Supplementary Figure 1 Disruption of lattice periodicities at grain boundary. (a-c) left panels are bias-dependent images recorded at the same boundary region, showing the atomic structure of the GB between Grain I and II (8 × 4 nm²; a, \( V_{\text{Tip}} = 1.2 \) V; b, \( V_{\text{Tip}} = 1.0 \) V; c, \( V_{\text{Tip}} = -0.5 \) V); and right panels are the corresponding lateral profiles of the black and blue lines denoted in left panels. The GB is featured as bright protrusions with a width of \( \approx 1.3 \) nm at \( V_{\text{tip}} = 1.2 \) V in (a). When the \( V_{\text{tip}} \) is reduced to 1.0 V and -0.5 V in (b) and (c) respectively, the bright features disappear. Obviously, the MoS₂ lattice periodicities are broken at the GB and a transition phase possessing a different packing structure forms there. The disruption of the MoS₂ lattice periodicity at the boundary can be also revealed by the lateral profiles shown in the right panels, where the edges of Grains I and II are denoted by the black and blue triangles respectively.
Supplementary Figure 2 A possible atomic model of the GB with 18° misorientation. It is proposed that the GB is composed of two regions, a transition phase (atoms are highlighted by yellow haloes) and a strain relaxation region. As the two grains meet during the CVD process, a transition phase of Mo and S, together with other impurities, may form in the 1.3 nm wide GB region. Compared to the periodic MoS$_2$ intrinsic lattices, the transition phase is relatively disordered without a periodic unit cell (neither in the direction parallel nor perpendicular to the boundary). This proposed model suggests that the transition phase between Grain I and II is mainly constructed by distorted MoS$_2$ lattices. The ~ 4 nm region from the GB edge to each domain acts as a distortion relaxation length between the transition phase and the pristine MoS$_2$. It is reasonable to have the magnitude of the strain field in the relaxation region decrease as d increase, and hence contribute to the tunalibility of the electronic bandgap we observed at the GB.
Supplementary Figure 3 A schematic diagram of the bandgap ($E_g$) change with respect to the distance ($d$) from GBs. The red one is for the case demonstrated in Figure 3 with 18° misorientation, and the blue one based on the Figure 4 with 3° misorientation. $E_g$ of 2.4 eV remains constant at the regions far away from the GBs, i.e., $d$ is larger than 4 nm; and decreases to a minima at $d = 0$ for both cases. In the diagram, the red (black) squares represent the measurements taken at grain I (II), and the blue (green) triangles represent that at grain III (IV). It is interesting to note that the decay of $E_g$ at grains I and II (or grain III and IV) are similar and symmetrical. The decrease of the bandgap at the GB can be as large as 0.85 eV when the misorientation between the two neighboring grains is 18°, but is only 0.17 eV when the misorientation is 3°.
Supplementary Figure 4 Complex band structure (CBS). CBS plots of ideal MoS$_2$ monolayer along the zigzag direction (a) and armchair direction (b). Software package SIESTA and SCARLET are used to calculate CBS, while the VBM and CBM are shifted by a scissor operator to match the experimental 2.4 eV bandgap determined by STS.

Supplementary Note 1

Decay behavior of defect states predicted by calculated complex band structures

While the observed long-range and smooth variation in bandgap is most likely due to strain, we also seek to address other physical effects that may also result in a smooth change in bandgap with distance. Specifically, we consider the possibility of bandgap modulation due to the decay of defect/impurity states from the GB into the interior. A defect may introduce a state near the CBM or VBM, which reduces the bandgap at the GB region, and as the state decays away from the GB, the bandgap widens to the pristine one. Regardless of the nature of the defect states, in general, states with energy $E$ introduced in the band gap of a material, e.g. interface states, or metal-induced gap states, have imaginary wave vectors that decay exponentially into the material, as $|\varphi(x)|^2 = Ae^{-kx}$, where $k$ can be determined for $E$ from a complex band structure (CBS) calculation. From our CBS calculations (Supplementary
Figure 4), we see that $k$ increases as $E$ moves away from the valence or conduction band edges, reaching a maximum of 0.470 Å$^{-1}$ at mid-gap for the fastest decaying mode. Reading from the plot, the decay length of defect states that may have resulted in a 0.85 eV reduction in band gap would be at most $\sim$5.6 Å for both the zigzag (Supplementary Fig. 4a) and armchair (Supplementary Fig. 4b) directions (taking, for the slowest decay, defect levels $\sim$0.4 eV below the conduction band minimum and $\sim$0.4 eV above the valence band maximum). Here, we define the decay length to be $1/k$. This decay length is much smaller than the range at which the bandgap variation is observed in experiment ($\sim$4 nm). Indeed, explicit calculations of different defect states also show that the wavefunctions tend to be localized near the defects$^{1,2}$. Thus, the much smaller decay distance of defect states obtained from CBS prediction indicates that it is unlikely to be the dominant reason for the observed bandgap modulation.

**Supplementary References:**