Supporting Information

Electron density modulation of metallic GeSb monolayer by pnictogen doping for excellent hydrogen evolution

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Table Caption

Table ST1. Calculated Löwdin charges for each atom of ML with and without Hydrogen adsorption.

Figure Captions

Figure SF1. Top and Side views of charge density contour plot for (a) pristine and hydrogen adsorbed 2x2 GeSb monolayer at (b) Ge-top site (c) Hollow site and (d) Sb-top site, respectively.

Figure SF2. Top and Side view of charge density plot of (a) As-doped GeSb ML and (b) Sb-H site (c) Hollow-H site, (d) Sb -H site hydrogen adsorbed GeSb monolayer respectively.

Figure SF3. Top and Side views of charge density contour plot of Bi-doped GeSb ML before (a) and after hydrogen adsorption over (b) Sb-top site (c) Hollow site and (d) Bi-top site, respectively.

Charge Density Contour and Charge transfer Analysis

Pristine and As-Bi doped GeSb ML

To gain better understanding of interaction taking place between hydrogen and the monolayer (ML) and to confirm the bond formation between them, we have performed charge transfer and charge density analysis of the pristine and As/Bi doped GeSb ML before and after adsorbing hydrogen along the preferential plane. Before adsorption of hydrogen over GeSb ML, we can observe charge distribution between Ge and Sb atoms with slightly more charge accumulated near the Sb sites (see Fig. SF1(a)). This can be expected due to the higher

electronegative nature of the Sb atoms. Further, the charge sharing taking place between them can be attributed to covalent bond formation. In the case of As doped-GeSb, we observed that the As atom shows polar-covalent bonding formation with Ge atom as it exhibits highest electronegativity as compared to Ge, Sb, Bi and H atoms. Therefore, more charge accumulation is observed near As atom. Moving towards the next case, the Bi-doped GeSb ML shows similar trend as that of pristine ML due to their similar electronegativity.

Hydrogen adsorbed over Pristine and As/Bi doped GeSb ML

Apart from the pristine and As/Bi doped GeSb ML, we further analysed the difference in the charge sharing and bond formation profiles of the ML atoms subjected to hydrogen adsorption by computing charge density contour and L**ö**wdin charge analysis for pristine, As/Bi doped GeSb ML after adsorption of hydrogen over three distinct sites.

At first, we have analysed the charge transfer and charge density of the hydrogen adsorption over three distinct sites; i.e., Ge-top, Hollow and Sb-top sites for pristine ML. We found that the electronic charge of the hydrogen adsorbed Ge atom decreases from 4.14*e* to 4.06*e*, and that of hydrogen increases from 1.0*e* to 1.63*e*, suggesting transfer of charge from ML to hydrogen atom leading to polar-covalent character in line agreement with the charge density contour plot (see Fig. SF1(b)). In the case of Hollow site, the analysis of interaction chemistry suggests transfer of charge from ML to hydrogen atom via markable reduction in the charge of Sb atom from 4.81*e* to 4.59*e*. The reduction in charge of Sb atom results in enhancement of the charge of hydrogen with magnitude 1.71*e* which indicates strong interaction between the ML and hydrogen showing polar-covalent character. Further, the modified Löwdin charges in Sb-top case are 4.58*e* and 1.70*e* on Sb and H atoms, respectively which also confirms the polar covalent character. In a nut-shell, we observed, more charge density towards hydrogen in all three sites indicating polar-covalent character of the system

as the electronegativity of hydrogen is more as compared to Ge and Sb atoms (see Figure SF1(b-d)).

