Single orientation graphene synthesized on iridium thin films grown by molecular beam epitaxy


Citation: Journal of Applied Physics 120, 075304 (2016); doi: 10.1063/1.4960804
View online: http://dx.doi.org/10.1063/1.4960804
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/120/7?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Structural properties of Bi2Te3 topological insulator thin films grown by molecular beam epitaxy on (111) BaF2 substrates
J. Appl. Phys. 119, 165303 (2016); 10.1063/1.4947266

Epitaxial (111) films of Cu, Ni, and CuxNiy on α-Al2O3 (0001) for graphene growth by chemical vapor deposition

Epitaxial graphene prepared by chemical vapor deposition on single crystal thin iridium films on sapphire
Appl. Phys. Lett. 98, 181903 (2011); 10.1063/1.3585126

Single-crystalline aluminum grown on MgAl2O4 spinel using molecular-beam epitaxy
J. Vac. Sci. Technol. B 29, 03C128 (2011); 10.1116/1.3570869

Defects in HgTe grown by molecular beam epitaxy on (211)B-oriented CdZnTe substrates
Single orientation graphene synthesized on iridium thin films grown by molecular beam epitaxy

A. Dangwal Pandey,1,a) K. Krausert,1,2 D. Franz,1,2 E. Gränäsa, R. Shaydukb, P. Müller,1,2 T. F. Keller,1,2 H. Noeib,1 V. Vonk,1 and A. Stierle1,2,b)
1Deutsches Elektronen-Synchrotron (DESY), D-22607 Hamburg, Germany
2Fachbereich Physik, Universität Hamburg, D-22607 Hamburg, Germany

(Received 14 April 2016; accepted 11 July 2016; published online 16 August 2016)

Heteroepitaxial iridium thin films were deposited on (0001) sapphire substrates by means of molecular beam epitaxy, and subsequently, one monolayer of graphene was synthesized by chemical vapor deposition. The influence of the growth parameters on the quality of the Ir films, as well as of graphene, was investigated systematically by means of low energy electron diffraction, x-ray reflectivity, x-ray diffraction, Auger electron spectroscopy, scanning electron microscopy, and atomic force microscopy. Our study reveals (111) oriented iridium films with high crystalline quality and extremely low surface roughness, on which the formation of large-area epitaxial graphene is achieved. The presence of defects, like dislocations, twins, and 30° rotated domains in the iridium films is also discussed. The coverage of graphene was found to be influenced by the presence of 30° rotated domains and an almost complete coverage of graphene was obtained. This synthesis route yields inexpensive, air-stable, and large-area graphene with a well-defined orientation, making it accessible to a wider community of researchers for numerous experiments or applications, including those which use destructive analysis techniques or irreversible processes. Moreover, this approach can be used to tune the structural quality of graphene, allowing a systematic study of the influence of defects in various processes like intercalation below graphene. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4960804]

