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Multi-layer and multi-component intercalation at the graphene/Ir(111) interface

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We present a scanning tunneling microscopy study of Fe and Co intercalated at the graphene–Ir(111) interface. In the case of Fe, we investigate the morphology of the surface with respect to the annealing temperature, which activates the intercalation, and as a function of coverage. By increasing the coverage we show that it is possible to intercalate multilayers at the interface. Finally, we demonstrate that the successive intercalation of Co and Fe for the same sample leads to distinct adjacent intercalation areas.

1. Introduction

The choice of the substrate on which a graphene layer can be grown is crucial in order to tailor the electronic properties of graphene or to create new graphene-based materials and devices. However, having graphene on a well-defined and clean substrate can be a challenge [1]. In order to broaden the choice of substrates or to change the graphene–substrate interactions, it is possible to intercalate specific elements at the pre-formed graphene–substrate interface. This method has recently become an active research area [2–12]. Furthermore, it has been reported recently that the intercalation method often leads to well-defined and highly uniform systems, which allow for the precise study of physical properties [8, 1,13,14]. In particular, the intercalation of magnetic materials is of prime interest [8,9,15–22]. Magnetic layers obtained in this way are very resistant against oxidation [23], i.e., a sample exposed to air and transferred back into the ultra-high vacuum (UHV) chamber still exhibits the same structure. It has been shown that these intercalated magnetic layers induce magnetism in graphene itself [9,15,16,22]. So far, a thorough study of the growth mode and a temperature- and coverage-dependent investigation of Fe and Co intercalation of graphene on Ir(111) is still lacking.

In this work, we present a scanning tunneling microscopy (STM) study of iron- and cobalt-intercalated graphene/Ir(111) systems. In both cases, the intercalation leads to well-defined epitaxial layers and the intercalated areas are characterized by a moiré pattern, which adopts the same symmetry and periodicity as the graphene/Ir(111) moiré [24]. The different surface morphologies, which result from a change of amount of Fe as well as annealing temperatures for the intercalation, are presented. Comparing the intercalation of Fe and Co, we find a layer by layer interstitial growth for both species but a higher mobility of Co compared to Fe at the graphene–Ir(111) interface. We also show that samples with both Co and Fe intercalated regions can be prepared.

2. Experimental details

Clean Ir(111) substrates are obtained by repeated cycles of Ar$^+$ sputtering ($E = 1$ kV, $I_{emission} = 10$ mA, $P_{Ar+} = 4.6^{-6}$ mbar, 30 min), annealing in O_2 atmosphere ($P_{O_2} = 1 \cdot 10^{-7}$ mbar , $T = 900$ K to 1500 K, 30 min) and flash annealing ($T = 1500$ K, 3 min). The graphene layer is obtained by a CVD process: the Ir(111) surface is exposed to a partial pressure of ethylene gas ($P_{C_2H_4} = 5 \cdot 10^{-8}$ mbar) while held at 1300 K for 10 min and then flashed for 45 s at 1500 K [24,25]. Co and Fe are deposited on the Ir(111) surface covered by a full graphene (Gr) layer. The intercalation process is activated by annealing the sample during deposition. The annealing is terminated directly after the end of the deposition. Our heater was calibrated using a dummy sample with a spot-welded K-type thermocouple under thermal equilibrium conditions. Note that the thermocouple is connected over a regular stainless steel feedthrough, therefore the measured temperatures are expected to be lower by up to a 100 K due to voltage drop on the resistance of the connectors.

A series of control experiments has been carried out: First, intercalation of Fe and Co on samples covered with graphene islands

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of several up to several hundreds of nm in diameter (details can be found in [9,15,16]). Second, an intercalation of Fe under a full graphene layer by post deposition annealing, which proved to be unsuccessful. In this case we observed only small areas of intercalated material and big Fe clusters on top of graphene.

All topographs shown in this letter were acquired in the constant current mode, at a temperature of ~30 K, using a home-built variable-temperature STM [26].

The amount of evaporated material was controlled using an ion flux in the evaporator. The deposition rate was calibrated by deposition of Fe or Co on a clean Ir(111) crystal and subsequent characterization by means of STM, yielding 0.5 ML/min. Note that for elevated temperatures the sticking coefficient is lowered and the deposition rate is then substantially reduced yielding 0.1 ML/min for 470 K and 0.05 ML/min for 600 K.

3. Results and discussion

The temperature dependence of the intercalation process is elucidated for a nominal deposition of 0.5 ML Fe in Fig. 1. When depositing Fe on the Gr/Ir(111) sample held at 420 K, only a part of the deposited Fe intercalates and Fe clusters remain on top of Gr as depicted in Fig. 1(a). Similar clusters with comparable size and morphology are also present when Fe is deposited at 300 K.

However, when annealing at a slightly higher temperature (470 K), all deposited Fe intercalates and forms well-defined intercalation areas with monolayer high Fe islands underneath Gr as illustrated in Fig. 1(b). These areas are characterized by a highly corrugated moiré pattern described recently [16,27]. It has been shown that the Fe monolayer is pseudomorphic with the Ir(111) surface and that the moiré pattern arises from the lattice mismatch in addition to the twisting angle that can arise between the graphene and the Fe monolayer. In the following, we define the highest positions of the Gr/Fe/Ir(111) moiré pattern as the hills and the lowest positions as the valleys, without distinction between fcc, hcp, and intermediate positions within valleys. Note that the apparent corrugation of the G/Fe/Ir(111) (from 110 pm to 150 pm depending on tunneling parameters) and G/Co/Ir(111) (from 120 pm to 180 pm depending on tunneling parameters) is an order of magnitude higher than the one of G/Ir(111) (from 20 pm to 60 pm depending on tunneling parameters). We have adjusted the gray scale so that the relevant moiré pattern on the intercalated areas is best visible.

