Amorphous W-S-N Thin Films: the Atomic Structure Behind Ultra-low Friction

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Amorphous W-S-N in the form of thin films has been identified experimentally as an ultra-low friction material, enabling easy sliding by the formation of a WS₂ tribofilm. However, the atomic-level structure and bonding arrangements in amorphous W-S-N, which give such optimum conditions for WS₂ formation and ultra-low friction, are not known. In this study, amorphous thin films with up to 37 at.% of N are deposited, and experimental as well as state-of-the-art *ab initio* techniques are employed to reveal the complex structure of W-S-N at the atomic level. Excellent agreement between experimental and calculated coordination numbers and bond distances is demonstrated. Furthermore, the simulated structures are found to contain N bonded in molecular form, i.e. N₂, which is experimentally confirmed by NEXAFS and XPS analysis. Such N₂ units are located in cages in the material, where they are coordinated mainly by S atoms. Thus this ultra-low friction material is shown to be a

complex amorphous network of W, S and N atoms, with easy access to W and S for continuous formation of WS₂ in the contact region, and with the possibility of swift removal of excess nitrogen present as N₂ molecules.

Keywords: tribology, thin films, ab initio calculations, EXAFS, WS₂

1. Introduction

In many applications where surfaces slide against each other, low friction and low wear of the surfaces is desired for optimum performance, efficient use of energy, and long component lifetimes. A particularly attractive solution is self-lubricating surfaces, which provide low friction and low wear also under unlubricated conditions. While the bulk material of a component is often selected based on other demands, the surface properties can be tailored for optimal tribological performance by, for example, deposition of thin films. Transition metal dichalcogenides (TMDs), such as WS₂, are intrinsic solid lubricants and can provide low friction especially under dry conditions. To make full use of the possibility of WS₂ superlubricity, one would like a stable surface with good load-bearing capacity and wear resistance, on which a tribofilm of aligned WS₂ crystallites is formed. To obtain this, WS₂ and MoS₂ have been combined with metals, for example Ti,[[1](#), [2](#)] Cr,[[3](#), [4](#)] Ni,[[5](#)] Au[[6](#), [7](#)] and Pb,[[8](#)] as well as non-metals, such as C [[9-11](#)] and N.[[10](#)] The film itself then contains embedded nanocrystalline TMD grains, and in some cases no distinguishable TMD phase at all. Even so, crystalline WS₂ or MoS₂ can be formed during tribological contact to provide low friction, in a process where WS₂ or MoS₂ is formed at the surface, by transport of relevant atomic species from the inner part of the film. These TMD-based materials are therefore self-lubricating. To meet the demand of low and stable friction it is important, however, that the added element does not disturb the formation of a lubricating tribofilm. For example, formation of high-friction metal oxides may hinder the formation and decrease the

stability of the WS₂ tribofilm. For optimizing the benefits of WS₂ lubrication, non-metallic nitrogen should thus be a good candidate as the added element, and Nossa and Cavaleiro [10, 12-15] first demonstrated low-friction W-S-N films. The concept was further investigated in a recent study by Gustavsson et al., who demonstrated ultra-low friction ($\mu < 0.003$) for an amorphous W-S-N film.[16]

This has potential in opening up new ways to find low-friction surfaces and is a small breakthrough in the field of solid-state lubrication. However, the atomic arrangement of W-S-N films has not been established, which excludes a microscopical understanding. It stands clear that with such a high N content, and lack of WS₂ crystallites, the chemical bonding and internal structure of the material must be widely different from that of WS₂. The bonding conditions also cannot be analogous to that of other doped TMD systems, in which excess dopant atoms can be found in metal grains or as a carbon matrix. The fact that nitrogen and its oxides are gases also means that the nitrogen may leave the material as a molecular entity, as N₂ or nitrogen oxide, instead of remaining in the tribological contact where it could disturb the tribofilm formation. W-S-N films could therefore offer optimal conditions for formation of well-functioning WS₂ tribofilms and low friction levels.

The aim of this study is to elucidate the nature of the chemical bonding and structure of amorphous W-S-N films, and to connect this to their excellent tribological performance. To this end, we have used experimental as well as theoretical means. Both long-range and short-range structures have been investigated by different experimental techniques. These experimental structures have been compared to models obtained from first principles theory and *ab initio* molecular dynamics, which also address the nature of chemical bonding in the films. Excellent agreement is found between calculated and measured data, and we can

therefore present a detailed structural and chemical description of this ultra-low friction material.

2. Methods

2.1 Experimental Details

The films were deposited by reactive DC magnetron sputtering from a WS₂ target and N₂ gas.