I. INTRODUCTION

The preparation of large-area graphene with high structural quality is in demand to exploit its two-dimensional nature with unique physical properties for diverse applications, including future electronic devices and sensors.1,2 Chemical vapor deposition (CVD) has become an established method to deposit epitaxial graphene on transition metal single crystals,3–5 and it was further demonstrated that epitaxial graphene with a preselected orientation can be synthesized using this route.6–10 CVD growth of graphene on Ir and Pt is self-limiting, which results exactly in one monolayer of graphene coverage of the surface.11 Graphene is found to interact weakly with the surfaces of Ir(111) and Pt(111) and is of high quality on these substrates.12–15 Moreover, a weak interaction between graphene and support might favor the formation of different coexisting domains of graphene.16 For example, non-rotated graphene on Pt (111) with a periodicity of 2.2 nm, 1.5° rotated graphene with a periodicity of 2 nm, and a 90° rotated graphene with a periodicity of 0.5 nm.17 On Ir(111), the most abundant form of graphene is non-rotated (R0) with respect to its support, while 30° rotated, 18.5° rotated, and 14° rotated forms of graphene are also reported.18 The non-rotated graphene can be grown as a single, millimeter sized, layer on Ir(111) single crystals,9 where the moiré structure of R0 graphene exhibits a periodicity of 2.53 nm and 0.02 nm vertical corrugations.19,20 A lattice mismatch between the metal substrates and graphene leads to a slight, but periodic, undulation of graphene on the top. These undulations in graphene are imaged by means of scanning tunneling microscopy (STM) as moiré structures.21–24 Graphene moiré on Ir(111) has been exploited as an active template to grow highly ordered lattice of variety of metal clusters such as Ir, Pt, W, Re, Au, and Iron.19,23 A regular array of monodispersed metal nanoclusters forms a model system to study various physical phenomena or chemical processes like heterogeneous catalysis, electrical transport, magnetism, etc. However, here the use of expensive single crystals makes this synthesis route less convenient for a wide community of researchers to conduct various possible experiments on the nicely formed cluster lattice on graphene moiré. A possible approach to circumvent this problem is to synthesize epitaxial graphene on Ir(111) thin films grown on an inexpensive substrate. Only few studies were reported on synthesizing graphene on iridium films, where sapphire(0001)24 or Si(111) with yttria-stabilized zirconia (YSZ) buffer layer25,26 was used as a support. Sapphire crystals are widely used as substrates to grow metal films due to their high thermal and chemical stabilities, necessary for withstanding the harsh conditions of the CVD process required for the synthesis of high-quality graphene.27–30 Single crystal iridium(111) films can be deposited by pulsed laser deposition (PLD)24 and metal-organic CVD31 on (0001) sapphire single crystals. Deposition of epitaxial iridium films on other orientations of sapphire was also reported by using the method of metal-organic CVD and an epitaxial relationship between different orientations.

a)Electronic mail: arti.pandey@desy.de
b)Electronic mail: andreas.stierle@desy.de
of the deposited film and the substrate was obtained from x-ray diffraction (XRD) measurements. Apart from these, the growth of (111) oriented Ir films on sapphire substrates is not explored systematically, and to the best of the authors’ knowledge, no report on (111) oriented iridium films grown on c-plane sapphire substrates using molecular beam epitaxy (MBE) is available up to date.

Here, we report on the deposition of epitaxial Ir(111) thin films on (0001) oriented sapphire single crystals by means of MBE and its use as a support to synthesize graphene monolayer by CVD. Various techniques were employed to characterize the iridium films, grown with systematically varying deposition parameters, and the subsequently synthesized graphene. Low energy electron diffraction (LEED) and x-ray diffraction (XRD) confirm that the (111) oriented iridium films are highly crystalline, and x-ray reflectivity (XRR) measurements verify their extremely low surface roughness. The presence of defects like dislocations, and rotated and twin domains in the film were also studied and their influence on the graphene was observed. An almost full coverage of graphene on the iridium films was confirmed by Auger electron spectroscopy (AES), and its perfect alignment with respect to the underlying Ir lattice was verified by LEED. The surface morphology and topography mapped by means of scanning electron microscopy (SEM) and non-contact atomic force microscopy (NC-AFM) revealed a homogeneous coverage and an atomically smooth surface of graphene on top. This is further corroborated by the XRR measurements showing the signature of the graphene layer on top of the iridium film.

II. EXPERIMENTAL

Sapphire (0001) crystals with a surface area of 10 $\times$ 10 mm$^2$ and low miscut ($<0.1^\circ$) were used as substrates. The as-received crystals were broken into two parts (for growing two samples at the same time) and cleaned with acetone, ethanol, and isopropanol successively in an ultrasonic bath. Sapphire surfaces were prepared by heat treatment at 1000 K in UHV for 40 min and treatment with atomic oxygen from a thermal cracker, followed by a flash annealing above 1200 K in UHV. Iridium films of various thicknesses were deposited by molecular beam epitaxy in an UHV chamber (base pressure of 5 $\times$ 10$^{-11}$ mbar), using an e-beam evaporator. The growth rate was varied as summarized in Table I, between 0.06 nm/min and 1.2 nm/min for different iridium films. During deposition, all the samples were kept at 700 K unless mentioned otherwise. For the highest growth rate, the growth temperature was 800 K. In another case (sample 13 A), a differential growth temperature was used, i.e., 1000 K in the beginning for one third of the deposition time and 700 K for the rest of the deposition. A post-annealing treatment was employed for all samples by a successive heating at 1100 K for 30 min. Graphene was synthesized by exposing the iridium film to ethylene with a partial pressure of $\sim$10$^{-7}$ mbar until a complete coverage at room temperature and then at temperatures above 1050 K. More details on graphene synthesis are given in Section III B.

