

Electronic Supplementary Information for

Initial oxidation of GaAs(100) under near-realistic environments revealed by *in situ* AP-XPS

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1. Details of experimental and analytical methods

As mentioned in the main text, all the AP-XPS measurements were performed at beamline 13B at the Photon Factory of the High Energy Accelerator Research Organization (KEK-PF) in Tsukuba, Japan.¹ An undoped semi-insulating GaAs(100) wafer was purchased from Wafer Technology Ltd., UK. The typical electrical resistivity and each pit density (EPD) are 10 M Ω cm and 2000 cm⁻², respectively. AP-XPS measurements were performed by a home-made vacuum chamber.² In the high-pressure analysis chamber, the sample was heated from the backside by a pyrolytic boron nitride heater. The temperature was measured by a K-type thermocouple attached near the sample surface. The photon energy of 150 eV was used to obtain the Ga 3d and As 3d XP spectra. The X-ray incident and photoelectron emission angles are 75° and 0° from the surface normal, respectively. The approximate X-ray spot size is 120 μ m (V) \times 630 μ m (H). Here, the analyzing depth is estimated about 1.5 nm. The binding energy is calibrated based on a previous report; a sharp GaAs peak of As 3d_{5/2} level is aligned at 40.9 eV. It is noted that a small trace of oxide peak is observed in As 3d and Ga 3d levels before gas exposure, due to the present highly surface sensitive condition. XP spectra for the as-prepared GaAs surface are recorded to identify the surface chemical state before oxidation (Fig. S1). Fig. S1(a) shows a wide range XP spectrum, and there are some contributions from residual oxide (O) and carbon (C) contaminations. With correcting by the photoelectron-cross-section, the ratio of C and O species to the GaAs substrate are estimated to be about 19 and 5%, respectively. Fig. S1(b) shows narrow scans of As 3d and Ga 3d for the as-prepared GaAs surface. A shoulder structure arising from the Ga oxide is observed at about 20.5 eV in the Ga 3d XPS. A very weak peak originating from the As oxide is also observed at about 44.5 eV in the As 3d XPS. LEED pattern was also checked for an as-prepared GaAs surface: Although the (1 \times 1) spots from the bulk structure were observed, no surface-induced periodic structure was observed.

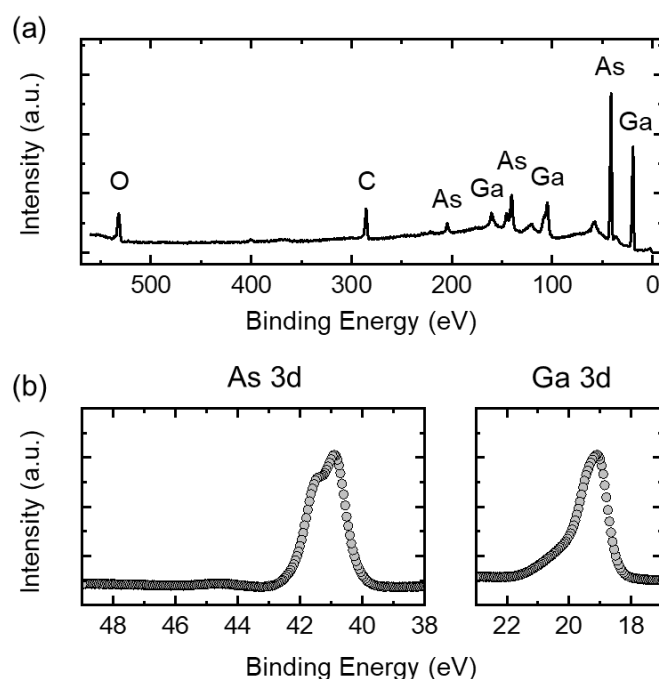


Fig. S1. XP spectra of wide range scan (a) and As 3d and Ga 3d narrow scans (b) taken from an as-prepared GaAs(100) surface. Here, the incident photon energies were tuned to 630 and 150 eV for the wide range scan and As 3d and Ga 3d levels, respectively.

Ga 3d and As 3d XP spectra are curve-fitted by the convolution of Doniach–Šunjić and Gaussian functions and Shirley-type background. The Ga 3d and As 3d peaks intrinsically split into two branches, resulting from the spin–orbit interaction. The GaAs and elemental As (As⁰) components are curve-fitted by the doublet line profiles, whereas oxide components are curve-fitted by a single Gaussian-like profile, which is probably due to the overlap of multiple contributions from slightly different chemical environments. Resultant binding energy (BE) and full width at half maxima (FWHM) are summarized in Table S1.

Table S1. Summary of parameters of curve-fitting analysis for the Ga 3d and As 3d levels.

