ADVANCED MATERIALS INTERFACES

Supporting Information

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MoS_2 Synthesized by Atomic Layer Deposition as Cu Diffusion Barrier

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Supporting information

Title: *MoS$_2$ synthesized by atomic layer deposition as Cu diffusion barrier*

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S1: Thickness measurement by atomic force microscopy

The thickness of each film was measured by atomic force microscopy (AFM) line scan profiles. Each sample was scratched with a pair of tweezers to remove the MoS$_2$ film and to create a height difference between the remaining MoS$_2$ film and the Si substrate with SiO$_2$. The height difference between the bare Si substrate with SiO$_2$ and the MoS$_2$ film was determined by AFM. Figure S1 shows the AFM line scan profiles for each thickness.

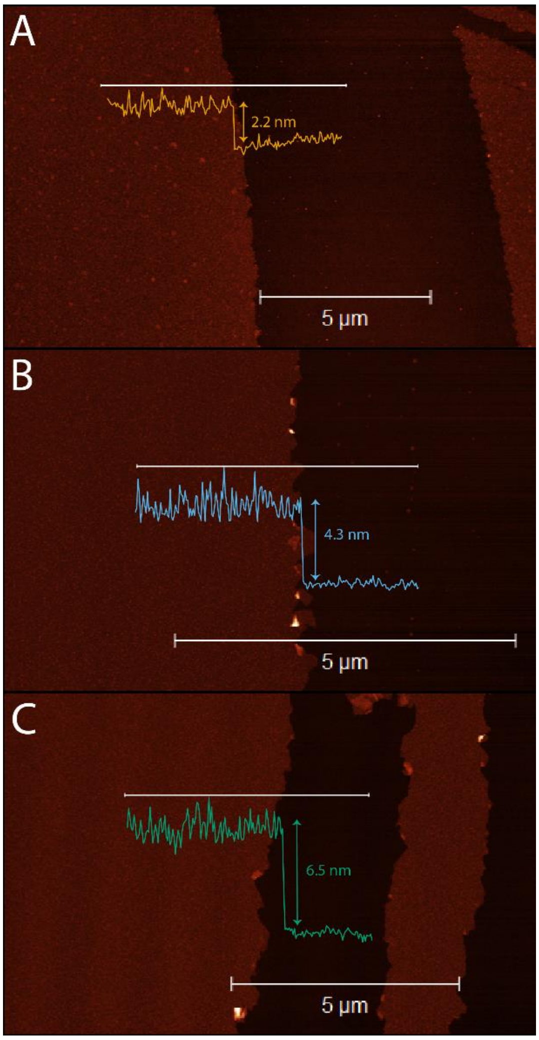

Figure S1: AFM images and line scan profiles of the different MoS$_2$ thicknesses. The height difference is created by removal of the MoS$_2$ film by scratching with a pair of tweezers.

S2: Crystallinity of the MoS_2 films

The crystallinity of the MoS_2 films was investigated by Raman spectroscopy. The Raman spectra of each thickness of MoS_2 on 90 nm SiO_2 is shown in Figure S2. Both the characteristic E^1_{2g} and A_{1g} peak corresponding to the 2H phase of MoS_2 are visible in the spectrum for all films as is expected from crystalline MoS_2 films.