LEED and AES measurements were performed in situ after each step of surface cleaning, iridium deposition, and graphene synthesis, to study the structure and composition of the surface. The deposited iridium films were contacted by a tantalum foil to minimize the charging of the insulating sapphire substrate during LEED measurements. For further characterization, the samples were stored under ambient conditions.

X-ray reflectivity and diffraction experiments were conducted for a detailed structural characterization of the surface and bulk of the samples. X-ray reflectivity is used to determine the film thickness, surface roughness, interfacial roughness, and the electron density profile perpendicular to the film plane. Out-of-plane Bragg scans (or radial scans measured in high angle regime) at a reciprocal-lattice point along the growth direction of the film yields information on the crystalline perfection and mosaicity. Specular rods were simulated by using the software ROD.$^{32}$ In-plane Bragg scans, performed at a grazing angle of incidence equal to the critical angle for the total external reflection for iridium to achieve a maximum signal to noise ratio, are used to determine the epitaxial relationship between the deposited iridium film and the substrate, average in-plane crystallite size, and mosaicity. A four-circle reflectometer with a Mo K$_\alpha$ source and a six-circle diffractometer with Cu K$_\alpha$ source were used for x-ray reflectivity and diffraction measurements.

To probe the reciprocal space of the Ir(111) film, an orientation matrix was set in terms of hexagonal surface coordinates, with lattice parameters: $a = b = \frac{a_0}{\sqrt{3}}, c = a_0 \cdot \sqrt{3}$, and $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ with Ir bulk lattice parameter $a_0 = 3.8392$ Å. In this article, we used the notation $(h k l)$ for bulk coordinates and $(H K L)_s$ for surface co-ordinates of the (111) oriented face centered cubic (fcc) iridium films. The transformation between bulk and surface co-ordinates is as follows:

$$\begin{pmatrix} h \\ k \\ l \end{pmatrix} = \frac{1}{3} \begin{pmatrix} 2 & -2 & 1 \\ 2 & 4 & 1 \\ -4 & -2 & 1 \end{pmatrix} \begin{pmatrix} H \\ K \\ L \end{pmatrix}_s$$

The surface topography of a fresh graphene covered iridium film was measured at room temperature by NC-AFM.
with a base pressure of $<5 \times 10^{-11}$ mbar. Some samples were also examined by NC-AFM under ambient conditions. The surface morphology of bare and graphene covered iridium films was additionally characterized using SEM.

III. RESULTS AND DISCUSSION

A. Growth of iridium films on (0001) sapphire

The cleaned and annealed sapphire crystal surface shows a bright $(1 \times 1)$ LEED pattern with clear threefold symmetry. Well-defined hexagonal spots in the LEED pattern were obtained after the iridium deposition, as given in Fig. 1(a), in line with a $(111)$ oriented surface. In a particular case, when the iridium film was deposited at a high growth rate of 1.2 nm/min, additional LEED spots rotated by 30° with respect to the normal LEED pattern were observed (Fig. 1(b)), which verify the existence of 30° rotated domains in the film.

AES data were collected from an annealed sapphire crystal surface before and after the deposition of iridium films, as given in Fig. 1(c). For a comparison, an Auger spectrum from an Ir(111) single crystal, measured in the same set-up, is also plotted in Fig. 1(c). The bare sapphire shows no contaminants, and after the deposition of iridium, the characteristic peaks for iridium, comparable to that from an Ir(111) single crystal, are observed, while the AES oxygen KLL signal from the sapphire substrate is completely absent. The absence of the O KLL signal demonstrates that the iridium film deposited on sapphire is completely closed. A shift of about 4 eV in the spectrum of the Ir-film arises because of charging of the film deposited on an insulating substrate.

