1.3.13 Synthesis and properties of van der Waals heterostructures

Van der Waals heterostructures (vdWh) are "designer heterostructures" made by assembling two-dimensional (2D) sheets in a precisely chosen sequence. They are a playground for fundamental studies with the potential to reveal unusual properties and new phenomena. Before 2014, vdWh presented limited lateral dimensions, being obtained via mechanical exfoliation of bulk crystals and a cumbersome process of mechanical assembly. This hindered not only the technological prospects of vdWh, but also their accessibility to a number of techniques of interest for fundamental studies. We demonstrated that it is possible to synthesize a large number of high-quality and scalable vdWh via chemical vapor deposition (CVD) and that these materials host enticing optical, electronic and nanomechanical properties and significant applicative prospects.

In the last years we have demonstrated the synthesis and investigated the properties and applicative prospects of different vdWh that can be grouped as follows: (i) vdWh based on 2D transition metal dichalcogenides (TMDs); (ii) vdWh based on uncharted 2D materials; (iii) twisted vdWh with controlled azimuthal angles.

(i) By 2014, a large plethora of 2D materials beyond graphene had been isolated via mechanical exfoliation. Among them, 2D semiconducting TMDs displayed strong appeal for fundamental studies (e.g. direct bandgap transition, extraordinary photoluminescence, giant exciton binding energies, sizable spin-splitting, valley degree of freedom) and great applicative potential in optoelectronics and spintronics. The combination in a vertical structure of semimetallic graphene and 2D TMDs was identified as a largely uncharted and extremely exciting playground to realize and to investigate. The first results in this direction were published in Ref. [1], where we demonstrated a critical step in the scalable CVD synthesis of vdWh by reporting for the first time the direct growth of a continuous atomic-thick layer of tungsten disulfide (WS_2) on different 2D materials such as hexagonal boron nitride (hBN) and graphene. In view of applications where the transduction of quantum information is crucial (e.g., electro-optical transducers), this work showed that the synthesized heterostacks present a remarkable conservation of polarization peaking at 74%. Furthermore, we presented an approach for the bottom-up fabrication of photoconductive and photoemitting patterns in WS_2 on epitaxial graphene on silicon carbide (SiC), where the quantum-optical properties of WS_2 can be combined with the outstanding ballistic transport properties of graphene [1]. Among the heterostacks demonstrated in Ref. [1], we selected that of WS_2 on epitaxial graphene on SiC as the ideal one to further adopt for fundamental investigations because of its extreme cleanliness. Microscopic and spectroscopic characterization by using in-house and synchrotron facilities demonstrated a 0° azimuthal alignment of graphene and WS_2 as well as the largest reported spin-orbit splitting for monolayer WS_2 (i.e., 462 meV) [2]. With tailored nanotribological studies, we also demonstrated superlubric sliding of WS_2 on graphene on SiC induced by scanning microscopy techniques [3]. We interpreted the reported experimental results by means of classical molecular dynamics simulations which indicated that an ultra-low friction motion is triggered by the tip-sample interaction. Further experiments presented in the paper demonstrated that our growth approach led to an atomically sharp WS_2/graphene interface, which is ideal for nanotribology investigations. The aging of monolayer WS_2 synthesized on epitaxial graphene was thoroughly studied and the effect of defects

in accelerating the aging process assessed and modeled [4]. Spectroscopic ellipsometry was used to investigate the complex dielectric function of WS_2 flakes on epitaxial graphene [5]. Also, we recently reported the direct evidence for efficient ultrafast charge separation in WS_2/graphene heterostructures by performing time- and angle-resolved photoemission spectroscopy (tr-ARPES) investigations [6]. After having explored the optical, electronic, chemical and nanotribological properties of this heterostack [1-6], we tested its application in the field of optoelectronics. In Refs. [7] and [8], we reported original approaches for the fabrication of optoelectronic devices on up to 4 inches wafers. Thanks to these approaches, low contact resistance, band alignment control, and ultimately high-performing devices could be achieved. In Ref. [7], a wavelength dependent persistent photocurrent (PPC) was observed, making this system interesting for the implementation of 2D-based data storage devices. As SiC is often considered a niche substrate for device fabrication, we recently demonstrated the possibility to obtain WS_2/graphene arrays (that behave as unipolar optoelectronic component) on the technologically relevant substrate SiO_2/Si [9]. Also, we reported on the possibility of using TMD/graphene stacks for realizing low-voltage field-effect-transistors (FETs) for digital and analog electronics [10].

