CrI$_3$-WTe$_2$: A Novel Two-Dimensional Heterostructure as Multisensor for BrF$_3$ and COCl$_2$ Toxic Gases.

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A new multisensor (i.e., resistive and magnetic) CrI$_3$-WTe$_2$ heterostructure (HS) to detect the toxic gases BrF$_3$ and COCl$_2$ (Phosgene) has been theoretically studied in our present investigation. The HS has demonstrated sensitivity towards both the gases by varying its electronic and magnetic properties when gas molecule interacts with the HS. Fast recovery time (< 0.14 fs) under UV radiation has been observed. We have considered two configurations of BrF$_3$ adsorbed HS: 1) when F ion interacts with HS (C1) and 2) when Br ion interacts with HS (C2). In C1 case the adsorption energy $E_{\text{ad}}$ is observed to be -0.66 eV while in C2 it is -0.95 eV. On the other hand in case of COCl$_2$, $E_{\text{ad}}$ is found to be -0.42 eV. Magnetic moments of atoms are also found to vary upon gas adsorption indicates the suitability of the HS as a magnetic gas sensor. Our observations suggests the suitability of CrI$_3$-WTe$_2$ HS to respond detection of the toxic gases like BrF$_3$ and COCl$_2$.

I. INTRODUCTION

Gas detection for environmental monitoring has innumerable applications in field such as industries and agriculture, medical diagnosis, military etc.¹,² that utilizes the adsorption of gas molecules over materials. For the great technological perspective, it necessitates the material to have superior physical and chemical stability as well as the accessibility for chip-scale miniaturization of sensing elements for the low cost. Owing to the advent in 2D materials and increasing mass-market applications, the research in the gas sensors field have elevated rapidly due to continuing need for the highly sensitive, selective and faster response and recovery dynamics towards gas adsorption. The first 2D atomic crystal graphene has for a long time enticed because of its extraordinary mechanical and electronic properties. The desired requirement of high surface area, carrier mobility, chemical and thermal stability with low electronic temperature noise, power consumption and higher response time promises graphene to be used in the next generation devices employed in gas sensing and bio-sensing³,⁴. Since each atom in graphene is a surface atom, it results in the ultrasensitive sensor response. It has been seen that the epitaxially grown graphene based sensors are ultrasensitive towards NO$_2$ gases⁴. However, pristine graphene limits its potential upon physical adsorption of common gas molecules⁵–⁷ because of no dangling bonds. Thus for the chemisorptive enhancements, the surface is functionalized through polymers or metallic coating⁸,⁹. Other forms of the graphene like graphene oxide (GO) or reduced GO do serve as a dynamic material for high performance molecular sensors¹⁰. Inspired by the performance of first 2D material, the gas sensing communities captured several hundreds of different 2D materials including elemental allotropes such as silicene, germanene borophene etc., and compound like transition metal dichalcogenides (TMDs)²¹. These have been tremendously successful in detecting even the traces of gas molecules like NO$_2$, SO$_2$, NH$_3$ etc.²²–²⁵. The forte of these materials are their ability to engineer artificial heterostructures (HS). Because of the van der Waal interactions between the HS the lattice mismatching is not there that ultimately minimize the interfacial damages and chemical modification²⁶. Recently the integration between magnetic layer and semiconductors initiate a new generation of advanced functional materials. By manipulating the exchange interactions the electronic structure in 2D materials can be altered²⁷–²⁹. Generally, the gas sensing mechanism is based on the principle of change in electronic properties with gas adsorption. Variation in magnetic properties upon gas adsorption has never been realized. We have investigated here the gas sensing ability of a magnetic HS with the magnetic CrI$_3$ integrated over WTe$_2$ monolayer upon interaction with noxious gases BrF$_3$ and phosgene (COCl$_2$). The BrF$_3$ a hazardous gas used mainly in processing of nuclear fuel. It is corrosive to metals and tissues and irritates the respiratory upon inhalation. On the other hand, phosgene is highly toxic gas used in industries for production of pesticides and its immediate reaction starts even below 2-3 ppm. So far no investigation has been done on BrF$_3$ gas adsorption on sensor layer. Thus this paper focusses on the study of how the gas molecules (BrF$_3$ and COCl$_2$) interfere with the electrical and magnetic properties upon interaction. We have also investigated the nature of adsorption and selectivity towards each gaseous molecules. Practically, a sensor’s recovery time ($R_T$) is crucial for technological applications, thus $R_T$ for the highly selective gas molecule is calculated for this system.

