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The influence of chemical reactivity of surface defects on ambient-stable InSe-based nanodevices†

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We demonstrate that, in contrast to most two-dimensional materials, ultrathin flakes of InSe are stable under ambient conditions. Despite their ambient stability, InSe-based nanodevices show an environmental p-type doping, suppressed by capping InSe with hexagonal boron nitride. By means of transport experiments, density functional theory and vibrational spectroscopy, we attribute the p-type doping assumed by uncapped InSe under an ambient atmosphere to the decomposition of water at Se vacancies. We have estimated the site-dependent adsorption energy of O₂, N₂, H₂O, CO and CO₂ on InSe. A stable adsorption is found only for the case of H₂O, with a charge transfer of only 0.01 electrons per water molecule.

1 Introduction

Two-dimensional (2D) materials had a groundbreaking impact on science and technology.¹ Their use for the fabrication of nanodevices strongly depends on their electronic band gap. As an example, the gapless spectrum of graphene² avoids the effective switching of its conductivity in electronic devices and, moreover, the achievement of a high ON–OFF ratio.³ Thus,

there is a continuous effort in the search for novel materials with finite and direct band gaps.³

Nature provides a variety of layered materials “beyond graphene”⁴ (semimetals, semiconductors, insulators) with electronic band gaps shifting from the infrared to the ultraviolet.

The synthesis of novel 2D materials,⁴ such as transition-metal dichalcogenides (MoS₂,^{5–8} WS₂,⁹ MoSe,^{10,11} WSe₂,¹² MXene compounds¹³) or atomically thin elemental materials (silicene,¹⁴ germanene,¹⁵ phosphorene,¹⁶ stanene¹⁷) promises a revolutionary step-change. Such innovative 2D materials allow for combining flexibility^{18,19} and transparency²⁰ with an existing electronic band gap.¹⁹

However, the unfeasibility to exfoliate silicene and germanene poses severe limits to their technological use.²⁰ On the other hand, the band gap of MoS₂ (1.29 eV²¹ for the bulk and ~1.8 eV for the monolayer²²) is relatively large and does not overlap well with the visible spectrum, making it intrinsically non-ideal for its use as an active element for optoelectronics in the visible domain. In principle, black phosphorus could be a more suitable material for photodetection of visible light, since it is a narrow-gap van der Waals semiconductor,^{14,23,24} which can be exfoliated in phosphorene layers. However, black-phosphorus flakes are found to chemically degrade upon exposure to ambient conditions.²⁵ The ambient degradation of black-phosphorus-based nanodevices causes large increases in the threshold voltage after six hours in air, followed by a remarkable decrease in mobility^{25–27} and in the ON/OFF ratio. Black phosphorus also increases over 200% in volume in a few days, as a consequence of water absorption.²⁶

A suitable solution to overcome the above-mentioned problems might be represented by InSe, which is a layered semiconductor made of stacked layers of Se–In–In–Se atoms with van der Waals bonds between quadruple layers. InSe is a direct band-gap semiconductor with an energy gap of ~1.25 eV at room temperature.²⁸ Many recent studies have reported the superb performance of InSe-based optoelectronic devices.^{29–33} InSe-based field-effect transistors (FETs) exhibit unprecedentedly high mobility transport.^{29,30,34–36} The mobility of bulk InSe is near 10³ cm² (V s)^{–1} at room temperature,³⁴ making it a

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promising candidate for next-generation high-performance 2D semiconductor devices.^{29,30,36} Together with potential optoelectronic applications, InSe also offers intriguing prospects for strain engineering,³⁷ nonlinear optics,³⁸ and photovoltaics.³⁹

However, the ambient stability of InSe is an essential prerequisite for the sustainability of InSe-based technology. Other valuable information would be represented by the effect of surface chemical reactions on transport properties. Both aspects have not been investigated yet.