(ii) In Ref. [11] and [12], we realized novel 2D materials by intercalating a single layer of copper and gold atoms, respectively, in between SiC and graphene. In particular, in Ref. [12] we were the first to report on the synthesis and properties of 2D gold (2D-Au). We demonstrated that graphene imposes a crystalline order on the gold layer, thereby allowing its electronic properties to unravel. ARPES studies showed that 2D-Au is remarkably a semiconductor with the valence band maximum 50 meV below the Fermi level, significant spin-orbit splitting, and a saddle point at −400 meV, meaning that the van Hove singularity (vHS) in the density of states is at an energy at reach for electronic measurements (Fig. 1). This makes this system an appealing platform for the exploration of collective phenomena at low temperatures and non-linear optics effects.

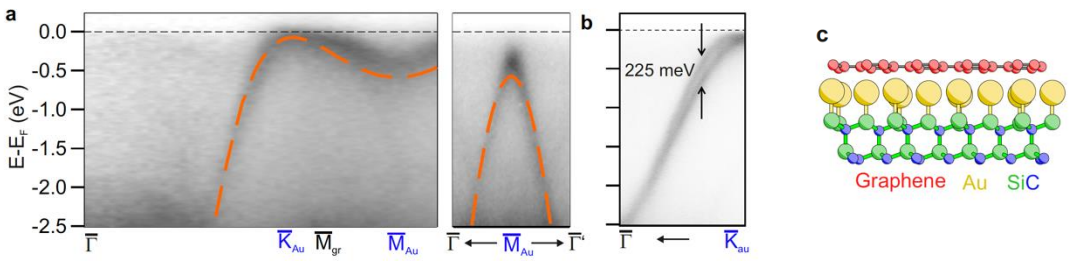

Figure 1. Electronic band structure of 2D-Au. (a) ARPES cut along k_y showing the Au bands dispersion (left panel) and spectrum cuts along k_x direction (right panel). The orange dashed lines superimposed to the data are tight-binding bands. (b) Au bands dispersion along the ky direction highlighting their spin-orbit splitting. Photon energy is 95 eV. (c) Ball-stick model of the gold atoms intercalated between graphene and SiC(0001).

(iii) Twisted heterostructures of layered 2D materials are currently a central topic in science, boosting research efforts at the intersection of condensed-matter physics and nanotechnology. Despite the exciting results recently achieved by the community, the relative orientation of the individual layers typically relies on the researchers' manual crafts, which is unavoidably limited in control and

reproducibility. With our work we have demonstrated that CVD can be used to obtain large-scale heterostructures with controlled angles. In Ref. [12], we investigated the properties of graphene grown on hBN with different rotation angle by Raman spectroscopy. Recently, in collaboration with Harvard University, we took the challenge of controlling the twist angle of graphene bilayers during their growth by CVD, focusing on the case of the incommensurate dodecagonal quasicrystals formed at 30° (30TBLG). We concentrated on this system because of recent reports of multiplication of the Dirac cones revealed by photoemission experiments, indicating important modification of the low-energy electronic structure. We were the first to report on the low-temperature transport and magnetotransport properties of 30TBLG. We obtained samples with excellent crystalline quality and carrier mobilities up to 10^5 cm^2/Vs, indicating low disorder, and found that the graphene quasicrystals effectively behave as uncoupled layers, showing 8-fold degenerate quantum Hall states (Fig. 2) [13]. With this result we could provide an answer to the debate whether the Dirac cones replica detected by previous photo-emission experiments could contribute to the electrical transport.