II. COMPUTATIONAL DETAILS

At ambient temperature and pressure conditions the crystal structure of CrI$_3$-WTe$_2$ HS is shown in Fig 1(a). The results presented here are obtained using first-principles approach which based on density func-
tional theory\textsuperscript{41} as implemented in Quantum Espresso package\textsuperscript{42}. Ideally, $\text{CrI}_3$ exists in two crystal structures: 1) $\text{AlCl}_3$ type monoclinic array and 2) $\text{BiI}_3$ type rhombohedral order\textsuperscript{31}. Here we report our findings for monoclinic assembly of $\text{CrI}_3$ deposited over hexagonal structure of WTe\textsubscript{2}\textsuperscript{27}. In order to explore the electronic structure of pure and BrF\subscript{3}/Phosgene gas adsorbed $\text{CrI}_3$-WTe\textsubscript{2} HS we have employed plane-wave ultrasoft pseudopotential method to trace the valance electron interactions. To serve the exchange-correlation potential, generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)\textsuperscript{43} has been implemented. A supercell of $2 \times 2 \times 1$ has been used to construct $\text{CrI}_3$-WTe\textsubscript{2} HS. The cut-off kinetic energy of 760 eV has been applied with $7 \times 7 \times 1$ K-mesh for Brillouin zones sampling. We have used these values after complete optimization process. To avoid any interaction among atomic orbitals we have provided a large vacuum of 17\textdegree A along z direction. The $\text{CrI}_3$-WTe\textsubscript{2} HS has been allowed to fully relax under the convergence of total energy and total forces which are found to be better than 1.0 meV. For gas sensing calculations, we have kept the structural geometry of $\text{CrI}_3$-WTe\textsubscript{2} HS fixed and periodically moved the gas molecules BrF\subscript{3} and Phosgene COCl\textsubscript{2} (one at a time) along z direction in order to acquire the equilibrium distance $d_{eq}$ between the HS and gas molecule. In case of BrF\subscript{3} gas molecule we have studied its interaction with the HS along two different orientations 1) F atom is interacting with HS surface and 2) Br atom is interacting with HS surface. The value of $d_{eq}$ obtained in BrF\subscript{3} in case 1 is $\sim 2.25$\textdegree A whereas in case 2 it is observed to be $\sim 2.04$\textdegree A. Moreover in case of Phosgene gas molecule $d_{eq}$ is found within the range of $\sim 2.32$\textdegree A to $\sim 2.34$\textdegree A. The adsorption energy of gas molecules BrF\subscript{3} (in both cases) and Phosgene adsorbed over $\text{CrI}_3$-WTe\textsubscript{2} HS was defined as:

$$E_{ad} = E_{\text{molecule}}/\text{CrI}_3$-WTe\textsubscript{2}HS$ - E_{\text{CrI}_3$-WTe\textsubscript{2}HS} - E_{\text{molecule}}$$

(1)

where $E_{\text{CrI}_3$-WTe\textsubscript{2}HS} and $E_{\text{molecule}}$ indicates the total ground state energy of HS and gas molecule before adsorption take place respectively and $E_{\text{molecule}}/\text{CrI}_3$-WTe\textsubscript{2}HS shows the total ground state energy of gas molecule adsorbed HS.

### III. RESULTS AND DISCUSSION

In the present investigation we have studied the HS which is comprised of monolayer of $\text{CrI}_3$ deposited over the honeycomb WTe\textsubscript{2} monolayer. Because of the presence of magnetic $\text{Cr}^{3+}$ ion in $\text{CrI}_3$ layer of HS, we have first carried out calculation for two different magnetic configurations namely, ferromagnetic (FM) and antiferromagnetic (AFM) spin states at Cr site. Since the AFM state gives higher energy as compared to FM one, thus FM configuration is the stable magnetic state which is in accordance with the previous reports\textsuperscript{31}. Hence, the further investigations have been done for FM configuration only.

