Applied Surface Science 305 (2014) 203–213

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Understanding the effects of sputter damage in W–S thin films by HAXPES

Jill Sundberg[a,*], Rebecka Lindblad[b], Mihaela Gorgoi[c], Håkan Rensmo[b], Ulf Jansson[a], Andreas Lindblad[a,b]

[a] *Department of Chemistry - Ångström Laboratory, Uppsala University, Box 538, 751 21 Uppsala, Sweden*
[b] *Department of Physics and Astronomy, Uppsala University, Box 516, 751 20 Uppsala, Sweden*
[c] *Helmholtz Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Str. 15, Berlin 12489, Germany*

ARTICLE INFO

Article history:
Received 20 November 2013
Received in revised form 23 January 2014
Accepted 5 March 2014
Available online 15 March 2014

Keywords:
HIKE-XPS
HAXPES
XPS
WS_2
Sputtering
Preferential sputtering

ABSTRACT

WS_2 is an excellent solid lubricant in dry conditions, and can be applied as thin films. The analysis of WS_2 and WS_2-based films by x-ray photoelectron spectroscopy (XPS) can be challenging, due to contamination and oxidized material on the surface. The investigations have traditionally therefore included sputter etching by ion bombardment, which however leads to changes of the remaining material. In this study, hard x-ray photoelectron spectroscopy (HAXPES) has been used to study W–S films deposited by magnetron sputtering. High-resolution reference measurements for crystalline WS_2 and metallic W are also presented. The W–S films were analyzed before and after sputter cleaning by Ar^+ ion bombardment, using photon energies of 3 and 6 keV. The as-deposited films were found to consist mainly of a WS_x phase, similar to WS_2 but with a broader range of chemical states. It is shown that ion bombardment of the surface not only removes the outermost oxidized material, but also leads to preferential sputtering of sulfur and the formation of metallic tungsten. The results are of strong interest for the analysis of WS_2-based materials, as they demonstrate that spectra from sputter-cleaned films include effects of sputter damage, and may not be representative of the original sample.

Introduction

Transition metal dichalcogenides (TMDs) have a general formula of MeX_2, with the metal Me usually being Mo or W, and the chalcogen X being S or Se. They have a layered structure, where the sheets of metal atoms are sandwiched between sheets of chalcogen atoms. Each metal atom is coordinated by a trigonal prism of chalcogen atoms, and the chemical bonds within each sandwich unit are covalent. The bonds between chalcogen layers, i.e. between the sandwich units, consist of van der Waals interactions and are considerably weaker [1]. The highly anisotropic structure of the materials makes them interesting for photovoltaic as well as tribological applications. In the latter case, the weak bonding between sandwiches makes the material easily sheared, which leads to low friction and motivates the use of TMDs as solid lubricants [2]. Thin films of WS_2 can be deposited by magnetron sputtering, and used for example in aerospace applications. Pure WS_2 is very soft, and other elements such as C [3–6], N [5,6], Cr [7], or Ti [8,9], can be added to improve the mechanical properties.

While the bulk material is relatively stable, the plane edges contain dangling bonds, and they and other defect sites in WS_2 and other TMDs are easily oxidized in ambient conditions. Thin films of these materials often contain a relatively large proportion of edge sites and defects, leading to the outermost surface consisting mainly of metal oxide along with adsorbed contaminants. XPS is often used to analyze the chemical bonding and phase content of TMD-based films. The surface sensitivity of the technique makes sputter cleaning necessary in order to study the material beneath the contaminated and oxidized surface. However, the bombardment of ions during sputter etching induces changes in the material, such as preferential sputtering of sulfur, which is much lighter than W (or Mo) [10–13]. Effects from differences in weight also occurs during sputter deposition of, e.g., WS_2 and MoS_2, as the target surface composition changes during deposition, and as larger proportion of the metal atoms than of the sulfur atoms reach and stay on the substrate [14]. The deposited films are thus usually substoichiometric in sulfur, even though the original target composition is stoichiometric. The sulfide phase in sputter deposited films should

---

* Corresponding author. Tel.: +46 184713775.
E-mail address: jill.sundberg@kemi.uu.se (J. Sundberg).

http://dx.doi.org/10.1016/j.apsusc.2014.03.038
0169-4332/

therefore more correctly be referred to as WS_x, where likely $x < 2$ [15].

Studies on bulk crystals of MoS_2 or WS_2 have shown that ion bombardment leads to a decrease in sulfur content on the surface, and the appearance of a reduced, metallic species [10–13]. The presence of metallic species has been observed also in XPS studies of sputter-deposited, polycrystalline films as well as for nanocomposites containing TMD grains [16], but has not previously been systematically studied for thin films, even though it is well-known and studied for crystalline bulk materials. The change in composition and the chemical shift of the metallic component may cause significant challenges when interpreting core level spectra, especially when several phases may be present. To evaluate spectra by curve fitting is thus necessary, but complicated, especially in the case of complex regions such as W4f, where each chemical state of W gives rise to three close-lying lines ($W4f_{7/2}$, $W4f_{5/2}$, and $W5p_{3/2}$).

