Superlattices in van der Waals materials: a low-energy electron microscopy study

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SUMMARY

This thesis considers how lattices of different periodicities combine in two-dimensional materials. When adding two signals of different frequency, a modulation of the signal with the difference of the constituting frequencies occurs, commonly known as a beating pattern. The same effect can occur both in space and in time. In particular, the spatial variant occurs when combining two different two-dimensional lattices: an additional periodicity not present in the constituting lattices appears, with its spatial frequencies (inverses of the lattice periods) equal to the difference of the frequencies of the original lattices. If the difference in periods is small, the resulting pattern has a much larger periodicity, which is why they are sometimes called 'superlattices'. Such patterns are named 'moiré patterns', after a type of French textile consisting of two layers of fabric pressed together, yielding a watered pattern due to the interference of the two layers. Another common occurrence of this effect in daily life can be seen when two mesh fences overlap and one is slightly distorted by the perspective.

The same effect also occurs on the atomic scale when combining two-dimensional materials, also known as van der Waals materials. In such a combined system, the moiré periodicity can have surprising effects on the electronic properties of the combined materials. In this thesis, moiré patterns are studied in two different two-dimensional materials: graphene, the 2D form of carbon, and tantalum disulfide (denoted TaS_2). The latter is a transition metal dichalcogenide (TMD), a layered material that can be exfoliated to 2D just like graphite. This particular TMD is interesting because as a function of temperature it exhibits a variety of charge density wave (CDW) states.

Of all the many possible combinations of different two-dimensional materials, probably the most amazing example of new electronic properties occurs in the original 2D material, graphene, when combined with itself: When two graphene layers are combined at a specific 'magic' angle of about one degree, the resulting 'magic angle twisted bilayer graphene' (MABLG) turns out to become superconducting at low temperatures, an effect directly connected to a flat band in the band structure of the system and the moiré pattern that causes it.

In this thesis, I use Low-Energy Electron Microscopy (LEEM) to study moiré patterns in twisted bilayer graphene (TBG) and some other combinations of two-dimensional materials. LEEM has advantages in studying 2D materials compared to other imaging techniques. Unlike Transmission Electron Microscopy (TEM), it reflects electrons off the sample surface at low energies and is therefore inherently surface sensitive and much less prone to damaging the material itself. However, the electrons still penetrate the material to some depth and interact with the material in a way that depends on their precise landing energy. Due to the different interactions with different materials, there are variations in the amount of electrons reflected, causing so-called amplitude contrast between areas of different materials. As the reflectivity depends on the landing energy, the contrast can invert as a function of energy, where the 'darker' area (relative to another

area) at one landing energy becomes 'brighter' than the other area at another landing energy. This contrast mechanism enables for example counting the number of graphene layers on top of a substrate and imaging the local stacking of the first few layers of atoms and therefore any stacking domains forming between the layers.

Just like in any other modern microscopy technique, obtaining LEEM images is only part of the work. In so-called spectroscopy experiments, an image is taken for a range of different landing energies, to fully capture the energy-dependent reflectivity of the sample. To extract the most from such data, it is necessary to properly calibrate the data and correct for sample drift. The necessary techniques, which are applied throughout this thesis are described in Chapter 3. The calibration techniques are adopted from astronomy. First, a dark count image is subtracted from the data. Second, a flat field correction is applied by dividing out an evenly illuminated image to compensate for uneven detector gain. Furthermore, we describe a procedure to actively tune the (exponential) gain of the detector to obtain accurate reflectivity values over four orders of magnitude.

From TEM, we adopt a statistically averaged cross-correlation technique to register LEEM images of the same area. Here, the key components are to apply an edge-detection filter first to deal with contrast inversions and to compare all possible pairs of images to obtain sub-pixel accuracy. Finally, we highlight the use of Principal Component Analysis (PCA) to reduce the number of dimensions in the dataset and visualize the data in a few images and showcase that this corrected and reduced data is amenable to automatic clustering algorithms such as the k-means algorithm.

In Chapter 4, we use a specific imaging mode called Dark Field LEEM, which breaks rotational symmetry, to distinguish all the possible different stackings of bilayer and trilayer graphene. We show that in epitaxial graphene on silicon carbide stacking domains form from a moiré pattern between the graphene layer and the underlying buffer layer. We conclude that these stacking domains are intrinsic to (few-layer) epitaxial graphene on SiC, as the moiré pattern is due to the strain exerted on the buffer layer by the SiC substrate.

Furthermore, we show that these domains have implications for the process of hydrogen intercalation, which is used to create so-called quasi-free standing graphene. We conclude that the hydrogen, despite its small size, does not penetrate the pristine graphene. It only penetrates at pre-existing point defects in the graphene, and travels below the graphene, preferentially along the domain boundaries.

Extending on this, Chapter 5 explores how in few-layer graphene, the domain boundaries themselves can be directly imaged using LEEM and we compare the contrast mechanism in twisted bilayer graphene and in the strained graphene on SiC. We show that for large domains the contrast is a pure amplitude contrast caused by the local relative stacking of the layers. The measured reflectivity therefore matches well with computations of the reflectivity of such different stackings. For small domains on the other hand, a different contrast mechanism becomes dominant, namely phase contrast, where interference of the phase of the electron waves reflecting of neighboring areas creates contrast. The contribution of this contrast mechanism yields a higher visibility of the moiré pattern, in particular in thicker sandwiches such as twisted bilayer-on-bilayer graphene.

The imaging of the domain boundaries in this way is applied to twisted bilayer graphene (TBG) in Chapter 6 to characterize the spatial variations of the moiré pattern, which gov-

ern the electronic properties of such samples. Additionally, we show that LEEM can be used to measure temporal fluctuations of the moiré lattice in TBG. Although these fluctuations correspond to collective atomic movements of less than 70 pm, which is much smaller than the resolution of the LEEM, they can be imaged using a magnification factor due to the moiré pattern itself. The same magnification enables the imaging of edge dislocations in the atomic lattice.

In Chapter 7, the same imaging mechanism is applied to study the morphology of the stacking domains in several samples of high-quality graphene on SiC. The morphology of the stacking domains highlights that even in the most homogeneous of such samples, there is an intrinsic strain disorder, caused by a spontaneous symmetry breaking due to both atomic edge dislocations and the coexistence of striped and triangular domains. This can help explain the observation of varying electronic properties of the graphene in such samples and help further optimize the growth processes.

In Chapter 8, we change gears and use LEEM to study the combination of different lattices occurring in TaS_2. In this material, such superlattices are caused by two completely different aspects. First, the charge density wave (CDW) states cause an extra periodicity larger than the atomic lattice, where the precise periodicity depends on the temperature. Second, this TMD occurs in different polytypes, i.e. different internal arrangements of the atoms within the Van der Waals layers with slightly different lattice constants. After demonstrating that LEEM can be used to distinguish different stackings of mixes of such polytypes, we study the combination of the temperature dependent CDW lattice occurring in the 1T polytype of TaS_2 with the atomic lattice. We show that in mixed polytype samples, in-plane domains of the two possible orientations of the CDW lattice occur at room temperature at an angle which is not the same as the angle in bulk 1T-TaS_2. We find that the transition temperatures between the different CDW states depend on the precise local polytype stacking and that the angle of the CDW lattice seems linked with the size of the in-plane orientational domains. As the different CDW states have a strong influence on the conductivity, this would make mixed polytype TaS_2 interesting for sensor applications if a controlled way to engineer different polytype stackings could be found.