

Nanoplatelets made from MoS_2 and WS_2

N. Bertram ^a, J. Cordes ^a, Y.D. Kim ^a, G. Ganteför ^{a,*}, S. Gemming ^b, G. Seifert ^b

^a *Fachbereich Physik, Universität Konstanz, Fakultät für Physik, D-78457 Konstanz, Germany*

^b *Institut für Physikalische Chemie und Elektrochemie, Technische Universität Dresden, D-01062 Dresden, Germany*

Abstract

Free clusters of the layered semiconductor materials of type MS_2 ($M = \text{Mo}, \text{W}$) are studied using mass and photoelectron spectroscopy and compared to theoretical predictions. In contrast to carbon fullerenes, these clusters prefer planar platelet structures. The dangling bonds at the edges are stabilized by excess S atoms. For W_nS_m^- we find that platelet structures dominate for clusters larger than $\text{W}_{10}\text{S}_{30}$, the most stable species are $\text{W}_{15}\text{S}_{42}$ and $\text{W}_{21}\text{S}_{56}$. These platelets have a metallic character and are chemically inert making them interesting building blocks for future nanoelectronics.

Carbon clusters and nanoparticles form a large variety of different structures such as fullerenes and nanotubes. These systems derive from the layered structure of bulk graphite avoiding dangling bonds at the edges by the formation of π -bonds, resulting in a hollow sphere structure. Similar structures might exist for other materials forming layered structures like the metal-chalcogenides MS_2 ($M = \text{Mo}, \text{W}$). Indeed, for nanoparticles of these materials nanotubes and onion-like structures have been observed [1–9]. However, until now the structures of MS_2 nanoclusters in the size regime of fullerenes are unknown. The observation of onion-like MS_2 nanoparticles might be taken as an indication for the existence of MS_2 fullerene structures. However, there are two aspects opposing this assumption:

- (i) The energy required to bend a single MS_2 sheet is larger than the corresponding bending energy in graphite [10,11]. The MS_2 sheets consist of a triple layer with the metal atoms in between two S layers. Therefore, larger structures might be similar to carbon, but for nanoclusters differences are likely to appear.

- (ii) The edges of planar fragments of a MS_2 sheet can be stabilized by additional S atoms. Therefore, the formation of S-stabilized platelets might be preferred over fullerene formation [11].

Such platelet structures might be of use for future nanoelectronic devices, because they are chemically rather inert and stable even at ambient conditions. In addition, they might exhibit a size-dependent HOMO–LUMO gap like other nanoparticles consisting of materials which are semiconducting in the bulk. Triangular MoS_2 nanoplatelets on an Au substrate have been studied by scanning tunnelling microscopy [12–14]. However, since the method of generation from 2-dimensional metal islands exposed to H_2S strongly prefers the formation of 2-dimensional structures, the most stable structure of free MS_2 nanoclusters is still unclear. It could be platelets or fullerenes or other structures.

We therefore studied clusters of MS_2 theoretically and experimentally. Triangular metallic platelets are found to be the favored structure in the size regime from 10 to 100 MS_2 units with a considerable excess of S atoms stabilizing the edges. Below about 10 MS_2 units 3-D compact cluster structures are preferred. Larger clusters have the double and triple mass of these magic platelets indicating the

* Corresponding author. Fax: +49 7531 885133.

E-mail address: gerd.gantefoer@uni-konstanz.de (G. Ganteför).

growth of sandwich-like nanocrystals already resembling the bulk crystal structure. In agreement with our calculations we find no indication for fullerene structures but for nanoplatelets. The difference between carbon and MS_2 is the saturation of the dangling bonds of the MS_2 nanoplatelets by additional S atoms. For carbon dangling bonds can only be avoided assuming a fullerene structure.

Experimentally we produced free MS_2 nanoparticles by two methods based on the pulsed arc cluster ion source [15,16]. First, bulk MS_2 is evaporated by a pulsed electric arc and charged and neutral M_nS_m clusters grow within an inert seeding gas (Helium). A mass spectrum of negatively charged W_nS_m^- clusters is displayed in Fig. 1 (top trace). For $n > 4$ only one dominant feature (A) is observed consisting of four peaks with a spacing corresponding to the mass of WS_3 . The first peak can be assigned to $\text{W}_{15}\text{S}_{42}$ plus two additional S atoms.

