Formation and structural analysis of twisted bilayer graphene on Ni(111) thin films

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ABSTRACT

We synthesized twisted bilayer graphene on single crystalline Ni(111) thin films to analyze the statistical twist angle distribution on a large scale. The twisted bilayer graphene was formed by combining two growth methods, namely the catalytic surface reaction of hydrocarbons and carbon segregation from Ni. Low energy electron diffraction (LEED) investigations directly revealed dominant twist angles of 13°, 22°, 38°, and 47°. We show that the angle distribution is closely related to the sizes of Moiré superlattices which form at commensurate rotation angles. In addition to the commensurate angles, quasi-periodic Moiré structures were also formed in the vicinity of the dominant angles, confirmed by microscopic observations with low energy electron microscopy and scanning tunneling microscopy (STM). The quasi-periodic Moiré patterns are presumably caused by insufficient mobility of carbon atoms during the segregation growth while cooling. Micro-LEED studies reveal that the size of single twisted domains is below 400 nm. Atomic-scale characterization by STM indicates that the twisted layer grown by segregation is located underneath the layer grown by surface reaction, i.e. between the Ni surface and the top single-crystal graphene layer.

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1. Introduction

The electronic properties of mono- and few-layer graphene strongly depend on the number of carbon layers. The π-bands of monolayer graphene exhibit a linear electronic dispersion at the $\overline{K}$-point of the graphene Brillouin zone [1]. When two graphene monolayers are stacked with the same in-plane rotational orientation, they form an AB-stacked bilayer. Then, the π-bands have two branches and take on a parabolic dispersion [2]. Monolayer graphene as well as charge-neutral bilayer graphene is a semi-metal without a band-gap. Bilayer graphene, however, can turn into a semiconductor with a tunable band-gap [3]. This can be accomplished by doping [4,5] or an electric field [6]. It should be noted that then – in addition – the parabolic dispersion is disturbed. For even thicker graphene slabs, e.g. trilayer graphene, not only the number of layers, but also the stacking sequence of the layers affects the electronic properties [7–9]. In addition, the relative orientation of the layers is important. Two adjacent graphene layers that are rotated with respect to each other are referred to as twisted layers [10]. The interaction between such layers is strongly dependent on the twist angle [10]. Small twist angles can lead to unique electronic properties as recently

demonstrated in scanning tunneling spectroscopy (STS) measurements [11]. These experiments revealed the existence of a van Hove singularity close to the Fermi level, with its exact energetic position depending on the twist angle. Upon twisting the two layers, the Dirac cones of the rotated layer are split away from the Dirac cones of the unrotated layer and the dispersion close to the charge neutrality point is back to linear. Furthermore, the Fermi velocity at the $\overline{K}$-point is renormalized. It decreases with decreasing twist angle. These changes in the electronic structure are interesting both from a theoretical [12] and an experimental [13] point of view. Since all these properties vary with the twist angle, a geometrical analysis of twisted graphene layers addressing the angular distribution and the statistics is crucial. Several studies have been carried out for graphene stacks on the C-face of SiC using scanning tunneling microscopy (STM) [14,15], low energy electron diffraction (LEED) [14], and small-angle X-ray diffraction [16]. However, the number of layers is difficult to control for this system and a superposition of different angles is frequently observed. Twisted graphene multilayers were also found on Ni thin films in previous work [17,18]. Yet, precise information on the twist angle could not be obtained, since the experiments were done on polycrystalline Ni thin films. In that case, the reference angle i.e., the orientation of the substrate, varies, and it is difficult to carry out a statistical study of the twist angle. Only individual regions were analyzed using local probe methods such as STM and transmission electron

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microscopy. To overcome this obstacle, we have fabricated twisted bilayer graphene on single crystalline Ni(111) thin films. [19] This route enables us to perform a structural analysis across a large area and makes it possible to determine the distribution of twist angles by means of LEED. In addition, the detailed structure of the twisted patches was investigated on a smaller scale by low energy electron microscopy (LEEM), micro-LEED and STM.

Two methods can be applied to synthesize graphene on metal surfaces. The first utilizes the catalytic dehydrogenation reaction of hydrocarbons or the dissociation of carbon oxide gas on a metal surface [19–24]. When the metal surface is exposed to a hydrocarbon gas, the catalytic reaction produces carbon atoms or clusters [25] which start to nucleate and under suitable conditions form graphene. This process automatically stops when the graphene covers the entire surface of the metal. The catalytic reaction cannot proceed on top of the graphene layer and, hence, this growth mechanism is self-terminating. It has been established that on Ni(111) the graphene grown by the catalytic surface reaction technique follows the surface structure of the substrate. The graphene can be a flat single crystalline layer, because the lattice mismatch is small [19–21]. The second method to synthesize graphene is based on the segregation of carbon atoms to the surface from inside the metal bulk [26–31]. Carbon atoms that are present in the metal either as impurities or because they have been dissolved by a high temperature gas treatment, migrate to the metal surface during cooling. The segregated carbon atoms cover the metal surface as adatoms and form a twisted graphene lattice [17,18]. Therefore, sequential segregation growth after the formation of a single-crystalline graphene layer with the catalytic surface reaction should result in twisted bilayer graphene. Here, we have synthesized and studied such twisted graphene layers on Ni surfaces obtained with this method. The fixed angle of the first graphene layer grown by the catalytic surface reaction provides a single reference orientation and hence a large area statistical analysis of the twist angle makes sense. We note for the sake of completeness that the formation of twisted bilayer graphene has been recently reported as well for graphene on Ir(111) [32]. However, in that work, the first graphene layer is not in registry with the Ir(111) lattice, and thus already the first layer does not have a single orientation. In contrast, in the present work, only the graphene layer grown by segregation is twisted, so that the twist angle distribution can be directly detected by LEED through reference to the Ni(111) substrate.

