

SUPPLEMENTARY INFORMATION

Abnormal electronic structure of chemically modified n-InP(100) surfaces

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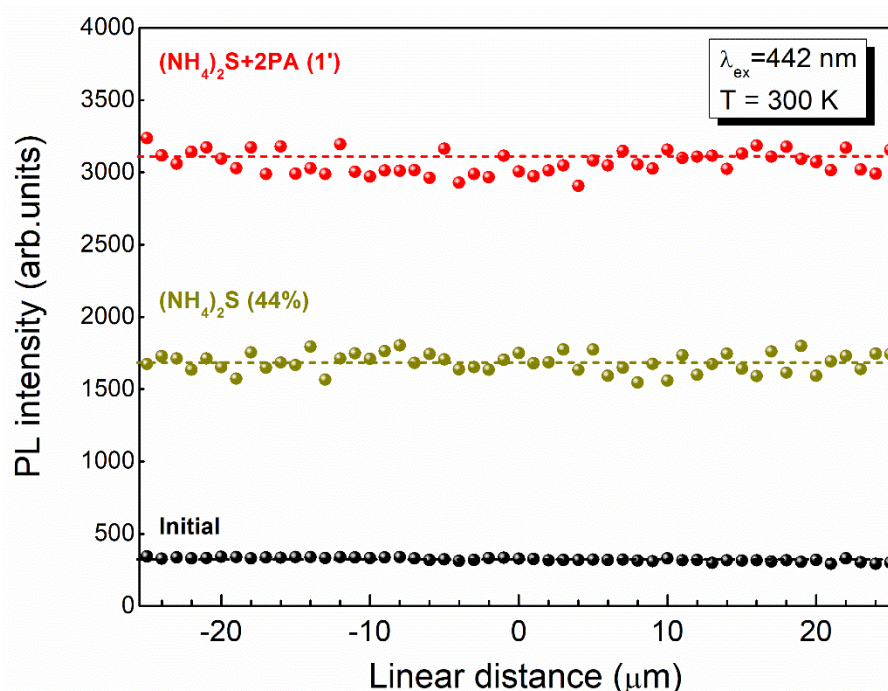


Fig. S1. Spatial distribution of the photoluminescence intensity over the native-oxide-covered n-InP(100) surface before and after passivation with indicated sulfide solutions. Dashed lines indicate average PL intensity values used in Fig. 1a and Table 1. Zero on the distance axis denotes an arbitrary point approximately in the middle of each sample.

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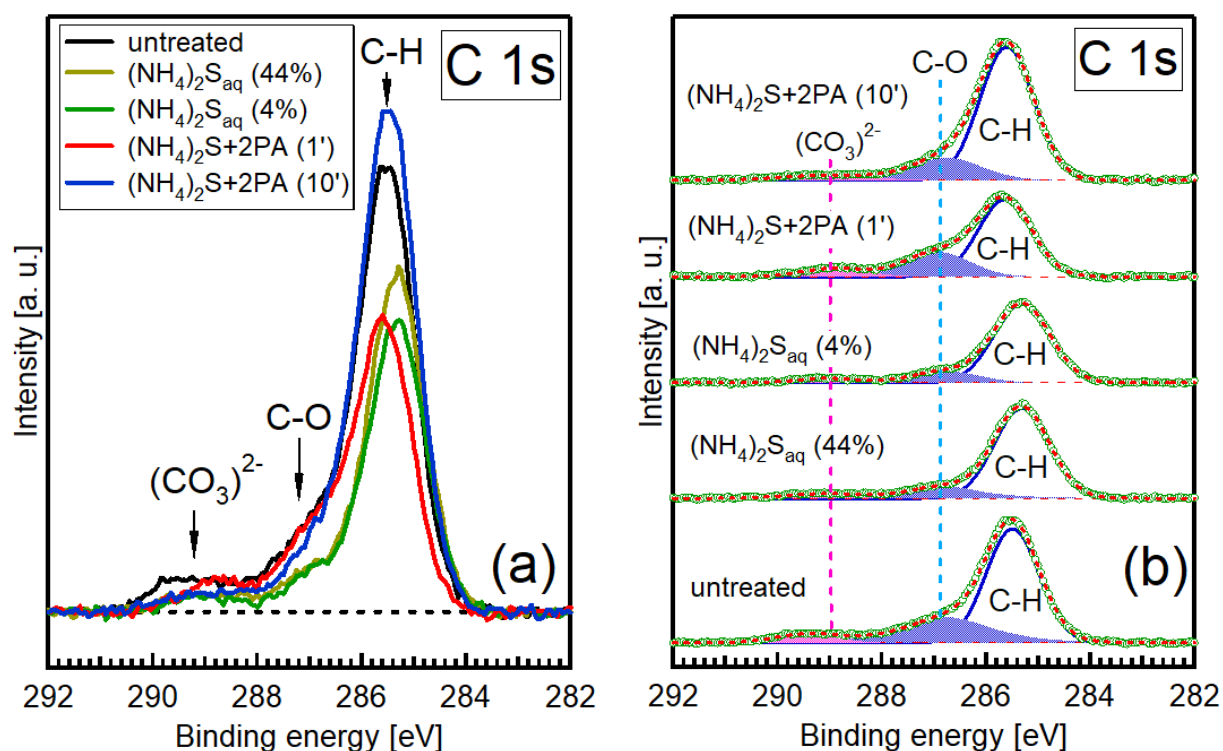