Level	Species	BE (eV)	FWHM ^{a)} (eV)
Ga 3d	GaAs	19.1	0.65
	Ga ₂ O ₃	20.4	1.4
As 3d	GaAs	40.9	0.60
	As ⁰	41.2	0.65
	As ₂ O ₃	44.4	1.5
	As ₂ O ₅	45.9	1.6

^{a)} The FWHMs for GaAs and As⁰ peaks are calculated by the Ga 3d_{5/2} and As 3d_{5/2} line profiles, whereas the FWHMs for Ga₂O₃, and As₂O₃ and As₂O₅ are calculated by the Ga 3d and As 3d line profiles.

2. Thickness of the oxide layer

Oxide thickness d is quantitatively estimated using XPS peak areas I of substrate (S) and oxide (O) as follows;

$$d = \lambda_0 \sin \theta \times \ln \left(\frac{\sigma_S n_S \lambda_S I_O}{\sigma_O n_O \lambda_O I_S} + 1 \right).$$

where λ , σ and n are the inelastic mean free path (IMFP), photoionization cross-section and density, respectively. θ is electron emission angle. The thickness is an averaged value on the surface. Here, the oxide is modelled as a flat layer on the substrate. The Ga and As oxides are modeled as a homogeneously mixed oxide. The intensity of elemental As is taken into account as a substrate component. Fig. S2 shows the XP spectra of As 3d and Ga 3d levels taken from a GaAs(100) surface at 573 K and 4600 s under 10 mTorr O₂ ambient (a), and the evolution of calculated oxide thickness as a function of oxidation time (b). Finally, the thickness reaches about 1 nm, thus in the present AP-XPS experiments we observe the initial oxidation process.

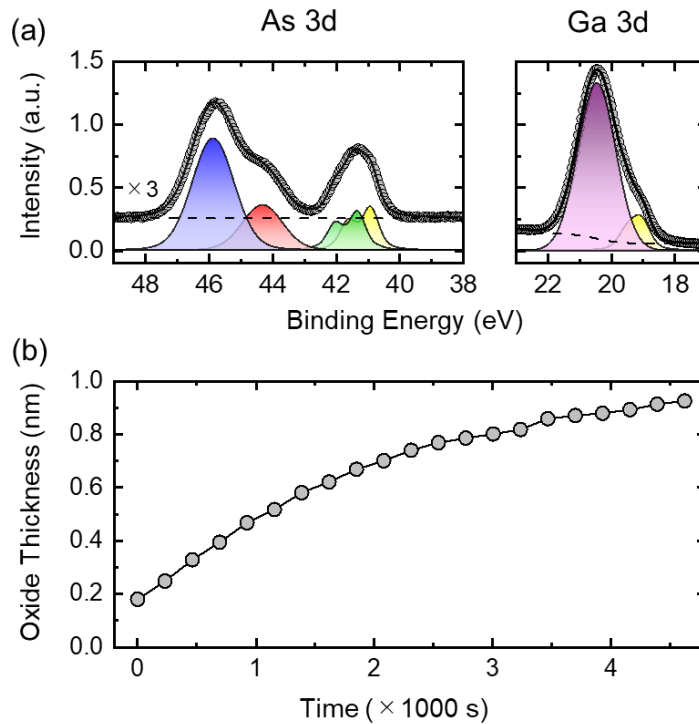


Fig. S2 (a) XP spectra of As 3d and Ga 3d levels taken from GaAs(100) surface at 573 K and 4600 s under O₂ ambient (10 mTorr). The XP spectra are curve-fitted and each distinct component is color-coded as follows: GaAs bulk, yellow; elemental As, green; As₂O₃, red; As₂O₅, blue; Ga₂O₃, purple. Details of the peak assignments are provided in the main text. Here the incident photon energies were tuned to 150 eV. (b) Calculated oxide thickness formed on the GaAs(100) surface as a function of oxidation time.

3. Cross-sectional STEM/EDX images of oxidized GaAs

The local structure of GaAs surface is characterized by the scanning transmission electron microscope (STEM) analysis (Fig. S3). The data was recorded using FEI Tecnai Osiris system. The electron energy was set to 200 keV. Here, the GaAs sample surface was covered by a native oxide. The sample was capped by Os layer, and cross-sectioned by focused ion beam processing.

As shown in Fig. S3(a), the bright-field (BF) image indicates that the GaAs surface is covered by two stacking layers with different contrasts. Energy-dispersive X-ray spectroscopy (EDX) images of O, Ga and As show that the topmost layer is Ga-rich oxide layer, and the second layer is As-rich layer. The line analysis along the vertical white lines on EDX images is shown in Fig. S3(b). It is noted that the sample was cross-sectioned by using Ga ion, therefore the Ga signal is normalized by the GaAs bulk (20 nm to 25 nm in Fig. S3(b)) as the Ga/As ratio is unity. It elucidates that the topmost oxide layer is Ga-rich oxide composition, whereas the second underneath layer is As-rich composition. These results are consistent with the observation of elemental As, which is likely to be segregated at the oxide/substrate interface, as shown in Fig. 2.