2. Experimental

Single crystalline Ni(111) thin films were deposited on MgO(111) substrates [19,33,34]. A low temperature buffer layer technique was applied to obtain a flat Ni surface, as described in detail previously [19]. After depositing the Ni thin film, the sample was transferred through air and mounted in an ultra-high vacuum (UHV) chamber. We intentionally avoided a complete removal of carbon impurities introduced during the Ni deposition and/or air transfer while cleaning the Ni thin film by cycles of Ar^+ sputtering and heating. Single crystal monolayer graphene was grown on top of the Ni film using propylene gas at a pressure of 1.0×10^{-6} mbar for 5 min at 600–680 °C. Then, the sample was cooled down to room temperature. During cooling, carbon impurities remaining in the Ni film segregate to the surface and form twisted graphene domains. In order to ensure an unequivocal determination of the twist angle and obtain isolated twisted bilayer regions, we aimed at an intermediate graphene coverage between a single layer and a bilayer. The average layer thickness of the samples prepared in this study is 1.1–1.5 layers of graphene as measured with X-ray photoelectron spectroscopy (XPS).

XPS measurements were carried out with Mg Kα or monochromatized Al Kα radiation using a hemispherical analyzer for electron detection. The graphene layer thickness was determined by a C 1s/Ni 2p peak ratio using a monolayer sample as a reference [19]. The characterization with LEED and XPS has been conducted in-situ in the same UHV system. The background pressure was maintained in the low 10^{-10} mbar regime in all the UHV chambers. The scanning electron and scanning Auger microscopy (SEM/SAM) measurements were performed using a JEOL JAMP 7810 Auger micro probe system with an acceleration voltage of 20 kV. For SAM, the intensity of the C_{KLL} and Ni_{LMM} Auger transition was used. The LEEM images were acquired using an Elmitec LEEM III. STM was measured at 40 K. The data was evaluated using the WSxM software [35]. The SEM/SAM, LEEM, and STM measurements were done ex-situ after the graphene growth.

3. Results and discussion

Fig. 1(a) and (b) depicts an SEM image and a SAM image, respectively, for the same surface area of a sample containing both mono- and bilayer graphene. The selected region contains domains of different contrast in both SEM and SAM. The domains which appear darker in SEM and brighter in SAM (corresponding to a larger carbon signal) are assigned to bilayer graphene by spatially resolved Auger electron spectroscopy (AES) measurements (bottom curve in Fig. 1(c)). Those with brighter SEM and darker SAM contrast correspond to monolayer graphene (top curve). Note that the first layer grown by the catalytic surface reaction is single crystalline and covers the entire sample. It follows the Ni(111) surface structure and grows continuously over substrate steps [19,23]. Only the second layer (in the bilayer domains) formed during the segregation process of carbon atoms out of the Ni film upon cooling has a non-uniform coverage. It should be emphasized that it is well known, that even at such low temperatures as in our experiments, strong segregation of C occurs in Ni [36]. Some carbon impurities might participate in the formation of the first single-crystal layer, but most of them remain near the surface, segregate during cooling and form the second twist layer.

Fig. 2 shows the LEED patterns after the first growth step based on the catalytic reaction alone (panel (a)) and after the second growth step using segregation (panel (b)). In panel (a) the LEED pattern exhibits six sharp diffraction spots which is characteristic of the single-crystal structure of monolayer graphene on Ni(111) [19]. The graphene film grows in (1 × 1) periodicity on Ni(111), so that the graphene diffraction spots appear at the same position as the substrate spots. Note that the intensity vs. energy spectra (so called I–V curves) of the spots are quite different for the bare Ni(111) substrate and the graphene/Ni system due to multiple scattering of the low-energy electrons. This is illustrated in panel (c) for the two inequivalent first order diffraction spots (10) and (01) (black vs. red curve). In panel (b) a weak ring-like feature has appeared in addition to the main spots. This ring originates from those regions where twisted bilayer graphene has formed. Part of this diffraction pattern enclosed by the yellow boundary has been magnified on the right. The diffraction intensity is not distributed uniformly along the ring. Instead, the intensity is
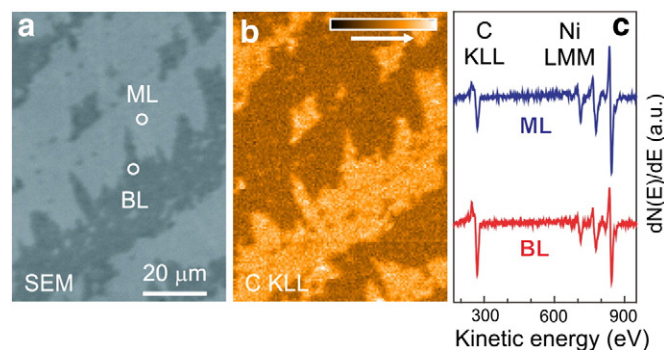
Fig. 1. Microscopic images of adjacent domains of monolayer (ML) and twisted bilayer (BL) graphene on a Ni(111) thin film. (a) SEM image and (b) SAM image mapping the intensity of the C_{KLL} Auger transition. (c) Differential Auger spectra from the two positions marked in panel a.