The substrates were single-crystal Si (100) wafers, which were cleaned by plasma etching in the deposition chamber. A titanium adhesion layer with a thickness of approximately 100 nm was then deposited. During deposition of the W-S-N films, the total gas flow (of Ar and N₂) and the total pressure were kept constant at 100 sccm and 5 mTorr, respectively. The composition of the deposited coating was varied by changing the flow of N₂ gas between 0 and 60 sccm. The substrates were not heated during deposition, and they were rotated and kept at floating bias. Deposition times were between 130 and 220 minutes, leading to film thicknesses of between 1.3 and 2.1 μm . The elemental compositions of the films were determined by energy dispersive X-ray spectroscopy (EDS) in a Zeiss 1550 scanning electron microscope (SEM), which was also used to obtain electron micrographs of the films. A reference sample of commercially available (NH₄)₂WS₄ powder was used to confirm the accuracy of the EDS elemental quantification. The crystallographic structure was analyzed by X-ray diffraction (XRD) in grazing incidence mode with an incidence angle of 1° in parallel beam geometry, on a Siemens D5000 instrument with Cu K α radiation. The chemical bonding was analyzed by X-ray photoelectron spectroscopy (XPS) on a PHI Quantum 200 instrument with monochromatic Al K α radiation. In some cases, the samples were sputter etched with 500 eV Ar⁺ ions for 5 min. X-ray absorption measurements on the N 1s $\rightarrow\pi^*$ resonance were performed at the SurICat endstation of beamline PM3 at the HZB/BESSY synchrotron light source (Berlin, Germany) [17].

2.2 Computational Details

First-principles calculations were performed by means of the density functional theory [18, 19] and projector augmented wave [20, 21] method as implemented in the Vienna *ab initio* simulation package (VASP) [22-24]. The exchange-correlation energy was calculated using the generalized gradient approximation with the Perdew, Burke, and Ernzerhof functional [25], including the valence states $5d^46s^2$ for W, $3s^23p^4$ for S and $2s^22p^3$ for N. This scheme is known to accurately describe the physical properties of transition metal carbides and nitrides.[26-30] The amorphous structures were generated by means of *ab initio* molecular dynamics using canonical (NVT) ensembles applying the VASP package. In the initial structures, 200 atoms were both spatially and chemically randomly distributed in a cubic unit cell with a density equal to the experimental one ($\rho = 7 \text{ g/cm}^3$). The ensembles were melted and equilibrated at high temperature (5000 K), then cooled down to 300 K following a path of exponentially decreasing temperature. The duration of the cooling process was 20 ps. Finally, the structures were equilibrated at 300 K. The temperature was controlled using the Andersen thermostat [31] with collision probability $\alpha=0.7$. Our choice of α yields theoretical structures that are in excellent agreement with the experimentally synthesized films, regarding bond lengths and atomic coordination. Slightly different values of α do not change this picture. The calculations were performed using the Γ k -point. The cutoff energy of 550 eV together with $6\times6\times6$ k -point Monkhorst-Pack mesh [32] and Methfessel-Paxton smearing [33] of $\sigma=0.2$ eV were used for electronic structure calculations. The atomic charges were determined from Bader analysis [34-36].

3. Results and discussion

A series of five samples was deposited and their compositions, determined by EDS, varied with the flow of N_2 during deposition (**Table 1**). Signals from oxygen were also detected, but corresponded only to 3-4 at.% for all samples except the N-0 film for which it was higher,

since it is pure W-S and therefore more porous. The oxygen signals, as well as signals from carbon, and in the case of the N-0 film also from nitrogen, were disregarded for the determined compositions. It can be noted that all films, including the W-S film (N-0), which was deposited without N₂ and thus only from the WS₂ target, had a S/W ratio close to 1. Substoichiometry with respect to sulfur is often observed in films sputtered from WS₂ targets, and the sulfide could therefore be referred to as WS_x rather than WS₂ [37].

Table 1. Compositions of the different samples, estimated from EDS measurements.

Sample	N ₂ flow [sccm]	W [at%]	S [at%]	N [at%]
N-0	0	50	50	0
N-19	5	39	42	19
N-22	10	35	43	22
N-31	30	34	35	31
N-37	60	33	30	37

The crystallographic structure of the films was analyzed by XRD (**Figure 1**). For the pure W-S film (N-0), broad peaks can be observed around the positions of reflections from WS₂, although the crystallinity is poor. For all samples containing N, only a broad bump is observed, implying that the films are X-ray amorphous. The phenomenon of decreasing crystallinity with increasing addition of another element has previously been observed for WS₂, and the related MoS₂, on addition of a wide range of elements, such as N [10], C [9-11], Ti [1, 2], Cr [4, 38], and Au [6, 7]. Furthermore, the lack of substrate heating decreases the possibilities of the atoms to arrange themselves on arrival to the substrate, meaning that the pure W-S film is also of relatively poor crystallinity.