Fig. S2. C 1s core level spectra (a) and their fitting (b) for different n-InP(100) surfaces under investigation. Spectra are fitted with 3 components that can be assigned to surface carbonates $(\text{CO}_3)^{2-}$, oxy-carbons C–O, and hydrocarbons C–H.

Table S1. Calculation of indium oxide content in total O 1s spectra.

Sample treatment	C–O _x /C 1s	C–O _x /In 4d	Oxides/In 4d = (O 1s–C–O _x)/In 4d
Initial (untreated)	0.34	0.55	0.83–0.55 = 0.28
$(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%)	0.19	0.14	0.16–0.14 = ~0.02
$(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%)	0.21	0.33	0.32–0.33 = ~0
$(\text{NH}_4)_2\text{S} + 2\text{PA}$, 10 min	0.23	0.39	0.39–0.35 = ~0
$(\text{NH}_4)_2\text{S} + 2\text{PA}$, 1 min	0.35	0.32	0.29–0.32 = ~0

Column [C–O_x/C 1s] is the ratio of C–O and carbonates $(\text{CO}_3)^{2-}$ components to the total area of the C 1 s spectra (Fig. S2b). Column [C–O_x/In 4d] is obtained by multiplication of the column [C 1s/In 4d] from Table 2 by column [C–O_x/C 1s] from Table S1. The column [C–O_x/In 4d] is a rough estimation of the amount of oxygen atoms involved to bonding with surface carbon atoms. The other oxygen atoms (column [Oxides/In 4d]) are supposed to be involved to bonding with surface In (and phosphorous) atoms. Thus, the present estimations show that roughly all oxygen remaining at the surface after treatment with any of the sulfide solutions belongs to carbon-related contamination rather than to passivating layer.