NC-AFM investigations were performed ex situ to image the surface topography of the iridium films. Fig. 1(d) shows the scanned area of $2.2\times2.2\ \mu m^2$ over a 10 nm thick iridium film. The film surface is relatively smooth as depicted from the roughness profile, and the root mean square roughness value of 0.15 nm was obtained for the film surface.

1. X-ray reflectivity studies

The x-ray reflectivity curves show the intensity of specularly reflected x-rays at small angles, which depend on the average electron density profile of the material perpendicular to its surface. Figure 2 shows the reflectivity data for iridium films with varying thickness from 10 nm to 40 nm together with their respective fits. For a better comparison, the intensity is plotted as a function of Q. Iridium films of 13 nm and 10 nm show distinct oscillations in the reflectivity curves, while thickness oscillations are strongly damped for 30 nm and 40 nm iridium films. To fit the reflectivity data, we used Parratt formalism for x-ray reflectivity, with a modification to include the contribution of roughness at the interfaces. In the case of damped reflectivity oscillations, the film thickness was determined by using the Scherrer equation for the Ir(111) reflection, and this value was used for the fit. For the electron density of the iridium film, we have assumed the bulk value. The parameters deduced from the fit are summarized in Table I.

On comparing the surface roughness of all iridium films, we find that the highest value of 0.16 nm is observed for the film grown with high deposition rate (1.2 nm/min), while extremely smooth surfaces are achieved (surface roughness $<0.1$ nm) for the films deposited at a rate of 0.6 nm/min or lower. The in-air NC-AFM results on a 10 nm iridium film grown with a rate of 0.06 nm/min, as shown in Fig. 1(d), provide similar roughness values. Since the microscopy techniques probe the sample locally, we believe that the surfaces of iridium films deposited on sapphire are extremely smooth.
over the entire surface as depicted by XRR measurements, which is advantageous for successive high-quality graphene growth.

Two samples of 13 nm iridium film thickness were grown with a similar deposition rate but at different growth temperatures: one at 700 K and the other at 1000 K for one third of deposition time and at 700 K afterwards. In the latter case, a higher growth temperature in the beginning of the growth process was intended to study its influence on the crystallinity of the film. In both cases, clear oscillations in a wide angular range are observed, and extremely low values for surface roughness (<0.06 nm) are obtained. Moreover, a small interface roughness (<0.2 nm) between iridium films and sapphire matches closely to the atomic step height in (0001) sapphire crystal surface.

The origin of damped reflectivity oscillations for 30 nm and 40 nm iridium films is found to be a gradient in the film thickness due to a small distance between the sample and the Ir-evaporator during the film growth. This was confirmed by performing radial Bragg scans with smaller x-ray beam footprint at different points on the film surface and the variation in the film thickness up to ∼1 nm/mm was obtained. The very high values of the interface roughness (>1.5 nm) for these films are artefacts that are caused by the thickness gradients leading to a smearing out of the thickness oscillations.

2. Out-of-plane Bragg scan results

Crystalline thin films, when consisting of N coherently scattering lattice planes, are characterized by Bragg reflections with satellite fringes of Laue oscillations given by \[ I = \sin^2 \left( \frac{Q L_c}{2} \right) \sin^2 \left( \frac{Q t}{2} \right), \] where \( t \) is the interplanar spacing corresponding to the angular position of Bragg reflection, \( L_c = N \cdot d \) is the coherent thickness, and \( Q = \left( \frac{2 \pi}{\lambda} \right) \sin \theta \) is the magnitude of the scattering vector.

Fig. 3 shows a radial Bragg scan through the Ir(111) reflection for a 13 nm iridium film. The observed out-of-plane epitaxial relationship is Ir(111)∥Al2O3(0001). The experimental \( d_{111} \) value is 2.2187 (±0.0015) Å, which is close to that for bulk iridium (2.2167 Å). Laue oscillations of the Ir(111) Bragg reflection are very prominent in these measurements. \( L_c \) is calculated to be 13.3 nm from the period of Laue oscillations, which is approximately identical to the thickness of the film retrieved from the reflectivity curve. The coherence thicknesses obtained for different films are summarized in Table I, matching closely to the film thicknesses retrieved from the reflectivity measurements. This confirms that these iridium films are completely made up of coherently scattering (111) planes in the vertical direction.