XPS is often performed using Mg Kα or Al Kα radiation, which have energies of 1253.6 and 1486.7 eV, respectively [17]. The use of synchrotron radiation offers the possibility of tuning the energy, as well as giving access to higher energies up to hard x–rays. XPS using x-rays in the range of 2–12 keV is often referred to as hard x-ray photoelectron spectroscopy (HAXPES) or high kinetic energy XPS (HIKE-XPS). Higher kinetic energies of the photoelectrons give a larger probing depth in the range of 10–30 nm, well above the reach of “classic” photoemission, thus making possible the investigation of the true bulk of materials below the surface in a non-destructive and less surface-sensitive manner. For example, it is possible to measure beneath the oxidized surface of a thin film. An additional advantage of HAXPES is that core levels at binding energies not reachable with Mg or Al anode sources can be studied, for example W3d and S1s. The interpretation of spectral features from these core levels is often more straightforward – for example, the energy split between the $W3d_{5/2}$ and $W3d_{3/2}$ in metallic tungsten is 63 eV, while the split between $W4f_{7/2}$ and $W4f_{5/2}$ is only 2 eV. Further details can be found in references [18] and [19].

The aim of the current work is to use HAXPES to study as-deposited and sputter-etched W–S films deposited by magnetron sputtering, in order to gain understanding of the unaffected film material as well as the effects of sputter cleaning. The results are discussed in conjunction with reference measurements performed on a WS_2 crystal and on pure, metallic tungsten.

Experimental

The W–S thin films were deposited by pulsed, non-reactive DC magnetron sputtering from a sintered WS_2 target (99.98%). A power of 450 W was applied to the target, which had a diameter of 4″. The films were deposited on single-crystalline (1 0 0) silicon wafers, which were cleaned prior to deposition by argon etching in the deposition chamber for 20 min at a bias of −600 V. The discharge pressure during deposition was 4 mTorr and the substrates were rotated and kept at floating potential. The deposition time was 105 min. One of the films was deposited during heating of the substrate to approximately 300 °C, while the other was deposited at room temperature. The heated and non-heated samples are denoted by W–S HT (high temperature) and W–S RT (room temperature), respectively. The WS_2 reference was a commercially available bulk single crystal, and the W reference was pure W foil, The W foil reference sample was sputter etched with Ar^+ ions to remove oxidized material on the outermost surface.

The films were imaged by scanning electron microscopy (SEM) in top-view mode and as fractured cross-sections using a Zeiss 1550 instrument with a field emission gun as the electron source. The structure of the films was studied by x-ray diffraction (XRD) on Siemens D5000 diffractometers with Cu Kα radiation. The measurements were performed at grazing incidence with an incidence angle of 1° in parallel beam geometry, and in θ–2θ mode with focusing geometry. HAXPES measurements were performed at the BESSY II Synchrotron at Helmholtz–Zentrum Berlin using the HIKE end-station [18] at beamline KMC-1 [20]. At this beamline, x-rays are generated with a bending magnet and energies are selected with a double crystal monochromator (DCM). In the current study the Si(1 1 1) and Si(4 2 2) crystal pairs were used to select the photon energies of 3000 and 6000 eV, respectively. In the case of reference samples, the measurements were performed using the Si(1 1 1) crystal pair and photon energies of 3000 and 6015 eV, where the latter was measured with the third order light of 2005 eV provided by the Si(1 1 1) crystal pair. The HIKE station is equipped with a Scienta R4000 spectrometer optimized for high kinetic energies up to 10 keV. The measurements were performed close to normal emission of the photoelectrons. The total energy resolution of the experiment was 0.5 eV for 3 keV excitation energy and 0.3 eV for 6 keV. All binding energies are referenced to measurements on a gold foil in electric contact with the sample. The Au $4f_{7/2}$ core level of gold was set to a binding energy of 84.0 eV [21]. To study the effect of surface cleaning and sputter damage, the samples were sputtered in the HAXPES analysis chamber with Ar^+ ions (where the emission current in the electron gun was 10 mA, the acceleration voltage 1 kV and the Ar pressure 2×10^{-7} mbar, giving a sample current of around 2 μA). The base pressure in the analysis chamber was in the low 10^{-8} mbar range. The measured spectra were fitted using Casa XPS software. The baseline was determined using a Shirley background correction function and the curves used for fitting were Voigt profiles. Background intensities are used for normalization of the spectra in order to remove intensity variations caused by variations of the synchrotron ring current.

Results and discussion

Sample morphology and structure

As seen by the SEM images in Fig. 1a and b, the W–S HT film has a columnar morphology that is typical for sputter deposited MoS_2 and WS_2 films [15,22–24]. The film has a thickness of 2.2 μm and consists of thin platelets growing perpendicular to the surface, making the film highly porous. To the bare eye, the film has a black and matte appearance. It can also be noted that it has a very low adhesion to the substrate, which can be related to the standing platelets. The W–S RT film (Fig. 1c and d) instead has a dense and featureless morphology, and a thickness of 0.9 μm. The film looks grey, and has a metallic luster when observed with the naked eye.

The x-ray diffractograms for both samples, in grazing incidence (GI) and in θ–2θ mode, can be seen in Fig. 2. For the W–S HT sample, the GI diffractogram features a diffraction pattern typical for sputtered WS_2 [7,23,25], with two asymmetric peaks as its most prominent features. For the RT sample, only broad peaks are observed in similar positions as the reflections for the W–S HT film. The W–S RT sample is thus nanocrystalline, which is consistent with the difference in morphology observed by SEM, and can be explained by the lower surface mobility of atoms during deposition. The microstructure of the W–S HT sample, observed in SEM, as well as the diffraction pattern is typical for WS_2 of the so-called type I, where the basal planes are perpendicular to the substrate surface, which is usually observed for sputtered W–S films [26–28]. Films may also grow with the basal planes parallel to the surface, in which case they are referred to as type II. The asymmetry, with a tail towards higher angles, is attributed to turbostratic stacking of the basal planes. The structure of WS_2 is hexagonal and layered, and can be said to consist of base planes perpendicular to the *c* axis. Turbostratic stacking can be described as disorder along the *c*