Herein, by means of transport experiments, density functional theory (DFT) calculations, and vibrational spectroscopy we explore the surface chemical reactivity of InSe toward ambient gases and, moreover, the stability of InSe-based nano-transistors in the atmosphere.

2 Results and discussion

To perform electrical measurements, devices with both uncapped and hexagonal boron nitride (h-BN)-capped InSe channels were fabricated.

The mechanically exfoliated InSe layers (with a thickness of ~20 nm) were placed on a p-type doped Si substrate with a 300 nm thick SiO₂ layer (Fig. 1a). The device fabrication was performed using electron-beam lithography for patterning the source (S) and drain (D) electrodes.^{40,41} Gold contacts with 70 nm thickness were deposited by electron-beam evaporation.

The h-BN capping of 2D materials has been proven to be beneficial for preserving the intrinsic electronic properties.^{41,42} More details on the nanofabrication process are reported in the ESI.†

In Fig. 1b, we report the I - V curve in the double V_G scan (−40 V to 40 V and back to −40 V) for uncapped and h-BN-capped InSe devices, where V_G is the gate voltage. The two

fabricated nano-devices show opposite transport types: uncapped InSe is dominated by p-type transport, while n-type transport is predominant in InSe capped with h-BN.

For negative voltage sweeping, both devices show p-type transport. In particular, uncapped InSe shows larger current. The difference observed in capped and uncapped InSe-based FETs is related to adsorbed contaminants from air, which induce a p-type doping.

Nevertheless, even the uncapped InSe FET shows stability under ambient conditions without any noticeable difference in the I - V curves repeated after two weeks (Fig. 2). Therefore, it could be suggested that no rapid degradation of the surface of few-layer InSe occurs, in contrast to the cases of black phosphorus,²⁶ Bi₂Se₃,⁴³ and MoS₂.⁴⁴

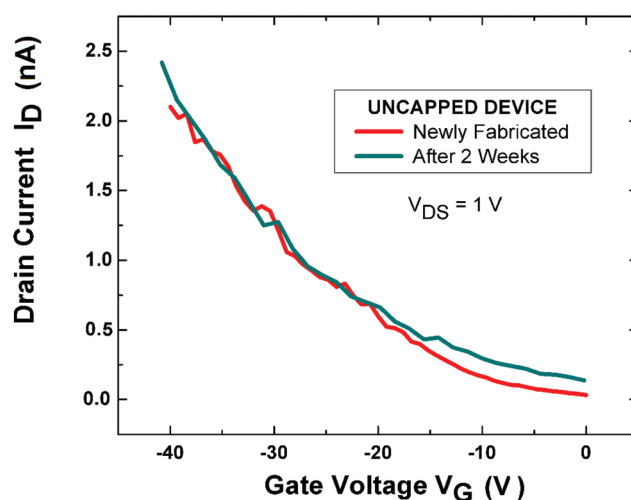


Fig. 2 I_{DS} - V_G curve of uncapped InSe-based transistors newly fabricated (red curve) and after two weeks (blue curve).