To allow for a controlled change of the metal-sulphur ratio a second method for cluster generation is used. Bulk metal (Mo, W) is vaporized and bare metal clusters are grown. Then a variable amount of H_2S is introduced into the source resulting in an unstructured mass spectrum of $\text{M}_n\text{S}_m\text{H}_x$ clusters. Within a weak electric discharge these clusters embedded in the seeding gas are heated up again and cooled down slowly. This annealing process [15] yields mass spectra with pronounced maxima (Fig. 1, middle and

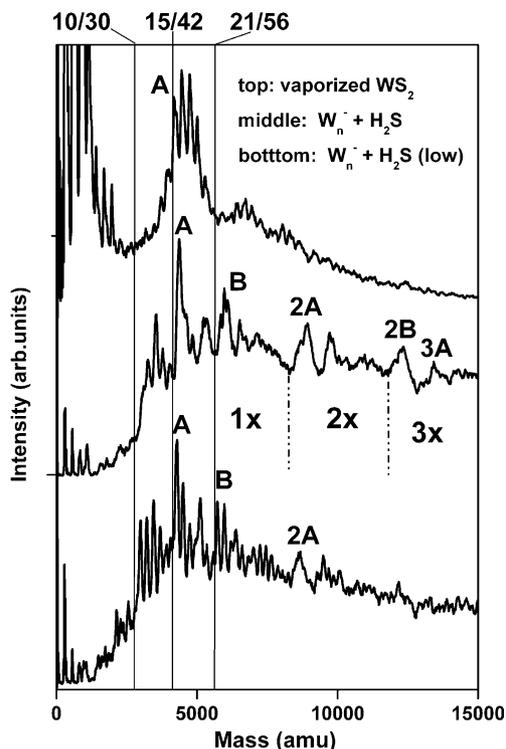


Fig. 1. Mass spectra of W_nS_m^- cluster anions generated by vaporization of WS_2 powder (top trace) and reaction of W_n^- clusters with H_2S and subsequent annealing (medium and bottom trace). With lower H_2S concentration all features shift to smaller mass (bottom trace). The vertical lines mark the masses of the platelets $\text{W}_{10}\text{S}_{30}$, $\text{W}_{15}\text{S}_{42}$, and $\text{W}_{21}\text{S}_{56}$. For a discussion of the marked features see text.

bottom traces). For small M_nS_m cluster anions with $n < 5$ generated using this method we could find no hints of H contamination [17]. However, for the larger clusters discussed here we cannot exclude this.

The second method yields structured mass spectra dominated again by one feature (Fig. 1, middle trace, marked A) similar to the one observed for WS_2 vaporization. The position of peak A depends strongly on the amount of H_2S introduced. At low H_2S concentration (lower trace) it almost coincides with the first peak of feature A in the top trace. The spacing between neighboring peaks corresponds to the mass of WS_2 and is different from the one in the top trace (WS_3). This can be explained by the different growth paths of the two different methods for generation used here.

For a better understanding of the experimental results we performed density-functional based calculations on various possible structures of such clusters. The calculations have been performed only for Mo_nS_m clusters, whereas most experiments have been done on the W_nS_m system because of the large difference in mass between S and W giving simple mass spectra. In a recent publication we demonstrated that indeed the systems W_nS_m and Mo_nS_m are very similar [17], i.e., we expect that the results of our calculations can also be applied to a large extent to the W_nS_m clusters.