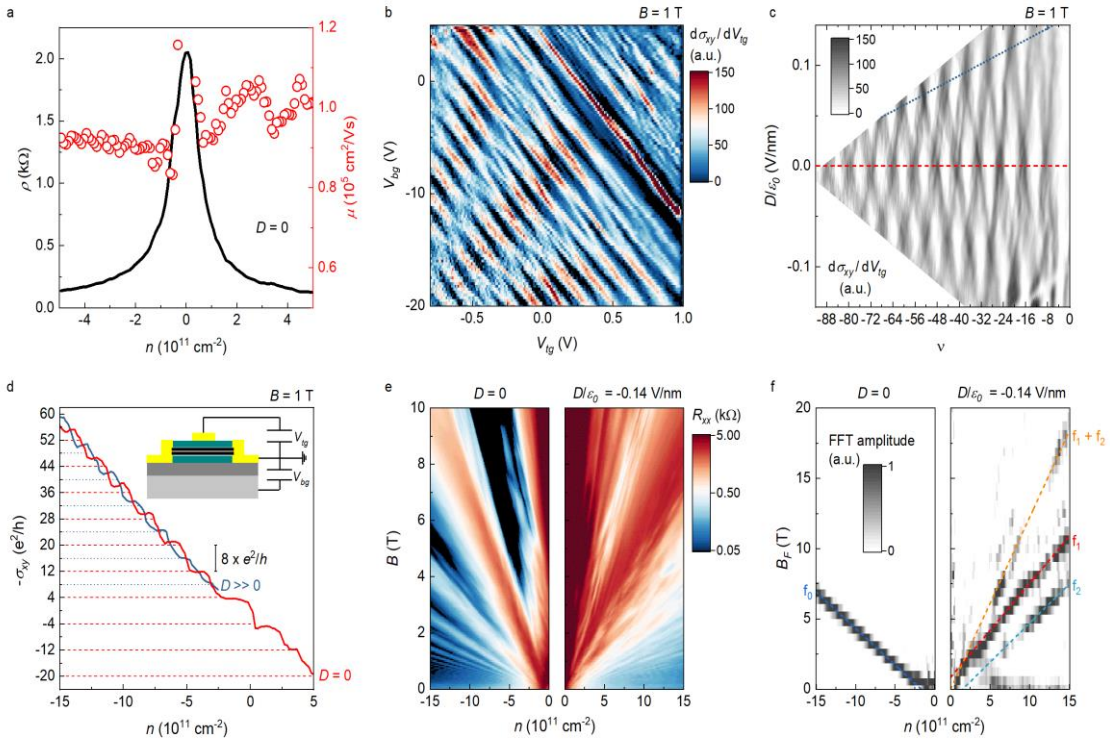

Figure 2. (a) Resistivity (black line) and carrier mobility (red circles) of 30TBLG as a function of carrier density n, at zero displacement field D. (b) First derivative of the Hall conductivity σ_{xy} as a function of V_{tg} and V_{bg}, at B = 1 T. (c) Same data of (b) as a function of ν and D/ε_0. The red dashed line marks D = 0. (d) Hall conductivity as a function of carrier density at B = 1 T, for D = 0 (red line) and D >> 0 (blue line). The inset shows a schematic cross section of the devices studied (light grey = Si; dark grey = SiO_2; black = graphene; dark cyan = hBN; yellow = Cr/Au). (e) Longitudinal resistance as a function of carrier density for zero (left panel) and finite (right) displacement field. (f) Fast Fourier transform (FFT) of the oscillatory component of the resistance data in (e). The dashed lines $f_{0,1,2}$ are fits of the main peaks in the FFT spectra as a function of n, while f_1+f_2 is the sum of the fits to the two split components. All the data were acquired at T = 4.2 K.

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