Scanning electron micrographs of fractured cross-sections (**Figure 2**) show a change in morphology with the addition of N. The W-S film (N-0) is porous, but does not contain the

distinct lamellae often seen in more crystalline W-S films. However, the morphology is typical of poorly crystalline sputtered W-S, or W-S-based, films. In this case the poor crystallinity is related to the low deposition temperature, but a similar morphology can be observed in films where the crystallinity is decreased by doping with another element. The N-containing films are dense and featureless, and show no indications of porosity in SEM.

To study the structure of the W-S-N material on an atomic level, the material was simulated by first principles theory (see Methods). For the theoretical simulations a composition of $W_{0.33}S_{0.33}N_{0.34}$ was chosen, similar to the N-31 film, and to W-S-N with 34 at.% of N for which ultra-low friction was observed [16]. The simulations consisted of 66 W, 66 S, and 68 N atoms, giving a total of 200 atoms. Three different theoretical structures with this composition were generated from separate molecular dynamics simulations, and are referred to as STR-A, STR-B and STR-C, respectively. All generated structures were found to be amorphous with no partial crystallization. To examine the reliability of our theoretical structures, EXAFS oscillations (referred to as $\chi(k)$) were simulated from the geometries of STR-A, STR-B and STR-C using theoretical local structural information. Since from experimental EXAFS one derives the average local information, we also made an average $\chi(k)$ from the individual $\chi_i(k)$'s ($i = A, B, C$) giving a fourth theoretical curve. We then compared the simulated EXAFS oscillations of $W_{0.33}S_{0.33}N_{0.34}$ with the experimental signal (see Methods) for the N-31 film. The simulated curves are presented alongside the experimental one in **Figure 3**. A remarkable agreement between theory and experiment is seen up to $9 \text{ \AA}^{-1}$ in k space, with STR-A giving the best agreement with the experimental results. This illustrates the computational efficiency and accuracy of the molecular dynamics technique for amorphous materials. We proceed with the structural analysis of the atomic configurations of $W_{0.33}S_{0.33}N_{0.34}$ as represented by the radial distribution function (RDF)

(**Figure S1**). The RDFs show short range order up to 6 Å for the W-S, W-N, S-N and N-N pairs, and up to 7 Å for W-W and S-S pairs. The peaks in the RDFs are clearly identified and correspond to the nearest neighbor (NN) distances for each of the atomic pairs. The theoretical NN distances and experimental bond lengths obtained from EXAFS are presented in **Table 2**, along with the corresponding bond lengths in selected reference systems.

Table 2. Theoretical and experimental nearest neighbor distances in amorphous $W_{0.33}S_{0.33}N_{0.34}$ and the N-31 film, respectively. The distances in the corresponding crystalline or organometallic materials are listed for comparison. The numbers given in parentheses correspond to the separate peaks in the RDFs.

Atomic pair	Theoretical distances [Å]			Experimental distance [Å]	Reference bond distance [Å]	
	<i>STR-A</i>	<i>STR-B</i>	<i>STR-C</i>		Bond distance [Å]	Material
W-W	2.921	2.835	2.844	-	2.826 ^[39]	WN (hexagonal)
W-S	2.389	2.366	2.387	2.387 ± 0.015	2.478 ^[40] , 2.411 ^[41] , 2.405 ^[4]	WS ₂ (hexagonal)
W-N	1.941	1.955	1.964	1.925 ± 0.027	2.188 ^[39]	WN (hexagonal)
					1.967 ^[43] , 1.972 ^[43]	W-N ₂ complex ^{a)}
					1.991 ^[44]	W-N ₂ complex ^{b)}
S-S	3.326	3.423	3.103	-	2.031 - 2.045 ^[45]	S ₈ (orthorhombic)
			(2.101)			
S-N	3.193	3.137	3.186	-	1.596 – 1.634 ^[46]	S ₄ N ₄
	(1.650)		(1.577)			
N-N	1.118	1.130	1.174	-	1.095 ^[47]	N ₂ (g)

^{a)} W(N₂)₂(depr)(PPh₂Me)₂]; ^{b)} W-N₂ complex bearing PNP-type pincer ligands

The theoretical W-W NN distances were compared with bond lengths in crystalline solids, since in EXAFS analysis W-W interactions were ignored due to a broad distribution of bond lengths. We found that the theoretical W-W distances for the amorphous material (2.835 – 2.921 Å) were slightly larger than the W-W bond length in hexagonal WN (2.826 Å and 2.893 Å ^[39]), and larger than in *bcc* W (2.735 Å ^[48]), suggesting a weaker bonding between W atoms in amorphous $W_{0.33}S_{0.33}N_{0.34}$ compared to these crystalline materials. The theoretical

