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# Preparation and characterisation of carbon-free Cu(111) films on sapphire for graphene synthesis

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**Abstract.** This work presents an investigation of carbon formed on polycrystalline Cu(111) thin films prepared by ion beam sputtering at room temperature on c-plane Al<sub>2</sub>O<sub>3</sub> after thermal treatment in a temperature range between 300 and 1020 °C. The crystallinity of the Cu films was studied by XRD and RBS/channeling and the surface was characterised by Raman spectroscopy, XPS and AFM for each annealing temperature. RBS measurements revealed the diffusion of the Cu into the Al<sub>2</sub>O<sub>3</sub> substrate at high temperatures of > 700 °C. Furthermore, a cleaning procedure using UV ozone treatment is presented to remove the carbon from the surface which yields essentially carbon-free Cu films that open the possibility to synthesize graphene of well-controlled thickness (layer number).

## 1. Introduction

In recent years, a large research effort has been invested on graphene because of its unique physical, mechanical, and electronic properties [1, 2]. Graphene is attractive for a wide variety of applications including semiconductor and high frequency devices [3, 4], optoelectronics [5], spintronics [6] or even catalysis [7] or sensor applications [8]. There are many synthesis routes for graphene [9], some of them employ metallic substrates, for example chemical vapour deposition (CVD) [10, 11] or carbon ion implantation. Indeed, several studies of graphene synthesis using carbon ion implantation can be found in the literature that employ either polycrystalline Ni [12, 13, 14, 15] or Cu foils [16, 17, 18] as substrate for graphene growth. The latter are advantageous due to the large Cu grain sizes in the range of mm achieved after thermal treatment [19]. Note that the Cu foils in these studies had a Cu(200) orientation which results in a lattice mismatch of 19.9% between graphene and the underlying Cu substrate. In contrast, Cu(111) substrates would allow for a lattice mismatch of only 3.8% [20, 21, 22, 23] and are therefore desirable for growth of high quality graphene.

It is essential to start with a carbon-free substrate for the synthesis, in order to have full control on the layer number of the synthesized graphene and therefore on its physical properties, e.g. the behaviour as semiconductor or conductor [24, 25]. Any additional contribution from intrinsic carbon that may have been incorporated into the Cu film during its preparation process has to be avoided. This carbon mostly comes from the residual gas within the deposition chamber. Note that the Cu-foils used in graphene synthesis so far may also not be free of carbon [17].



The aim of this study is the preparation of Cu(111) thin films that are essentially free of carbon and can therefore serve as substrates for high quality graphene growth. For this purpose, Cu(111) thin films sputtered on Al<sub>2</sub>O<sub>3</sub> substrates were thermally annealed and the formation of carbon on the surface of the Cu films studied as a function of annealing temperature. The origin of the carbon is discussed and an UV ozone treatment described that allows obtaining carbon-free Cu substrates for subsequent graphene synthesis.

## 2. Experimental details

The Cu films with a thickness of 200 nm and 450 nm were prepared on 1 cm<sup>2</sup> *c*-plane Al<sub>2</sub>O<sub>3</sub> at room temperature by magnetron and ion beam sputtering, respectively (see section 1 in supplementary material). The 200 nm films were annealed in vacuum ( $\approx 5 \times 10^{-7}$  mbar) at 300 °C, 500 °C, 700 °C, 750 °C, 800 °C, 850 °C, 900 °C for 1 h, whereas the 450 nm films were annealed at 1020 °C for 20 min.

The chemical composition of the surface of the deposited Cu films on sapphire was determined after annealing with X-ray photoelectron spectroscopy (XPS). Monochromatic Al K $\alpha$  X-rays with 1486.6 eV energy were used for photoelectron emission. Quantification was done with the help of the program UNIFIT (Unifit, Leipzig) using the experimentally estimated analyser transmission functions. For further investigations, Raman measurements were performed with a 473 nm laser excitation to reduce the fluorescence background from the Cu substrate. The laser was coupled on a LabRam HR Evolution spectrometer with a resolution of 1.3 cm<sup>-1</sup> (600 l mm<sup>-1</sup> grid) and an Olympus MPlan N 100x/0.90 objective.

