

MOIRÉ SUPERLATTICES

Twistronics and the small-angle magic

Understanding, at the atomic level, the effect of the stacking and twisting of different layered two-dimensional materials is a major challenge for the future of twistronics. Optical excitations evidence twist-angle-dependent whirlpool-shaped distortions in such materials.

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A new perspective for materials design has been opened with the ability to isolate and relocate two-dimensional materials, usually laminar in their bulk form. Imagine a single-layered material, where all (or most of) the atoms are at the surface. By laying down one on top of the other, the interlayer surface interaction will be playing a role in the entire new system. This defines the field of van der Waals heterostructures¹. Now, imagine that you rotate the crystalline orientation of one layer with respect to the other. For each rotation angle θ , you will have the formation of θ -dependent moiré superstructures (Fig. 1a), with different sets of interactions among the atoms from the two different layers. This θ -dependent structure gives rise to the field of twistronics². Now, writing in *Nature Materials*, Jungcheol Kim and co-authors³ report that they have built such a heterostructure by stacking two monolayers of different transition metal dichalcogenides, one monolayer of molybdenum disulfide (MoS_2) and one of tungsten diselenide (WSe_2) (Fig. 2). Then, the authors studied what happens to the bilayer system when stacking them with different twist angles. By analysing the emerging intralayer vibrational modes, they show that strong interactions take place and that these interactions become larger for smaller twist angles ($\theta < 7^\circ$).

Gaining a clear understanding of what happens to every atom when you stack two monolayers into a van der Waals heterostructure with a twist is far from trivial. Kim and co-authors, by looking at the way atoms vibrate, realized that whirlpool-shaped periodic lattice distortions arise (Fig. 1b). When the two monolayers were coupled, an emerging interlayer breathing mode was observed in their Raman spectra, and, by lowering the twist angle θ below 7° , the authors observed increased broadening of this breathing-mode peak. The fuzziness in vibrational frequency is an indication of non-uniform interlayer interaction, as clarified based on first-principles calculations. Furthermore, the authors also

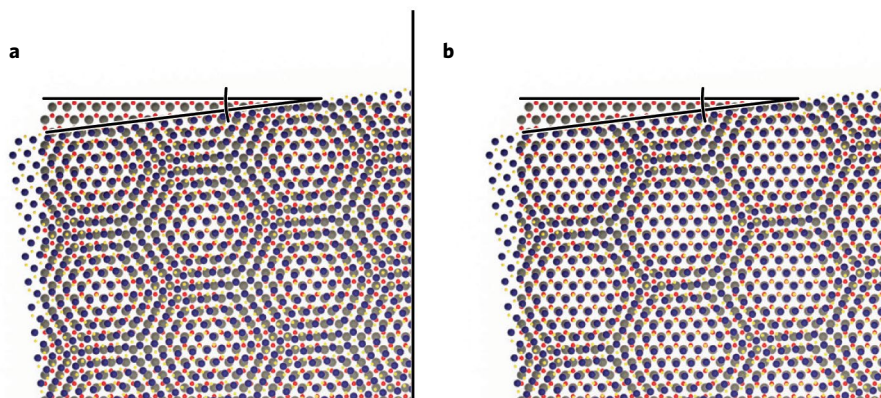


Fig. 1 | Artistic representations of the moiré superstructures formed when rotating two two-dimensional crystals with respect to one another by an angle θ . **a**, Top view of two different transition metal dichalcogenide structures rotated by $\theta = 7^\circ$. **b**, The same as in **a** with the addition of whirlpool-shaped counter-rotations (-7°) in the top layer, centred on each supercell in the moiré superstructure. Credit: Cassiano Rabelo.

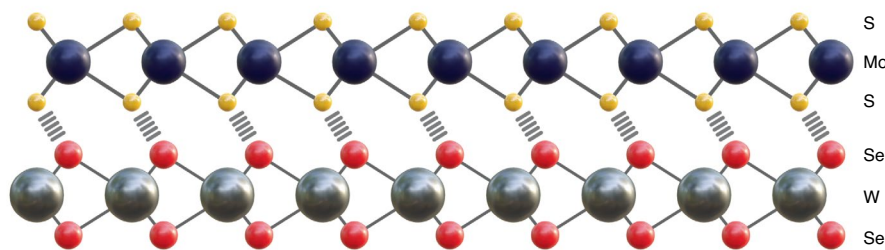


Fig. 2 | Side view artistic representations of two different transition metal dichalcogenides forming a bilayer van der Waals heterostructure. The different colours and sizes of the spheres represent the different atoms of MoS_2 (top) and WSe_2 (bottom). Credit: Cassiano Rabelo.

analysed intralayer atomic vibrations, and identified that the deformations happen mostly on the softer crystal, namely the MoS_2 , with the S atoms facing the WSe_2 crystal exhibiting much larger changes compared with the Se atoms. Besides, the local torsion of the Mo and the S atoms changes chirality within a moiré unit cell, due to the different local interlayer matchings. The first-principles calculations also show that when the twist angle decreases below 7° , the magnitude of the

out-of-plane distortion quickly increases and the average interlayer spacing, as well as the average interlayer distance between the W and the Mo atoms, decreases. Finally, having established the vibrational structure of their bilayer two-dimensional system, the authors studied the optical reflectance and showed that the exciton energies are generally redshifted, but the energy displacements for the MoS_2 exciton in a small-twist-angle ($\theta < 5^\circ$) van der Waals heterostructure were much larger³.