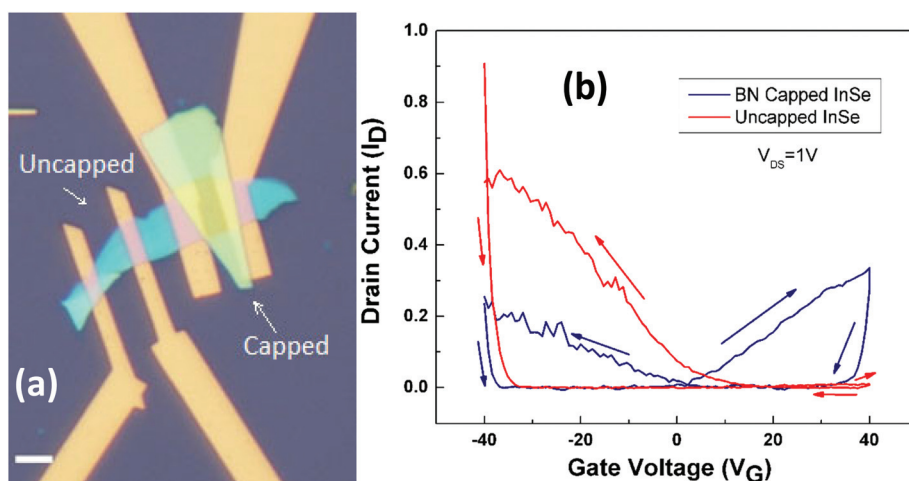


Fig. 1 (a) Optical image of typical InSe back-gate transistor devices: one device has its channel capped with an h-BN flake, while the other channel is open to environment. (b) The I_{DS} - V_G curve of capped and uncapped InSe-based transistors. For each measurement, gate is swept from −40 V to 40 V and back to −40 V. Although with large hysteresis, the uncapped device shows dominant p-type transport, whereas the capped device clearly exhibits ambipolar transport.

Previously, it has been reported that the interaction of 2D materials with ambient air humidity introduces p-type doping in graphene.⁴⁵ Concerning transition-metal dichalcogenides, H₂O-induced depletion of n-type has been found in MoS₂ and MoSe₂,⁴⁶ while the opposite occurs in WSe₂.⁴⁶

To elucidate the p-type doping and the ambient stability of InSe-based nanodevices, we have studied the relationship between the surface chemical reactivity, the ambient doping and the influence of defects on InSe by means of DFT calculations of the atomic structure and the energetics of various configurations of chemical species adsorbed on the InSe surface (Fig. 3 and 5). The energy cost E was calculated by a standard formula:

$$E = E_{\text{InSe+molecule}} - (E_{\text{InSe}} + E_{\text{molecule}}),$$

where E_{InSe} and $E_{\text{InSe+molecule}}$ are the energies of pristine or defective (see below) monolayer InSe before and after adsorption of a single molecule and E_{molecule} is the energy of molecules in an empty box. Note that positive energies correspond to endothermic processes.

The adsorption of two possible contaminants from air has been evaluated for two different adsorption sites on defect-free InSe: over Se atoms, which are the outermost surface atoms of the InSe monolayer (top position, Fig. 3c and d), and over the centers of hexagons (hole position, Fig. 3a and b). Theoretical findings, reported in Table 1, evidence that for all investigated species (H₂O, CO, CO₂, N₂, O₂) the adsorption over hole sites is more energetically favorable than in the on-top position with respect to Se atoms.

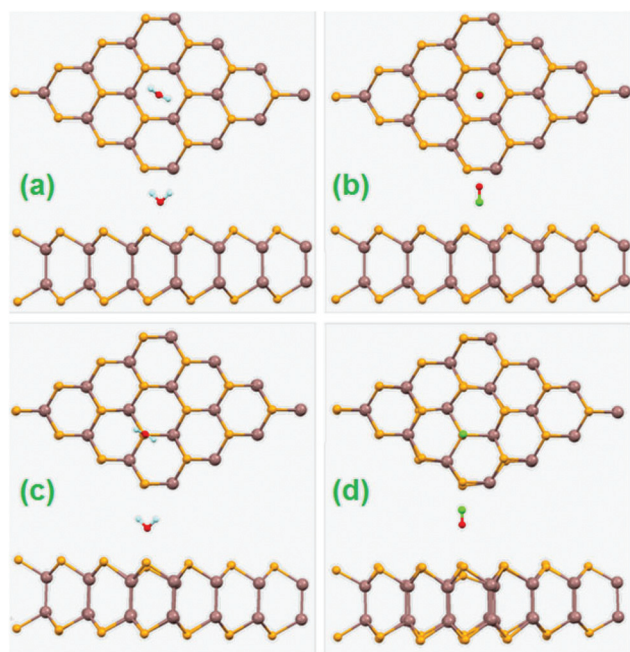


Fig. 3 Top and side views of the atomic structure of the InSe monolayer with adsorbed H₂O (a, c) and CO (b, d) molecules over hole sites (a, b) and on-top sites (c, d) with respect to Se atoms.