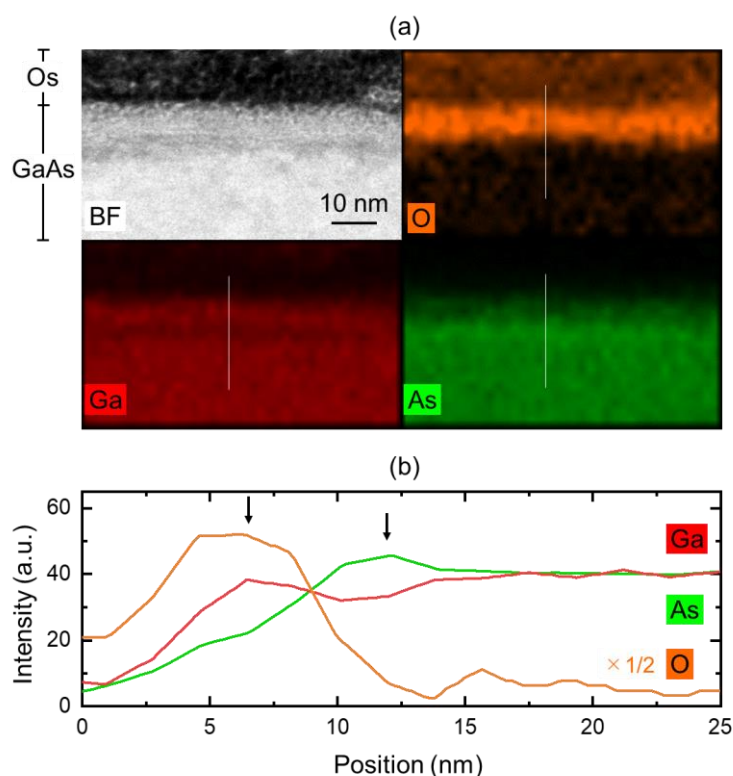


Fig. S3 (a) Bright-field (BF) and energy dispersive X-ray spectroscopy (EDX) images taken from GaAs substrate. (b) Line-profiles of O, Ga, and As analyzed along the vertical white lines shown in the EDX images of (a). The topmost Ga-rich oxide and underneath As-rich (Ga-poor) layers are marked by the arrows.

4. Evolution of the As fraction under oxidizing conditions

The evolution of Ga/As composition during oxidation in 10 mTorr O₂ ambient is estimated by analyzing XPS data. Here, the integrated XPS peak areas of Ga 3d and As 3d levels, from which the background contributions are subtracted, are compared. The evolution of Ga/As composition ratio, which is estimated as As / (Ga + As), is shown in Fig. S4. It is noted that the estimated value refers to the composition only near the surface region due to the limitation of XPS analyzing depth. Initially, the Ga/As composition ratio of the surface was estimated to be less than half; about 40% with a deviation of 2-3%. This is probably because some of As was sublimated during the heating up to 673 K in the surface cleaning process. Changes in the GaAs composition ratio during oxidation are traced at 373 K, 473 K and 573 K. As the oxidation progresses, the surface gradually changes to an As-poor (Ga-rich) composition. The line-slope becomes steeper as temperature increases. This result indicates that a part of As migrates underneath the surface, in other words, surface segregation of Ga from bulk takes place during the oxidation process. This is consistent with the results of STEM/EDX analysis (Fig. S3).

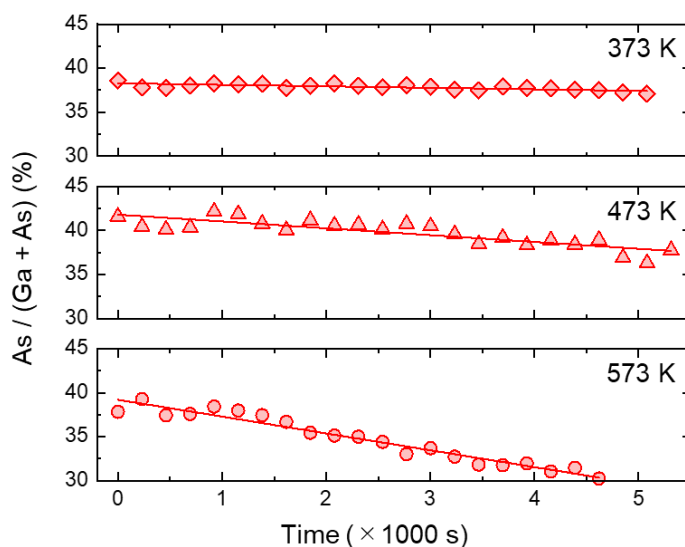


Fig. S4 Evolution of the As fraction during oxidation on GaAs(100) surface under 10 mTorr O₂ as a function of time. The As fraction is deduced from the corresponding XPS data shown in Fig. 2.

5. References

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