂ regions was detached by the tape, as shown in Figure 3f. All the test results above indicate that TaSₓ can serve as a favorable liner for Cu.

Figure 3. Device structures and tests of liner properties of 400 °C TaSₓ. a) AFM profile of 1.5 nm TaSₓ grown at 400 °C. This film is used for all the liner and barrier tests. b) Sample fabrication procedure. Ta/Cu stack is deposited in situ, while TaSₓ has been exposed to air before Cu deposition. An in situ Cu deposition on TaSₓ could bring an even better performance. c) Cu thin film patterned into Kelvin structure for resistance measurements. Ultrathin Cu film patterned into Kelvin structure for resistance measurements. d) Cu resistivity on various surfaces. In general, thinner Cu is expected to have a higher resistivity. Nevertheless, the thinnest Cu (13 nm) on TaSₓ has the lowest resistivity, indicating suppression of surface scattering at the TaSₓ/Cu interface. e) Wetting properties of Cu tested by depositing ultrathin Cu (≈10 nm) on different surfaces. Numbers of cracks can be observed when Cu is on SiO₂, while Cu on 1.5 nm Ta and 1.5 nm TaSₓ have smooth morphologies. The results show that TaSₓ can provide a good surface as Ta does for Cu seeding layers, which is important for the subsequent Cu electroplating. f) Adhesion tests using the tape method. ≈80 nm Cu is deposited on TaSₓ or SiO₂. After detaching the tape, only Cu on TaSₓ remains, indicating that TaSₓ is a good liner for Cu to survive CMP processes. The scale bars are 1 µm and 500 nm in (a) and (e), respectively.
The diffusion barrier properties of TaS\textsubscript{x} were tested by time-dependent dielectric breakdown (TDDB) measurements.\textsuperscript{[33–36]} TDDB measurement is a standard test method to evaluate gate dielectric reliability as well as Cu diffusion in the dielectrics (IMDs) of interconnects. Here, a capacitor structure\textsuperscript{[34]} was adopted for TDDB measurements to study the intrinsic diffusion barrier properties of TaS\textsubscript{x}. Extrinsic breakdown\textsuperscript{[34,37]} due to the CMP process can occur in interconnect damascene structures, which affects a sensitive evaluation of TaS\textsubscript{x} for the barrier application. In the measurement, a constant electric field was applied across a capacitor structure to drive Cu ions into the dielectric, as depicted in the inset of Figure 4a. Note that the mass transport of Cu ions driven by the electric field is actually “Cu drift.” Nevertheless, we still denote it as “Cu diffusion” because of the conventional terminology used in the field. The Cu ions driven into the dielectric can cause Cu-induced breakdown by forming conductive paths and/or by lowering the barrier of trap-assisted tunneling/conduction.\textsuperscript{[35]} A superior diffusion barrier is expected to mitigate Cu diffusion, which prolongs the time-to-breakdown (t\textsubscript{BD}) of the devices. Figure 4a shows the current evolution with the stress time at 7 MV cm\textsuperscript{-1} of multiple devices. Sudden current jumps.
indicate device breakdown. It can be observed that $t_{BD}$ of most devices increases when Ta is converted to TaS$_x$, suggesting improved diffusion barrier properties. The values of $t_{BD}$ of multiple devices were further plotted in the statistical distribution shown in Figure 4b, where each point was obtained from one device. At a certain electric field, the device with the shorter/longer $t_{BD}$ was assigned to have the lower/higher value of the cumulative probability. Therefore, a straight line with a positive slope can be obtained. Medium time-to-failure ($TTF_{50\%}$) was extracted from the figure for an easier comparison between different materials. From Figure 4b, it is obvious that TaS$_x$ devices have ≈6 times longer lifetime than Ta devices at 7 MV cm$^{-1}$.

Although TaN mainly enables the diffusion barrier function in the conventional barrier/linear bilayer, Ta can also contribute to the blocking of Cu diffusion. Figure 4c indicates that 1.5 nm TaS$_x$ has similar barrier properties as 3 nm Ta, which is essential to the barrier/liner thickness scaling requirement. Since TaN plays the dominant role in mitigating Cu diffusion, TaS$_x$ is also benchmarked to TaN results from other work.[8] It can be observed in Figure 4d that 1.5 nm TaS$_x$ has similar performance as 2 nm TaN in terms of mitigating Cu diffusion. Based on the experimental results of liner and diffusion barrier properties, it is possible to decrease a 5 nm TaN/Ta stack (2 nm TaN + 3 nm Ta) to a 3 nm TaS$_x$ layer while maintaining or even improving

Figure 5. DFT calculations of Cu diffusion through a 2D TaS$_2$ barrier. A) Illustration of grain-boundary (GB) and interlayer diffusion. b) Atomic structure of Cu bound at GB of TaS$_2$. c) Atomic pathway of intralayer diffusion of Cu in layered TaS$_2$. d) Energies of the states along the diffusion pathway. e) Comparison of the energy barriers for Cu diffusion through GBs of various materials. The values for TaN and graphene are from other works.[38,39,41] The calculation indicates TaS$_2$ has a sufficient energy barrier of at least 1.5 eV to block Cu diffusion.
the barrier/liner performance. Further scaling can be achieved given the 2D material nature of TaS\(_x\). The projection of significant resistance reduction benefitting from the maximized Cu volume is provided in Figure 4e. In addition to the electrical tests, material analyses on Cu diffusion were also conducted, as discussed in Figures S3–S6 (Supporting Information).