Preliminary calculations on small fullerene-like structures of Mo_nS_m clusters did not yield stable structures and will not be discussed here, but calculations on 2-dimensional structures give promising results. Starting from MoS_6 with the trigonal prismatic coordination of Mo, as it appears in bulk MoS_2 , subsequent series of triangular platelet structures were constructed and optimized, using a density-functional based tight-binding (DFTB) method [10,18]. This method has already been used successfully for MoS_2 nanotubes [10,11]. With the integer number k as the number of Mo atoms along a side of the triangle the following relations for Mo_nS_m have been obtained:

$$n = k(k+1)/2; \quad m = 2n + 2(k+l).$$

As an example Fig. 2 displays the geometric structure of $\text{Mo}_{15}\text{S}_{42}$. Each Mo atom is coordinated with six S atoms. The edges are stabilized by pairs of bridge-bonded S atoms, while at each corner two single-coordinated S atoms appear. The total number of S atoms (42 in Fig. 2) can be varied with no considerable loss of relative stability. In a recent study of small Mo_nS_m and W_nS_m clusters we found that apart from single S atoms also polysulfide-like S_3 chains can bind to the metal atoms [19]. With such a mechanism many more S atoms can be bound to the platelet.

The smallest platelets following the structural motif displayed in Fig. 2 are Mo_3S_{12} and Mo_6S_{20} . For such small platelets all Mo atoms can be considered edge-atoms. Starting from $\text{Mo}_{10}\text{S}_{30}$ bulk-like coordinated metal atoms appear in the centre of the platelets. In contrast to the expectation based on the finite size behavior of other semi-

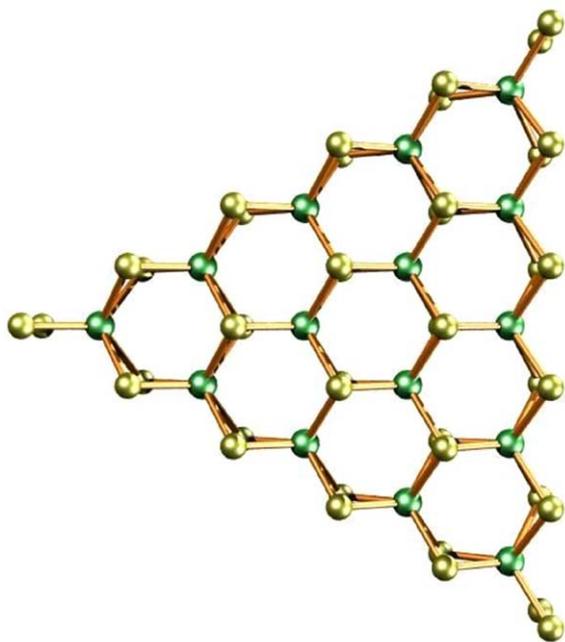


Fig. 2. Calculated structure of the neutral $W_{15}S_{42}$ platelet.

conductor clusters, our calculations indicate that the larger platelets ($k > 5$) have a vanishing HOMO–LUMO gap and can be considered metal-like.

With these theoretical findings now several features observed in the mass spectra displayed in Fig. 1 can be understood. Peak A dominating all three spectra is assigned to $W_{15}S_{42}$. The mass is slightly higher, which can be explained by the tendency to add more S atoms by formation of S_3 bridges. All spectra show an increase of intensity at the mass corresponding to $W_{10}S_{30}$. Smaller platelets have not been observed although we intensely searched for them. A possible explanation is that small platelets are not stable if there are edge-sites for the W atoms only. This is the case for W_3S_{12} and W_6S_{18} . According to our photoelectron spectra, these clusters have different but yet unknown structure.

The next triangular platelet beyond $W_{15}S_{42}$ is $W_{21}S_{56}$. Indeed, such a peak (B) at a position corresponding to a slightly larger mass is observed in the spectra generated using method II. Again its position depends sensitively on the S excess and at very low H_2S concentration it shifts to a mass almost coinciding with the one of $W_{21}S_{56}$ (lower trace).

The maxima at higher masses do not fit to any progression of larger triangular platelets. However, these peaks can be understood in terms of a repetition of the first part of the mass spectrum (e.g., the peaks labelled 2A, 3A and 2B). We tentatively assign these features to bulk-like sandwich structures consisting of two or three Van der Waals bound platelets resembling bulk microcrystals.

