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Scalable synthesis of graphene on single crystal Ir(111) films

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ABSTRACT

We have investigated single crystal Ir(111) films grown heteroepitaxially on Si(111) wafers with yttria-stabilized zirconia (YSZ) buffer layers as possible substrates for an up-scalable synthesis of graphene. Graphene was grown by chemical vapor deposition (CVD) of ethylene. As surface analytical techniques we have used scanning tunneling microscopy (STM), low-energy electron diffraction, scanning electron microscopy, and atomic force microscopy. The mosaic spread of the metal films was below 0.2° similar to or even below that of standard Ir bulk single crystals, and the films were basically twin-free. The film surfaces could be improved by annealing so that they attained the perfection of bulk single crystals. Depending on the CVD conditions a lattice-aligned graphene layer or a film consisting of different rotational domains were obtained. STM data of the non-rotated phase and of the phases rotated by 14° and 19° were acquired. The quality of the graphene was comparable to graphene grown on bulk Ir(111) single crystals.

1. Introduction

A strong driving force for the current scientific interest in graphene is its high charge carrier mobility which could facilitate ultra high speed electronic devices [1]. Due to the limited size of graphene flakes obtained by mechanical exfoliation from graphite this technique cannot provide a technological concept for future graphene based electronics. Two alternative approaches are the graphenization of SiC and the synthesis of graphene on single crystal metal surfaces [2,3]. Both concepts could provide a route towards wafer scale graphene layers provided that appropriate substrates are available [4,5].

The metal route starts with deposition of carbon atoms on a suitable metal surface, mostly by chemical vapor deposition (CVD) of hydrocarbon molecules [6–8]. Alternatively, carbon atoms dissolved in the metal can be segregated to the surface [9,10], or they can be evaporated from a solid carbon source onto the metal surface [11]. At sufficiently high temperatures the carbon atoms can form graphene at the surface of the metal. The graphene layer is then detached from the metal, typically by wet chemical etching, and transferred to an insulating support. It is obvious that a technological synthesis of large area graphene layers on the metal route requires thin metal films because large bulk metal crystals are out of the question for economic reasons.

The general feasibility of this route has been shown [5,7,8,12–16], but with regard to a viable technology a suitable material system has to fulfill various requirements. Firstly, the metal films have to be monocrystalline with minimum mosaic spread and without small angle grain boundaries. On a polycrystalline support, the orientational spread of the graphene nuclei would inevitably lead to a polycrystalline graphene layer. Although graphene can overgrow domain boundaries on metal surfaces this can most likely not cure a massive initial disorder [17]. Then both, the single crystal metal film as well as the support of the metal film, should withstand the high temperatures during the CVD process that are required for a defect-free growth of the graphene film. Finally, the support structure should ideally be compatible with common procedures in current microelectronics processing.

Several material systems have been investigated, mainly using polycrystalline Ni and Cu films [12,13,18,19]. Only few studies up to now addressed monocrystalline metal layers, namely films of Ir(111) [20], Ru(0001) [15], Cu(111) [21], Co(0001) [22] on sapphire(0001) supports, Ni(111) [16], and Co(0001) [23] on MgO(111), and Rh(111) [24] and Ir(111) [25] on a Si(111) support with an yttria-stabilized zirconia (YSZ) buffer layer.

Heteroepitaxial metal growth on Si(111) with YSZ buffer layers is a technique that has been developed in the last years and is well established in the meantime [26,27]. It has the advantage that, using Si wafers, it can be more easily implemented into standard Si technology than processes based on other supports. The fabrication can be upscaled, and Ir/YSZ/Si(111) wafers of 4 inch diameter have already been prepared. It has been shown that a liquid precursor (acetone) can be decomposed on Ir(111)/YSZ/Si(111) to form graphene [25].

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However, the quality of the graphene overlayer grown on metal/YSZ/Si(111) substrates and possible methods and limits to improve the order have not been systematically investigated. Such an investigation is presented here for the case of iridium. It involves the surface morphology of the Ir(111) films, namely atomic scale flatness and types of defects, which will affect the quality of the graphene layer grown on such a substrate. We investigated the possibility of a morphology improvement by annealing, and explored the limits of the thermal stability for the heteroepitaxial Ir films. We have then studied the structure of graphene layers that were grown by CVD of ethylene in an ultra-high vacuum (UHV) chamber on the Ir layers. Their structural quality is compared with that of graphene layers prepared on bulk Ir(111) crystals. As analytical techniques we used scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), scanning electron microscopy (SEM), and atomic force microscopy (AFM).

2. Experimental

The Ir/YSZ/Si(111) multilayer system was prepared according to a previously described method [26]. In brief, a (111)-oriented Si wafer was first covered by a YSZ layer (40–150 nm) by means of pulsed laser deposition (KrF excimer laser, pulse duration 25 ns, pulse energy 850 mJ) from a ZrO_2 target containing 21.4 mol% $YO_{1.5}$. The YSZ serves as buffer layer preventing silicide formation of the metal with the subjacent silicon. In addition it has to transfer the epitaxial orientation from the Si single crystal to the metal film. On top of the YSZ layer a 150 nm thick Ir film was deposited by e-beam evaporation at substrate temperatures between 600 and 700 °C. A recently developed two-step process was applied with an ultralow deposition rate for the first 10 nm. X-ray diffraction (XRD) showed that the Ir film was (111)-oriented with epitaxial alignment to the Si(111) substrate [26]. X-ray rocking curve measurements of the Ir(111) reflections perpendicular to the surface and azimuthal scans at a polar angle of 70.5° revealed a low mosaic spread of 0.18° and 0.20° for the tilt and twist component, respectively [26]. The fraction of the twin orientation was lower than 0.1% [26]. Two previous XRD investigations of single crystal metal films, which were grown on a sapphire support and then used for graphene synthesis, reported a mosaic spread of 1° [20] or pronounced twin formation of the metal film [21].