Annealing at higher temperatures (600 K) leads to a change of the intercalation area when imaged with STM, as shown in Fig. 1(c). Although the periodicity and orientation of the moiré pattern can still be discerned, by comparing Fig. 1(b) and (c) a striking loss of homogeneity is observed, i.e., some valleys are at the same apparent height as hills. High resolution STM topographs such as the one presented in the inset of Fig. 1(c) reveal that the Gr layer itself is continuous across intercalated and non-intercalated areas. It is worth noticing that prolonged ($t > 1$ h) annealing at temperatures around 470 K leads to a similar effect. Therefore the annealing should be stopped as soon as the intercalation process has finished, before other processes are triggered.

We observed the surface morphology of the Fe-intercalated Gr/Ir(111) sample with different amounts of Fe deposited, while keeping the annealing temperature at 470 K during sample preparation, as in the case described in Fig. 1(b). In Fig. 2(a)–(d) STM topographs obtained after deposition of nominal 0.2 ML, 0.7 ML, 1.1 ML, and 8 ML, respectively, are presented. At low 0.2 ML nominal Fe coverage (Fig. 2(a)), we observe islands of the intercalation areas located mostly in the middle of terraces. These islands are ≈240 pm high as measured between top sites of clean Gr/Ir(111) and intercalated graphene moiré patterns. The exact height varies with tunneling parameters. After a nominal deposition of 0.7 ML Fe (Fig. 2) (b), we find extended intercalated Fe-islands as well as step decoration at Ir-step edges. The intercalation with nominal 1.1 ML deposited Fe leads to a complete layer of intercalated material and some ≈240 pm high islands, as measured betweeen the top position of the graphene moiré on the complete intercalation layer and the top position of the graphene moiré on the Fe island. At highest nominal coverage of 8 ML, we observe a complete continuous intercalation layer with additional islands and some crystalline bulk-like Fe islands on top of graphene. It is interesting to note that these latter islands are flat and that their edges follow the high symmetry directions of the underlying moiré.

In the sub-monolayer regime, the ≈240 pm high islands are ascribed to areas with one layer of intercalated Fe underneath Gr as discussed earlier [15, 16]. The fact that the islands are located in the middle of terraces indicates that the intercalation starts at defects of the graphene layer consistent with a recent report by Schumacher et al. in the case of Eu intercalation [7]. Such defects are even visible as darker spots on the graphene/Ir(111) parts in Fig. 2(a). Graphene is known to be very sensitive to ion bombardment [28–30]. In fact since a fraction of material deposited onto the surface is ionized, such ions may induce defects into the graphene lattice [31]. This would enable penetration through defects in an otherwise perfect graphene lattice. However, a longer evaporation time would lead to increase in the density of defects which we do not observe. Therefore we conclude that in our case Fe is intercalating by defects in graphene.

For the nominal coverage of 0.7 ML we have only a first layer Fe underneath Gr. However, in the experiment with 1.1 ML nominal coverage, besides a complete first Fe layer underneath Gr, the observed

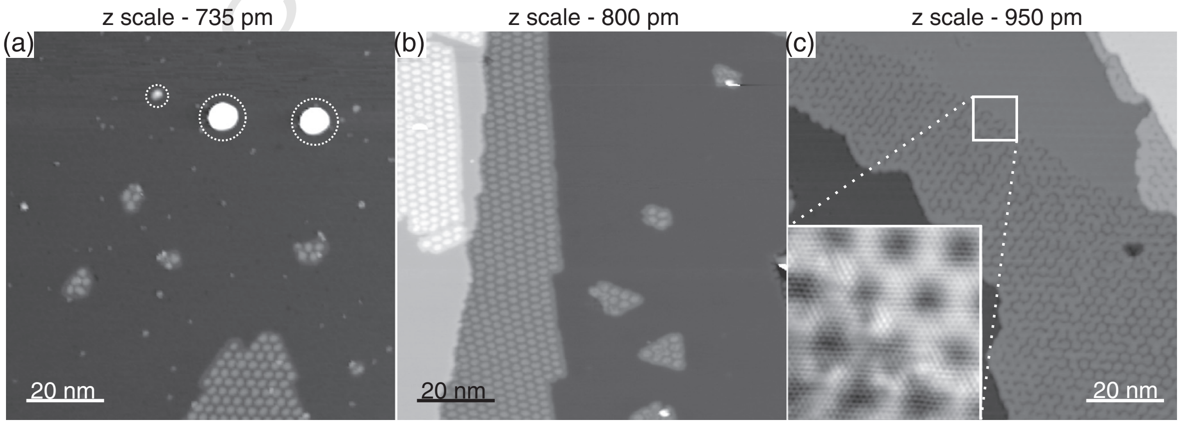

Fig. 1. Fe-intercalated graphene (Gr)/Ir(111) surfaces held at different temperatures during annealing. On the one hand, Fe clusters marked by circles in (a) are visible on top of Gr when the sample is held at a temperature of 420 K. These clusters are absent when annealing at $T = 470$ K, as depicted in (b). On the other hand, after annealing at 600 K (c), the typical moiré pattern of Gr/Fe/Ir(111) is no longer preserved indicating a modification of the intercalant layer or the Gr/Ir(111) interface. The inset in (c) is a high-resolution STM image of the marked area. The Gr layer is continuous across the [Gr/Ir]–[Gr/Fe/Ir] boundary.

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