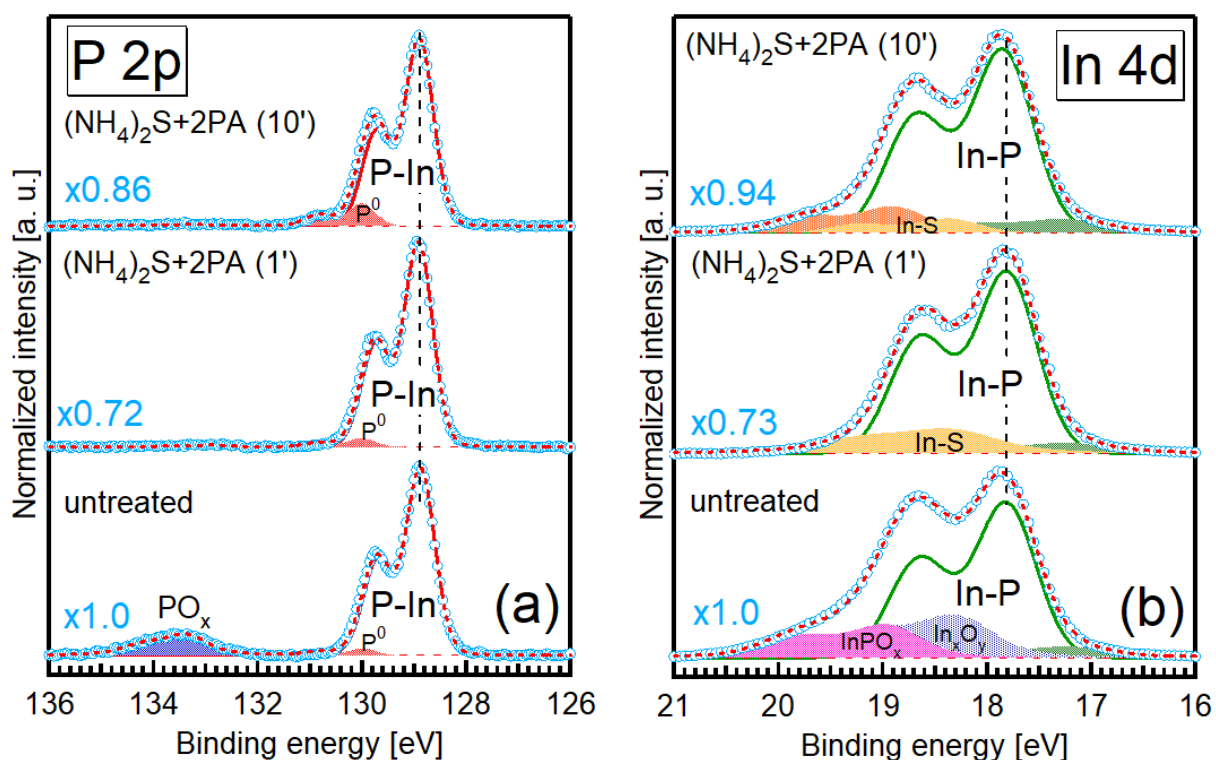


Fig. S3. Fitting of P 2p (a) and In 4d (b) core level spectra of the native-oxide-covered n-InP(100) surface measured before and after treatment with diluted (4%) solution of aqueous ammonium sulfide (NH₄)₂S in 2-propyl alcohol (2PA) for 1 and 10 min. Dashed red line is a fit with indicated components. Spectra are normalized to maximum intensity. Scaling factors are given with respect to the intensities of the spectra of untreated n-InP(100) surface.

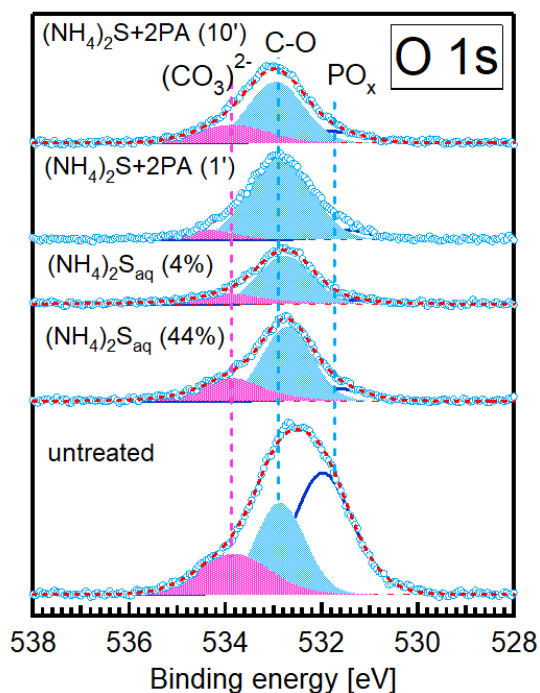


Fig. S4. Fitting of O 1s core level spectra of the native-oxide-covered n-InP(100) surface measured before and after treatment with different sulfide solutions. Dashed red line is a fit with indicated components.