In this work 10 mm x 10 mm pieces were cut from the wafers, mounted to a sample holder on a piece of Ta sheet and introduced into a UHV chamber (base pressure 1×10^{-10} Torr). The chamber was equipped with a home-built STM, an Auger electron spectrometer, and LEED optics. X-ray photoelectron spectroscopy (XPS) was available in another UHV system. The sample temperature was measured by an infrared pyrometer. The samples were cleaned by oxidation (2×10^{-7} Torr of O_2 at 400 °C for 0.5 to 1 h), annealing (at 800 to 900 °C for 1 to 2 h), Ar^+-sputtering (0.8 keV, 5 μA, for 5 to 15 min), and finally flash annealing to 800 °C. The first annealing after oxidation of a fresh sample caused some segregation of Si, C, and Ca to the surface. However, already after the following first sputtering and annealing step the sample was clean according to Auger electron spectroscopy (AES). LEED showed sharp spots of (111)-oriented, single crystal Ir across the entire sample surface, indicating that the orientation and quality of the original film was not affected by the surface preparation in UHV.

Graphene was grown by CVD of ethylene at temperatures between 700 and 800 °C. Ethylene pressures were between 2×10^{-9} and 2×10^{-8} Torr, and a dose of 18 L was sufficient to form one monolayer ($1\ \mathrm{L}=1\times10^{-6}$ Torr s). The graphene layers could be completely removed by oxidation in 2×10^{-7} Torr of O_2 at 400 °C and flash annealing to 800 °C. For further investigation by SEM [Jeol JSM-6500F with energy-dispersive X-ray (EDX) detector] and AFM (NanoINK DPN station with tapping mode AFM) the sample was removed from the UHV chamber.

3. Results and discussion

3.1. Characterization of the Ir(111) films

As described in the experimental section the preparation technique leads to basically twin-free heteroepitaxial Ir(111) films on the YSZ/Si(111) support with low mosaic spread (≤0.20°). AFM and SEM of freshly prepared Ir films, before annealing and sputtering in the UHV chamber and before preparation of graphene, showed flat surfaces without any grain boundaries [Fig. 1(a) and (b)]. The only marked defects were pinholes, probably residues of grain boundaries most of which were removed in coalescence processes during film growth. The pinhole density was approximately 7.5 μm^{-2}. The structureless surface and the pinholes were also visible in STM [Fig. 1(c)]. In the AFM and STM data the pinholes appeared as 40 to 90 nm wide and 2 to 5 nm deep holes (same diameters as in the SEM micrographs), suggesting that they do not penetrate the entire Ir film. However, the finite AFM and STM tip diameters prohibit a definite conclusion about the actual depth of the holes.

After transfer of the samples to UHV and surface preparation as described above we tried to reduce the number and diameters of the pinholes by annealing the Ir films at 900 °C for 2 h. AFM, SEM and STM measurements substantiated that the holes had then completely disappeared [an example of an STM image is shown in Fig. 1(d)]. This behavior is different from observations by Vo-Van et al. for Ir films on sapphire [20]. In this work, annealing at 1127 °C reoriented the originally twinned films into the single crystal orientation. In our case twinning was not an issue in the as-grown layers. The special growth procedure of the Ir/YSZ/Si(111) multilayer system already provided twin-free heteroepitaxial films. The surface after annealing consisted of approximately 1000 Å wide terraces separated by irregular monatomic, double and triple steps [Fig. 1(d)], closely resembling surfaces of bulk single crystals. The only difference to bulk single crystals were additional straight steps that run along the closed-packed directions of the Ir(111) surface, crossing “normal” steps, and crossing each other at 60° angles [Fig. 1(d)]. The height of these steps was identical to the atomic layer distance of 2.22 Å of Ir(111), ruling out that they were replicas of steps in the underlying

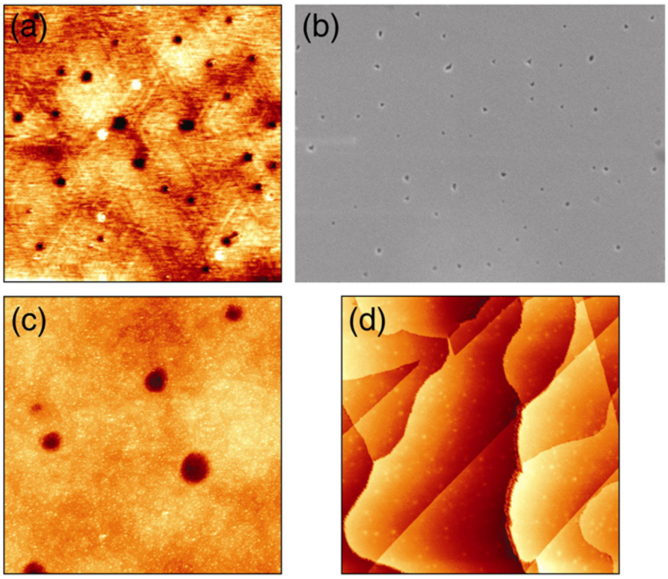

Fig. 1. Morphology of the Ir(111) film on the YSZ/Si(111) support. (a) AFM image of an as-grown film (2 μm × 2 μm); (b) SEM image of the same sample as in (a) (3.4 μm × 2.6 μm); (c) STM image (6000 Å × 6000 Å) (taken with $V_t = +0.7$ V, $I_t = 0.3$ nA; (d) STM image (5000 Å × 5000 Å) after annealing for 2 h at 900 °C, taken with $V_t = +0.7$ V, $I_t = 0.1$ nA.