#### A. Structural Analysis

The pristine HS shown in Fig 1(a) is composed of WTe\textsubscript{2} and $\text{CrI}_3$ monolayers. From Fig 1(a) we can see that in WTe\textsubscript{2}, the W ions forms a zig-zag pattern along a-axis resulting in slightly distorted hexagonal symmetry. The Te ions constitute an octahedral environment accompanied with strong intra-layer covalent bonding w.r.t W ions. Whereas, in the $\text{CrI}_3$ layer of HS, $\text{Cr}^{3+}$ ions form a honeycomb lattice. The I- ions create an edge sharing octahedrally coordinated network w.r.t. $\text{Cr}^{3+}$ ions such that the three I- ions are coordinated at the top and bottom layer of Cr ions. The two parent compounds (WTe\textsubscript{2} and $\text{CrI}_3$ monolayer) are vertically stacked together along c-axis to form a $\text{CrI}_3$-WTe\textsubscript{2} HS with interfacial bonds linking I and Te ions. The $(\text{Te}-\text{I})$ average bond length at the interface is 2.61\textdegree A. An overall compression along c-axis has also been observed among the parent compounds of the HS which may affect its electronic structure. Table I. displays the comparison of experimental and calculated bond length in HS.

|                          | Exp (\textdegree A) | Calculations (\textdegree A) |
|--------------------------|---------------------|-------------------------------|
| W-W                      | 3.6                 | 3.2                           |
| W-Te                     | 2.769               | 1.448                         |
| Cr-Cr$^{3+}$             | 3.96                | 2.16                          |
| I-I$^{3+}$ (axis)         | 3.86                | 2.04                          |
| Cr-I$^{3+}$              | 2.72                | 1.43                          |

From the results obtained in Table I we observed a net compression in the HS (i.e. $< 45\%$) except for $(W-W)$ ($\sim 11\%$) due to its relatively heavy atomic mass which obstructs any significant variation in its bond length as compared to other atoms. Hence the compression is emerging due to the interfacial bonds formed among the parent compounds of the HS (i.e. WTe\textsubscript{2} and $\text{CrI}_3$). These bonds are occurring from the charge transfer from Te ions to I ions (charges flows from low electronegativity $(\text{Te}= 2.1$ Pauling scale$)$ to high electronegativity $(I= 2.6$ Pauling scale$)$). This process of bond formation at the interface of HS in turn results in compression of bond...
length among the atoms upon optimization. The electronic properties of the HS may get influenced due to this compression which has been discussed in detail in the following section. The interaction of BrF₃ on HS can occur through two possible orientations: by forming an interfacial bond between (1) F and HS as shown in Fig 1(b) (C1 configuration), (2) Br and HS as shown in Fig 1(c) (C2 configuration). The \( F - Br - F \) bond angle is \( 86^\circ \) with the \( Br - F \) bond length along axial and equatorial plane as 1.72 Å and 1.81 Å respectively. The equilibrium distance \( d_{eq} \) in C1 and C2 case is 2.25 Å and 2.04 Å respectively. For the COCl₂ gas the bond angle and bond length is \( 124^\circ \) \( (Cl - C - O) \) and 1.76 Å \( (Cl - C) \), 1.19 Å \( (C - O) \) respectively. Unlike BrF₃, only single orientation of COCl₂ has been considered (CI linked with HS) as presented in Fig 1(d) due to larger reduced mass of Cl w.r.t O (about \( \sim 10\% \)) ions. The \( d_{eq} \) varies from 2.32-2.34 Å for this case.

**B. Electronic Structure**

In order to investigate the gas sensing effect of the HS, we have first studied the electronic density of states (DOS) prior to the gas adsorption. When no gas molecules were adsorbed, the total DOS of HS (Fig 2(a)) shows a spectral weight of 11.83 states/eV at Fermi level (FL). Small amount of metalliclicity is induced because of Cr-3d and I-5p orbitals of CrI₃ layer of HS. This induced metalliclicity is emerging from the compressed bond length of the atoms upon optimization as discussed above. Whereas the WTe₂ counterpart displays an insulating behaviour with a gap of 1.31 eV between majority and minority spin channels. Experimentally, CrI₃ layer is insulating in nature but in CrI₃-WTe₂ HS, half-metallicity is observed. This might be due to the electron doping of CrI₃ layer induced by WTe₂ as reported previously. Near FL (\( E = -0.48 \) eV) only contributions from W-5d orbital and Te-5p orbital dominates whereas Cr-3d and I-5p orbital state lies 1.32 eV below FL. For pristine HS the total bandwidth for metallic state is observed to be 0.02 eV (Fig 2(a)) with the majority spin carriers separated from minority spin carriers by 0.88 eV.