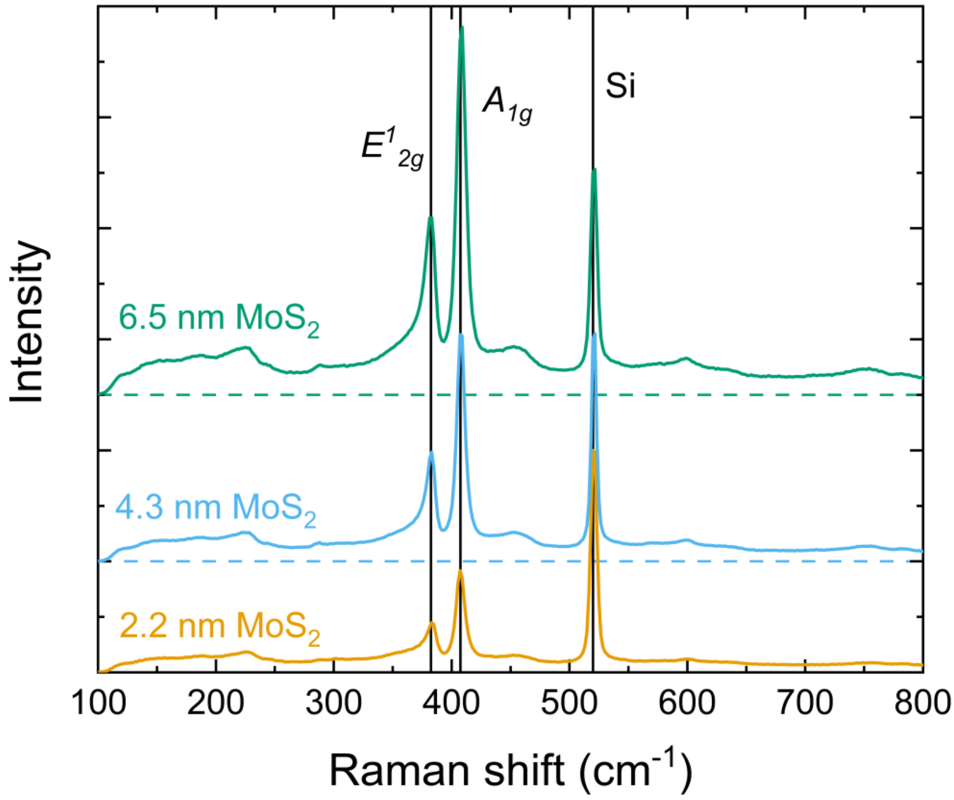

Figure S2: Raman spectra of the MoS_2 films. Spectra are scaled to the Si peak and shifted vertically for clarity.

S3: Number of fins on MoS_2 films

Fins (vertical structures) are visible in the top-view high-angle annular dark field scanning transmission electron microscopy (HAADF STEM) images. The number of fins on a surface varies with thickness. For each thickness the number of fins was analyzed by investigating several different TEM images with a magnification of 2,500,000. The average number of fins per nm^2 is displayed in Figure S3. Since the 2.2 nm MoS_2 TEM window contains some contamination, counting the number of fins is less straightforward for this sample. Small white spots in the image can be either contamination or a small fin. In Figure S4 two different count methods for 2.2 nm MoS_2, conservative and liberal, are illustrated on a TEM image. In Figure S3 both the resulting number of fins from the liberal and conservative count method are displayed. The different counting methods are not necessary for the 4.3 and 6.5 nm MoS_2 films, since these are clean enough to clearly distinguish fins. From the data, it can be concluded that from 4.3 nm to 6.5 nm MoS_2 the number of fins increases with increasing thickness, but a trend down to 2.2 nm MoS_2 cannot be established.