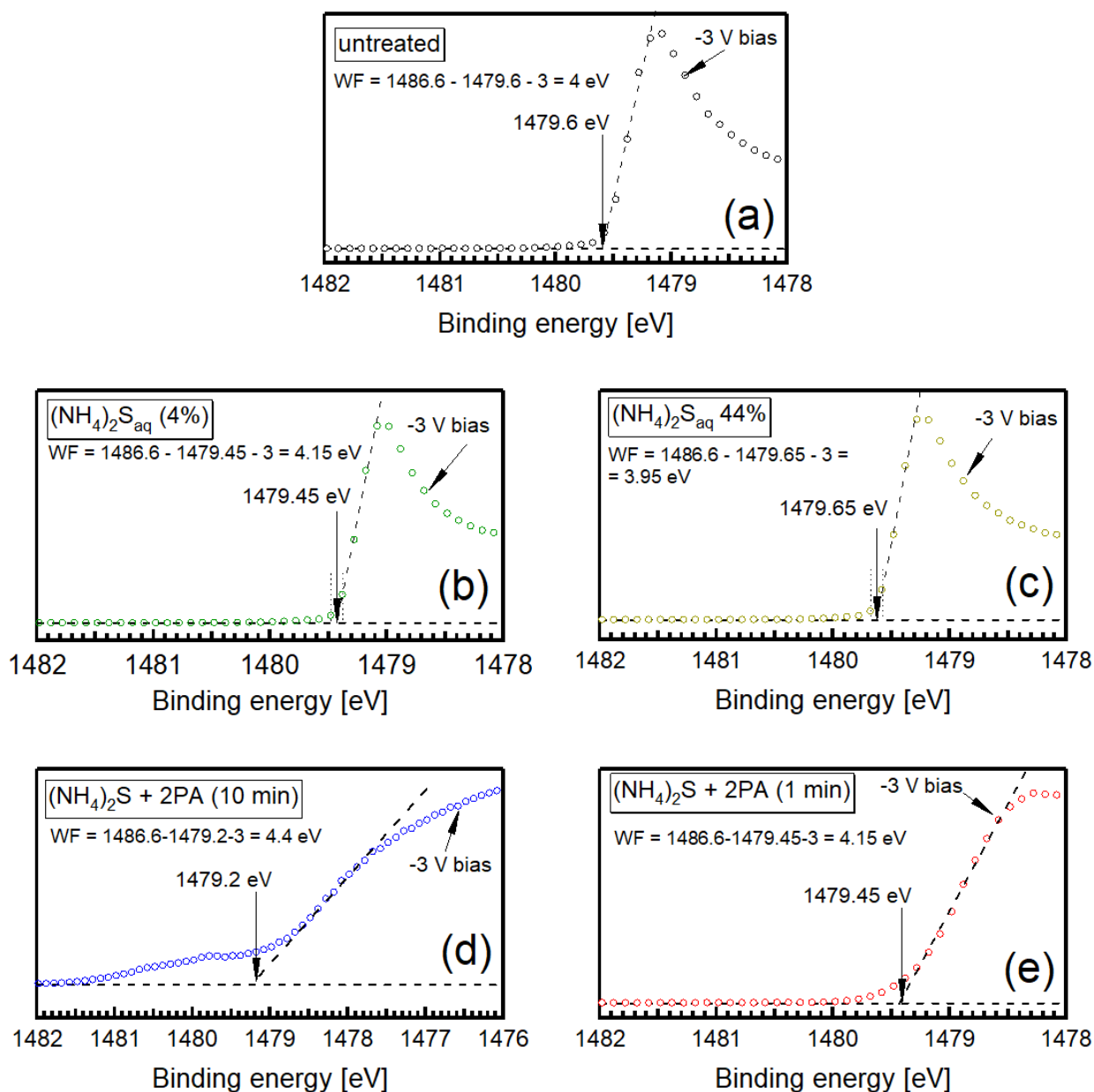


Fig. S5. Secondary electron cutoffs of the native-oxide-covered n-InP(100) surface measured using a bias of -3V before (a) and after (b–e) treatment with different sulfide solutions. The cutoff binding energy ($\text{BE}_{\text{cutoff}}$) shown in each figure is determined by linear extrapolation of the secondary edge to zero signal level. The work function (WF) is determined as the cutoff kinetic energy (excitation energy ($=1486.6 \text{ eV}$) $- \text{BE}_{\text{cutoff}}$) minus bias applied to the sample (3 V in the present case).