Table 1 Adsorption energies (in eV) of various species abundant in the air over hole and over the top of Se atoms

Species/position	Hole	Top
H ₂ O	-0.139	0.69
CO	0.014	2.75
CO ₂	0.244	2.05
N ₂	0.097	1.15
O ₂	0.705	3.67

Results in Table 1 indicate that the energy cost for the adsorption over Se atoms is minimal for the cases of water molecules and carbon monoxide, while it is rather high for the adsorption of other molecules. In particular, the adsorption energy is negative only for the case of H₂O on hole sites.

On the basis of these findings, we have calculated the charge transfer for adsorbates with minimal adsorption energies, *i.e.* water and carbon monoxide, for the case of defect-free InSe. The adsorption of water molecules over hole sites induces a charge transfer of only 0.01 electrons (e^-) for each molecule, resulting in a slightly p-doped InSe surface. By contrast, 0.14 e^- is back-donated from InSe to CO molecules. Nevertheless, in spite of the lower adsorption energy, CO adsorption on the InSe surface is less stable compared to water.

Thus, we can conclude that, among the ambient gases at room temperature, only water could form covalent bonds with InSe. It is also worth mentioning that the formation of strong bonds between H₂O molecules and Se atoms induces noticeable displacement of Se atoms from their positions in the pristine InSe (Fig. 3a and c).

To investigate the nature of the water–InSe interaction, we have carried out vibrational experiments on water-exposed InSe, by means of the high-resolution electron energy loss spectroscopy (HREELS) technique. The vibrational spectrum of water-exposed InSe (Fig. 4) shows an intense peak at 450 meV, assigned to the O–H stretching vibration in –OH groups.⁴⁷

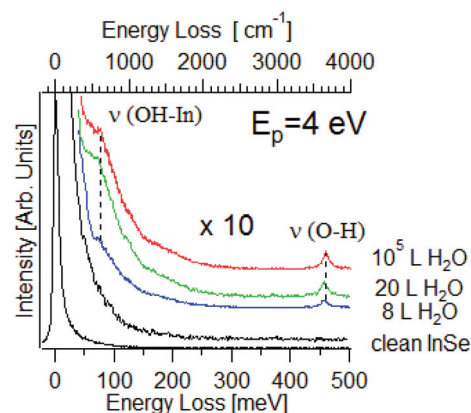


Fig. 4 Vibrational spectrum of water-dosed InSe. The impinging energy is 4 eV. The incidence and the scattering angles are 55° with respect to the sample normal. We remind that a dose of 1 L corresponds to 1.33 × 10⁻⁶ mbar s.

This result represents direct evidence of water dissociation at the InSe surface. In fact, undissociated water molecules would show O–H vibration energy in the 410–420 meV range.⁴⁸ Moreover, we also observe a broad band centered at ~ 70 meV, assigned to the OH–In stretching.⁴⁹

On the basis of vibrational experiments, we can affirm that water adsorption on InSe at room temperature is completely dissociative, with a saturation coverage estimated to be 0.05 ML.

Calculations on water decomposition on the InSe substrate confirm our experimental findings. In detail, we calculated the energy cost of water decomposition for the cases of pristine and defective InSe monolayers. We studied several types of possible defects: single In and Se vacancies, the joint presence of single In and Se vacancies, and Stone–Wales defects. We find that water decomposition over InSe without defects is energetically unfavorable (energy cost higher than 2 eV, Fig. 5a). Similarly to the case of graphene,⁵⁰ the presence of

defects significantly decreases the energy cost of chemisorption by a value that depends on the type of defect. The presence of In vacancies reduces the energy cost for water decomposition to 1.85 eV (Fig. 5b). Water decomposition is particularly favorable on Se vacancies, where the energy cost is only 0.29 eV (Fig. 5c). For the case of the joint presence of single In and Se vacancies, we find that the energy cost for decomposition is about 1 eV (Fig. 5d), while it is ~ 0.7 eV for the case of Stone–Wales defects (Fig. 5e).