1) BrF₃ Adsorbed HS:

When BrF₃ gas molecule is adsorbed on the HS the metalliclicity is enhanced in both the orientations which can be seen from Fig 2(b) and Fig 2(c). In C1 configuration (Fig 2(b)), when F directly forms an interfacial bonding with HS, the bandwidth increases to 0.67 eV. At FL, the dominant contribution is coming from Cr-3d states with the spectral weight for up and down spin density being 0.85 states/eV and 1.56 states/eV respectively. Feeble participation of W-5d (up 0.33 states/eV, down 0.77 states/eV) and Te-5p (up 0.14 states/eV, down 0.21 states/eV) and I-5p states(up 0.23 states/eV, down 0.37 states/eV) are also observed at FL. The adsorbed BrF₃ gas molecule in C1 have enhanced spin up DOS at FL.
In principle, the charges should flow from Br (low electronegativity) to F (high electronegativity) ions but due to the large (Br – F) bond length (< 1.7 Å) the charge hopping takes place at slower rate resulting in higher spectral weight of Br (2.08 states/eV) ion as compared to F (0.97 states/eV) ions at FL. On the other side for C2 configuration (Fig 2(c)), when Br interacts directly with HS, the bandwidth further intensifies to 0.76 eV at FL. Likewise in C1, here also the Cr-3d states are pronounced at FL with spectral weight of 2.08 states/eV as compared to C and HS, we have studied the charge density results of a) C1 configuration of BrF3 adsorbed HS showing the charge transfer network among the HS and gas molecule. This also confirms the presence of chemisorptive nature of bond which has influenced the electronic structure of pristine HS. b) C2 configuration of BrF3 adsorbed HS. The charges are appeared to flow from I ions to the gas molecule. Among all the atomic species present in the HS and the gas molecule, maximum electronegativity is possessed by F ions hence charges will get accumulate at F ions site.

In HS to the gas molecule which causes the accumulation of carriers at COCl2. The above observations suggest that C13-WTe2 HS serve as a potential gas sensor for BrF3 and COCl2 gas molecule.

C. Magnetic Properties

In HS the magnetic contribution is coming due CrI3 layer which has FM ordering with total spin magnetic moment of 5.35 μB. And the magnetic moment per Cr
and I ions are 2.86 \( \mu_B \) and 0.041 \( \mu_B \) respectively. This is in good agreement with the saturation moment (3.1 \( \mu_B/\text{Cr} \)) measured experimentally\textsuperscript{31}. The low magnetic moment of I ions is due to the transfer of unpaired 4s electron from Cr to I, resulting in stable 5p states. This delocalization of charges causes reduced moment at I-site. On the other hand, the WTe\(_2\) layer in HS remains non-magnetic. With the exposure of BrF\(_3\) gas molecule in C1 configuration, the delocalization effects dominate in Cr ions resulting in decreased magnetic moment. The Br and F ions on the other hand acquire charges from HS have higher mag moment (0.088 \( \mu_B \) for Br and 0.005 \( \mu_B \), 0.144 \( \mu_B \), 0.0268 \( \mu_B \) per F ion) as compared to Cr\(^{3+}\) (0.009 \( \mu_B \)). As discussed above that due to difference in (Br – F) bond lengths uneven charge flow takes places to form dissimilar magnetic moment per F ion. In C2 configuration when Br directly bonded with HS layer total magnetic moment is almost negligible. This is in accordance with the DOS of C2 (Fig 2(c)) where the net reduction in spectral weight was observed. Due to the continuous charge transfer path (I-Br-F) the delocalization of electrons causes the moments to drop. The same scenario has been observed when Phosgene is exposed to HS. The overall reduction in magnetic moment is observed here as well. The variation in magnetic moments of the HS upon interaction of gas molecules suggests that CrI\(_3\)-WTe\(_2\) HS can be used as a magnetic gas sensor as well as resistive gas sensor. There are many studies over the latter type but only few experimental studies are performed on the former type of gas sensor which detects the perturbation in the magnetic properties when gas molecules interact with the sensor material\textsuperscript{33}. A few magnetic gas sensors so far studied are nanoparticles of CuFe\(_2\)O\(_4\) which was used for the detection of volatile organic compounds (VOCs)\textsuperscript{34}, Co/ZnO nanorods to detect H\(_2\) and CO molecules\textsuperscript{35}, Co/ZnO hybrid nanostructures for the detection of C\(_3\)H\(_6\)O, CO and H\(_2\) target gases\textsuperscript{36} etc.

