Supplementary material

Emergence of Dirac-like bands in the monolayer limit of epitaxial Ge films on Au(111)

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1. **Au 4f peaks: suppression of Au(111) surface state and formation of new interface environment**

The 4f core levels of pristine Au(111) surfaces display splittings within the 4f$_{7/2}$ and 4f$_{5/2}$ peaks due to the different chemical shifts in the bulk and on the surface, as can be seen in Figure S1. However, the Au(111) surface peak is completely suppressed by the time the first ML of Ge is deposited, as a new Au-Ge interface environment develops. This interface layer has its own signature (labelled Int) as a shoulder at higher binding energy than the bulk peaks. The overall intensity of the Au substrate core levels is reduced as additional Ge is deposited on top, but the interface layer becomes relatively more pronounced compared to the bulk contribution as the layers build up. These results are comparable to the data shown in M. E. Dávila, L. Xian, S. Cahangirov, A. Rubio, G. L. Lay, New J. Phys. 2014, 16, 095002.

![Figure S1: Stacked XPS spectra covering the Au 4f core levels, obtained with 120 eV photon energy at 10 K in normal emission. Intensities are normalized to background at 80 eV binding energy.](image-url)
2. The role of Bi as a surfactant

The role of a surfactant in thin-film growth is to encourage a change in the growth mode from 3D to epitaxial 2D growth. Sb (isovalent to Bi) was shown to be an effective surfactant for Ge film growth on Si(111) (T. Schmidt, R. Kröger, T. Clausen, J. Falta, A. Janzen, M. Kammler, P. Kury, P. Zahl, M. Horn-von Hoegen, Appl. Phys. Lett. 2005, 86, 111910), thus Bi is likely to play this role in germanene growth as well.

Bi 4f core levels: Bi rises to the top

A well-calibrated small quantity of Bi surfactant is deposited first onto the Au substrate, before the Ge deposition. However, it seems that after the growth, Bi is always found on the top surface of the sample, once the few-layer germanene is grown. The evidence for this is that the Ge 4f peak height is completely independent of germanene thickness, as shown in Figure S2. This is in contrast to the suppression of the underlying substrate Au 4f peaks, which occurs due to the surface-sensitivity of photoemission.
Figure S2: Core level photoemission spectrum containing Bi 4f and Ge 3d peaks. The intensity of the Bi 4f peaks is independent of thickness. Data obtained with 120 eV photon energy. The data is normalized to the background.
3. Film characterization: LEED

**Figure S3:** a) LEED obtained at ~55 eV incident energy, on different samples. Red hexagons are used to indicate the first order Au(111) substrate peaks. Note that due to small distortions in the LEED images, in some places the spots deviate slightly from a perfect hexagon. Apart from the sub-ML coverage, all subsequent layers display qualitatively equivalent spectra, although the quality of the spectra is sample dependent (for a mixture of intrinsic and extrinsic reasons). The 2 ML* sample was not used for ARPES measurements. e-g) LEED at various energies on the 2 ML* sample; some prominent peaks associated with the dominant 8x8 reconstruction are circled in red. h) Detail of the 56 eV data from panel d). Orange and green circles highlight spots which do not conform to the 8x8 reconstruction, as discussed.

**Submonolayer case: linking the LEED pattern with replica bands observed by ARPES**

For the sub-ML case, the LEED pattern is qualitatively different to both the pristine Au(111) and the epitaxial few-layer films. One study (M. E. Dávila, G. Le Lay, Sci. Rep. 2016, 6, 20714) indexed a sub-ML LEED pattern of Ge on Au(111) to a combination of 19x19R(23.4°), 5x5, and 7x7R(19.1°) reconstructions, suggesting a number of variants are possible depending on the coverage; here the inclusion of Bi is also likely to play a role. In our sub-ML sample, a few weaker spots in the LEED pattern might be associated with a 5x5 pattern, but the most prominent spots are found as a regular hexagon around the first order substrate peak, which could be indexed to approximately a 15x15 surface reconstruction. Due to this surface
superstructure, it is to be expected that replica substrate bands could be observed in ARPES measurements, with the magnitude of the shift in momentum space being linked to the periodicity of the of the superstructure, as is discussed in the main text.