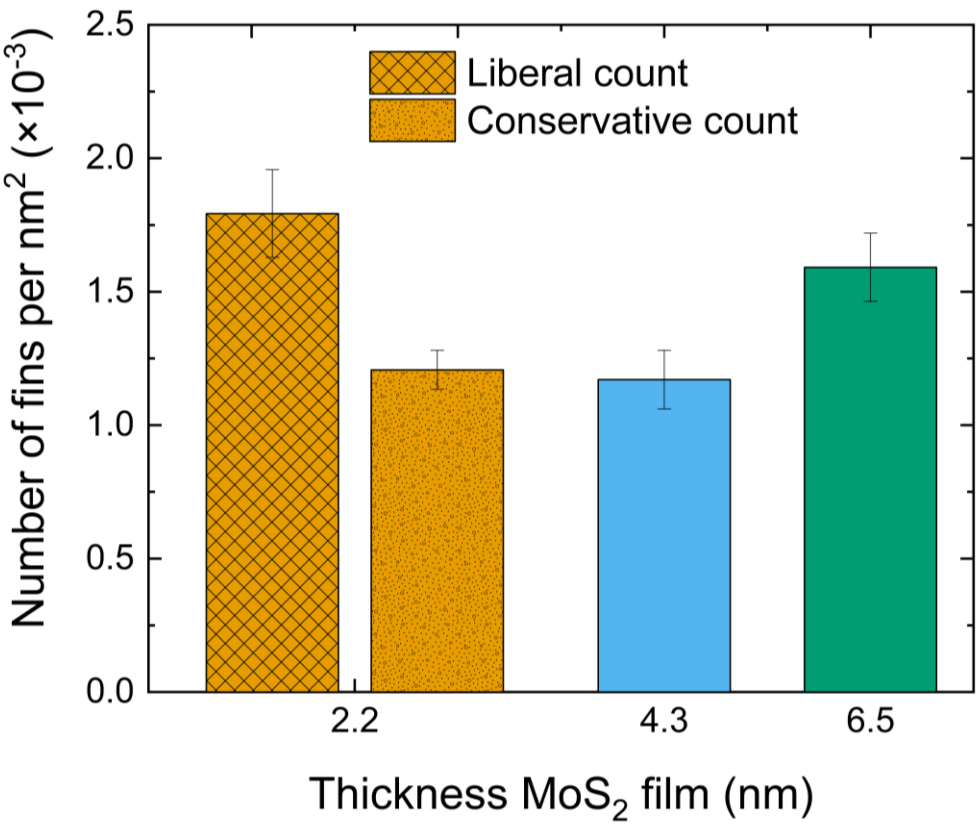

Figure S3: Average number of fins per nm^2 for different thicknesses of MoS_2 film. For the 2.2 nm thick MoS_2 both the liberal and conservative count are indicated.

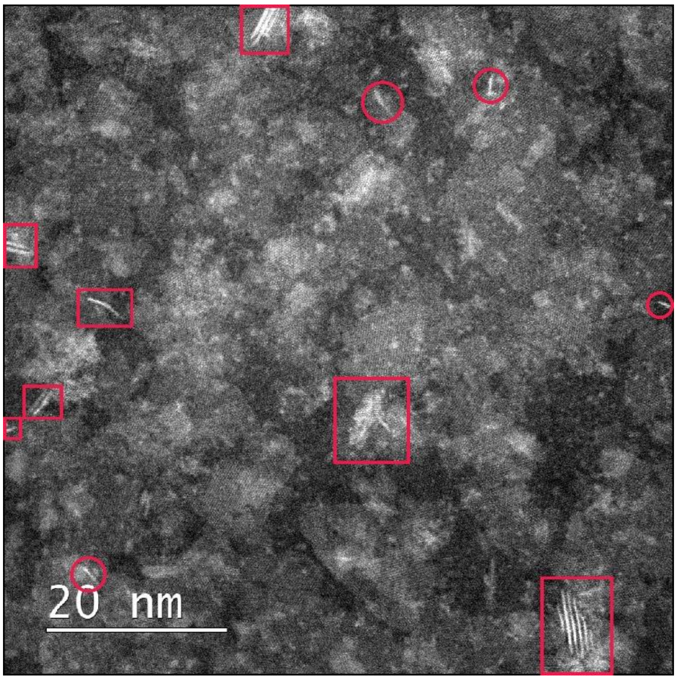

Figure S4: HAADF top-view STEM images of 2.2 nm ALD MoS_2 at 2.5 million times magnification. The conservative count consists of the fins in the rectangles. The liberal count consists of fins in the rectangles as well as fins in the circles.