Based on the relationship between calculated DFT energies and temperatures of reactions,⁵¹ we conclude that reactions with energies below 0.5 eV, *i.e.* the case of water decomposition at Se vacancies, occur at room temperature with a rather high rate.

Finally, it is worthwhile mentioning that we have also checked whether the presence of defects could play a role in CO adsorption. We have calculated the adsorption energy of CO over the hole in the vicinity of Stone–Wales defects. However, we find that adsorption on these sites is even less energetically favorable (+0.105 eV) than on undefective areas.

3 Conclusions

We have demonstrated that atomic sheets of InSe are stable under ambient conditions, contrarily to the case of most 2D materials, which usually react and decompose in air, thus severely hindering their application capabilities.

Despite their ambient stability, InSe-based FETs exhibit an environmental p-type doping, arising from the decomposition of water molecules at Se vacancies. We estimate that the charge per molecule transferred from InSe is only $0.01 e^-$. The information on chemical reactivity of surface defects is also important for engineering selective sensor applications of 2D materials.^{52,53}

By means of h-BN capping, ambipolar transport is achieved, with the suppression of environmental doping.

Our results pave the way for an InSe-based nano-electronics, which could overcome the possible limitations of the technology based on other 2D materials.

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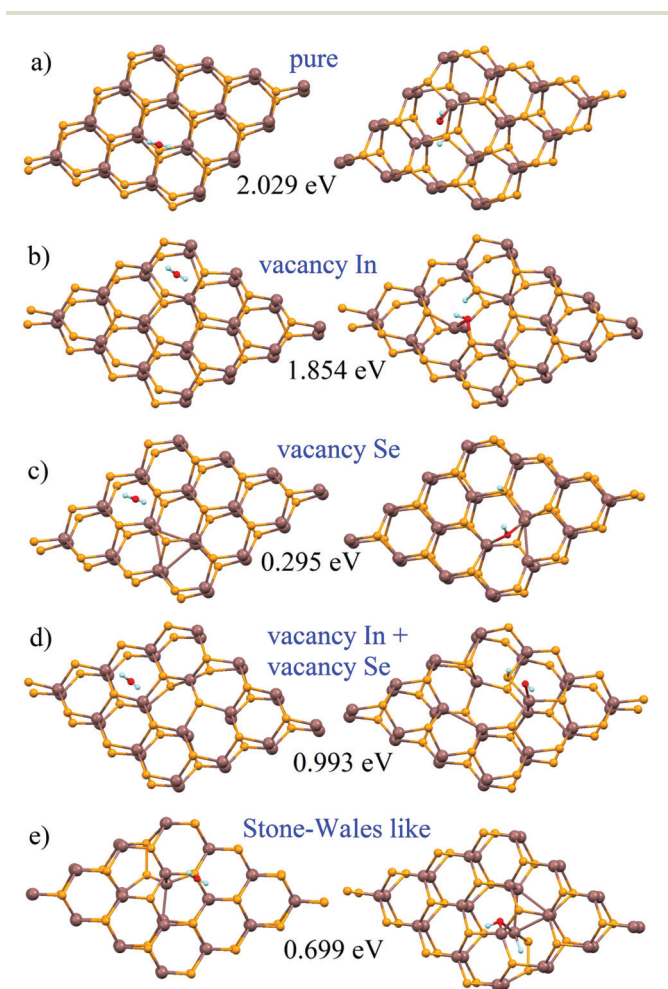


Fig. 5 Atomic structure of pristine (a) and defective (b–e) InSe monolayers before (left) and after (right) water decomposition. The reported numbers indicate the energy cost of water decomposition for the various cases.

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