A rocking scan obtained with a fixed detector at the position for the Ir(111) reflection is given in the inset of Fig. 3, which provides information on the mosaicity normal to film plane. This rocking curve shows two components: a resolution limited sharp Bragg component with FWHM of 0.12° superimposed on a broader diffuse component with FWHM of ∼0.54°. Lattice distortions are found to be responsible for giving rise to such a broad diffuse component in the rocking scans of epitaxial films. The lateral coherence length of 23 nm is derived from the FWHM of the diffuse component, which represents the average distance between dislocations in the film. The presence of structural defects (such as dislocations, local deformation of lattice planes, and twinned domains), based on x-ray and microscopy measurements, was reported for epitaxially grown (111) oriented fcc metal films on sapphire substrates. The existence of twinned domains in the here discussed iridium films will be discussed in the following subsection.

![FIG. 3. Radial Bragg scan of Ir(111) reflection for a 13 nm iridium film. Inset: rocking curve at Ir(111) Bragg peak. The data points are indicated with circles and the fit to the broad component is indicated with line.](image-url)
3. Grazing incidence x-ray diffraction results

To characterize the in-plane structure of the Ir films in detail, we performed in-plane Bragg scans at a grazing angle of 0.597°, which is the critical angle of incidence for total external reflection by iridium for Cu Kα radiation. Figure 4 shows a plot of theta-scans for iridium films, in which the sample was rotated around the film surface normal and the detector was kept fixed at the Ir (2 0 2) Bragg peak position. We observe that main Bragg reflections appear around −85°, −25°, 35°, 95°, and 155°, in line with the six-fold symmetry of (2 0 2) and equivalent reflections. The variation in the intensities of reflections is caused by the rectangular geometry of the sample. A 40 nm iridium film at the highest deposition rate of 1.2 nm/min showed intense reflections at 30° intervals in addition to the 60° reflections. This is in line with the LEED observations on this sample (Fig. 1(b)), indicating that the 30° rotated domains exist over the whole film thickness. In the case of a 15 nm film deposited with a rate of ∼0.2 nm/min, no additional 30° reflections were observed, suggesting the suppression of 30° rotated domains in the iridium films by lowering the growth rate. The in-plane mosaicity for all iridium films, as derived from the FWHM of the in-plane reflections, lies within the range of 0.6–1°. A higher value of 1.9° is obtained for the 40 nm Ir film with 30° rotated domains (see Table I).

The in-plane epitaxial relationship for the here discussed Ir film on (0001) sapphire is Ir[1 1 1] || Al2O3[1 1 2 0]. The in-plane radial scan for a 13 nm iridium film at the (2 2 0) bulk reflection ((1 1 0)S) provides a value of d_{220} = 1.354 (±0.001) Å, close to the bulk value for iridium (1.3574 Å), and ~1.5% smaller than d_{030} of the sapphire substrate.

It has been reported that homo- or heteroepitaxial Ir(111) films grown by physical vapor deposition (PVD) suffer from twinning. The presence of twin-domains can be investigated by some particular lines in reciprocal space with momentum transfer perpendicular to the surface. Fig. 5(b) shows a sketch of the Bragg reflections in surface coordinates for a (111) oriented fcc surface: black dots indicate reflections from ABC stacked regular domains and orange dots indicate reflections from CBA stacked twinned domains. From this, one can easily recognize that Bragg reflections from normal and twinned domains overlap for L = 3n but are separated for L ≠ 3n.

A scan along the (10 L) rod, performed on a 13 nm iridium film grown at 700 K, is shown in Fig. 5(c). The presence of (101)₃, and (102)₃, Bragg reflections confirms the existence of twinned domains in the film. The same observation was made for all iridium films investigated in this study. No influence of deposition temperature and growth rates was found on the 60° twinning in the iridium films.

