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## Interaction of Li with the group IV selenide layer compounds at low temperature

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### Abstract

Li was deposited at low temperature (80 K) onto cleaved van der Waals surfaces of the layered compounds  $MSe_2$  ( $M \equiv Ti, Zr$  and  $Hf$ ). The adsorption systems were investigated by means of low-energy electron diffraction, work-function measurements and soft-x-ray photoelectron spectroscopy using a synchrotron radiation source. The results suggest that at low coverages, Li is uniformly distributed near the surface, leading via a decomposition reaction to the formation of  $Li_2Se$  and  $M^0$ . At high adsorbate concentration, some of the Li intercalates into the substrate in the interlayer region. The intercalation process seems to depend on the temperature and the lattice parameter of the substrate.

### 1. Introduction

The transition metal dichalcogenides (TMDC)  $MX_2$  are formed from two-dimensional sandwich layers of covalently bound  $X-M-X$  units which are separated from each other by a weak interlayer (van der Waals gap). Along these gaps the crystals can be cleaved very easily. The resulting (0001) surface is chemically saturated and therefore free of dangling bonds [1]. One interesting property of TMDC is the insertion of electron-donating atoms or molecules between the sandwich layers [2–6]. Such an insertion reaction is often called intercalation, if it does not lead to a chemical decomposition of the host. Many promising technological applications, such as battery systems [2, 3, 7, 8], superconductivity [9], and solar cells [1], involve intercalation compounds of layered materials. In addition, the intercalation process is of interest from a fundamental point of view, as the electronic and structural properties of the host may be changed considerably by the intercalate [4, 5].

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Within last three decades, the interaction of alkali atoms with layered chalcogenides has been investigated intensively [2–6, 10–14]. Among these investigations, a number concluded that alkali deposition on (0001) surfaces of the layer compounds could lead to the formation of different interfaces. Specifically, the possible cases are:

- (1) a non-reactive atomically abrupt interface [15–17];
- (2) an intercalated phase [18–24]; and
- (3) a chemical reaction which may start either near the surface [20] or in the bulk after initial intercalation [25].

The kind of interface formed depends on the substrate and its temperature, and the size and flux of the alkali atoms.

Despite of the intensive investigation, the question of the interaction of the alkali with the layer compounds has not been settled yet. In this investigation, we study Li deposition on the (0001) van der Waals surfaces of 1T-MSe<sub>2</sub> (M ≡ Ti, Zr and Hf) layer compounds at low temperature (80 K). The experiments were carried out by means of low-energy electron diffraction (LEED), work-function (WF) measurements and soft-x-ray photoelectron spectroscopy (SXPS) using a synchrotron radiation source.

## 2. Experimental details

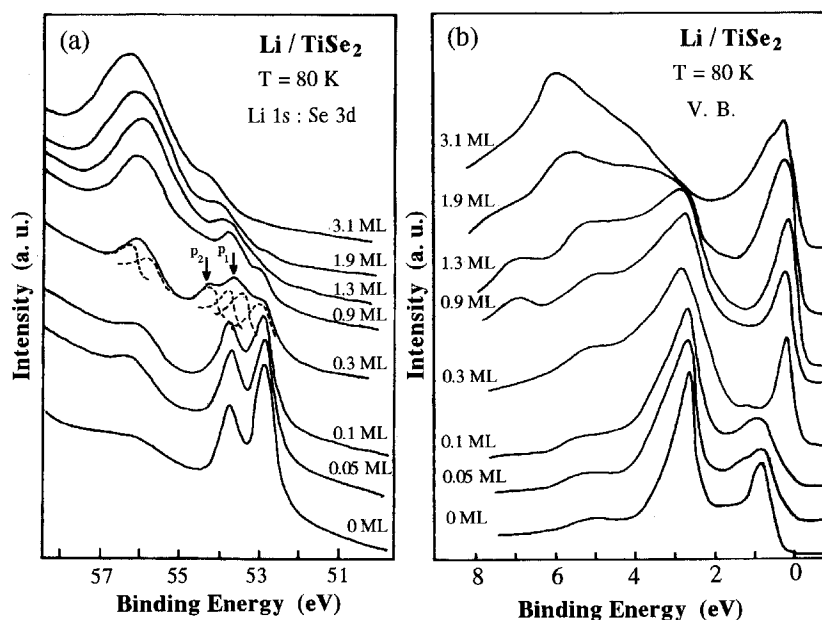
The experiments were performed in an ultrahigh-vacuum (UHV) system, with a base pressure close to  $5 \times 10^{-11}$  mbar. The system was equipped with a quadrupole mass spectrometer (QMS) and a LEED system. Photoemission measurements (normal emission) were performed with a commercial spectrometer, VG ADES 500. As an excitation source, synchrotron light (BESSY storage ring, TGM 7,  $h\nu = 10\text{--}120$  eV) was used [26]. The overall energy resolution achieved at the full width at half-maximum (FWHM) was about 0.3 eV. The spectra were taken in normal emission with photon energy 70 eV and were given versus binding energy (BE). A negative bias voltage of 6 eV was applied to the sample. All the spectra were referenced to the Fermi level ( $E_F$ ) of a Cu support (BE = 0 eV). The Cu support was cleaned by Ar-ion bombardment before cleaving the layer compound crystals. The WF of the sample was determined from the cut-off of the secondary electrons.

