Amorphous W–S–N thin films: The atomic structure behind ultra-low friction

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Abstract—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 WS_2 tribofilm. However, the atomic-level structure and bonding arrangements in amorphous W–S–N, which give such optimum conditions for WS_2 formation and ultra-low friction, are not known. In this study, amorphous thin films with up to 37 at.% 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. N_2, which is experimentally confirmed by near edge X-ray absorption fine structure and X-ray photoelectron spectroscopy analysis. Such N_2 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 WS_2 in the contact region, and with the possibility of swift removal of excess nitrogen present as N_2 molecules.
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1. Introduction

In many applications where surfaces slide against each other, low friction and low wear of the surfaces are 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 even 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 WS_2, are intrinsic solid lubricants and can provide low friction, especially under dry conditions. To make full use of the possibility of WS_2 superlubricity, one would require a stable surface with good load-bearing capacity and wear resistance, on which a tribofilm of

aligned WS_2 crystallites is formed. To obtain this, WS_2 and MoS_2 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 WS_2 or MoS_2 can be formed during tribological contact to provide low friction, in a process where WS_2 or MoS_2 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, the formation of high-friction metal oxides may hinder the formation and decrease the stability of the WS_2 tribofilm. For optimizing the benefits of WS_2 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].

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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, and this excludes a microscopical understanding. It is clear that with such a high N content, and lack of WS_2 crystallites, the chemical bonding and internal structure of the material must be widely different from that of WS_2. 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 N_2 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 the formation of well-functioning WS_2 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 using 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 WS_2 target and N_2 gas. The substrates were single-crystal Si (1 0 0) wafers, which were cleaned by plasma etching in the deposition chamber. A titanium adhesion layer with a thickness of ∼100 nm was then deposited. During deposition of the W–S–N films, the total gas flow (of Ar and N_2) and the total pressure were kept constant at 100 sccm and 5 m Torr, respectively. The composition of the deposited coating was varied by changing the flow of N_2 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 min, 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 $(NH_4)_2WS_4$ 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 → π^* 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 ($\rho = 7$ 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 $6 \times 6 \times 6$ 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 N_2 and thus only from the WS_2 target, had a S/W ratio close to 1. Substoichiometry with respect to sulfur is often observed in films sputtered from WS_2 targets, and the sulfide could therefore be referred to as WS_x rather than WS_2 [37].

The crystallographic structure of the films was analyzed by XRD (Fig. 1). For the pure W–S film (N-0), broad peaks can be observed around the positions of reflections from WS_2, 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 WS_2, and the related MoS_2, on addition of a wide range of elements, such