On recently reported epitaxial iridium films on (0001) sapphire, grown by pulsed laser deposition at a substrate temperature of 700 K, the annealing treatment of the films to 1100 K successfully removed twin formation. From the pole figure in Figure 1(a) of Ref. 24, it becomes evident that after the procedure discussed in Ref. 24, reciprocal planes with threefold symmetry around the surface normal are parallel for Al2O3(0001) and Ir(111). This corresponds to an epitaxial relationship of Ir[1 1 1] || Al2O3[1 0 1 0], which is exactly 30° rotated compared to the epitaxial relationship found in our study after MBE growth.

We may speculate that the difference in in-plane orientation is responsible for the removal of the twinning in PLD.

---

**FIG. 4.** Theta-scan of Ir (2 2 0) in-plane reflections indicating a six-fold symmetry for iridium films of 13 nm thickness (orange) and 40 nm thickness (magenta). Additional 30° reflections are observed for 40 nm iridium film.
grown heteroepitaxial iridium films because of a change in interfacial energy. Other factors such as differences in the growth mode between PLD and MBE, a different miscut, or different pre-treatment of the substrates might be responsible for the observed variation in in-plane orientation.

From the FWHM of the (101) reflection along L, an out-of-plane crystallite size of 9.2 nm is retrieved, which is significantly smaller than the total film thickness. Dislocations or stacking faults might be responsible for a reduced crystallite size along the film normal compared to the total film thickness. The scan given in Fig. 5(d) provides information on the in-plane domain size. The FWHM of the (011) reflection along K is 0.0165 and corresponds to an in-plane crystallite size of 16.45 nm. This is close to the average distance between the dislocations/defects obtained from the out-of-plane rocking scan of the Ir(111) reflection. Moreover, approximately the same values of FWHMs of K scans, \( D_K = 0.0165 \) at \( K = 1 \) and \( D_K = 0.0166 \) at \( K = 2 \), suggest that the film is nearly free from in-plane strain gradients.

**B. Graphene synthesis on Ir(111) film**

After the deposition of highly crystalline Ir(111) films with atomically flat surfaces, we synthesized graphene by exposing the films at room temperature to ethylene until saturation \((10^{-7} \text{ mbar})\), followed by annealing at very high temperatures \((>1200 \text{ K})\) for aligning graphene domains parallel to the surface lattice. Further exposure of ethylene was performed in the range 1050–1150 K CVD temperature for 40 min to achieve maximum graphene coverage on the sample surface. For graphene growth on iridium single crystals, the reported annealing and CVD temperatures are \(~1500 \text{ K}\) and \(~1000 \text{ K}\), respectively.\(^{40}\) Due to a mismatch in the thermal expansion coefficients of sapphire and iridium, we expect crack formation in the iridium film by the rapid temperature changes. For this reason, we have modified the temperatures for the graphene growth. In the case of iridium films with 15 nm, 12 nm, and 40 nm thickness, we used an annealing temperature of 1220 K and a CVD temperature of 1120 K, while 30 nm and 10 nm thick iridium films were treated at an annealing temperature of 1250 K and a CVD temperature of 1050 K for graphene synthesis.

LEED patterns after graphene growth on a 15 nm film are given in Fig. 6(a), which shows clearly the formation of “\( R_0 \)” graphene, non-rotated with respect to the Ir(111) film. No other orientations of graphene are observed, which were reported for graphene growth at lower temperatures on Ir(111) single crystals.\(^6,18\) Distinct hexagonal spots are observed as a signature of multiple diffraction events, which are typical for electron diffraction. For a comparison with graphene grown on a Ir(111) single crystal, a corresponding LEED pattern is also given in Fig. 6(b). We observe that each hexagonal spot is slightly elongated in the tangential direction for graphene on iridium films, while the spots are circular in the case of iridium single crystal. This suggests the formation of slightly less-ordered graphene domains on iridium films, analogous to graphene grown on Ir(111) crystals at temperatures below 1300 K.\(^{41}\) To check the graphene quality over the whole sample, the electron beam was scanned in steps over the whole sample and similar LEED patterns were recorded at all positions. This suggests the presence of a homogeneous, non-rotated, graphene layer formed on top of the iridium film.