S4: Comparison between different 2D barriers

Besides MoS_2, other 2D materials have been investigated as Cu diffusion barrier in the literature [1]–[3]. The overview of the median-time-to-failure with extrapolation to lower E-fields is shown in Figure S5 and the $TTF_{50\%}$ values are displayed in Table S1.

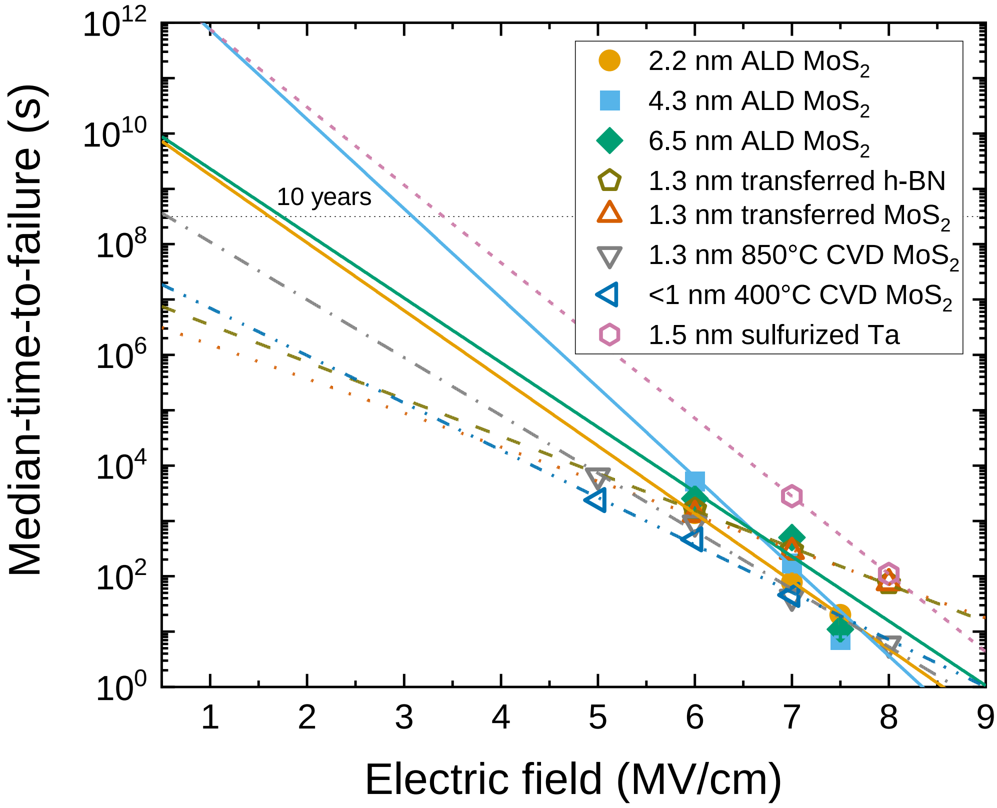

Figure S5: Extrapolation of the median-time-to-failure data to low electric fields, shown by the linear fit according to the E-model [4]. The dashed line indicates a time of 10 years. ALD MoS_2 results are from this work. Transferred h-BN, transferred MoS_2 and 850°C CVD MoS_2 results are from Lo *et al.* (2017) [1], 400°C CVD MoS_2 results are from Lo *et al.* (2018) [2] and sulfurized Ta results are from Lo *et al.* (2019) [3].

Table S1: Overview of TDDB results of different 2D barriers from this work and as reported in the literature.