We found the interesting charge modulations due to the incorporation of As atom in GeSb ML due to its higher electronegativity. The Löwdin charge analysis Ge-top case for As doped ML suggests reduction in the charges acquired by all atomic species with magnitudes 3.95*e* to 3.84*e* for Ge, 5.70*e* to 5.62*e* for As and, from 4.77*e* to 4.67*e* for Sb, respectively. This modulation in the charge is counter balanced by the hydrogen atom with significant rise in its intrinsic charge from 1*e* to 1.79*e* hydrogen adsorbed over the Ge atom shows the polar-covalent character. The Hollow site of As-doped GeSb ML, shows similar results with slight modification in the charge magnitudes of Ge (3.91*e*), As (5.61*e*), Sb (4.63*e*) and H (1.66*e*) atoms which is attributed to charge transfer between the ML and H. Further, looking at the charge transfer mechanism, in the As-top case, it is observed that all atoms acquire moderately depleted charges with magnitude 3.9*e*, 5.64*e* and 4.66*e* for Ge, As and Sb atoms, respectively. The depleted charge is shared by the adsorbed hydrogen atom with net magnitude of 1.5*e*; this suggests balanced transfer of charge from ML to hydrogen which forms polar covalent bond

The overall analysis for As doped ML under H-adsorption suggests that there is structural distortion in case of H-adsorbed over Ge-site due to steric effect between H and Ge atoms with polar-covalent bond forming between Sb and H, whereas in the case of Hollow (As-top) site, it prefers to be at the top of (Sb) As atom. This reduces the steric effect leading to minimal structural changes and shows polar-covalent character. The ML shows charge sharing between adsorbate and adsorbent which is more as compared to other considered systems due to change in their electronegativity which leads to more covalent character instead of polar-covalent character. Furthermore, the As-top site adsorbed hydrogen shows strong interaction with the ML suggesting covalent nature of bonding (see Fig. SF2 (d)).

The hydrogen adsorption over the Bi doped GeSb ML shows similar trend as pristine ML, as the electronegativity of Bi atom differs very slightly than Ge and Sb atoms. We observe that the significantly reduced Löwdin charges over all atoms of the ML are Ge (4*e*), Bi (4.62*e*) and Sb (4.73*e*) are compensated by the enhanced charge on the H (1.83*e*). Further, the charge density contour plot (see Fig. SF3(b)) indicates depletion between the shared electronic orbitals of Ge-Sb pair near adsorption site subjected to H adsorption in Ge-top case. In Hollow case, the Löwdin charge analysis suggests that the average charges on the atoms Ge, Bi and Sb get reduced with magnitudes 4.09e, 4.59e and 4.70e, respectively. In the Bi-top case, analysis of charge transfer indicates that except for the Ge atom which possesses 4.10*e* charge is slightly more than the Hollow site H-adsorbed case, and all remaining atoms possess similar magnitudes of charges. This causes reduction in the charge of the adsorbed H-atom from 1.7*e* (Hollow site) to 1.69*e*. At the end, validation of the bond formation is done by the charge density contour plot that clearly shows overlapping atomic orbitals of H and Bi atoms (see Fig. SF3).We observed that the hydrogen prefers to be at Bi site in all three configurations. Moreover, markable distortion is observed when the H-atom resides in between the planes of Ge and Bi atoms due to the increment of the steric effect in the system; instead, when H resides the on the top of the Sb-atom the steric effect of the system is reduced making the structure stable. In all the three cases of Bi-doped GeSb ML, we observed the polar-covalent type bond formation with the adsorbed hydrogen.

Table ST1. Calculate Löwdin charges for each atom of ML with and without Hydrogen adsorption

Atom	GeSb ML	H-Adsorbed over site			As doped GeSb ML	H-Adsorbed over site			Bi doped GeSb ML	H-Adsorbed over site		
		Ge-top	Hollow	Sb-top		Ge-top	Hollow	As-top		Ge-top	Hollow	Bi-top
Ge	4.14*e*	4.06*e*	4.12*e*	4.13*e*	3.95*e*	3.84*e*	3.91*e*	3.9*e*	4.14*e*	4*e*	4.09*e*	4.10*e*
Sb	4.81*e*	4.64*e*	4.59*e*	4.58*e*	4.77*e*	4.67*e*	4.63*e*	4.66*e*	4.80*e*	4.73*e*	4.70*e*	4.70*e*
As/Bi	-	-	-	-	5.70*e*	5.62*e*	5.61*e*	5.64*e*	4.81*e*	4.62*e*	4.59*e*	4.59*e*
H	1*e*	1.63*e*	1.71*e*	1.70*e*	1*e*	1.79*e*	1.66*e*	1.5*e*	1*e*	1.83*e*	1.7*e*	1.69*e*