The single crystals of TiSe<sub>2</sub>, ZrSe<sub>2</sub>, HfSe<sub>2</sub> and TiS<sub>2</sub> were prepared by halogen transport in sealed glass tubes according to [27]. The samples were attached via a thin conducting layer of Ag epoxy to Cu plates, which were mechanically pressed to the sample holder for good thermal and electrical contact. The crystal holder was mounted on an X, Y, Z manipulator and could be cooled down to about 80 K with liquid nitrogen. Clean (0001) faces were produced by cleaving the crystals in UHV. Lithium was deposited from SAES getter evaporation sources. During Li deposition the pressure was less than  $5 \times 10^{-10}$  mbar. The Li surface stoichiometry was determined from the intensity of the photoelectron spectra corrected by theoretical photoionization cross-sections [28] and normalized by Li QMS measurements. The Li deposition flux was estimated to be 0.1 ML/dose.

## 3. Results and discussion

### 3.1. LEED and WF measurements

The hexagonal LEED pattern for the three MSe<sub>2</sub> substrates becomes more diffuse and the background of the picture increases substantially with Li deposition at 80 K. At high coverages



**Figure 1.** SXPS spectra of the (a) Li 1s and Se 3d core levels and (b) VB spectra for Li deposition on  $\text{TiSe}_2$  at 80 K.

the LEED pattern disappears in a high background. This shows that Li destroys the lattice near the surface, possibly because of a strong interaction with the substrate.

The WF of the surfaces, as measured from the cut-offs of the electron distribution curves, are 5.3 eV for  $\text{TiSe}_2$ , 5 eV for  $\text{ZrSe}_2$  and 4.8 eV for  $\text{HfSe}_2$ . After Li deposition of 2 ML, the WF of every substrate decreases by 3.6, 2.3 and 3.4 eV for  $\text{TiSe}_2$ ,  $\text{ZrSe}_2$  and  $\text{HfSe}_2$  respectively. Such relatively large WF changes have also been observed during Li deposition on S-covered Ni(100) surfaces and has been attributed to the alkali-S interaction on the surface [29]. So, in our case, the large WF changes probably indicate that most of the Li atoms remain on the surface, reacting with the outermost Se atoms and forming chemical compounds. This is in agreement with the LEED observations.

### 3.2. Photoemission measurements

**3.2.1. Li on  $\text{TiSe}_2$ .** The SXPS spectra of Li 1s, Se 3d and the valence band (VB) region in the course of Li deposition on  $\text{TiSe}_2$  at 80 K are summarized in figure 1. The Ti 3p core level was very weak and broad and it is not shown here. In figure 1(a), the Li 1s core level appears initially at about 56.2 eV and shifts slightly to lower BE by  $\approx 0.2$  eV as the Li coverage increases. At the same time the peak looks asymmetric, becoming gradually broader. The FWHM increase indicates that Li 1s emission is superposed by two different contributions (see the dashed curves in figure 1(a)). Drastic changes happen for the Se 3d doublet as well. For Li coverages,  $\Theta_{\text{Li}} \leq 0.1$  ML, the relative intensity ratio of the  $d_{3/2}$  and  $d_{5/2}$  lines changes. For  $\Theta_{\text{Li}} = 0.3$  ML, the doublet is drastically affected by the appearance of two new peaks  $p_1$  and  $p_2$  at about 53.5 and 54.2 eV respectively. Analysis of this SXPS spectrum reveals that, next to the original Se 3d doublet, a new one develops, as shown by the dashed curves. At high  $\Theta_{\text{Li}}$ , the Se 3d doublet almost disappears because of the Li 1s broadening. In figure 1(b), the

