Potassium adsorption on MoS$_2$(0001) at low temperature

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Abstract. In this work we report on the properties of potassium on MoS$_2$(0001) at 100 K as deduced from LEED, AES, EELS and TDS measurements. Potassium grows in a layer-by-layer mode on the surface of MoS$_2$. The intercalation of K into MoS$_2$, which occurs at RT, is negligible at LT. At low coverages K is deposited in ionic form, whereas for $\theta_K > 0.5$ there is clear evidence of metallization of the K overlayer on MoS$_2$.

1. Introduction

Recently, there has been considerable interest in the adsorption of alkali on transition metal dichalcogenide (TX$_2$) layered compounds [1–9]. Layered semiconductors are ideal substrates to study fundamental aspects of the metal–semiconductor interaction as the van der Waals cleavage plane (0001) is extremely inert [2,4]. Alkali metals are of importance in catalysis because of their ability to modify activity and selectivity [3,10,11]. Interaction of alkali on layered materials also has outstanding potential for electrochemical energy storage [12] and solar energy conversion [5].

Despite this effort, the behaviour and properties of alkali metals on layered compounds are not yet understood. Recent studies suggest that high coverages of Na on WSe$_2$(0001) at low temperature (LT) form two-dimensional (2D) metallic layers [1,5,13], whereas at room temperature (RT) they form 2D and 3D clusters [6,9]. Also Cs forms clusters on MoS$_2$, at both RT and LT [1]. However, Cs on WSe$_2$ grows in clusters only at RT, while at LT it forms uniform metallic layers [13]. The adsorption of K on MoS$_2$(0001) has been studied recently at RT [6,7]. It has been shown that part of the adsorbed K is intercalated in the bulk while the rest remains on the MoS$_2$ surface. At low coverages, all the K adatoms are bound in ionic form directly to the surface of MoS$_2$ and tend to form 2D islands which, at higher coverages, coalesce and grow to 3D clusters. Apart from the size of the adsorbed alkali atoms, their intercalation and surface structure depend on the nature and temperature of the substrate layer compound. Therefore it is important to continue studies of K on the basal plane of MoS$_2$ at LT.

In this work low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS) and thermal desorption spectroscopy (TDS) measurements are used to study the behaviour and properties of K on MoS$_2$(0001) at 100 K in comparison with RT results [6,7].

2. Experimental details

The experiments were performed in a commercial ultra-high-vacuum (UHV) chamber equipped with four-grid LEED optics, a semicylindrical mirror analyser for AES and EELS measurements and a quadrupole mass spectrometer for TDS measurements. K was deposited from an SAES Getter source. The background pressure during K deposition was less than 5×10^{-10} Torr. The K flux was measured by a modified surface ionization probe and was constant at $(9\pm1) \times 10^{11}$ cm^{-2} s^{-1}. The MoS$_2$(0001) sample was cleaved in air. In UHV the sample could be heated by passing current through a 0.05 mm Ta strip uniformly pressed between the sample and a Ta foil case and could be cooled at 100 K by liquid nitrogen. The temperature of the sample was measured by a Cr–Al thermocouple spot-welded on the case and calibrated with an infrared pyrometer in the range 900–1200 K.

3. Results and discussion

Adsorption of K on MoS$_2$(0001) at 100 K caused a background increase in the LEED pattern while the integer order beams became diffused. At high coverages the LEED pattern was covered completely by a high background, indicating that, at 100 K, K formed uniform disordered layers on MoS$_2$.
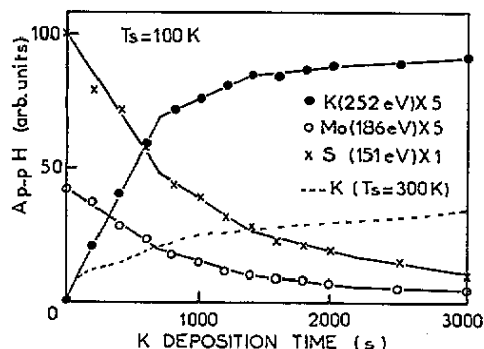

Figure 1. Auger peak to peak height (Ap–pH) of K (252 eV), S (151 eV) and Mo (186 eV) versus K deposition time on MoS$_2$(0001) at 100 K, as compared to the variation of K (252 eV) Ap–pH during K deposition on MoS$_2$ at RT (dashed line).

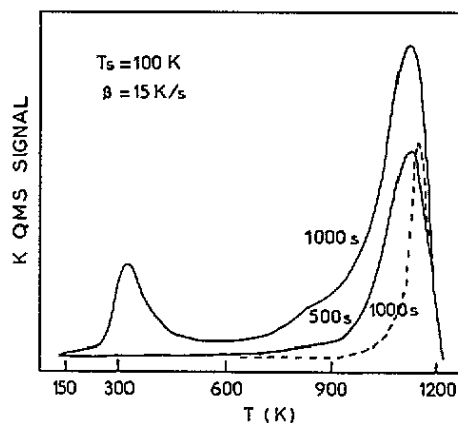**Figure 2.** Thermal deposition spectra of K from K-covered MoS$_2$(0001) at 100 K, as compared to that at RT (dashed line).

