1. Bulk GaAs samples and surface band alignment

Two-inch epi-ready GaAs wafers were obtained from commercial suppliers and cleaved into smaller pieces for spin-coating and measurements. All samples were n-type silicon doped with doping levels, in units $10^{18} \text{ cm}^{-3}$, of 2.5, 5.4 and 1.4 for (100), (110) and (111) A and B samples respectively, confirmed by Hall effect measurements. Surface orientations were specified within ±0.05° of the crystallographic normal. The bulk Fermi level for GaAs doped by silicon in the $10^{18} \text{ cm}^{-3}$ range and at room temperature can be estimated using standard semiconductor statistics and parameters. This is shown in Fig. S1. For the range of bulk doping levels used in the main experiments, the variation is only 16 meV.

![Figure S1](image.png)

**Figure S1** Bulk Fermi level in GaAs as a function of Si doping level. Horizontal lines show the variation of Fermi level over the range of doping in the bulk samples used in these experiments.

The variation of work function across different crystal faces is therefore dominated by differences in both band bending and surface dipoles. Both may arise through changes in the structure of the native oxide on the different crystal faces. On GaAs, the effective surface acceptor density will change the degree of upward band bending (in the depletion approximation the band bending varies as the square of surface acceptor density). Independently, the local vacuum level can be changed by any net dipole in the outermost atomic layers of the material. PEI adsorption certainly changes the surface dipole so as to lower the local vacuum level, but since PEI can also act as a surface donor it may compensate some surface acceptors as well.
2. Heterostructure and Kelvin probe force microscopy

Figure S2  Schematic GaAs heterostructure used in KPFM experiments (not to scale). Green and red regions are respectively p- and n-doped. Thin grey regions are AlAs spacer layers.

Figure S3  Averaged KPFM line scan across the GaAs heterostructure, whose layers are superimposed as colours corresponding to Fig. S2. The horizontal axis represents
distance in the [100] direction, with zero at the sample’s (100) surface, and the vertical axis is CPD.
The GaAs(100) heterostructure is shown in Fig. S2. Samples were grown by molecular beam epitaxy on semi-insulating GaAs(100) wafers. Green and red regions are respectively p- and n-doped. A (110) plane is exposed by cleaving to allow PEI deposition and KPFM measurements, but the wafer is too thin to allow Kelvin probe measurements with a 2 mm tip.

KPFM experiments were performed using a Bruker Multi-Mode 8 microscope operating in nitrogen atmosphere and using a Pt-Ir tipped probe with nominal tip diameter 20 nm, cantilever resonant frequency 75 kHz and spring constant 3 Nm⁻¹. The microscope was operated in frequency modulation mode to make the KPFM measurements: the shift of the resonance frequency of the cantilever through the force gradient induced by the electrical field between tip and sample surface is used to measure the CPD [C. Li et al., *PeakForce Kelvin probe force microscopy*, Bruker Application Note 140, 2013, p1-14].

Fig. S3 shows a typical averaged linescan of CPD along the [100] direction. This averaged linescan was obtained from an integration region of about 1 μm width and about 5 μm length along the [100] growth direction, averaging in the perpendicular [010] direction. Due to the relative shift of the Fermi level from the mid-gap position, the p-doped (green) layers show a higher work function than the n-doped regions (red). A doping level decrease is seen in the p-doped regions starting at 2.5 μm, but doping level seems to have little effect on the measured CPD, with all values being within 100 mV of each other. It is possible to distinguish the individual doping levels however, unlike the n-doped region where the increase in CPD due to doping was far less obvious. The line scan shifts in CPD crossing the pn-junction from a lower CPD to a higher CPD, behaving in a similar way in the regions as seen in the isolated regions deeper within the sample.

