

# Synthesis of graphite monolayer stripes on stepped Ni(771) surface

© A.M. Shikin, G.V. Prudnikova, V.K. Adamchuk, W.-H. Soe\*, K.-H. Rieder\*, S.L. Molodtsov\*\*, C. Laubschat\*\*

Institute of Physics, St. Petersburg State University,  
198904 St. Petersburg, Russia

\* Institut für Experimentalphysik, Freie Universität Berlin,  
D-14195 Berlin, Germany

\*\* Institut für Oberflächen- und Mikrostrukturphysik, Technische Universität Dresden,  
D-01062 Dresden, Germany

Graphite stripes on stepped Ni(771) substrate were grown *in-situ* by cracking of propylene followed by annealing at optimal temperatures between 450 and 590°C. The samples were studied by means of C 1s and Ni 3p core-level photoemission and high resolution electron energy loss spectroscopy. The C 1s spectra reveal dominant graphite-like character. The phonon spectra measured in the direction parallel and perpendicular to the steps display certain differences, which can be explained on the basis of size-limited effects.

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In the recent past, a large number of experimental studies related to quantization of the electronic states in low-dimensional structures in the direction perpendicular to the surface was published in the literature (see, for instance, [1–4]). On the other hand, much less attention was paid to the search and studies of the systems where size-limited effects could be observed in the direction parallel to the surfaces. The latter can likely be explained by difficulties in formation of this kind of systems. One of the possibilities to prepare them is *in-situ* deposition of investigated materials onto stepped surfaces of monocrystals of various metals. In this way, stripes of the deposited substances with well defined thicknesses and widths may be grown on top of the terrace surfaces.

The present work is devoted to the analysis of conditions for synthesis of graphite stripes formed by cracking of carbon-containing gases on top of vicinal Ni(771) surfaces. The *in-situ* grown samples were studied by means of C 1s and Ni 3p core-level photoemission (PE) and high resolution electron energy loss spectroscopy (HREELS) of phonon excitations measured in the directions parallel and perpendicular to the steps at the Ni(771) substrate. It was found that such a system is characterized by graphite stripes, which have (i) monolayer thicknesses (monolayer graphite stripes, MGS), since the cracking is terminated when the whole Ni(771) substrate is covered by C atoms [5–9]; and (ii) fixed width defined by regularly-stepped character of Ni(771).