The chemical composition of the surface was checked before and after graphene synthesis, by means of AES measurements (Fig. 6(c)), and the results were compared with graphene synthesized on an Ir(111) single crystal. The appearance of the KLL transition at 270 eV corresponds to

![LEED patterns](image.png)
carbon and is in line with graphene formation. It was demonstrated that almost 100% full coverage of one monolayer graphene is achieved on Ir(111) single crystals with the described procedure.\textsuperscript{42} Identical heights of the C-peak for graphene on a 15 nm Ir film and graphene on an Ir single crystal suggests nearly full coverage of the iridium film by graphene, mainly limited by possible defects present on the film surface. On the other hand, a slightly smaller C-peak and higher Ir peaks are observed for the 40 nm iridium film, containing rotated domains, which hints for an incomplete graphene coverage on its surface; possibly, the C-coverage is limited by the larger amount of grain boundaries.

The surface topography of a freshly prepared graphene layer on top of a 13 nm iridium film is shown in Fig. 7, which was measured by NC-AFM in UHV. The straight line marked by an arrow most probably represents an atomic step originating from the sapphire miscut. The image reveals a rather high density of steps on the graphene covered Ir surface, with the steps not showing any clear preferential direction. Some islands exhibit edges which are rotated 120° with respect to each other, while others appear more curved. The angular edges are typical for Ir(111) islands, while the curved features most probably correspond to the iridium grain boundaries. These observations of angular and curved edges are similar to what has been reported for insufficiently annealed pulsed laser deposited iridium films containing the twinned domains\textsuperscript{24} and also for graphene grown on Cu(111) on sapphire prior to annealing.\textsuperscript{27} The domain size of the Ir islands as observed in the NC-AFM images lies between 10 nm and 100 nm, while in-plane domain size retrieved from XRD investigations is \(\sim14\) nm. This difference can be understood from the fact that XRD experiments provide representative information about the whole sample, while AFM measurements give the local information about the probed area, which is 500 nm \(\times\) 500 nm in this case.

Graphene seems to follow the iridium film topography consistently with an atomically smooth surface over the grains, depicting its perfect orientation with respect to the substrate. There are also some regions, as indicated by dotted lines in the AFM micrograph, where the surface appears significantly rougher, as seen in the corresponding line scan. Higher roughness might come from not-perfectly grown graphene domains due to the defects on the iridium film surface, or adsorbates on those regions. More investigation is needed to understand this in detail. A line scan along a segment crossing two grains evidences atomically smooth area on both sides of the step. The height of the steps in both of the line scans is \(\sim0.22\) nm and corresponds to an iridium-on-iridium atomic step height.

Large-area surface morphologies for different samples were investigated via SEM before and after graphene synthesis. A homogeneous surface was observed for all of the as-deposited iridium films. After the graphene synthesis, a non-homogeneous surface was obtained for the 40 nm iridium film with rotated domains (Fig. 8(a)), indicating a partial graphene coverage, in line with the AES results from this sample. In contrast to this, the film surface was homogeneous for rest of the samples after graphene growth, as shown in Fig. 8(b) for the 10 nm iridium film. In a large area SEM micrograph (Fig. 8(c)) of the 10 nm iridium film, a high number of defects are observed on the surface. In-air AFM measurements revealed the presence of holes of approximately 1 \(\mu\)m width in these areas of the film, as shown in Fig. 8(d). We believe this to be a signature of dewetting of the iridium film arising from the rapid temperature changes during the CVD growth of graphene. Large dewetting features of \(\sim50\) \(\mu\)m size have been observed by SEM on high-temperature annealed films of Cu(111) grown on sapphire\textsuperscript{27} and Ir(111) grown on YSZ/Si(111).\textsuperscript{25} The dewetting of the films could be avoided by an additional acid cleaning of sapphire in the former case, and use of thicker YSZ buffer layer on Si(111) in the latter case. For here discussed iridium films, growing thicker films might be helpful to overcome dewetting problem and investigations are going on in this direction.