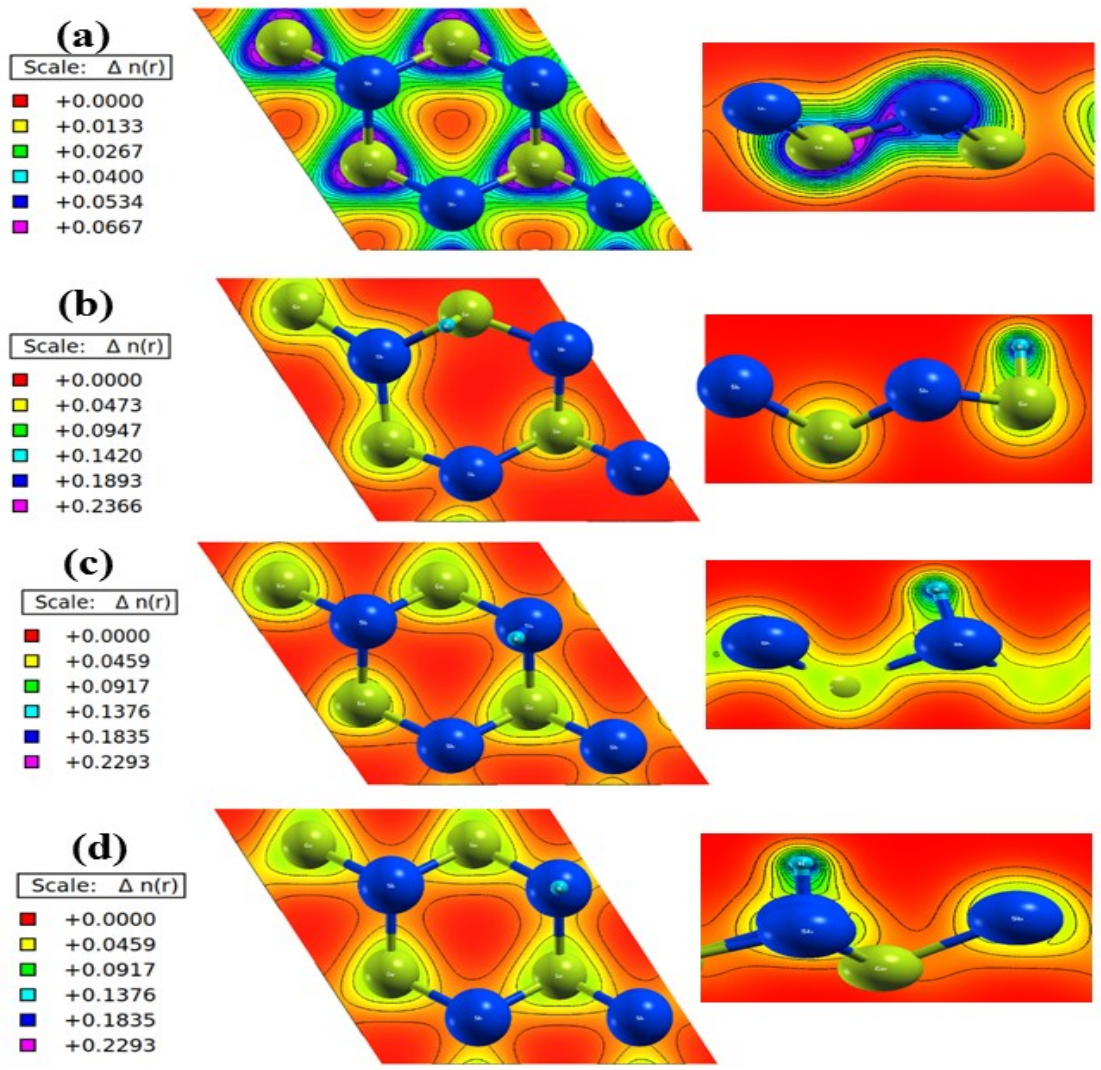

Figure SF1. Top and Side views of charge density contour plot for (a) pristine and hydrogen adsorbed 2x2 GeSb monolayer at (b) Ge-top site (c) Hollow site and (d) Sb-top site, respectively.