Figure 1 shows the Auger peak to peak height (Ap–pH) of K L$_{111}$M$_{23}$M$_{23}$(250 eV), S L$_{III}$M$_{23}$M$_{23}$(151 eV) and Mo M$_v$N$_{23}$N$_{45}$ (186 eV) versus K deposition time, t_K, at 100 K, as compared to the variation of K (252 eV) Ap–pH during K deposition on MoS$_2$ at RT (dashed line) from [6]. The variation of the dashed curve was related to the clustering of the adsorbed K on the surface of MoS$_2$(0001) and the intercalation of part of it into MoS$_2$ at RT [6,7]. The reported [7] deintercalation of K caused by oxygen coadsorption on MoS$_2$ confirmed the intercalation of K into MoS$_2$ and

precluded a possible decrease in sticking coefficient at RT. The K (252 eV) Ap–pH–t_K curve at LT is obviously different from that at RT. Except for the early stages of K adsorption, the Auger peak heights for the same t_K and flux are substantially greater at LT than that at RT. The greater Ap–pH at LT, for the same flux and t_K, indicates that at LT almost all of the K remains on the surface of MoS$_2$(0001) forming uniform layers. Moreover, at LT the K Ap–pH increases linearly with periodic distinct breaks which appear at periods of 700 s. This behaviour is characteristic of layer-by-layer growth of K on MoS$_2$ [14]. At very low coverages ($t < 100$ s) the slope of the K Auger curve is slightly greater than that measured at RT (dashed line) which implies that the initial sticking coefficient, s_0, of K on MoS$_2$ at LT is about equal to or greater than that at RT. The linearity of the K Auger curve and the constant deposition time intervals (700 s) between the successive breaks of the curve (figure 1) suggest that the sticking coefficient of K on MoS$_2$ at LT s_0, remains constant. From the K flux measurements we can estimate the coverage, if the sticking coefficient of K on MoS$_2$ is known. In a recent report the initial sticking coefficient of K on MoS$_2$ at RT was estimated to be 0.7 [6,7]. According to the comparison of the initial slopes of K Auger curves at RT and LT (figure 1) the s_0 at LT should be $\geqslant 0.7$. If we assume that at 100 K the sticking coefficient of K on MoS$_2$ is unity as for alkali on metals, we find that the coverage at the first Auger break is 5.8×10^{14} cm^{-2} or 0.5 ML. This coverage is close to those reported for K close packed monolayers on metallic substrates (5.4×10^{14} cm^{-2}) [15,16]. From the attenuation of the Mo (186 eV) Auger peak in figure 1 we can estimate the thickness of the K layer at the first break using the following equation:

$$I = I_0 \exp(-d/\lambda \, \cos \, \theta) \qquad (1)$$

where I_0 and I are the Ap–pH of Mo (186 eV) of clean and K-covered MoS$_2$, respectively, λ is the mean free path, $\theta = 42°$ for CMA and d is the thickness of the K adlayer. From the mean free path of electrons versus their energy curve [17] we estimate an inelastic mean free path of $\lambda = 7$ Å for the 186 eV electrons. Using this value of λ in (1) we find the thickness of the K monolayer to be 4 Å, which is close to the thickness of a single layer of K. Therefore each break on the Auger curve (figure 1) corresponds to the completion of a K layer with coverage of 0.5 ML. In other words, at LT (100 K) K is deposited on the surface in a uniform layer-by-layer growth mode and possible intercalation of K in the bulk of MoS$_2$ is almost precluded. This is in contrast to the RT adsorption where part of the K deposited on MoS$_2$(0001) is intercalated while that remaining on the surface forms clusters [7].

Figure 2 shows two thermal desorption spectra of K from MoS$_2$ covered at 100 K with $\theta_K = 0.36$ ML and 0.72 ML, respectively, as compared to the TD spectrum of K from 0.72 ML of K-covered MoS$_2$ at RT (dashed line), from [6]. At $\theta = 0.36$ ML there is only one desorption state at high temperature (1150 K), whereas at $\theta = 0.72$ ML a second desorption state appears at T = 350 K. From Readhead's equation [18]

$$E = kT_p \left[\ln(\nu_1 T_p/\beta) - 3.64 \right] \qquad (2)$$

where k is the Boltzmann constant, T_p the TDS peak temperature, ν_1 the pre-exponential factor ($\nu_1 = 10^{13}$) and β the heating rate (15 K s^{-1}), we may calculate the binding energy which correspond to the thermal desorption peaks in figure 2.