It is well known that the columnar grain-boundaries (GB) structures in TaN/Ta provide paths for faster Cu diffusion\([38–40]\). It was also predicted that GBs should also be the dominant diffusion paths for Cu diffusion through 2D layered materials\([41]\). To better understand the Cu diffusion behavior through these new materials, we have performed density functional theory (DFT) calculations using TaS\(_2\) as the material for analysis. The computation details can be found in the Supporting Information. The energy barriers for Cu diffusion through GBs and through the intralayer were both calculated. The two types of diffusion were illustrated in Figure 5a. Various TaS\(_x\) GB structures were compared,\([42–44]\) as illustrated in Figure S7 (Supporting Information), to find the lowest energy configuration (Figure S8, Supporting Information). It is discovered that the energy of Cu adsorbed at the GB shown in Figure 5b is \(\approx 1.5\) eV lower than that at the interlayer site (the adsorption energies at the GB core and at the sites far from the GB core were calculated to be \(-4.154\) eV and around \(-2.6\) eV, respectively). This suggests that the energy barrier for Cu diffusion from the GB to the interlayer site should be at least 1.5 eV, which is higher than that of Ta/TaN\([38,39]\). We also find that the intralayer diffusion (Figure 5c) is very fast, with an energy barrier of only 0.25 eV, as shown in Figure 5d. These results summarized in Figure 5e suggest that the enhanced barrier performance of TaS\(_x\) compared with conventional TaN/Ta is likely to arise from the difference in GB, which blocks the Cu diffusion more effectively. Further improvement of the TaS\(_x\) grain size can lead to even better diffusion barrier properties\([9]\).

In summary, a \(\approx 1.5\) nm TaS\(_x\) barrier/liner is realized by converting Ta with PECVD at a BEOL-compatible temperature, providing a near-term solution for industry to improve the reliability/performance of current interconnect technology. This work considers critical integration aspects of this 2D material in terms of liner and barrier properties. The liner properties are evaluated based on i) surface scattering at various interfaces, ii) wettability that TaS\(_x\) can provide for the subsequent Cu seeding layers, and iii) adhesion of Cu to TaS\(_x\). The TaS\(_x\) film passes all the tests, which is demonstrated in 2D layered materials for the first time. The diffusion barrier properties are analyzed by TDDB measurements. The TDDB results show better barrier properties after Ta being converted to TaS\(_x\). Additionally, the benchmark of TaS\(_x\) to TaN indicates enhanced Cu blocking capability. The test results of liner and diffusion barrier properties are summarized in Table 1. Our accomplishments compared to other works are summarized in Table 2. Further improvement of the film quality can be expected to bring even better barrier performance. Based on the evaluations, a conventional TaN/Ta bilayer stack can be replaced by an ultrathin TaS\(_x\) layer to maximize the Cu volume for ultrascaled interconnects. Further development of CVD or ALD based growth methods may realize even thinner (single-layer; <1 nm) and more uniform 2D TaS\(_x\) barrier/liner.

**Experimental Section**

**Preparation of TaS\(_x\) Film:** Ta was first deposited by an e-beam evaporator on Si/SiO\(_2\) at a rate of \(\approx 0.5\) Å s\(^{-1}\). After loading the Ta sample to the PECVD system, the tube furnace was pumped down. Nitrogen purging/chamber pumping was conducted repeatedly for ten times to remove moisture and other possible contamination sources from the ambient during the sample loading step. Meanwhile, the temperature was set at 400 °C, which was reached after 5–10 min. After

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**Table 1.** Test results of liner and diffusion barrier properties. The liner properties are tested in three aspects, while the analysis of diffusion barrier property focuses on the capability of blocking Cu diffusion.

| Liner properties | Diffusion barrier property |
|------------------|---------------------------|
| Cu surface scattering | TaS\(_x\) reduces surface scattering → Cu resistivity decreases |
| Cu wetting | No obvious cracks in Cu thin films deposited on TaS\(_x\), → TaS\(_x\) provides a good surface for Cu seeding layer |
| Cu adhesion | Pass tape test → Could survive CMP process |

Compared to Ta Better
Compared to TaN Similar

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**Table 2.** Comparison of different works using 2D layered materials as Cu diffusion barriers. Only the TaS\(_x\) barrier/liner in this work satisfies all of the requirements.

