Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
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Supplementary Information

Formation of a two-dimensional oxide via oxidation of a layered material

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1. Estimating the escape depth

To estimate the effective inelastic mean free path (λ) in our X-ray photoemission spectroscopy (XPS) experiments, we have used the equation:

$$\lambda = IMFP \cdot (cos(\varphi)) \qquad (1)$$

where IMFP is obtained from the TPP-2M model[1] using the following parameters:

E_{kin}: 610 eV

Valence Electrons: 9

Molar mass: 147.512 g/mol

Density[2]: 5.556 g/cm^3

Band gap: 0.65 eV[3]

and φ is the angle between the detector and the direction normal to the sample surface, namely $60°$.

According to the above, λ in our experiment is 0.74 nm.

The escape depth is given by 3λ = 2.22 nm

2. Estimation of oxide overlayer thickness

We have estimated the thickness, L, of the oxide overlayer (approximated as a flat and uniform layer) from the exponential attenuation of the XPS intensity of the unoxidized Ge component that is reported in Figure 2c in the main text.

Notably, from the equation $exp(-L/\lambda) = 0.45$, we find L = 0.59 nm.

This number is smaller than the interlayer distance in GeAs (0.66 nm), meaning that the oxidation is taking place in the topmost GeAs monolayer.

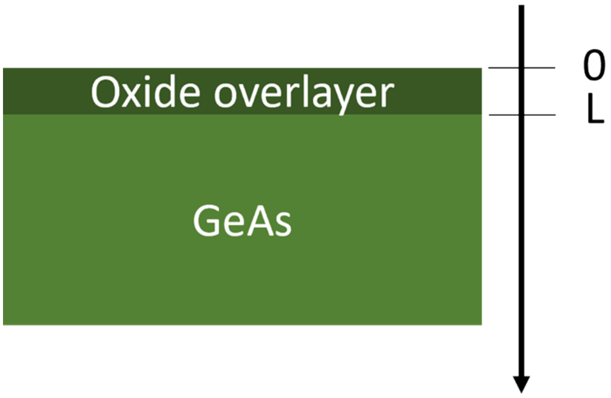

Figure S1. Sketch of the experimental system under investigation. An oxide layer with thickness L forms on top of GeAs upon oxidation.

3. Oxygen 1s and absence of features from Arsenic oxide

The XPS shown in Figure 2 in the main text was obtained by continuously collecting in a single spectrum-sweep both Ge 3d and As 3d core levels. Thus, since it was not possible to collect the oxygen signal during the oxidation (as it is in a different energy range), we performed another oxidation experiment on a freshly cleaved GeAs flakes where we collected sequentially Ge 3d, As 3d and O 1s as a function of oxidation time (namely, with oxygen inside the chamber, we collected Ge 3d, then As 3d, then O 1s and then back to Ge 3d to restart the cycle and so on). The results are shown in **Figure S2**. From this set of data, we can conclude that, similarly to the experiment shown in the main text, Ge is being oxidized (note the components at binding energies higher than 30 eV) while no arsenic oxide is being detected on the GeAs sample (note the absence of additional peaks in the binding energy range 44.9 eV to 46.2 eV, energies characteristics of As_2O_3 and As_2O_5 respectively[4]).