## 1. Experimental details

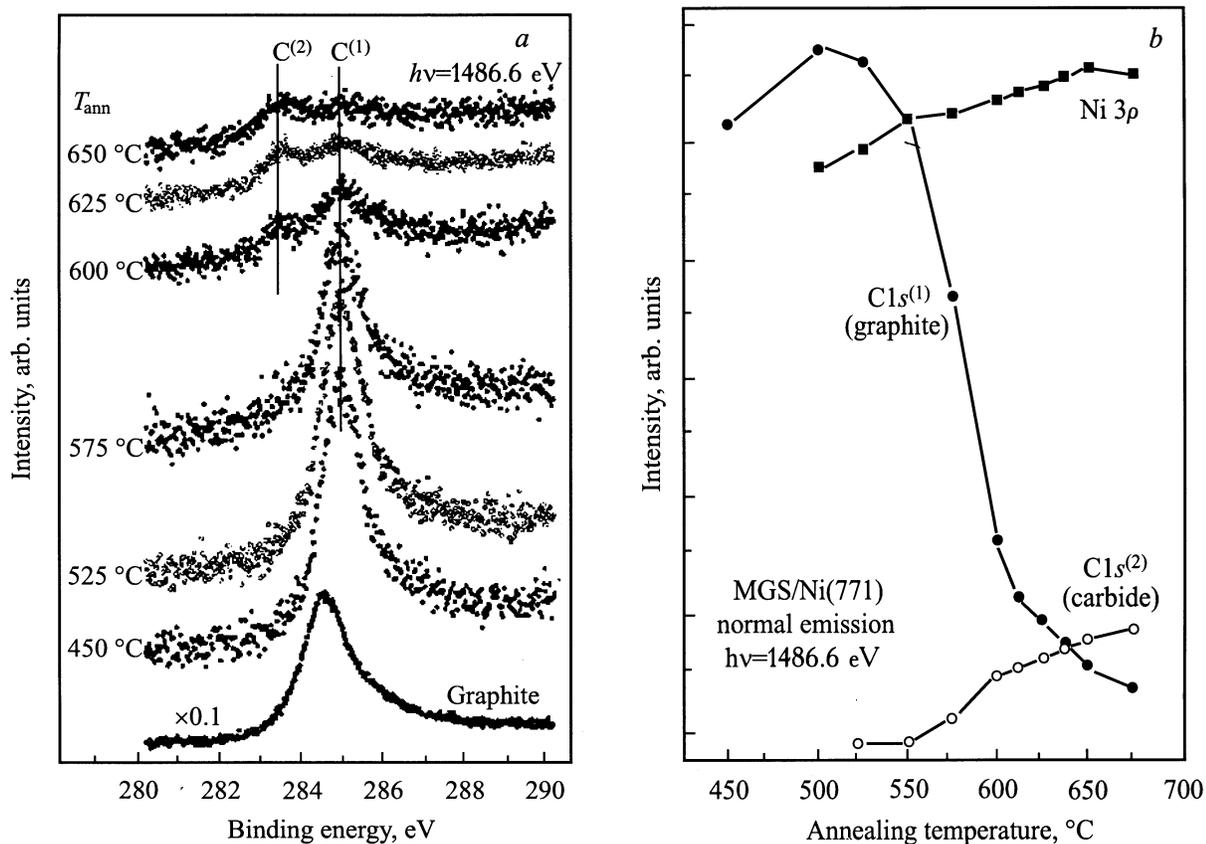
C 1s and Ni 3p core-level PE and HREELS spectra were taken for different annealing temperatures ( $T_{\text{ann}}$ ) beginning from  $T_{\text{ann}}$  lower than the cracking temperature up to the temperatures at which the destruction of the graphite stripes is observed. The core-level PE spectra were measured at the normal emission geometry using a X-ray source with the AlK $_{\alpha}$  radiation ( $h\nu = 1486.6$  eV)

and a CLAM-II analyzer. The HREELS experiments were conducted in a set-up equipped with a 127° deflector at a primary electron energy ( $E_p$ ) of 17.5 eV. The electron incident angles were set to 60 and 75° relative to the normal to the vicinal Ni(771) terraces having (110) orientation and a width of about 12.3 Å [10,11]. The detection angle was varied from 0 to 65° relative to the direction of the elastically reflected peak.

The Ni(771) substrate was preliminary cleaned by repeated cycles of Ar sputtering, treatment in oxygen and hydrogen atmospheres and thermal annealing at 700°C until a sharp low energy electron diffraction (LEED) pattern characteristic for vicinal Ni(771) surfaces was obtained [10,11]. Similar to the monolayer graphite (MG)/Ni(111) system [8,9], the graphite overlayer (i.e., graphite monolayer stripes) was formed by a 5-min cracking of propylene (C<sub>3</sub>H<sub>6</sub>) at sample temperature of about 500°C and pressure of  $1 \cdot 10^{-6}$  mbar. In the course of the measurements, the samples were annealed at different temperatures between 400 and 700°C. The base pressure in the CLAM and HREELS spectrometers during experiments was better than  $2 \cdot 10^{-10}$  mbar.

## 2. Experimental results and discussion

A series of C 1s core-level PE spectra measured at normal emission for the systems prepared by cracking of propylene and following annealings at temperatures between 450 and 650°C, is shown in Fig.1, a. For comparison, a C 1s spectrum of natural monocrystalline graphite is also presented in the bottom of the figure. The spectra taken after annealing between  $450 < T_{\text{ann}} < 575$ °C are characterized by a single pronounced peak at a binding energy (BE) of about 284.9 eV (marked C<sup>(1)</sup> in the figure) that is very close to the C 1s BE (284.5 eV, dotted line) characteristic for monocrystalline graphite. Similar C 1s spectra were obtained for the monolayer of graphite on top of Ni(111) [6] or for the graphite monolayer on a (111)