VB spectra are shown as  $\Theta_{\text{Li}}$  increases. The energy gap near the Fermi level decreases and finally disappears with a newly developing sharp peak for  $\Theta_{\text{Li}} \geq 0.3$  ML. This peak can be attributed to the metallic Ti 3d level. In the same coverage range, a new peak appears at about 5.2 eV below  $E_F$ . As  $\Theta_{\text{Li}}$  increases, this peak shifts to 5.8 eV, whereas the shape of the VB spectrum changes substantially.

From the above description of figure 1, it is clear that most of the changes in the spectra occur at 0.3 ML. The observed drastic changes, such as the new Se 3d doublet, the strong emission at  $E_F$  and the large WF decrease, are strong evidence of the interaction between Li and Se. In agreement with previous results [10, 30], this interaction leads to  $\text{Li}_2\text{Se}$  formation on the surface, according to the reaction



where  $\text{M} \equiv \text{Ti}$ .

So the new Se 3d doublet is due to the new chemical state of Se in  $\text{Li}_2\text{Se}$ . Also the 5.8 eV peak in the VB region is attributed to the Se VB in the compound formed. Another interesting point, which is related to the  $\text{Li}_2\text{Se}$  formation, is the Li 1s emission broadening. As has already been mentioned, the broadening is caused by two different contributions, at about 56.1 and 55.7 eV. In order to distinguish these contributions let us name the 56.1 eV peak the higher binding energy contribution (HBEC) and the 55.7 eV one the lower binding energy contribution (LBEC). Similar broadening and contributions have been reported for the Li 1s emission level, in the case of Li deposition on  $\text{WSe}_2$  and  $\text{WS}_2$  [10, 30].

In our case, because of the low diffusion rate of the Li atoms at low temperature, most of the deposited Li remains on the surface for low coverage. This portion of the Li is related to the HBEC and is attributed to the  $\text{Li}_2\text{Se}$  formation. As the coverage increases ( $\Theta_{\text{Li}} \geq 0.3$  ML), some of the Li intercalates into the substrate. The LBEC is probably related to the quantity of Li intercalated into the layer compound. As a consequence of the Li–Se interaction, metallic Ti is formed, explaining the strong emission of Ti 3d near  $E_F$  (figure 1(b)). The broadening of the Li 1s peak drastically affects the Se 3d doublet, via a strong overlap effect particularly at high coverage. In view of this problem, we also investigated the adsorption of Li onto  $\text{TiS}_2$  at 80 K. Figure 2 shows the development of the Li 1s emission in the course of increasing Li coverage. The main peak grows at about 56 eV, as observed also on  $\text{TiSe}_2$ , and is assigned to  $\text{Li}_2\text{S}$ . At 0.3 ML, the peak becomes broader due to a new contribution at lower BE clearly apparent at 1.9 ML. This peak is attributed to the Li intercalated into the layer compound.

**3.2.2. Li on  $\text{ZrSe}_2$ .** Figure 3 summarizes the Li 1s, Se 3d core levels and the VB region for Li deposition on the  $\text{ZrSe}_2$  surface at 80 K. At low  $\Theta_{\text{Li}}$ , the Li 1s emission appears at  $\text{BE} \approx 56.2$  eV. This emission is assigned to Li reacted with Se in the  $\text{Li}_2\text{Se}$ , in agreement with previous results [10, 22]. The FWHM of the Li 1s peak increases for coverage  $\Theta_{\text{Li}} \geq 0.1$  ML. This can again be explained by considering the Li 1s peak to consist of two separate peaks, i.e. the HBEC and the LBEC, where the average energy positions are indicated by arrows in figure 3(a). The LBEC strongly affects the spectrum at high Li coverage ( $\Theta_{\text{Li}} = 2.5$  ML) and is attributed to Li intercalated into the layer compound. This contribution dominates the spectrum, indicating that the quantity of Li intercalated is higher than the quantity that interacted.