W-S NN distances ($2.366 - 2.389 \text{ \AA}$) are in excellent agreement with the W-S bond length obtained from EXAFS measurements ($2.387 \pm 0.015 \text{ \AA}$), but are shorter compared to the W-S bond length in hexagonal WS_2 [40-42]. For the W-N atomic pair, theoretical NN distances ($1.941 - 1.964 \text{ \AA}$) are in good agreement with the experimental one ($1.925 \pm 0.027 \text{ \AA}$). The experimental and theoretical W-N NN distances are comparable to the W-N bond in crystalline tungsten nitride WN ($2.065 \text{ \AA}$ in cubic WN, [49] $2.188 \text{ \AA}$ in hexagonal WN [39]), as well as to W-N bonds in organometallic tungsten-dinitrogen complexes ($1.967\text{-}1.972 \text{ \AA}$, [43] $1.991 \text{ \AA}$ [44]). The shorter W-S and W-N bonds in amorphous $\text{W}_{0.33}\text{S}_{0.33}\text{N}_{0.34}$ compared to bonds in the corresponding crystals can be correlated with a reduced coordination of sulfur and nitrogen, respectively (**Figure 4 b and c**).

The theoretical S-S and S-N NN distances are significantly longer than the corresponding S-S and S-N bond lengths in crystalline S_8 [45] and tetrasulfur tetranitride S_4N_4 [46]. However, we found additional peaks in calculated S-S (STR-C) and S-N (STR-A and STR-C) RDFs, with smaller peaks of the RDF located at shorter distances. These peaks can be ascribed to the formation of S-S and S-N bonds with bond lengths of $2.101 \text{ \AA}$ and $1.577\text{-}1.650 \text{ \AA}$, which are in good agreement with those in S_8 and S_4N_4 .

Directing the attention to the N-N RDF curves (**Figure S1**), a separate peak at approximately $1 \text{ \AA}$, which corresponds to the formation of N_2 molecules, is clearly distinguished. Indeed, we found 7 N_2 molecules in STR-A, and 8 N_2 in STR-B and STR-C, corresponding to 21 % and 24 % of the total amount of nitrogen atoms in each theoretical structure, with the theoretical N-N NN distance being slightly larger than in gaseous N_2 [47]. Our simulations showed that nitrogen molecules accumulated together and were surrounded by S atoms, with the S-N distance varying from 2.776 to $4.186 \text{ \AA}$. These S-N distances are $1.2 - 2.8 \text{ \AA}$ longer than the

S-N bond lengths, indicating the absence of strong interaction between N₂ and S atoms in the cages. We also found that some of the N₂ molecules, located in smaller cages, were bonded to W atoms. The bond length in these N₂ molecules is in the range of 1.120 – 1.467 Å, which is larger compared to that of the quasi-free N₂ molecules (1.108 – 1.127 Å), as the W-N bond weakens the nitrogen triple bond in N₂. For STR-A, which gives the best atomic description of W_{0.33}S_{0.33}N_{0.34}, we show 5 out of 7 N₂ molecules surrounded by sulfur atoms and other neighboring N and W atoms in **Figure 5**. The nearest neighbor S atoms form a cage where the N₂ molecules are trapped. The length of this cage is equal to the length of a cubic unit cell used in the theoretical calculations (15.3 Å), while the diameter of the cross section is 10.6 - 11.5 Å. The number of atoms used in the theoretical calculations was enough to capture the formation of N₂ molecules and their clustering in a small region, however, the cages might be larger than our calculated unit cells. Formation of dimers has also been confirmed experimentally in amorphous alumina (a-Al₂O₃) [50] and silica (a-SiO₂) [51], where some of the O atoms were found to be present as O-O pairs.

Now we turn our attention to the atomic coordination numbers (**Table 3**) that we compare to the experimental EXAFS data. From theoretical calculations we obtained that on average, W atoms were coordinated by 3.2 W atoms, 2.7 S atoms and 2.7 N atoms. The latter two are in a good agreement with experimental coordination numbers $n_{NN}=2.7$ for S and $n_{NN}=2.7$ for N atoms. Analyzing the local environments for W atoms (Figure 4, we found that most W atoms had 2-4 W, 2-4 N and 2-3 S nearest neighbors. The average coordination number thus is decreased from 6 in crystalline WS₂ to 2.7 in amorphous W_{0.33}S_{0.33}N_{0.34}, which suggests that a substantial amount of WS₃ building blocks, characteristic to WS₂, are present in the amorphous structure.