Assuming first-order desorption, as for alkali on metallic and semiconducting surfaces [1, 9, 23] and using equation (2), we find the energy of the high-temperature peak to be ~3 eV which is close to the binding energy of the ionic bonds of K [19]. This means that at low coverages the K–MoS$_2$ binding is strong and most likely the K adatoms are in an ionic state. The binding energy of the low-temperature desorption state is 0.9 eV which is identical to the cohesive energy of metallic K [20], and thus it has been attributed to a metallic character of the K adlayer for $\theta_K > 0.5$ ML. The latter desorption state has not been observed at RT, even at high K deposition time (4000 s). This implies that at RT the K overlayer remains in the ionic state even at high coverages. From a comparison of the RT and LT desorption spectra for $\theta_K = 0.72$ ML, we conclude that, for the same t_K and K flux, the amount of desorbed K is much higher at LT. The greater peaks at LT than at RT for the same t_K and K flux may be attributed to the negligible intercalation of K into the bulk at LT [6, 7].
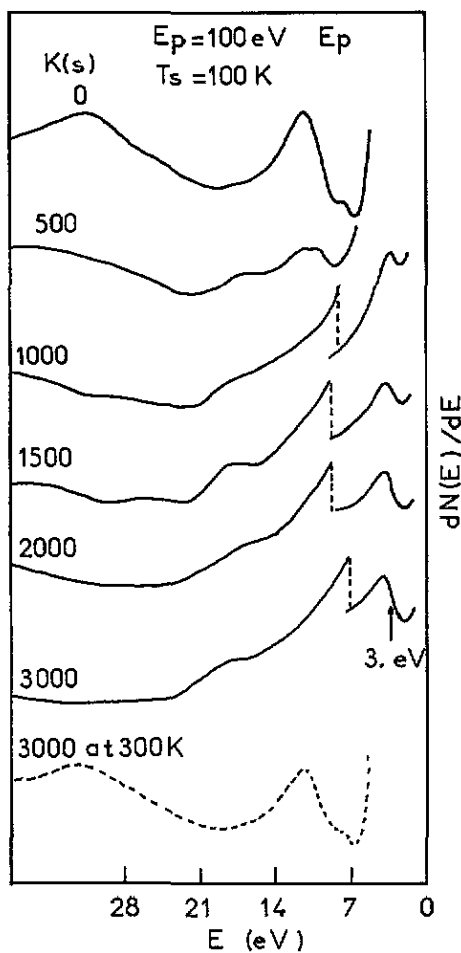

Figure 3. A series of EEL spectra of MoS$_2$ during K deposition on MoS$_2$ at 100 K, as compared to the EEL spectrum of K-covered MoS$_2$ at RT (dashed curve).

Figure 3 shows a series of EEL spectra of MoS$_2$ during K deposition on MoS$_2$ at 100 K, as compared to the EEL spectrum of K-covered MoS$_2$ at RT (dashed curve). During K deposition on MoS$_2$ at RT the EEL spectrum did not change; it remained

almost the same as that of clean MoS$_2$, shown by the dashed curve (figure 3). In contrast, at LT the spectrum showed interesting changes. Specifically, for $\theta < 0.5$ ML the intensity of the characteristic loss peaks of MoS$_2$ decreased rapidly. This is consistent with the layer-by-layer growth mode. For $\theta > 0.5$ ML the substrate peak almost disappeared while a new peak appeared at an energy of 3.0 eV. The energy of this peak is close to the energy of the surface plasmon of bulk K [21, 22] which is related to the bulk K plasmon peak 4.2 eV with $\omega_s = \omega/\sqrt{2}$. The presence of this EELS peak coincides with the appearance of the low-energy desorption state of K (figure 2) which has also been attributed to the metallization of the K overlayer. According to EELS measurements, the behaviour of K on MoS$_2$ at LT is different from that of Cs on MoS$_2$ at LT [1]. Deposition of Cs on MoS$_2$ at LT did not show any plasmon loss or low-temperature desorption state as did K [1]. This is consistent with the clustering of Cs on MoS$_2$ [1].

4. Summary

This work refers to adsorption of K on MoS$_2$ at 100 K. The investigation took place in a UHV system by means of LEED, AES, EELS and TDS measurements. The Auger measurements showed that, at 100 K, K grows in a layer-by-layer mode on the surface of MoS$_2$(0001), in contrast to the clustering at RT. The intercalation of K into MoS$_2$, which occurs at RT, is negligible at LT. At low coverages, K adatoms are in ionic form. The simultaneous appearance of a 3 eV K plasmon peak and a low-energy TDS peak (0.9 eV) for $\theta_K > 0.5$ supports the metallic character of the K overlayer at 100 K. This is in contrast to the RT adsorption of K which did not indicate any metallicity on MoS$_2$.

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