ESRF	**Experiment title:** "The role of the Ni(111) near-surface carbide in graphene growth studied by surface X-ray diffraction"	**Experiment number**: CH-3857
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Report:

Initially, a clean and crystallographically well ordered Ni(111) sample was prepared by 1 long cycle of Ar-sputtering ($p_{Ar} \sim 5 \cdot 10^{-6}$ mbar, $I_{Ar+} \sim 4$ μA, t ~ 49 min. T ~ RT), flash heating to 800 °C in $5 \cdot 10^{-7}$ mbar O_2, then to 600°C in $5 \cdot 10^{-7}$ mbar H_2. Thereafter, 6 short sputter anneal cycles, one oxidation cycle in O_2 and finally annealing in UHV ($8 \cdot 10^{-11}$ mbar) to 800°C led to an AES spectrum without detectable C signal.

I. From the clean sample, an in-plane mesh and CTR's (-1 1), (0 -1), (1 -1), (1 0), (0 1), (-1 1), (1 1), (2 -1), and (-1 0) were recorded as reference data for the later-prepared carbon-modified surfaces. Initially, AES showed an almost carbon-free sample. Prolonged irradiation of sample in residual CO containing background atmosphere led to weak reflections of surface carbide Ni_2C in a low order state. „Powder-like" rings in reciprocal carbide distance in the overview hk mesh may result from metastable arbitrarily rotated domains etc. This means that this structure does already form at RT from CO traces if radiation energy is introduced into the CO covered surface.

II. After flash annealing to 800 °C in UHV, a surface-limited "low-coverage" state of the Ni_2C carbide was prepared by 200 sec ethylene dosing at 270 °C/ ~ 5·10-8 mbar for 200 sec (10 L) to gain "monolayer" reference data for comparison with more C-rich and graphene modified surfaces expected from higher doses. An in-plane map of the complete carbide unit cell and the CTR's up to (-2 2) and (2 -2) were recorded, as well as the Ni_2C carbide rods: (-4 1), (4 1), (-2 1), (-2 2), (-1 1), (-2 0), (0 2), (3 1), (2 1), (2 2), (1 1), (2 1), (-2 1). III. A "high-coverage" state of the Ni_2C carbide, according to [1] close to the onset of graphene nucleation, was prepared by additional ethylene dosing onto the "low-coverage" state at elevated temperature ($p(C_2H_4) \sim 6 \cdot 10^{-7}$ mbar, $T_{sample} \sim 405$ °C, $t_{exposure} \sim 14$ min, 504 L) and cool down in ethylene to room temperature. Currently we analyze the data in view of the original idea of a potentially thicker (multilayered) carbide which may be proved or disproved from a detailed analysis of the STR data. In the hk map a gradual improvement of intensity and reflection sharpness was observed relative to II). The full dataset involves an in-plane map, CTR's (-1 0), (0 -1), (1 -1), (1 0), (0 1), (-1 1), (-1 2), (1 1), (2 -1), (1 -2), (-2 0), (0 2), (2 0), (0 -2) and Ni_2C carbide rods (0 2), (2 0), (2 2), and (3 1). A reference AES spectrum of the "high-coverage" carbide was recorded.

IV. After an additional 15 min $1.2 \text{x} 10^{-6}$ mbar exposure at 450 °C (+1080 L, total 1594 L) just one (1 0) STR and a hk in-plane map were recorded. In view of Jacobson et al. [2], this preparation might have yielded a maximum coverage of “rotated” graphene on top of a complete carbide surface layer. The actual effect was that no extra spots were seen, and too little changes for another full analysis were present. At least, the existence of rotated graphene domains could be excluded. The pronounced stability of the carbide somehow contracticted the “replacement” graphene growth picture by the “replacement mechanism” of [1]. As a reflectivity / specular rod measurement (up to L = 1.25) showed no major changes relative to the state in III., probably only traces of graphene were formed. A comparison with the carbon AES from III also showed no major changes.