We note that in case of proper model structure size (good statistics) and equilibration process there should be no significant differences between the three theoretical structures and the experimental one. This is what we see in Figure 3, where we find that all the three simulated EXAFS curves agree excellently with the experimental EXAFS signal. The small differences in nearest neighbor distances between the theoretical structures can be seen in Table 2. We find that the difference in the W-W, W-S and W-N bond lengths vary up to 3%, 1% and 1%, respectively, which is insignificant. The nearest neighbor distances between S atoms vary between 3% and 7%, however the S-S bond distance, which we obtained in structure STR-C, agrees well with that in crystalline sulfur, the deviation being about 3%. The difference in the theoretical S-N distances and N-N bond lengths are below 2% and 5%, respectively. The theoretical coordination numbers (Table 3) vary only slightly from structure to structure for most atomic pairs. We find larger differences in the N-S and S-N coordination numbers, which can be due to the fact that S and N atoms in the theoretical amorphous structures do not form bonds, and are located at distances much longer than the corresponding S-N bond length.

Table 3. Theoretical and experimental average coordination numbers in amorphous $\text{W}_{0.33}\text{S}_{0.33}\text{N}_{0.34}$. The rows represent the central atom, and the columns the surrounding atoms in the first coordination sphere.

	Theoretical CN												Experimental		
	STR-A			STR-B			STR-C			Average CN			CN		
	W	S	N	W	S	N	W	S	N	W	S	N	W	S	N
W	3.2	2.8	2.6	3.4	2.7	2.6	3.0	2.7	2.7	3.2	2.7	2.6	–	2.7	2.7
S	2.8	5.6	6.4	2.7	5.8	5.1	2.7	5.5	4.9	2.7	5.6	5.5	–	–	–
N	2.5	6.2	0.2	2.6	5.0	0.2	2.6	4.7	0.2	2.6	5.3	0.2	–	–	–

The chemical bonds in the films were also studied by XPS. Due to the surface sensitivity of the method, much of the signal comes from the oxidized outer surface. However, removal of this material by sputter etching may cause artefacts, since WS_2 -based materials are prone to

damage by ion bombardment [53-55]. Therefore, the spectra were measured on as-deposited films, but also after gentle sputter cleaning. The spectra for the W4f region of as-deposited films (**Figure 6a**) are dominated by a contribution from WO_3 , with the $\text{W4f}_{7/2}$ line at a binding energy of 35.8 eV. However, another contribution at a lower binding energy is also clearly seen. For the pure W-S film, it is situated at about 32.5 eV, which is similar to the 32.8 eV reported by Wagner for WS_2 [56] and it is ascribed to a WS_x phase. For the W-S film, there is also a small contribution at a lower binding energy of about 31.4 eV, which is the binding energy reported in literature for metallic W [57, 58]. However, the presence of such a phase does not in itself explain the sulfur substoichiometry of the film, and we conclude that $x < 2$ for the WS_x phase. For the W-S-N films, the contribution ascribed to WS_x in the N-0 film changes with the addition of N. Its binding energy increases with increasing N content, from 32.5 eV for N-0 up to 33.1 eV for N-37. The peak also broadens significantly, from a full width at half maximum (FWHM) of 1.0 eV in the N-free film, to 1.5 eV at 37 at.% N. It is thus clear that a change in the chemical bonding of W atoms occurs with the addition of N, so that there is more charge transfer from them. This is in line with N being more electronegative than S, and the reported binding energy levels for WN compounds are around 33 eV [58, 59]. The observed binding energies could mean that each W atom is bonded to a mix of S and, increasingly within the series, N. The average conditions thus shifts from W-S bonds towards W-N bonds within the series, explaining the chemical shift, and a larger number of atomic configurations for W atoms, explaining the increasing width. Another possibility is that the observed peak is a combination of two separate contributions, one from a W-S phase and one a W-N phase, with the latter becoming more significant with increasing N content. However, there is nothing in the shape of the peak indicating that it is a combination of two distinct contributions.

The spectra from the S2p region are shown in Figure 6b. For the W-S film, the spectrum displays a distinct doublet, with the S2p_{3/2} line at a binding energy of 162.2 eV. This contribution can be ascribed to the WS_x phase, and has a binding energy similar to but slightly lower than the 162.6 eV reported by Wagner for WS₂ [56]. With the addition of nitrogen, the shape of the spectrum becomes a flat plateau rather than two separate peaks and its center of mass shifts towards a lower binding energy. It is clear that the chemical bonding environment of the S atoms changes with the addition of N, and becomes more varied than in the pure W-S film. The spectra from as-deposited films also contain a small contribution from oxidized sulfur around 169 eV, which originates from surface contamination.