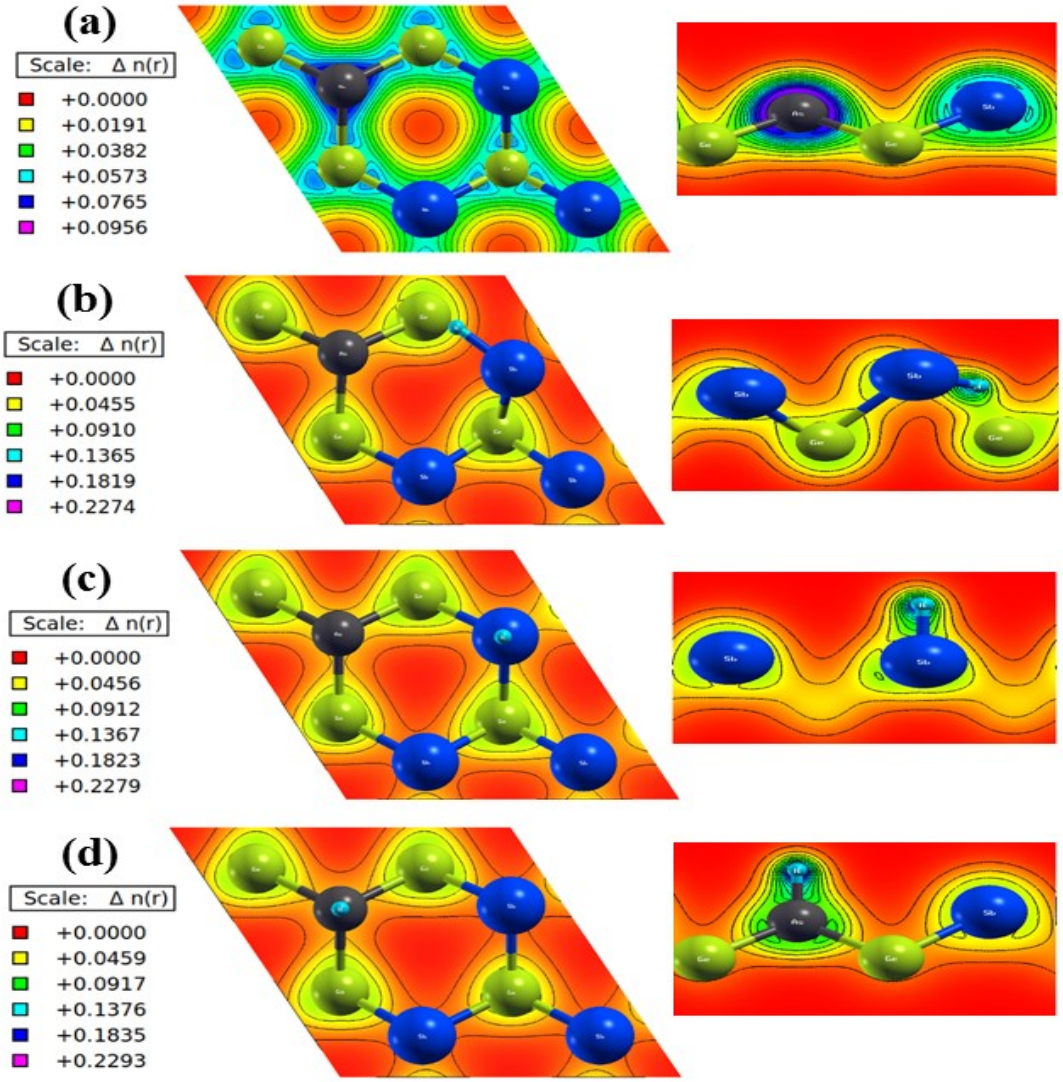

Figure SF2. Top and Side view of charge density plot of (a) As-doped GeSb ML and (b) Ge-H site (c) Hollow-H site, (d) As -H site hydrogen adsorbed GeSb monolayer respectively.