This universal θ -dependent behaviour, which is the basis for twistrionics, is curious, especially the interesting and pronounced behaviour for small θ . For comparison, the twistrionics of graphene has also revealed interesting phenomena, such as twist-angle energy-dependent peaks in the electronic density of states⁴ for ‘large twist angles’ ($\theta > 2^\circ$), strong quasiparticle correlation, including superconductivity⁵ at the ‘magic angle’ ($\theta \approx 1.1^\circ$), and atomic reconstruction with the formation of strain domain⁶ walls for ‘small twist angles’ ($\theta < 1^\circ$). These interesting phenomena are always related to the modulation of the emerging moiré superlattice, and in some cases (usually for small angles) generate a mesoscopic confinement of electrons and phonons⁷, resulting in flat bands and strong correlations⁸. The work from Kim and co-authors shows the universality of these concepts for van der Waals heterostructures, in agreement with theoretical expectations⁹.

These results are impactful for materials science in two ways. First, they show the richness of playing with dimensionality at the nanoscale — somehow similar

to what has been done by rolling up two-dimensional sheets into nanotubes, now we see novel properties appearing in the θ -dependent superlattices. Second, Raman spectroscopy is increasing in importance in the field of nanomaterials, always surprising researchers with the deep level of information one can obtain. Looking now at a broader perspective, it is astonishing to see the level that nanoscience is achieving. Going back two decades at most, materials scientists were struggling to control precisely how to build specific well-designed nanostructures, with bottom-up and top-down approaches. Such control is an absolutely necessary step for nanoscience to deliver on the promised wonderful emerging technologies, which are highly sensitive to the structure at the atomic level. The sudden arrival of these intriguing few-atoms-thick, pure-surface, two-dimensional materials has provided a natural platform for materials scientists to create all sorts of new electronic materials utilizing a microscope and a micro-manipulator. Now, we are facing all these beautiful and intriguing novelties, including the birth

of twistrionics, which might represent a significant leap in the transport and control of energy and information, comparable to how the traditional electrical and electronic technologies have shaped up our present lifestyle. □

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Competing interests

The author declares no competing interests.



HAFNIA FERROELECTRICS

Another route to ferroelectric HfO₂

Observation of large remnant polarization in epitaxial yttrium-doped hafnium oxide thin films demonstrates that small-grained or ultrathin microstructures are not required to achieve robust ferroelectric behaviour.

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The surprising discovery that hafnium oxide (HfO₂)-based thin films can be ferroelectric, first reported in 2011 by Böschke et al.¹, has spurred continually growing interest in understanding and optimizing the factors that control this behaviour. This is motivated both by the demonstrated compatibility of HfO₂ with silicon-based electronic devices, and by the desire to find alternatives, in the applications of ferroelectrics, to the use of well-established, but environmentally unfriendly, lead-containing materials such as PbTiO₃ or Pb(Zr_xTi_{1-x})O₃.

Ferroelectric materials exhibit switchable non-zero polarization. Only materials with a non-centrosymmetric structure can be ferroelectric, which means that the thermodynamically stable cubic, tetragonal and monoclinic phases of HfO₂

are not ferroelectric (Fig. 1). Previous studies have concluded that formation of a non-centrosymmetric orthorhombic structure of HfO₂, having space group *Pca*2₁, is the key to realizing ferroelectric behaviour², and thus determining the synthesis and processing conditions required to form this metastable phase has been the focus of many recent studies. A typical conclusion reached by many previous investigators is that ferroelectric behaviour in HfO₂-based materials can be observed only in nanocrystalline films with an average grain size no larger than about 10 nm (ref. ³). While several recent reports have demonstrated that epitaxial single-crystal HfO₂-based films can also exhibit ferroelectric behaviour, the remnant polarization (*P_r*) values reported in those studies were no larger than about

15 $\mu\text{C cm}^{-2}$ unless the films were limited to thicknesses of less than 10 nm (ref. ⁴). Even for much thinner epitaxial films, the maximum *P_r* value reported so far for HfO₂-based ferroelectric materials is 34 $\mu\text{C cm}^{-2}$ (refs. ^{5,6}). Similar maximum *P_r* values have been reported for nanocrystalline HfO₂-based films.

Now, writing in *Nature Materials*, Yu Yan, Pratyush Buragohain and co-authors report that they have succeeded in preparing ferroelectric 10-nm-thick epitaxial (111)-oriented yttrium-doped HfO₂ films that exhibit record-high room-temperature *P_r* values⁷ (Fig. 2), challenging the viewpoint that only ultrathin or nanocrystalline HfO₂-based films can exhibit large ferroelectric polarization. The 5% yttrium-doped HfO₂ films characterized in their study were grown by pulsed laser