Spectra measured for the N1s region (Figure 6c) show a large contribution from oxidized nitrogen species at a binding energy of about 402 eV. The main contribution from the film itself is found at 397.1-397.4 eV, with the lower binding energies for higher N contents. This contribution can thus be ascribed to N bonded to W [57]. Furthermore, there is another, smaller contribution at around 400 eV. This is similar to values reported for N-N bonds [60].

Measurements were also performed on the samples after sputter cleaning (not shown). It is well-known that sputter-etching of WS₂ (and MoS₂), leads to preferential sputtering of sulfur and the formation of a metallic phase [53-55, 61, 62], which was indeed observed, as the main contribution in the W4f region was found at 31.2 - 31.6 eV after sputter-etching. The spectra measured after etching thus show sputter-damaged material, but confirmed that the oxidized contributions in the W4f, S2p and N1s regions originated from contamination or oxidation of the outermost surface, which disappeared with sputter cleaning, while the N-N bonds are present in the bulk of the film.

To further study the N-N bonds, the film with 37 at.% N was also analyzed by NEXAFS. In a spectrum recorded around the photon energy range where a signal from molecular nitrogen would be expected (see e.g. reference [52]) a N_2 $N1s \rightarrow \pi^*$ resonance is clearly observed (Figure 6d). The results are compared to a spectrum recorded for gaseous N_2 , kindly supplied by the authors of reference [52]. The vibrations $v=0$ to 4 are clearly observed for this film. A least squares fit to the data gives a Lorentzian life-time broadening 0.6 eV larger than that obtained for the isolated nitrogen molecule. Similar effects have been observed for molecular nitrogen inside compound semiconductors [63] - a shorter lifetime suggests more pathways for the core hole to decay.

We proceed with the electronic properties of amorphous W-S-N. Total and partial densities of states (DOS) calculated for the structure STR-A of amorphous $W_{0.33}S_{0.33}N_{0.34}$ are shown in **Figure 7a**. Due to finite DOS at the Fermi level, we predict that amorphous $W_{0.33}S_{0.33}N_{0.34}$ has a metallic character, for optical properties as well as electron transport. States corresponding to metallic W-W bonds contribute to the Fermi level similarly to crystalline hexagonal WN (Figure 7b). Hexagonal WS_2 , however, is a semiconductor with a band gap of 2.1 eV [64] (Figure 7c). The resistivity in amorphous material is expected to be larger than in metallic crystalline WN, due to the presence of more scattering centers. In the case of metals, it is well-known that amorphous alloys have significantly higher resistivities than their crystalline counterparts [65]. Amorphous metal alloys generally have resistivities in the 100-200 $\mu\Omega \cdot \text{cm}$ range [65], but higher values up to around 600 $\mu\Omega \cdot \text{cm}$ have been reported for alloys containing metalloid elements [66]. The sheet resistance was measured for the W-S-N films at room temperature (**Table S3**). As expected from theory, for the N-31 film the measured resistivity 432 $\mu\Omega \cdot \text{cm}$, is in between values for WN (9 $\mu\Omega \cdot \text{cm}$ [67]) and WS_2 (10^5 $\mu\Omega \cdot \text{cm}$ [64]).

The analysis of orbital projected DOS shows that mainly W 5d orbitals, S 3p orbitals and N 2p orbitals hybridize at energies of -8 eV to 0 eV. This corresponds to the formation of strong covalent W-N and W-S bonds, similar to those of crystalline WN and WS₂ (Figure 7b and 6c). The W-N bonds are in general stronger than the W-S bonds, and, accordingly, they appear at overall lower energies with some overlap between the corresponding states. Despite the chemical preferences, the number of W-S bonds is slightly larger than that of the W-N bonds in all the three theoretical structures, since fewer N atoms are available to form W-N bonds, as some are present as N₂ molecules. The number of W-N and W-S bonds is almost twice as large as the number of metallic W-W bonds, i.e. W mainly forms covalent bonds with N or S. Bader analysis shows that W atoms have on average 4.41 valence electrons, meaning that almost 30% of their valence electrons are transferred to N and S atoms. In crystalline hexagonal WN and WS₂, W atoms have 4.71 and 4.97 valence electrons, i.e. the electron transfer from W atoms in amorphous W-S-N is larger compared to the crystalline systems discussed here. The average number of valence electrons for S atoms is increased to 6.64 in W-S-N compared to 6.52 in WS₂, indicating that S atoms gain more electrons in amorphous W-S-N. Nitrogen atoms in W-S-N have fewer valence electrons in the amorphous phase (on average 6.16) than in crystalline WN (6.29). In amorphous W-S-N, the N atoms which do not form N₂ molecules gain almost twice as many electrons as S atoms. This shows that both W-N and W-S covalent bonds are polarized, i.e. they have some ionic character.