Material	Deposition method	Thickness (nm)	Deposition temperature (°C)	$TTF_{50\%}$ (s)	E-field (MV/cm)	Reference
h-BN	Transferred	1-1.3	-	1623	6	[1]
h-BN	Transferred	1-1.3	-	297	7	[1]
h-BN	Transferred	1-1.3	-	74	8	[1]
MoS_2	Transferred	0.6-1.3	-	1305	6	[1]
MoS_2	Transferred	0.6-1.3	-	280	7	[1]
MoS_2	Transferred	0.6-1.3	-	76	8	[1]
MoS_2	850°C CVD	0.6-1.3	850	6500	5	[1]
MoS_2	850°C CVD	0.6-1.3	850	923	6	[1]
MoS_2	850°C CVD	0.6-1.3	850	42	7	[1]
MoS_2	850°C CVD	0.6-1.3	850	6	8	[1]
MoS_2	400°C CVD	0.62	400	2364	5	[2]
MoS_2	400°C CVD	0.62	400	463	6	[2]
MoS_2	400°C CVD	0.62	400	46	7	[2]
MoS_2	ALD	2.2	450	$(1.4 \pm 0.1)\cdot10^3$	6	This work
MoS_2	ALD	2.2	450	77 ± 7	7	This work
MoS_2	ALD	2.2	450	20 ± 1	7.5	This work
MoS_2	ALD	4.3	450	$(5.2 \pm 0.4)\cdot10^3$	6	This work
MoS_2	ALD	4.3	450	172 ± 7	7	This work
MoS_2	ALD	4.3	450	7 ± 1	7.5	This work
MoS_2	ALD	6.5	450	$(2.5 \pm 0.1)\cdot10^3$	6	This work
MoS_2	ALD	6.5	450	$(5.0 \pm 0.3)\cdot10^2$	7	This work
MoS_2	ALD	6.5	450	11 ± 1	7.5	This work
TaS_x	Plasma sulfurization	1.5	400	2800	7	[3]
TaS_x	Plasma sulfurization	1.5	400	110	8	[3]

S5: Adhesion

The adhesion of the MoS_2 barrier films to the Si substrate with SiO_2 and to the Cu/Al electrodes was investigated with the Scotch tape test method. The tested structure was a Si wafer with 450 nm thermal SiO_2, 6.5 nm MoS_2 and 30 nm Cu covering the full 1x1 cm^2 area of the sample. The Scotch tape was applied to part of the sample. After exfoliation the sample consisted only of SiO_2 with the same thickness as before the Scotch tape test. Both the MoS_2 and Cu films were removed by the Scotch tape, indicating that the adhesion of the MoS_2 to the SiO_2 substrate is limited. Figure S6 shows the sample where a part of the top film with MoS_2 and Cu is removed by the Scotch tape. The removal of the MoS_2 was confirmed by spectroscopic ellipsometry. The thicknesses of MoS_2 and SiO_2 are displayed in Table S2.

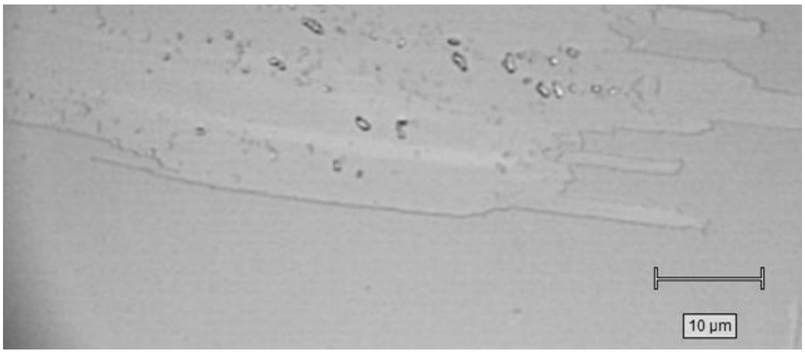

Figure S6: Photo, taken with an optical microscope, of a $Si/SiO_2/MoS_2/Cu$ sample where the top part was removed by the Scotch tape.

Table S2: MoS_2 and SiO_2 thicknesses before and after the Scotch tape test.

MoS_2 thickness (nm)		SiO_2 thickness (nm)	
Before	After	Before	After
6.5	0.0	442	445

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