## **Supporting Information**

## Phase Segregation Behavior of 2D Transition Metal Dichalcogenide Binary Alloys Induced by Dissimilar Substitution

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Fig. S1: Optical micrographs of the samples grown from different precursor ratio showing various morphologies. Scale bar =  $10\mu m$ .



Fig. S2 : XPS data for binary alloy grown from precursor ratio 1:4 and ternary sample grown from precursor ratio 1:4:8.

Figure S2 shows the XPS peaks for Mo 3d, W 4f, Sn 3d, and S 2p. Mo 3d binding energy peaks show splitting into two peaks, i.e., Mo  $3d_{3/2}$  and Mo  $3d_{5/2}$ , attributing to the Mo<sup>4+</sup> state. An additional peak at 227.14 eV corresponding to S 2s is also present. Similarly W 4f binding energy also splits into two peaks, namely,  $4f_{5/2}$  and  $4f_{7/2}$ , corresponding to W<sup>4+</sup>. In this case too an additional peak at 38.1 eV corresponding to W  $5p_{3/2}$  is also seen. Sn 3d binding energy shows two peaks,  $3d_{3/2}$  and  $3d_{5/2}$ , corresponding to 495.53 and 487.13 eV, respectively, confirming the Sn<sup>4+</sup>

binding state. However, these peaks are present only in the case of ternary alloy composition, thus confirming its presence. In addition to this, an additional broad auger electron peak at 492.52 eV attributing to Na KLL is present in both binary and ternary alloys which may be the result of contamination in the XPS chamber. At last, the S 2p binding energy plot shows a doublet at 162.74 eV, S  $2p_{3/2}$ , and 163.87 eV, S  $2p_{1/2}$ , confirming the presence of the S<sup>2–</sup> state. Overall, in Mo 3d, W 4f, and S 2p we see a shift toward the higher energy side in the ternary alloys due to the addition of Sn.

## Growth mechanism (Fig. 4g of main text):

For the binary precursors of MoO<sub>3</sub> and WO<sub>3</sub>, the molar ratio of the precursors in the gas phase is dependent on the vapor pressure of these precursors at the growth temperature of  $800^{\circ}$ C and the time evolution of this gaseous phase concentration determines the growth of alloys and heterostructures. For low concentrations of W (1:2 ratio of MoO<sub>3</sub> : WO<sub>3</sub>), MoS<sub>2</sub> lattice is formed preferentially first followed by an alloy of Mo<sub>x</sub>W<sub>1-x</sub>S<sub>2</sub> alloy as the outer region as the Mo concentration in the growth atmosphere reduces leading to a lateral heterostructure of MoS<sub>2</sub>/(Mo+W)S<sub>2</sub>. With increasing concentration of W in the growth atmosphere (1:4 case), we obtain a uniform alloy throughout as the molar ratio of Mo and W is maintained throughout the growth time. On further increasing the W concentration during growth, we obtain a lateral heterostructure of (Mo+W)S<sub>2</sub>/WS<sub>2</sub> as during the initial growth phase we have both Mo and W precursors in the growth atmosphere followed by a final phase of growth where Mo precursor is almost depleted.

The growth scenario becomes more interesting with the inclusion of a Sn precursor into the growth environment. As explained from the DFT calculations, Sn substitution in MoS<sub>2</sub> lattice generates a localized strain field which acts as a nucleation site for secondary layer growth. At lower concentrations of Sn in the growth atmosphere (1:1:1), uniform alloys of  $Mo_{1-x}W_xS_2$  were observed. To observe significant changes in growth scenario the concentration of Sn precursor was increased to eight times where there is significant amount of Sn precursor in the gaseous state during growth to influence the growth kinetics of (Mo+W)S<sub>2</sub>. For the growth scenario where the W concentration is less (1:2:8 of MoO<sub>3</sub> : WO<sub>3</sub> : SnO<sub>2</sub>), there is preferential substitution of Sn in the MoS<sub>2</sub> lattice which prevents W substitution in the MoS<sub>2</sub> lattice. This is followed by growth of WS<sub>2</sub> as an outer layer with substituted Sn. Due to the strain field of Sn, if the growth is allowed to

continue for larger time, then bi/multilayers start nucleating and growing from Sn substituents. We do observe that under optimized growth conditions very good phase separation is obtained between the  $MoS_2$  and  $WS_2$  regions without compromising on the quality of the heterostructures as evident from the PL data obtained from these crystals. With further increase in W concentration, we start observing alloys with microscopic phase segregation of  $MoS_2$  and  $WS_2$  lattices along with Sn substitution which promotes second layer growth. But as the Mo in the environment depletes we obtain preferential  $WS_2$  growth at the outer edges. On increasing the W concentration even more we obtain preferential growth of  $WS_2$  multilayers favored due to Sn substitution.



Fig S3: Calculated and fitted mixing energies of the 2D  $Mo_{1-x}Sn_xS_2$  alloy in the H phase per MX<sub>2</sub> unit. Large red circles show values obtained with DFT-LDA calculations, and small blue points show values from the cluster expansion fitting. Maximum mixing energy of 0.72 eV/MX<sub>2</sub> is at x=1/3.



## **References :**

1. Kresse G, Furthmüller J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B* 1996, **54:** 11169--11186.