In the lower part of Figure 7a we show the partial DOS for nitrogen atoms which in the low-energy region are clearly separated into contributions coming from nitrogen atoms of N₂ molecules, and those which are not bonded as N₂ molecules. In Figure 7a, N 2s and 2p orbitals of quasi-free N₂ molecules appear at very low energies (-23 eV), and correspond to σ_{2s} molecular orbital, similar to that in free N₂ molecules (**Figure S5**). There are two N₂

molecules in a smaller cage that are bonded to W atoms, and this is reflected in hybridization of N₂ N 2p states and W 5d states in the energy range from -8 eV to -5 eV. These W-N pairs have larger bond lengths (2.047 - 2.288 Å) compared to the average W-N bond length found for this amorphous material (1.941 Å).

Next we calculated the charge density distribution for STR-A. As it can be seen from Figures 6d and 6e, N atoms of N₂ molecules interact with S atoms of the cages, as well as with N atoms of other N₂ molecules. Though these interactions are significantly weaker than the strong covalent N-N bonds in N₂, they may keep N₂ molecules in the cages. We further calculated the number of valence electrons of N₂ molecules (10.02-10.25) and found extra charge on each molecule compared to the isolated N₂ (10.00), which implies a charge transfer from atoms of the cages to the N atoms in N₂.

We now discuss the implication of the structural information, discussed above, for the tribological properties. The low-friction properties of WS₂ and other TMDs are an effect of the weak bonding between the layers, which are only van der Waals interactions.[68, 69] Theoretically, TMD layers can slide against each other almost without friction [70]. However, even though the actual sliding occurs in a tribofilm of crystalline and aligned WS₂, optimum performance is not necessarily reached by depositing a crystalline and horizontally aligned film. In fact, a smooth and mechanically stable surface is desirable to support the tribofilm, and the addition of a third element to WS₂ is known to increase the density and hardness [2, 3, 10]. Such nanocomposite, or amorphous, W-S-X coatings, have been shown to be successful low-friction coatings due to the formation of WS₂ tribofilms. Among these, the amorphous W-S-N coatings have displayed exceptionally good lubricating properties in dry conditions [10, 16]. There is thus no reason to assume that the presence of crystalline or

nano-crystalline WS_2 in the as-deposited film is a prerequisite for formation of a well-functioning WS_2 tribofilm. On the other hand, there are several reports on the formation of WS_2 tribofilms with W coming from one source and S from another, such as S from a TiCS thin film and W from a tungsten counter-surface [26], or W from a W-doped DLC thin film and S from oil additives in a lubricated contact [71]. The key to successful tribofilm formation is thus not the initial presence of WS_2 , but the availability of its constituents. The tribofilm in a sliding contact is dynamic rather than static, as the location of the contact spots vary with time and material may be transferred, low and stable friction requires continuous formation of the solid lubricant. Thus WS_2 , or its constituents, must be fed to the outermost surface from the film material by atomic-level rearrangements. We suggest that this is more easily obtained by diffusion of individual atoms, than by movement and alignment of larger WS_2 platelets. As demonstrated in this work, amorphous W-S-N is an intricate elemental mixture, with good supply of W and S atoms to diffuse to wherever the contact spots are found in a given point in time, allowing for easy WS_2 formation at the surface. This is in line with the reports from Gustavsson et al. who showed that after sliding, the outermost surface on a W-S-N coating with 34 at.% N consisted of well-aligned WS_2 [16]. It is highly important that the added element does not hinder the formation of a lubricating tribofilm by, for example, remaining in the contact or forming other compounds which give high friction or wear. Nitrogen is an excellent addition element in this respect, considering that its oxides are gaseous and easily leave the contact. Furthermore, as has been shown in this work by theoretical as well as experimental means, part of the nitrogen in amorphous W-S-N is present as captured N_2 molecules, which may easily leave the material when exposed. Nitrogen is also found to be engaged in W-N bonds, but the material is amorphous and does not contain hard and abrasive nitride grains. We thus suggest that the excellent tribological properties of amorphous W-S-N can be derived from the dense and stable surface, the good

availability of W and S atoms to form WS₂ in the contact, the absence of high-friction or high-wear secondary phases, and the easy removal of excess nitrogen.