| Material | Growth temperature (BEOL-compatible?) | Transfer-free? | Barrier property? | Liner property? |
|----------|--------------------------------------|----------------|-----------------|----------------|
| Graphene\([8]\) | 1000 °C (NO) | NO | YES | NO |
| Graphene/graphene oxide\([7]\) | 750 °C (NO) | NO | YES | NO |
| Graphene\([6,8]\) | NO | NO | YES | NO |
| Graphene\([10]\) | 550 °C (NO) | YES | YES | NO |
| Graphene\([12]\) | 400 °C (YES) | YES | YES | NO |
| MoS\(_2\)\([11]\) | 850 °C (NO) | YES | YES | NO |
| TaS\(_x\)(this work) | 400 °C (YES) | YES | YES | YES |

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reaching the base pressure of ~10 mTorr, Ar with a flow rate of 10 sccm was introduced. The pressure at this time was ~180 mTorr. Then, H2S with a flow rate of 10 sccm was introduced and the pressure reached ~320 mTorr. After waiting for 5 min to stabilize the temperature and flow rate, plasma power was turned on and slowly increased to 70 W. At this power, the pressure changed to ~420 mTorr. After 20 min of growth, the plasma was turned off, followed by turning off the gases and the furnace heater.

XPS Analysis: Monochromatic XPS was employed in this work using a system described elsewhere. The AAnalyzer software was used for XPS core level analysis. Active Shirley background and Voigt line shape were employed for peak fitting. For all chemical states detected at Ta 4f core level, the binding energy separation between 4f5/2 and 4f7/2 is 1.9 eV with the same Lorentzian (0.11). The Gaussian component is larger for the Ta—O—S chemical state due to formation of new bonds. Similar for the S 2p core level, binding energy separation (1.1 eV) and Lorentzian (0.11) for 2p1/2 and 2p3/2 is the same for S—Ta and S—Ta—O chemical states. While the Gaussian component is larger and broader for S—Ta—O bonding corresponding to the Ta—S—O chemical state at S 2p and Ta 4f core spectra levels, an additional chemical state is observed in the O 1s core level at a lower binding energy (~330 eV).

TEM Analysis: Scanning transmission electron microscopy (STEM) cross-sectional samples were prepared with a FEI Nova 200 dual-beam FIB/SEM by using the lift-out method. The region of interest above the Al metal pad was protected during the focused ion beam milling, by depositing SiO2 and Pt layers on top of the sample. Both high-resolution transmission electron microscopy images, atomic STEM high-angle annular dark-field (HAADF) and bright field images, were obtained in a JEOL ARM200F microscope equipped with a spherical aberration (Cs) corrector (CEOS GmbH, Heidelberg, Germany) and operated at 200 kV. The corrector was carefully tuned by the Zemlin-tableau method with Cs = 0.5 μm and the resolution was demonstrated to be around 1 Å.

Fabrication of MOS Capacitor and Kelvin Structures: Heavily doped Si (resistivity ~5 mΩ cm) substrates with 90 nm SiO2 were used for all sample fabrication. Ta/Cu was always deposited in situ, while Ta3Sn/Cu encounter air exposure after the Ta deposition and Ta3Sn conversion. For the fabrication of capacitor structures, on top of Ta or Ta3Sn, Cu/Al (~30 nm/20 nm) electrodes with diameters of 100 μm were deposited by e-beam evaporation using a shadow mask, with Cu in contact with the 2D material and Al on the very top as a passivation layer. The sample was then coated with photoresist and placed into 6:1 buffered oxide etch to etch away the SiO2 on the back side of the Si substrate, followed by 50 nm Al deposition to form an ohmic contact to the Si substrate. Finally, the top photoresist was removed by acetone. For the Kelvin structure, the same Si/SiO2 substrate with Ta or Ta3Sn, top (or SiO2 only) was first coated with poly(methyl methacrylate) (PMMA). 30 min of forming gas annealing was used to remove residues on TaS, from the growth before PMMA coating. E-beam lithography was then used to write the desired patterns, followed by a development in isopropyl alcohol (IPA):water = 3:1. Cu was e-beam-evaporated on the sample. Finally, a lift-off process was used to form the desired Cu patterns.

DFT Calculations: DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) with projector augmented wave pseudopotentials[49] and Perdew–Burke–Erznerhof exchange-correlation functional.[50] A kinetic energy cut-off of 400 eV was used for the plane-wave expansion, and all atomic positions were fully relaxed until the final force on each atom was less than 0.01 eV Å⁻¹. The vdW interaction in layered systems was incorporated using Grimme’s method.[51] To model the interlayer diffusion, we used a 4 x 4 supercell of bilayer TaS2. The structures of GBs and their energies can be found in the Supporting Information.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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2D materials, Cu diffusion, interconnects, reliability

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