V. After an intermittent sample cleaning cycle (annealing to 850 °C in 5×10^{-7} mbar O_2, sputtering, annealing in UHV to 800 °C), the surface was exposed for 60 min to ethylene at ~ $2 \cdot 10^{-6}$ mbar at T_{sample} ~ 500 °C, immediately followed by 10 min exposure at the same pressure at T_{sample} ~ 400 °C. An in-plane map, and a mesh around the (-2 0) CTR were recorded in search of rotated graphene, but no indications were found. Thereafter, CTR‘s (-1 0), (0 -1), (1 -1), (1 0), (0 1), (-1 1), (-1 2), (1 1), (2 -1), (1 -2), (-2 0), (0 2), (2 0), (0 -2), (-1 0), (0 -1), (1 -1), (1 0), (0 1), (-1 1), (-1 2), (1 1), (2 -1), (1 -2), (-2 0), (0 2), (2 0), (0 -2), (0 1), (2 -1), (0 -2), (2 0), (0 2), (1 0), (-1 0), (0 -1), (1 -1), (-1 1), (-1 2), (1 1), (1 -2), (-2 0) and carbide rods: (2 0), (0 2), and (2 2) were recorded. The reflectivity / specular rod data were recorded but still need to be analyzed with respect to unrotated graphene on top of the carbide. AES showed increased amounts of carbon with graphitic/ graphene character, suggesting the presence of unrotated graphene domains (unrotated Ni_2C interlayer model of [2]).

VI. Starting out from V., the carbide interlayer was dissolved by isothermal UHV annealing at 430°C into the Ni bulk with the aim to deposit the graphene directly on bulk-terminated Ni(111). During the isothermal experiment, time resolved STR rod data of the carbide showed a gradual disappearance of the reflection intensity. A subsequent in-plane map showed the loss of the carbide pattern, despite the almost constant graphene intensity in the AES spectrum. Then, CTR‘s (-1 0), (0 -1), (1 -1), (1 0), (0 1), (-1 1), (-1 2), (1 1), (2 -1), (1 -2), (-2 0), (0 2), (2 0), (0 -2) and reflectivity/ specular rod data were recorded and are currently analysed for epitaxial graphene on top of bulk Ni(111).

VII. The sample of VI. with graphene residing directly on Ni(111) was cooled down to RT to exclude re-segregetion of the carbide phase upon cooling. An in-plane map, CTR‘s (-1 0), (0 -1), (1 -1), (1 0), (0 1), (-1 1), (-1 2), (1 1), (2 -1), (1 -2), (-2 0), (0 2), (2 0) and (0 -2) and the reflectivity / specular rod data were measured. AES showed no significant changes relative to VI.

VIII. Clean Ni(111) was re-established (flashing to 800°C in $5 \cdot 10^{-7}$ mbar O_2, sputtering and annealing to 850 °C) to provide reflectivity and CTR reference data of the clean sample with extended hk range in view of optimized detection of unrotated graphene from reflectivity and CTR data. An in-plane map and CTR‘s (-1 0), (0 -1), (1 -1), (1 0), (0 1), (-1 1), (-1 2), (1 1), (2 -1), (1 -2), (-2 0), (0 2), (2 0) and(0 -2), together with the reflectivity / specular rod data were scanned with enhanced range/ resolution. Prior to the scans, AES showed a carbon-free surface, despite the fact that some carbide reflection intensity reappeared in the in-plane map. Dissociation of residual CO or a “subsurface carbide” state are currently considered to cause this effect.

IX. With the improved reflectivity settings, the “pure” Ni_2C carbide on Ni(111) (prepared by $5 \cdot 10^{-7}$ mbar C_2H_4 exposure at 400 °C for 156 s) was again measured (in-plane map, CTR (1 0), carbide rod (2 0), reflectivity / specular rod). AES showed the typical carbide fingerprint.

X. With the improved reflectivity settings, the unrotated graphene/ carbide/ Ni(111) system was re-done (sample preparation as in V., in-plane map, CTR’s (1 0), (0 1), (1 1), reflectivity / specular rod). Distinct differences between purely carbide-covered, “interlayer” carbide supported [2] and directly Ni(111) supported graphene [3] are currently analysed. Figure 1 shows the characteristic difference of specular reflectivity between the purely carbide covered and the graphene-Ni2C-Ni(111) layered surface states.

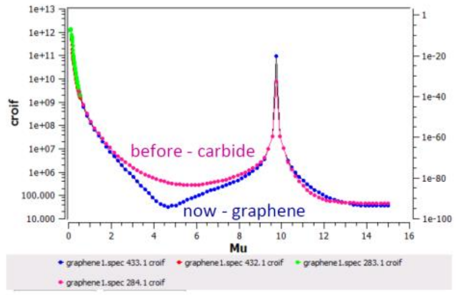

Figure1: Specular reflectivity data of purely carbide- and carbide-graphene covered Ni(111).

Literature:

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