The crystallinity was studied by X-ray diffraction (XRD) using a diffractometer Ultima IV equipped with a Cu anode X-ray tube, a graded multilayer mirror to obtain a parallel beam, a theta-theta goniometer, a parallel slit analyser and a scintillation detector.

Rutherford backscattering spectrometry (RBS) and ion channeling were performed to study the composition and crystalline quality of the Cu films as well as interdiffusion of Cu film and Al<sub>2</sub>O<sub>3</sub> substrate. For this purpose, a 2.07 MeV He<sup>+</sup> ion beam with a diameter of  $\approx 0.8$  mm was used. The film composition was determined from RBS data using XRUMP [26].

The surface topography was measured by atomic force microscopy (AFM) with a large sample scanning force microscope. The resolution was 1024  $\times$  1024 pixels for each measurement. The root mean square (RMS<sub>sq</sub>) roughness was calculated from the processed images.

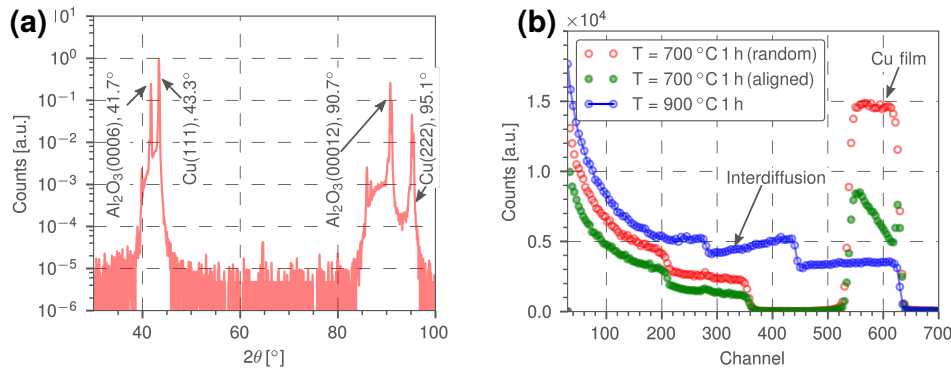
The carbon formed on the Cu surface was removed by UV-ozone treatment using a Xe<sub>2</sub>\* excimer lamp 172/630 Z lamp system, applying a VUV power of up to 30 mW cm<sup>-2</sup> and a distance from the sample of 2 cm. The excimer lamp has a continuous emission in the VUV wavelength range from  $\lambda = 160$  to 195 nm (photon energy 7.75 eV  $> E_{Ph} >$  6.36 eV; 614 kJ mol<sup>-1</sup>  $< \Delta E <$  748 kJ mol<sup>-1</sup>) with the maximum at 172 nm ( $E_{Ph} = 7.21$  eV; 696 kJ mol<sup>-1</sup>). Irradiation was carried out in a chamber flushed with nitrogen containing 0.25 vol.-% oxygen to minimize VUV absorption by molecular oxygen and ozone formation on one hand [27] and maintain oxidative conditions on the other, as published for the conversion of perhydropolysilazane to silica [28].

## 3. Results and discussion

### 3.1. Crystallinity

The XRD measurements reveal a Cu(111) orientation of the as-prepared Cu films (see fig. 1(a)). Note that no other crystal orientations were found. In contrast to the literature [23] the films were not single-crystalline but consisted of twinned Cu(111) crystals for all annealing treatments and film thicknesses studied here (see section 4 of supplementary material). The peaks at 41.7° and 90.8° shown in fig. 1(a) originate from the Al<sub>2</sub>O<sub>3</sub> substrate.