This lithium behaviour is different to that on  $\text{TiSe}_2$ , but it is consistent with the smaller WF change (2.3 eV). In figure 3(b) the VB region is shown with a new weak peak appearing at the Fermi level from low Li coverages. This peak is due to the metallic Zr produced on the surface after the Se–Li interaction according to the reaction (1), where  $\text{M} \equiv \text{Zr}$ .

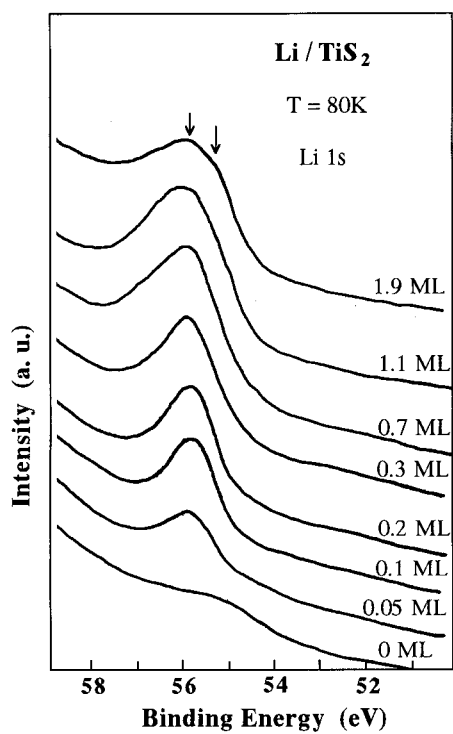


Figure 2. SXPS spectra for the Li 1s core level of the Li/TiS<sub>2</sub> interface at 80 K, in the course of increasing Li coverage.

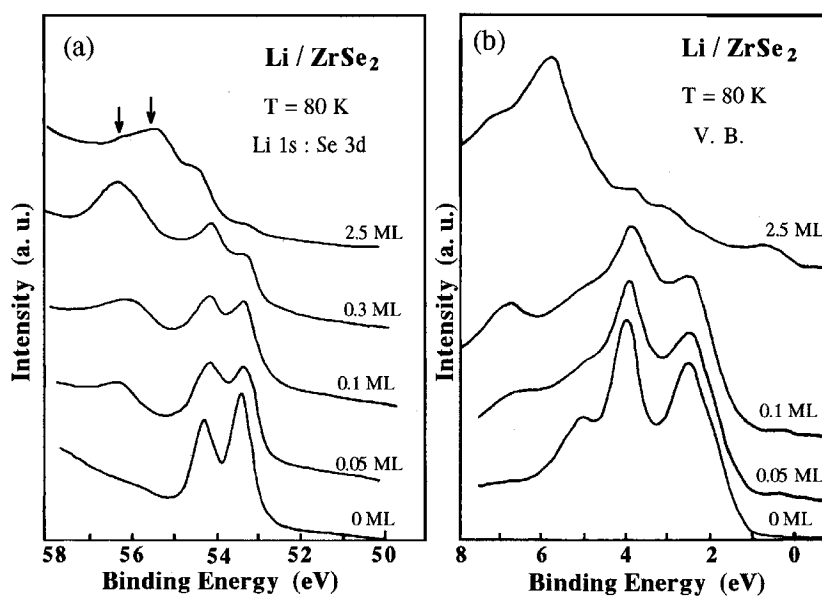
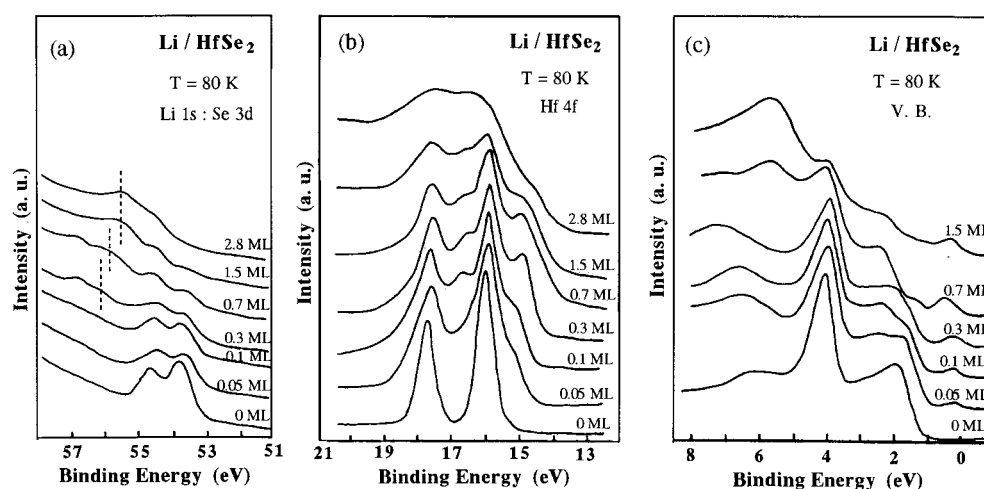