Average CPD values and corresponding standard deviation values were extracted from integration areas of about 3 to 4 μm width for each of the doped layers in the heterostructure from KPFM measurements performed before and after the PEI coating. The local work function reduction shown in the main paper is obtained by subtracting the CPD values after the PEI coating from the CPD values before PEI coating. The standard deviations were used to estimate the measurement uncertainties, which lie in the ±15 meV range.
3. Kelvin probe measurement and calibration

The KP010 Kelvin probe was supplied by KP Technology Ltd., UK. Measurements were made in a Faraday cage, in the dark and under ambient atmospheric conditions. A copper-beryllium clip was attached to the sample top surface during scans to aid charge neutralisation across the semiconductor wafers. As this process occurs, the measured CPD changes with time. To extract reliable CPD values, a simple MATLAB algorithm was used as illustrated in Figure S4. An initial mean of 100 points and their standard deviation were calculated, starting around 100 points from the end of the time series to avoid the initial charging region and any measurement termination effects. Data points within 2 standard deviations were then accepted into a “moving tunnel” which was propagated back in time with any points outside the tunnel being rejected. The mean CPD was updated continually. The number of accepted points above and below the mean was measured, and for any 100-point tunnel, if 66 or more points within the tunnel were above or below the mean, the propagation was terminated. The running average of all points taken later in time than this last 100 points was taken as the stable CPD. This allows the maximum number of points to be averaged for the CPD while avoiding the charge neutralisation region in a systematic way. The parameters of this algorithm (tunnel length, rejection criterion) have only a very small effect on the measurement outcome. The overall experimental error on the CPD measurements is better than 5 meV and in the main paper we quote CPD values to the nearest 0.01 eV.

![Figure S4](image.png)

**Figure S4** Example of CPD extraction form a typical Kelvin Probe time series plot.
4. XPS measurements and further data

Samples were attached to electrically-conductive carbon tape, mounted on to a sample bar and loaded in to a Kratos Axis Ultra DLD spectrometer with a monochromated Al Kα X-ray source. The measurements were conducted at room temperature and at a take-off angle of 90° with respect to the surface parallel. The core level spectra were recorded using a pass energy of 20 eV (resolution approx. 0.4 eV), from an analysis area of 300 μm x 700 μm. The work function and binding energy scale of the spectrometer were calibrated using the Fermi edge and 3d_{5/2} peak recorded from a polycrystalline Ag sample during the experiments. Data were fitted and quantified using the CasaXPS software. Normalised intensities are quoted after the appropriate atomic sensitivity factor has been applied. Data were analysed in the CasaXPS package using Shirley backgrounds and mixed were Gaussian-Lorentzian (Voigt) lineshapes. For compositional analysis, the analyser transmission function has been determined using clean metallic foils to determine the detection efficiency across the full binding energy range. The NIST database was used to guide fitting of the core level regions. Samples did not show any sign of charging over the duration of scanning, therefore were not charge referenced. The primary carbon component (C-C/C-H) in the C 1s at 286.1 eV is well within the expected position of this peak on a native oxide surface using results from the literature: up to 286.7 eV [Journal of Electron Spectroscopy and Related Phenomena 231, 2019, p75], 285.6 eV [Applied Surface Science 379, 2016, p1], 285.8 eV [Applied Surface Science 458, 2018, p849], up to 286.74 eV [Applied Surface Science 451, 2018, p99]. The N 1s spectra taken are in excellent agreement with Zhou et al. [Science, Volume 336, 2012], with the exception of the component in our study at binding energy of 401.5 eV. This is related to the degradation mechanism and was presumably not present in Zhou’s work as no time dependent XPS was explored there.

Figure S5 shows the Ga 3d spectra before and after a HCl:H2O 30 second etch. There is a spin orbit splitting of 0.46 eV, with the doublets plotted as dashed lines. Post-etch, the decrease in relative intensity of the Ga2O3 peak is apparent, as well as the appearance of a newer component at a higher binding energy. Identification of the Ga2O3 peak was aided by Carli et al. [Applied Surface Science 74, 1994, p99], with our component being within 0.1 eV of theirs. The GaCl2 component was identified by reference to the work of Bourque et al. [Dalton Transactions 45, 2016, p7678].