In order to investigate the crystallinity of the Cu films RBS-channeling measurements were performed. Figure 1(b) shows two spectra for a sample annealed at 700 °C for 1 h with random



**Figure 1.** (a) Typical XRD spectrum showing the Cu(111) crystal orientation and (b) RBS spectra of a sample (200 nm thickness) annealed at  $700^\circ\text{C}$  for 1 h for random and aligned crystal orientation as well as a spectrum of a Cu film annealed at  $900^\circ\text{C}$  (200 nm thickness) for 1 h showing strong interdiffusion of the Cu and the  $\text{Al}_2\text{O}_3$  substrate.

orientation (red circles) and after alignment of the Cu  $\langle 111 \rangle$  axis with respect to the ion beam (green full circles) indicating ion channelling of the  $\text{He}^+$  ions, respectively. For the normalised minimum yield  $\chi_{\min}$  values down to 0.22 were obtained indicating Cu(111) orientation of the film over macroscopic lateral extensions. Channeling into the  $\langle 111 \rangle$  axis is also possible when crystals are twinned around this axis.

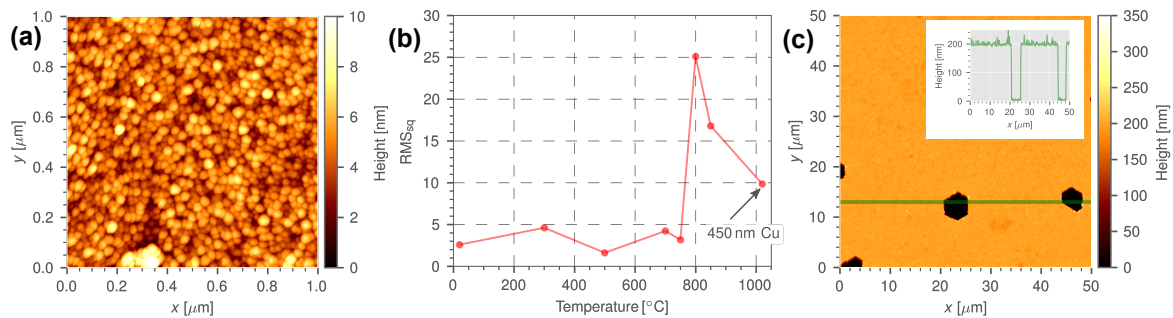
Furthermore, an RBS spectrum of a sample annealed at  $900^\circ\text{C}$  for 1 h (circle-line) is shown in fig. 1(b), which demonstrates the interdiffusion of Cu film and  $\text{Al}_2\text{O}_3$  substrate at this high temperature and long annealing time. Whereas the Cu film of the sample annealed at  $700^\circ\text{C}$  for 1 h still consists of pure Cu, the composition after  $900^\circ\text{C}$  for 1 h has changed to  $\text{Cu}_{0.12}\text{Al}_{0.36}\text{O}_{0.52}$  (see section 2 of supplementary material for details on RBS analysis). Due to this diffusion process the high temperature annealing steps above  $1000^\circ\text{C}$  were performed for the 450 nm thick Cu films and for 20 min only.

### 3.2. Surface topography

Prior thermal treatment the Cu film show grain sizes of around 50 nm (see fig. 2(a)). Annealing leads to an increase of the grain sizes to several  $\mu\text{m}$ . Figure 2(b) shows the  $\text{RMS}_{\text{sq}}$  roughness of the Cu films after the different annealing procedures. The  $\text{RMS}_{\text{sq}}$  roughness of Cu obtained after sputter deposition is drastically lower than the one measured for Cu foils of any quality used for graphene synthesis [16, 19]. This low roughness is beneficial for 2D graphene growth. The large roughness values for temperatures above  $800^\circ\text{C}$  originate from the presence of etch holes (see figure 2(c)). The etch holes are of hexagonal shape with a depth given by the thickness of the Cu film.