4. Conclusions

Thin films of the ultra-low friction material W-S-N were deposited by magnetron sputtering from a WS₂ target and N₂ gas. The nitrogen content was varied within the series, from 0 to 37 at.%. All W-S-N films were found to be X-ray amorphous, while the W-S film (0 at.% N) contained nanocrystalline tungsten sulfide, WS_x. The chemical bonding and local atomic structure in the films were further analyzed by XPS, NEXAFS and EXAFS. For a selected composition, W_{0.33}S_{0.33}N_{0.34}, amorphous structures were generated by *ab initio* molecular dynamics for a detailed investigation of the structural and electronic properties of the material. Simulated EXAFS oscillations were found to be in excellent agreement with the experimental EXAFS signal, confirming that our molecular dynamics simulations indeed provide an accurate representation of the material.

X-ray photoelectron spectra showed that W atoms were engaged in W-S and W-N bonds, with the latter increasing throughout the sample series, with increasing N content in the films. The electronic structure calculations for the 31 at.% N composition also showed that W atoms mainly formed strong covalent W-S and W-N bonds, the latter being relatively stronger. Both of these bonds have some ionic character, indicated by the charge transfer from W atoms to N and S atoms, with the N atoms gaining almost twice as much charge as S atoms. Due to the metallic W-W bonds and their contribution to the states at the Fermi level, amorphous W_{0.33}S_{0.33}N_{0.34} was predicted, and also experimentally confirmed, to exhibit metallic character.

The most striking feature of amorphous W-S-N is that 21-24% of the N atoms form quasi-free N₂ molecules, which are located in cages in the amorphous matrix and weakly interact with their local environment. The presence of N₂ molecules was predicted from theoretical simulations and confirmed experimentally by NEXAFS and XPS measurements. We suggest that ultra-low friction in W-S-N is due to a dense and stable surface, easy access to W and S atoms for continuous tribofilm formation, absence of high-friction and high-wear secondary phases, and release of nitrogen in molecular form. The mechanisms for excellent tribofilm formation discussed here are likely to be found in other materials as well, potentially allowing for formation of new groups of layered materials.

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Figure 1. Grazing incidence X-ray diffractograms for W-S-N films. The background has been removed, and the diffractograms are normalized, and offset for clarity.

Figure 2. Scanning electron micrographs of fractured cross-sections of samples with 0 (a), 22 (b) and 37 (c) at.% N. The W-S film is porous, while the W-S-N films have a dense and featureless morphology.

Figure 3. Comparative k-weighted $\chi(k)$ oscillations of the experimental EXAFS for the N-31 film and simulated EXAFS from the three different theoretical structures for $W_{0.33}S_{0.33}N_{0.34}$ as well as their weighted average.

Figure 4. Local environments calculated for three different structures of amorphous $W_{0.33}S_{0.33}N_{0.34}$ obtained by molecular dynamics simulations. n_W denotes the number of W atoms surrounded by the number n_{NN} of nearest neighbors.

Figure 5. The cross section (a) and side views (b) of a large cage, containing five N_2 molecules in the theoretical structure “STR-A” of amorphous $W_{0.33}S_{0.33}N_{0.34}$. W, S and N atoms are shown in grey, yellow and cyan, respectively.

Figure 6. XPS spectra for all films, and NEXAFS spectrum for the N-37 film. The N content (in at.%) is indicated for each spectrum.

- XPS W4f spectra, with the film contribution broadening and shifting towards higher E_b with increasing N content.
- XPS S2p spectra, with a broadening of the doublet peaks with increasing N content.
- XPS N1s spectra, displaying two contributions from the bulk of the film; N-N and N-W bonds.
- NEXAFS spectra for a N $1s \rightarrow \pi^*$ transition in N_2 . A spectrum measured for the N-37 film is compared to a reference spectrum of gaseous N_2 , kindly provided by the authors of [52]. The spectra have been normalized and offset for comparison of the fine structure.

Figure 7. (a) Partial density of states calculated for theoretical structure “STR-A” of amorphous $W_{0.33}S_{0.33}N_{0.34}$. In the lower part of (a) we show contributions to the DOS from N atoms of N_2 molecules (green dashed curve) and from those, which are not bonded in N_2 (dotted blue curve). The Fermi level, E_F , is shown by vertical dashed line. (b, c) Total and partial DOS calculated for hexagonal WN and WS₂. Charge density distribution between two N_2 molecules (d) and between a N_2 molecule and a S atom of the surrounding cage (e). The maximum isovalues for these isosurfaces are $0.007 \text{ \AA}^{-3}$ (d) and $0.009 \text{ \AA}^{-3}$ (e).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7