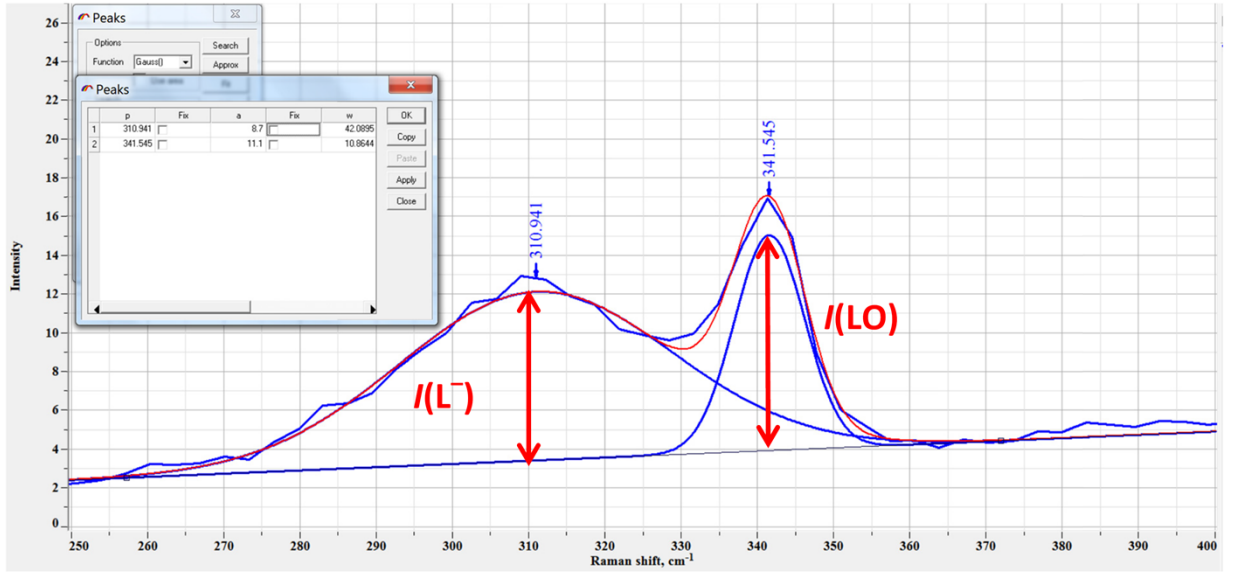


Fig. S6. Portion of the Raman spectrum of the native-oxide-covered n-InP(100) surface shown to indicate the procedure for determination of the $I(LO)/I(L^-)$ ratio. Fitting of Raman spectra and calculation of the $I(LO)$ and $I(L^-)$ peaks intensity values for all samples was performed using LabSpec (Version 5.36.11) software.

Calculation of δ from Raman spectra

The width of the surface space charge layer δ_0 for the untreated n-InP(100) surface is 15.6 nm (Table 1). The $I(LO)/I(L^-)$ ratio values were calculated by deconvolution of the Raman spectra (see Fig. S6, as an example) performed using LabSpec (Version 5.36.11) software. The experimentally determined ratios of peak intensities $I(LO)/I(L^-)$ for the reference (untreated) sample is 1.27 (Table 1, Fig. S6, ESI). These values, as well as $\alpha = 2.29 \times 10^5 \text{ cm}^{-1}$, are substituted to formula

$$\left\{ \frac{I(LO)}{I(L^-)} \right\}_{untreat} = \frac{I_0(LO)}{I_0(L^-)} \times \frac{(1 - \exp(-2\alpha\delta_0))}{\exp(-2\alpha\delta_0)} \quad (S1)$$

$$1.27 = \frac{I_0(LO)}{I_0(L^-)} \times \frac{(1 - \exp(-2 \times 2.29 \times 10^5 \times 15.6 \times 10^{-7}))}{\exp(-2 \times 2.29 \times 10^5 \times 15.6 \times 10^{-7})}$$

to obtain the $I_0(LO)/I_0(L^-)$ ratio. As a result, $I_0(LO)/I_0(L^-) = 1.218$.

The values δ_{pas} for passivated surfaces are calculated by formula

$$\left\{ \frac{I(LO)}{I(L^-)} \right\}_{pas} = \frac{I_0(LO)}{I_0(L^-)} \times \frac{(1 - \exp(-2\alpha\delta_{pas}))}{\exp(-2\alpha\delta_{pas})}, \quad (S2)$$

which can be transformed as follows

$$\left\{ \frac{I(LO)}{I(L^-)} \right\}_{pas} = R_{pas}; \frac{I_0(LO)}{I_0(L^-)} = R_0 = 1.218; \delta_{pas} = -\frac{1}{2\alpha} \times \ln\left(\frac{R_0}{R_0 + R_{pas}}\right)$$

Substituting as R_{pas} the value 0.55 for e.g. surface treated with the aqueous $(\text{NH}_4)_2\text{S}$ (4%) solution (Table 1), we can obtain

$$\delta_{pas} = -\frac{1}{2\alpha} \times \ln\left(\frac{R_0}{R_0 + R_{pas}}\right) = -\frac{1}{2 \times 2.29 \times 10^5} \times \ln\left(\frac{1.218}{1.218 + 0.55}\right) = 8.1 \text{ nm}$$

For other passivated surfaces from Fig. 1, the width of the surface space charge layer can be calculated in a similar way.