X-ray scattering measurements on the graphene covered sample provide details on the crystalline quality of the film after going through harsh CVD process for graphene synthesis. The reflectivity curve measured on a graphene covered 15 nm thick iridium film is shown in Fig. 9(a). The data are fitted with a model of a single layer graphene on an iridium film on a sapphire substrate. An excellent fit to the data was
achieved for an iridium film thickness of 14.78 nm with surface roughness of 0.05 nm and interface roughness of 0.15 nm, graphene thickness of 0.4 nm with surface roughness of 0.17 nm. The profile of electron density perpendicular to the surface of graphene on iridium film on sapphire is derived from the reflectivity fit and is given in the inset of Fig. 9(a). In this plot, the electron density is given in terms of $2\delta$, where $\delta$ is the decrement in the refractive index for x-rays due to dispersion. To check the sensitivity of x-ray reflectivity measurements to a single graphene monolayer, a simulated curve is also plotted in Figure 9(a) for the same iridium film on sapphire without considering the graphene layer on top. The difference is observable at higher incidence angles, where the reflectivity curve seems to be modulated by the presence of graphene layer. Interestingly, the distance between graphene to iridium top layer retrieved from the fit is $\sim$20% higher than that for graphene on Ir(111) single crystals. The presence of defects such as grain boundaries on the film surface might be responsible for this observation. Since it is known that a weak covalent bond exists between graphene layer and a perfect Ir(111) single crystal surface,20 the presence of grain boundaries might reduce its effect. Therefore, we speculate that the interaction between graphene and Ir(111) film on sapphire substrate is weaker than that between graphene and Ir(111) crystal.

The specular rod measurement of the same sample is given in Fig. 9(b), where we clearly observe the satellite fringes of Laue oscillations of the Ir(111) reflection, similar to that for bare iridium films. A curve is simulated for a single layer graphene on an iridium film on the sapphire substrate, which fits well to the data. Graphene layer is $\sim$0.4 nm above the iridium top layer, as retrieved from XRR curves and the coherence length for iridium is found to be 14.8 nm. As was observed for as-deposited iridium films, the coherence length is identical to the film thickness derived from the reflectivity curves. Thus, the crystallinity and morphology of the iridium films have been very well preserved after going through the graphene CVD process.

Grazing incidence x-ray diffraction measurements were also conducted on graphene covered iridium films. The in-plane mosaicity was observed to lie in the same range as for as-deposited iridium films. Reciprocal line scans gave similar results compared to that before the synthesis of graphene, and no significant changes in the in-plane and out-of-plane crystallite size and defect structure were observed afterwards.

IV. CONCLUSION

We have shown that heteroepitaxial Ir(111) thin films, grown by MBE on (0001) sapphire, act as a suitable support to grow large-area graphene of R0 orientation. We have studied the influence of the growth parameters on the quality of the iridium films deposited on sapphire (0001) single crystals, and subsequently on graphene layers synthesized by CVD on top. Higher iridium deposition rates resulted in the formation of 30° rotated domains, leading to an incomplete coverage of graphene. Lower growth rates lead to highly crystalline iridium films with atomically smooth surfaces, on which a very homogeneous and a nearly complete coverage of graphene is obtained and the grain boundaries of iridium are limiting the size of the graphene domains. As main defects, the formation of ABC and CBA stacked twin domains is observed in the iridium films.
Iridium films were found to be highly stable, and can be re-used for preparing fresh graphene, as done with bulk crystals. Analogous to the graphene moiré on metal single crystals, this system can be utilized for growing metal cluster superlattices on top. This opens the avenue for future studies in which processing of iridium films is involved. In conclusion, our work presented here shows that MBE grown (111) oriented iridium films on sapphire substrates may serve as good substitute for the expensive bulk single crystals presently used for large-area epitaxial graphene growth.

15A. Dahal and M. Batzill, Nanoscale 6, 2548 (2014).
37A. Dahal and M. Batzill, Nanoscale 6, 2548 (2014).