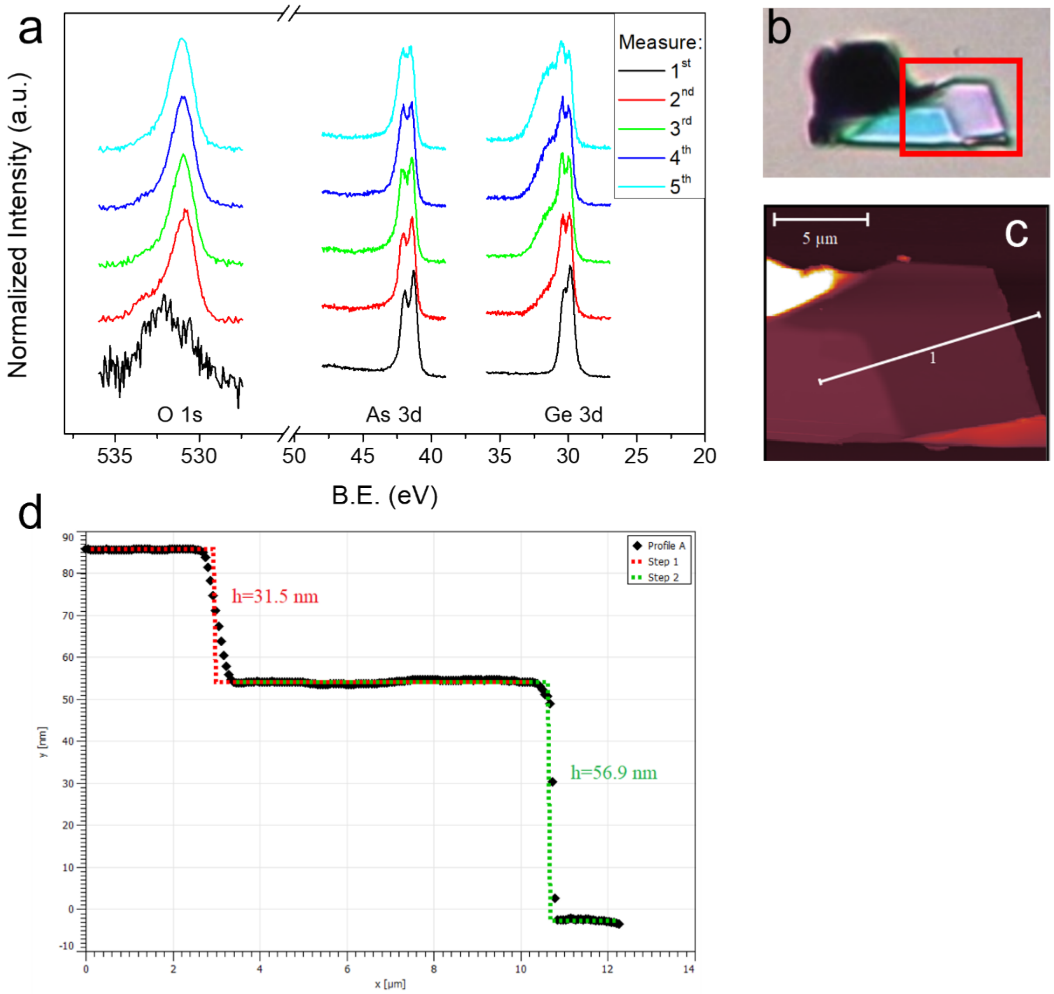

Figure S2. a) Sequential O 1s, Ge 3d and As 3d spectra (1 to 5) collected on an individual flake exposed to 1x10^{-6} mbar of molecular oxygen with photon energy of 648 eV. b) optical and c) atomic force microscope images of the studied flake. d) Line profile taken on the flake in the white line in c).

4. Derivation of eqn. 9 in main text

The photoelectron signal of As has been done using a similar approach to that employed for Germanium. In this case the $As^{(0)}$ intensity decreases over time, as explained in the main text.

The intensity of the $As^{(0)}$ signal due to n oxidized (hence, removed) MLs plus $j \leq 2$ layers of As, reads:

$$I_{As^{(0)}}(n,j) = \tilde{I}_0\left[e^{-na/\lambda}\left(\sum_{l=j+1}^{2} e^{-(l-1)d/\lambda}\right) + \left(\sum_{k=n+1}^{\infty} e^{-ka/\lambda}\right)\left(\sum_{l=1}^{2} e^{-(l-1)d/\lambda}\right)\right], \qquad (1)$$

that is rewritten as

$$I_{As^{(0)}}(n,j) = \tilde{I}_0\left[X^n\left(\sum_{l=j+1}^{2} z^{(l-1)}\right) + \frac{X^{n+1}}{1-X}B\right], \qquad (2)$$

where $z = e^{-d/\lambda}$, $B = 1 + z$ and $X = e^{-a/\lambda}$. Since $B = \sum_{l=1}^{2} z^{(l-1)} = \sum_{l=1}^{j} z^{(l-1)} + \sum_{l=j+1}^{2} z^{(l-1)}$, it follows $\sum_{l=j+1}^{2} z^{(l-1)} = B - \sum_{l=1}^{j} z^{(l-1)} = B - \sum_{m=0}^{j-1} z^m$ and eqn.2 becomes

$$I_{As^{(0)}}(n,j) = \tilde{I}_0\left[X^n(B - G(j)) + \frac{X^{n+1}}{1-X}B\right], \qquad (3)$$

with $G(j) = \sum_{m=0}^{j-1} z^m$. Normalization of the photoelectron signal to the value $I_{As^{(0)}}(0,0) = \frac{B}{1-X}$ provides, eventually

$$I'_{As^{(0)}} = \left[\frac{1 - X}{B} X^n (B - G(j)) + X^{n+1}\right], \tag{4}$$

that is eqn. 9 in the main text.

References

1. S. Tanuma et al. *Surf. Interface Anal* **35**, 268 – 275 (2003)
2. P. Wu et al. *Phys. St. Sol. b* **253**, 862 – 867 (2016)
3. S. Yang et al. *Adv. Func. Mat.* **28**, 1707379 (2018)
4. Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. Handbook of X-Ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data. Chastain, J., Ed.; PerkinElmer: Eden Prairie, MN, 1992; pp 94–95