Figure 3. SXPS spectra of the (a) Li 1s and Se 3d core levels and (b) VB spectra for Li deposition on ZrSe<sub>2</sub> at 80 K.



**Figure 4.** SXPS spectra of the (a) Li 1s and Se 3d core levels, (b) Hf 4f and (c) VB spectra for Li deposition on HfSe<sub>2</sub> at 80 K.

**3.2.3. Li on HfSe<sub>2</sub>.** Figure 4 shows the Li 1s, Se 3d, Hf 4f core levels and the VB spectrum in the course of Li deposition on HfSe<sub>2</sub> at 80 K. As figure 4(a) shows, a broad and weak double Li peak appears in the spectrum, around 56.7 and 56.0 eV at  $\Theta_{\text{Li}} = 0.3$  ML. At early Li deposition stages, a new Hf 4f doublet appears  $\approx 1$  eV to lower BE (figure 4(b)) while a new peak also appears near  $E_F$  in the VB spectra (figure 4(c)). As Li coverage increases, the 56 eV peak comes to dominate the spectrum and shifts to lower BE, overlapping with the Se 3d doublet at the same time. As regards the Li double peak, the 56 eV emission is attributed to Li interacted with Se resulting in the Li<sub>2</sub>Se compound, whereas the 56.7 eV one is attributed to Li intercalated into the substrate. The difference in BE of the intercalated Li between the Li in TiSe<sub>2</sub> and in HfSe<sub>2</sub> is due to the position of the Fermi level [10, 30]. The Li–Se interaction takes place according to the reaction (1), where  $M \equiv \text{Hf}$ . This is strongly supported first by the appearance of the new Hf 4f doublet and second by the peak near  $E_F$ . Both of these peaks attest to partial metallization of the Hf. In addition, the peak in the VB region at 5.8 eV can be attributed to the Se participating in the Li<sub>2</sub>Se compound.

#### 4. Thermodynamic and kinetic aspects

Our experimental results on Li deposition on the basal plane of the group IV selenide layer compounds at low temperature, indicates a strong chemical interaction with the substrate according to the reaction (1) with  $M \equiv \text{Ti, Zr and Hf}$ . This reaction seems to start from the early Li deposition stages, while at higher adsorbate concentration some of the Li intercalates into the substrate. The intercalation process is more drastic in the case of ZrSe<sub>2</sub> than in TiSe<sub>2</sub> and HfSe<sub>2</sub>, leading to a smaller final WF change (2.3 eV) than in the other two cases (3.6 and 3.4 eV respectively). A possible reason for this might be the bigger lattice parameter of ZrSe<sub>2</sub> (3.77 Å) compared to that of TiSe<sub>2</sub> (3.53 Å) [31]. Since Gibbs free energies of the selenide layer compounds and reactions are not available in the literature, we may only estimate the thermodynamic driving forces. The Gibbs free energy for Li intercalation into the layer compounds may be obtained from the determination of electromotive forces (EMF). The EMF can be derived from the difference between  $E_F$  for metallic Li (approximated by the