**LEED patterns in the few-multilayer regime**

In Figure S3b-d, we present LEED patterns at different coverages in the range of 1-3 ML, which show no qualitative change in the LEED pattern. This would appear to indicate that, at least in this regime, germanene grows epitaxially. This pattern was also seen by Davila et. al. (M. E. Dávila, G. Le Lay, Sci. Rep. 2016, 6, 20714), who suggested an 8×8 reconstruction of germanene on Au(111) (i.e., 8×8 relative to the Au(111) lattice). Indeed, we find that the peaks with the strongest intensity do match well to an 8×8 reconstruction, as indicated in Figure S3e-h. However, there are also indications that there are features beyond the 8×8 reconstruction (which can also be weakly observed in the LEED pattern of Davila et. al. (M. E. Dávila, G. Le Lay, Sci. Rep. 2016, 6, 20714)). Three different sets of peaks do not obey the 8×8 reconstruction. First, as seen most clearly in Figure S3d, the peak pattern seen around the main Au(111) substrate peaks is replicated at a 30° rotation, indicating the likely presence of 8×8R30° domains. Second, the spots marked in orange in Figure S3h, do not conform to any allowed 8×8 diffraction peak, but instead they may be attributed to a 6° rotation of the 8×8 structure (i.e., 8×8R6°). It seems probable that the azimuthal orientation of the Ge film is not strongly constrained, which may be related to the large size of the reconstruction. Third, the peaks marked in green in Figure S3h do not conform to the 8×8 structure. These may be tentatively associated with Bi surface ordering due to the fact that these peaks alone disappear in the range of 250-300°C (see below), as well as the fact that these peaks do not appear in the LEED data of Davila et. al. (M. E. Dávila, G. Le Lay, Sci. Rep. 2016, 6, 20714) where no surfactant was used.
Annealing analysis of a 3 ML sample

The as-grown 3 ML film features some spots consistent with an 8x8 reconstruction, but in place of the 8x8R6° peaks, a ring-like continuum of intensity from 6° to 24° rotation. It is likely that some rotational disorder of the growth occurs as the film thickness increases, which manifests as a ring-like structure. After annealing at 300°C, as shown in Figure S4c, these rings disappear and instead 8x8R6° spots emerge. This indicates that the annealing process aids the azimuthal rotational ordering of the germanene structure on Au(111), though there may still be several preferred orientations. In addition, the main 8x8 peaks appear sharper after the annealing process, indicating that the film quality is increased by the annealing.

Additionally, a set of spots labelled with green rings disappear at temperatures between 250 and 300°C reversibly, since they are present again in the final cooled data. One possible explanation for this is that these peaks are associated with the Bi atoms which are likely to sit in an ordered arrangement on the top surface of the sample. We also note that this annealing procedure gave no significant difference to the XPS spectrum, i.e., no significant desorption occurred at these temperatures.
Annealing also influences the quality of our ARPES data, as can be seen in Figures S4e-h. While the ~2ML as-grown film without annealing shows to rotationally smeared LEED spots (Figure 4e) and rotationally smeared Dirac bands (indicated by red arrows in Figure 4g), the ~3ML film after annealing shows a more discrete LEED pattern (Figure 4f) and band structure (Figure 4h), which suggests less rotational disorder.

4. Ge monolayer thickness determination via STM

We determined the thickness of a Ge film monolayer from preliminary STM measurements of a thick Germanium film (nominal thickness 3.3 Å) evaporated on Au(111), the topography of which is shown in Figure S5. The STM image shows a number of Ge islands that allowed us to determine a Ge monolayer thickness of ~2.5 Å.

The structural transition that is indicated by the LEED measurements shown in Figure 1b-c is a strong indicator that at least one full layer of Germanium is completed at the nominally 2.6 Å
thick films, which is also corroborated by the Ge appearance of a bulk (i.e. germanene) contribution in the Ge 3d core level peaks (shown in Fig 1a and S2). Due to the possibility of island growth, the film may be slightly thicker than one monolayer in some parts of the sample, but it is unlikely that two layers were completed in this film, since the interface component in the Ge 3d core level spectrum is still clearly present in Fig 1a for the nominally 2.6 Å thick film, but only fully suppressed for a ~2 ML thick film (shown in Fig SM2). Based on the STM measurements, quartz microbalance rate calibration, and core-level spectroscopy, we therefore conclude that the film with nominal thickness of 2.6 Å measured during our ARPES experiments is approximately at the monolayer limit.

5. **Influence of rotational disorder on the appearance of Dirac cones**

We observed the appearance of parallel lines on the equal energy surfaces shown in Figure 4(d). These lines can be understood from the suppositions of circular pockets with small rotational disorder, which will wash out the sides of the pocket, while leaving streaks of intensity tangential to the sense of the rotational disorder, as is illustrated by the simulation in Figure S6.

![Figure S6: Simulations of the effect of rotational disorder on the observations of Dirac cones. Here the “perfect” cone is centered at (-1,0), while in the right panel we sum intensities after continuously rotating the cone over -2.5° to 2.5° (the centre of rotation is (0 0)).](attachment:figure_s6.png)