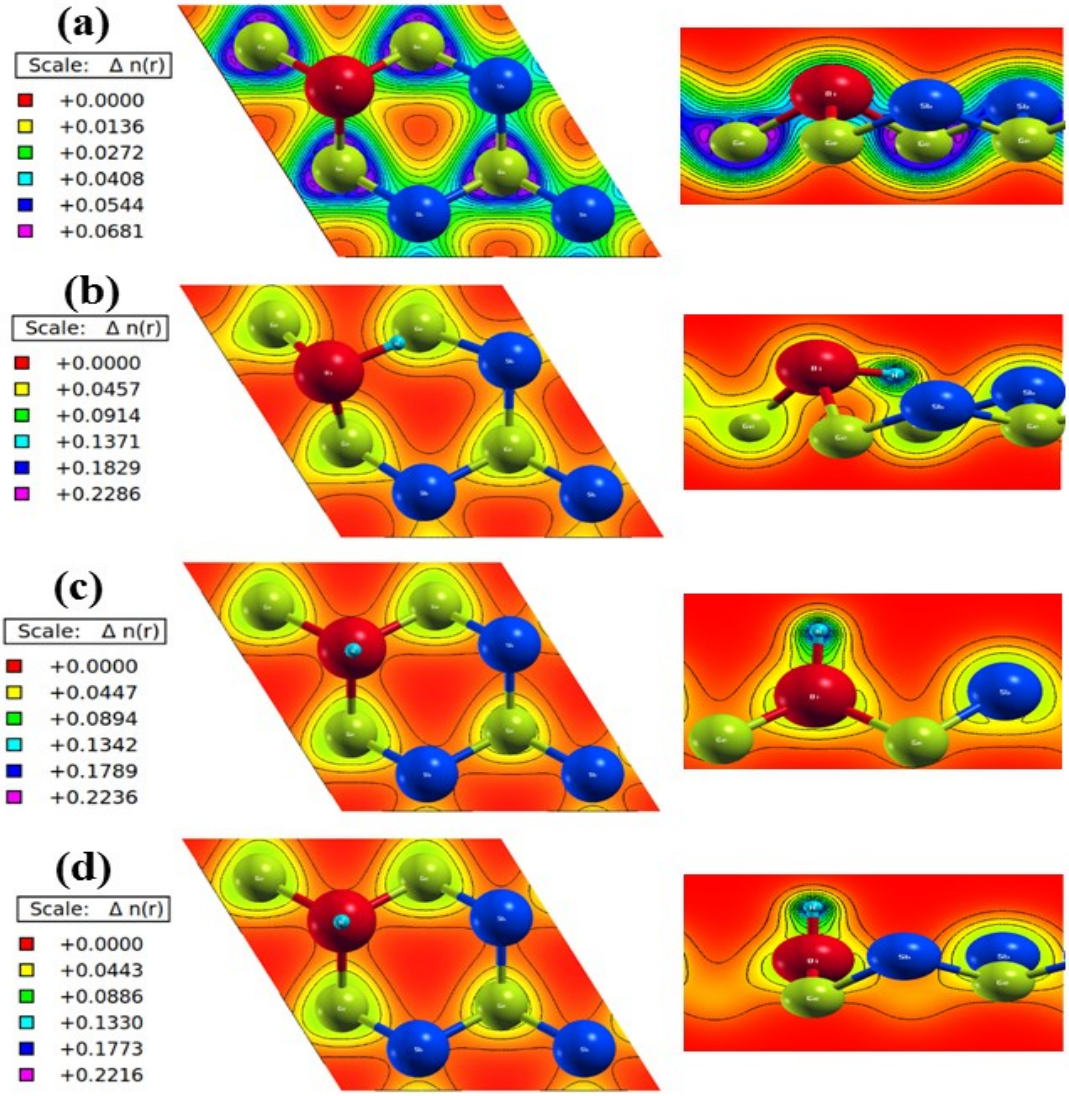

Figure SF3. Top and Side views of charge density contour plot of Bi-doped GeSb ML before (a) and after hydrogen adsorption over (b) Sb-top site (c) Hollow site and (d) Bi-top site, respectively.