### 3.3. Characterisation of carbon films

In order to investigate the formation of carbon on the surface of the Cu films and thus the diffusion of the impurity carbon atoms from the bulk of the film to its surface, Raman (range  $1000\text{cm}^{-1}$  to  $3000\text{cm}^{-1}$  to observe the graphite/graphene-related D-, G- and 2D-bands) and XPS measurements were performed. Directly after the deposition of the Cu on the  $\text{Al}_2\text{O}_3$  no carbon was found on the surface. After annealing within the  $300^\circ\text{C}$  to  $700^\circ\text{C}$  temperature range Raman spectra were obtained which indicate the presence of amorphous carbon at the surface (see fig. 3). This is supported by XPS measurements where an increase of the carbon content at the surface from 30 at.-% after the  $300^\circ\text{C}$  anneal to 67 at.-% after the  $700^\circ\text{C}$  anneal

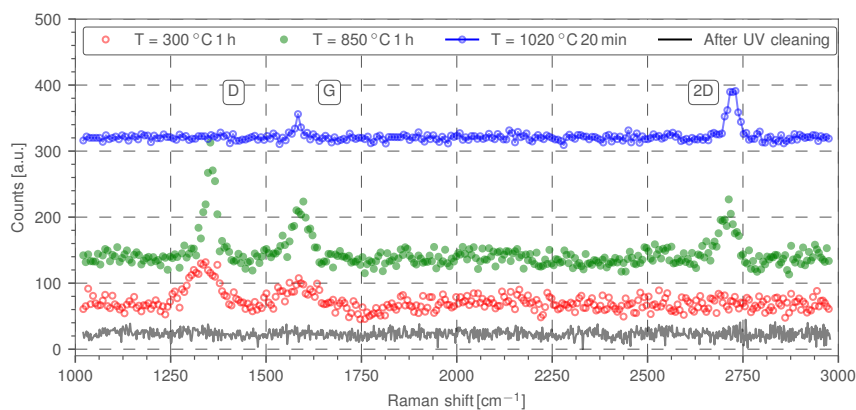


**Figure 2.** (a) Typical AFM image of a non-annealed sample showing Cu grains of 50 nm size. (b)  $\text{RMS}_{\text{sq}}$  roughness of the differently annealed Cu films and (c) an AFM scan and line plot of a Cu film annealed at 800 °C for 1 h showing etch holes of hexagonal shape and a depth of 200 nm.

has been observed. This carbon is believed to originate from surface adsorbates (see section 3 in supplementary information for more details). The samples annealed at 750 °C, however, showed no Raman bands, despite a carbon content of 56 at.-% as obtained by XPS studies. At temperatures above 800 °C the 2D-band which is indicative for graphene appears in the Raman spectra. This graphite/graphene is probably formed by carbon atoms that start to diffuse at this temperature from the bulk of the Cu film to the surface. From XPS analysis, the  $\text{sp}^2$ -content of the carbon was determined to 12.5% for an annealing temperature of 1020 °C. For the lower temperatures, the  $\text{sp}^2$ -content could not be unambiguously determined using XPS.

### 3.4. UV-ozone cleaning

The carbon formed at the surface during the thermal annealing could be removed by a UV ozone treatment for 30 min, which represents a radiant exposure of  $33 \text{ J cm}^{-2}$  at the sample height. During this process, the temperature of the sample increased to approximately 50 °C. After this UV ozone cleaning and an additional annealing step at 1020 °C no carbon signal was observed on the surface of the 450 nm Cu film demonstrating the purification of the Cu film with regard to carbon contamination.



**Figure 3.** Raman spectra of samples annealed at 300 °C and 850 °C for 1 h each as well as 1020 °C for 20 min. Furthermore, the removal of the carbon film after UV ozone cleaning is indicated by the missing Raman features of the grey curve.

#### 4. Conclusion

In this study, a pathway is shown to obtain carbon-free Cu(111) polycrystalline substrates for the synthesis of graphene. The substrate purity achieved with regard to carbon will enable better control of the layer number of the graphene by the synthesis process. It is also shown that a thermal anneal at temperatures above 850 °C is required for a sufficient mobility of the carbon atoms within the Cu film to allow for purification. In initial experiments, a diffusion of the Cu into the Al<sub>2</sub>O<sub>3</sub> was observed for temperatures above 700 °C, indicating that annealing times should be carefully chosen at high temperatures to preserve the metallic Cu film for further synthesis.

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