### D. Adsorption and recovery time

The adsorption energy describes the nature of stability among adsorbent (HS) and adsorbate (gas molecule). The process can take place in two modes (1) physisorption: which involves weak van der Waals forces between two reacting species. The electronic properties of adsorbent is barely perturbed during this mechanism; (2) chemisorption: here actual involvement of chemical bonds between species exists. This also require minimum activation energy to initiate the process. In C1 with BrF\(_3\) adsorption on HS, the adsorption energy is -0.66 eV while in C2 it increases to -0.95 eV. The increasing adsorption rate by 30% suggests the comparatively strong chemisorptive nature in C2. The existence of strong covalent bonding between HS and BrF\(_3\) (C1 and C2) have been observed from charge density results shown in Fig 3(a) and Fig 3(b). Similar studies for COCl\(_2\) adsorption shows the chemisorptive character but the \( E_{ad} (-0.42 \text{ eV}) \) is relatively smaller than that from BrF\(_3\) interaction. It is evident that as \( \alpha_{eq} \) increases, \( E_{ad} \) energy decreases. Thus, the higher \( \alpha_{eq} \) for COCl\(_2\) case is marked by decrease in \( E_{ad} \). Though the relative stability in COCl\(_2\) case is lesser than BrF\(_3\) but from previous literature COCl\(_2\) adsorption on BN nano tube (BNNT), BN nano rod (BNNR) and borophene reported to have \( E_{ad} = -0.18 \text{ eV}, -1.058 \text{ eV} \) and \(-0.306 \text{ eV} \) respectively\textsuperscript{37,38}. Hence, COCl\(_2\) adsorption on CrI\(_3\)-WTe\(_2\) HS has shown better performance as compared to previous reports with an exception of BNNR.

The recovery time \( R_T \) of a sensor is based on how fast the sensor retrieve its initial state. Based on the Arrhenius theory the sensor recovery time\textsuperscript{39} is related by:

\[
R_T = \nu^{-1} e^{-E_{ad}/kT}
\]

where, \( \nu \) is the operational frequency, \( E_{ad} \) is adsorbate energy, K is Boltzmann constant and T is the sensor’s operational temperature. For different attempt frequencies, the sensor’s recovery rate is affected as tabulated in Table 2. Under UV illumination the HS is showing faster \( R_T \) for all the cases. The recovery rate depends on the nature of adsorption. With relatively weak chemisorptive effect of COCl\(_2\) gas on HS, fastest recovery time is achieved.

### IV. CONCLUSIONS

We have theoretically investigated a new 2-dimensional CrI\(_3\)-WTe\(_2\) HS in the present work in order to explore the possibility as a multisensor (i.e. resistive and magnetic). Our results shows that upon interaction with the gas molecules BrF\(_3\) and COCl\(_2\) with HS the electronic as well as magnetic properties of pristine HS get altered. We have also determined that how swiftly the HS can get recover after detaching the gasous species from it by means of recovery time. We found that under UV illumination ultrafast recovery time is presented by the HS i.e. \(< 0.14 \text{ fs} \). Hence we conclude that CrI\(_3\)-WTe\(_2\) HS shows the chemisorptive character but the \( E_{ad} (-0.42 \text{ eV}) \) is relatively smaller than that from BrF\(_3\) interaction.

| \( E_{ad}(eV) \) | \( R_T \) (fs) | \( R_T \) (Visible) (fs) | \( R_T \) (UV) (fs) |
|---|---|---|---|
| BrF\(_3\) (C1) | -0.66 | 1302 | 13.02 | 0.13 |
| BrF\(_3\) (C2) | -0.95 | 1460 | 14.6 | 0.14 |
| COCl\(_2\) | -0.42 | 1180 | 11.8 | 0.12 |
offers it self as a multisensor for the detection of highly toxic gases like BrF₃ and COCl₂.

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