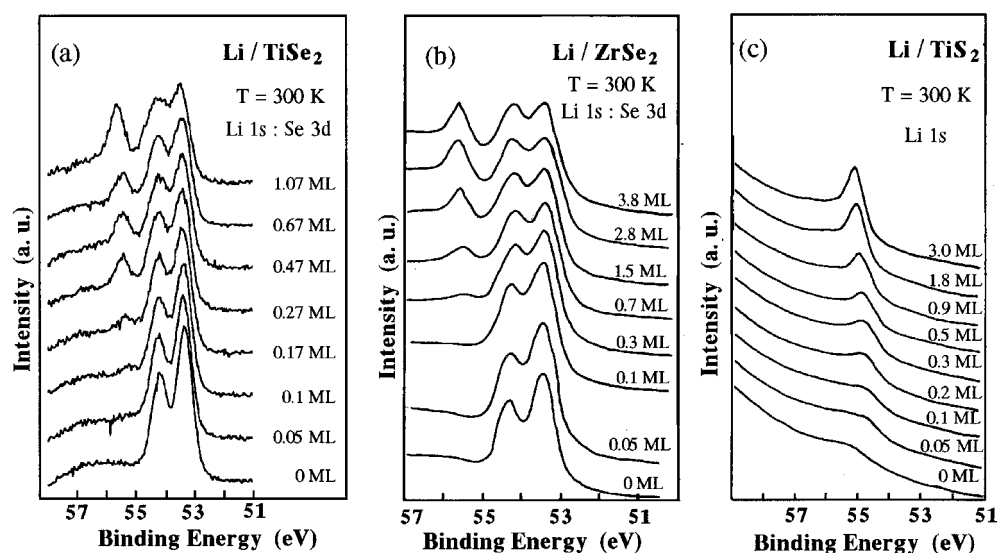


Figure 5. The SXPS Li 1s core level for Li deposition on (a)  $\text{TiSe}_2$ , (b)  $\text{ZrSe}_2$  and (c)  $\text{TiS}_2$  at RT.

Table 1. Energies of the Li intercalation into  $\text{MSe}_2$ , where M = Ti, Zr and Hf.

Layer compound	EMF (eV)	$\Delta G_{int}$ ( $\text{kJ mol}^{-1}$ )	$\Delta G_{dec}$ ( $\text{kJ mol}^{-1}$ )
$\text{TiSe}_2$	2.1	-200	-120
$\text{ZrSe}_2$	1.5	-145	-78
$\text{HfSe}_2$	1.1	-106	-75

WF = 2.9 eV) and the electron affinity of  $\text{MSe}_2$  layer compounds. The results are tabulated in table 1. The last column reports the Gibbs free energies for the decomposition reactions ( $\Delta G_{dec}$ ) of the respectively sulphide layer compounds according to the reaction (1) [3]. Assuming that these  $\Delta G_{dec}$  values are close to those of the selenide compounds, the results suggest an overwhelming driving force for the intercalation reaction for all the group IV selenide layer compounds. This implies that the intercalation reaction is thermodynamically favoured in all the substrates investigated in this work. However, the experimental results show that the decomposition reaction of the surface due to  $\text{Li}_2\text{Se}$  compound formation is favoured, particularly at low coverage. Evidently, kinetic factors help such a reaction. At low temperature, due to the slow diffusion rates, most of the deposited Li is concentrated near the surface. The accumulation of Li helps the decomposition reaction because the reaction (1) needs four Li atoms for each  $\text{MSe}_2$  molecule [10, 30]. Moreover, the group IV layer compounds adopt the 1T structure with octahedral coordination of the metal by chalcogens with a p-d hybrid antibonding conduction band. The Li 2s electron transferred to the conduction band leads to a destabilization of the crystal [5], resulting in the surface decomposition reaction. At room temperature (RT) these conditions do not exist because the diffusion rate of Li is large. Figure 5 shows the Li 1s core level in the course of Li deposition on (a)  $\text{TiSe}_2$ , (b)  $\text{ZrSe}_2$  and (c)  $\text{TiS}_2$  at RT. The sharpness and the constant FWHM of the peak are characteristic features of the intercalation process [10, 22, 24, 30].



## 5. Conclusions

In this study we investigated the Li deposition on the group IV layer compounds  $MSe_2$  ( $M \equiv Ti, Zr$  and  $Hf$ ) at 80 K. The experiments were carried out in UHV by means of SXPS, LEED and WF measurements. In all cases, at low coverages Li accumulates on the surface, interacting strongly with Se and forming the compound  $Li_2Se$  and  $M^0$ . This interaction leads to a partial metallization of the  $M^0$ . At higher adsorbate coverage, some of the Li intercalates into the layer compound. The intercalation process is more drastic for the  $ZrSe_2$  substrate than  $TiSe_2$  and  $HfSe_2$ . A possible reason for that may be the bigger lattice parameter in the case of  $ZrSe_2$ . Although the intercalation reaction is thermodynamically favoured, the decomposition reaction is also observed. This is helped by kinetic factors such as the low diffusion rate, which occurs at low temperature. In contrast, due to the higher diffusion rate at RT, the intercalation process becomes dominant.

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