Although we consider the mass spectra displayed in Fig. 1 a support of the theoretical predictions, an assignment to exact structures based on the mass spectra alone is rather uncertain. Therefore, we studied the cluster anions

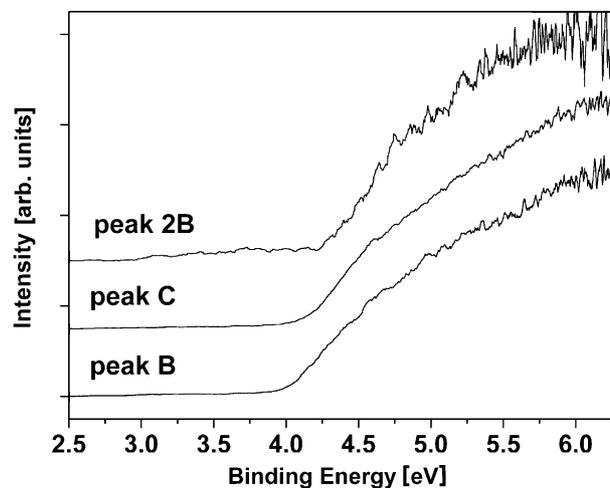


Fig. 3. Photoelectron spectra of the cluster anions corresponding to the peaks marked B, C and 2B in the Fig. 1. Each spectrum is a sum of single spectra taken at different source conditions. Independent of these conditions, a pronounced onset of the electron signal around 4 eV is observed. Similar spectra have been recorded for all features marked in Fig. 1. The spectra show no detectable HOMO–LUMO gap, i.e. the gaps are smaller than about 0.3 eV in good agreement with calculations.

corresponding to the main features shown in the lower trace of Fig. 1 by means of photoelectron spectroscopy. All photoelectron spectra of the various peaks are similar. As an example, Fig. 3 displays photoelectron spectra of the mass peaks labelled B, C and 2B. The signal rises at 4 ± 0.2 eV binding energy with no significant size dependence, and a monotonous increase up to the maximum binding energy observable with our set up (6.4 eV) is observed. This is in agreement with the theoretical predictions for $k > 5$. For the platelets $W_{15}S_{42}$, $W_{21}S_{56}$, $W_{28}S_{72}$, $W_{36}S_{90}$ and $W_{45}S_{110}$ vertical detachment energies of 4.3, 4.4, 4.2, 4.2 and 4.2 eV, respectively, have been calculated. The density of states close to the highest occupied molecular orbital is dominated by a metal d-band. For such clusters, it is known that the photoelectron spectra show a broad and unstructured maximum with a weak size dependence [20]. Because of the high electron affinity of the $W_nS_m^-$ clusters, we cannot observe the maximum but the increase on the low binding energy side only.

In conclusion, we present theoretical and experimental data which strongly support the idea of a triangular platelet structure for clusters of the layered semiconductor materials WS_2 and MoS_2 . We were able to investigate the electronic structure of free size-selected platelet nanoclusters for the first time. The dangling bonds at the edges of the nanoplatelets are passivated by additional S atoms. The nanoplatelets $W_{15}S_{42}$ and $W_{21}S_{56}$ have been identified as outstanding magic clusters. Both experimental and theoretical data indicate a nearly ‘metallic-like’ character of the platelets in contrast to the bulk electronic structures with a considerably larger band gap [21]. This result fits the experimental observation that MoS platelet clusters exhibit several metallic states [22]. However, the analysis of the electronic structure shows that these metallic-like

states are not localized at the edges of the platelets, as discussed by Bollinger et al. [22]. The states around the Fermi-energy (HOMO) are rather W-d states delocalized over the whole cluster. The metallic-like behavior (i.e., zero gap) is caused by the excess of sulfur at the edges of the W_mS_m platelets, compared to the ideal $\frac{m}{n} = 2$ ratio in the bulk WS_2 . With increasing cluster size and increasing k this ratio ($\frac{m}{n} = 2 + \frac{4}{k}$) converges asymptotically to the bulk value of 2. Larger clusters seem to consist of stacks of the magic triangular platelets already indicating a growth pattern similar to the bulk. This new class of stable and unreactive nanoclusters might be well suited for future nanoelectronics, e.g., as a part of a Nano-Schottky contact.

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