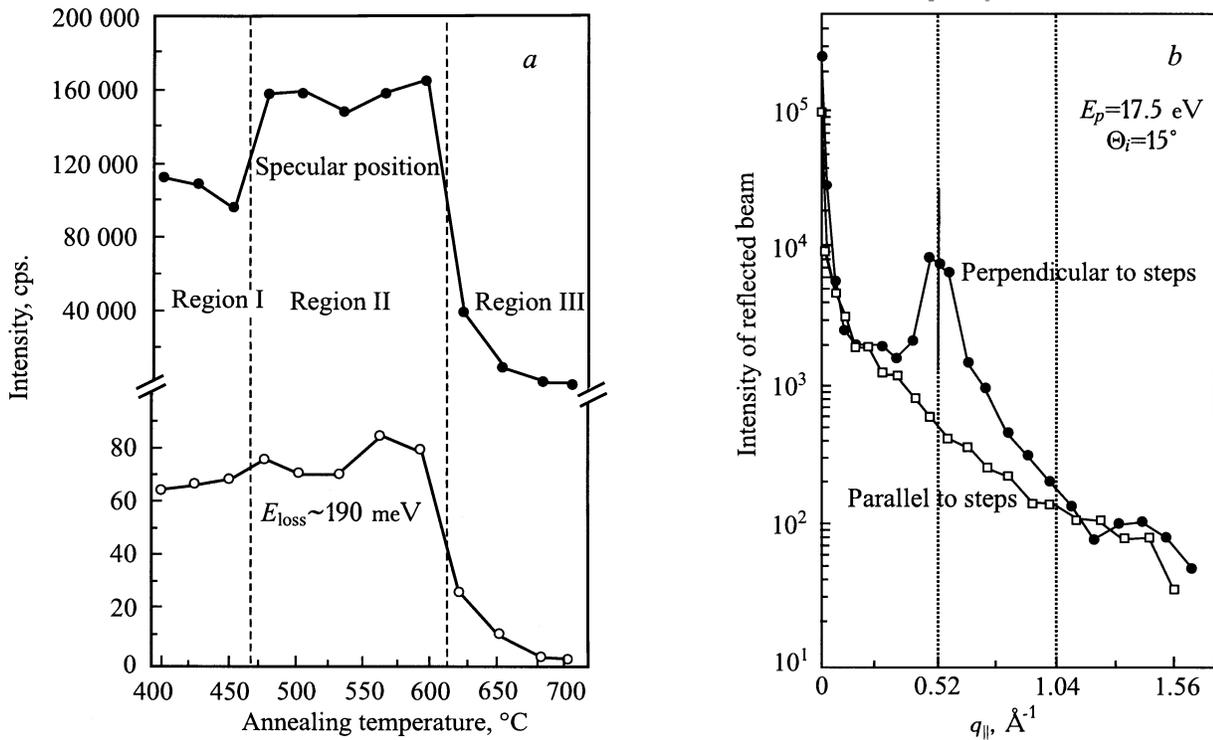
**Figure 1.** (a) C 1s core-level PE spectra taken for the MGS/Ni(771) system after annealing at different temperatures. (b) PE intensity of graphite- (solid circles) and carbide- (open circles) derived components in C 1s spectra as well as of Ni 3p core-level peak (solid squares) depending from the annealing temperatures.

surface of La-carbide [12], where the above small core-level energy shift was related to the bonding between the MG and the substrates. Obviously, an analogous situation occurs in the case of graphite coverage on Ni(771), where the interaction of the graphite layer (i.e., graphite monolayer stripes) with the Ni substrate is confirmed by an energy shift of the graphite-derived phonon modes, as obtained by the HREELS experiment.

With increase of the annealing temperature, the intensity of the C 1s peak decreases. Simultaneously, a new feature appears at the BE of about 283.4 eV (marked C<sup>(2)</sup> in the figure) that is very close to values typical for carbides of *d*-metals and rare-earth's [12,13]. LEED patterns at these annealing temperatures reveal a (4 × 1) overstructure, which is usually ascribed to formation of carbide-like constructions at the surface of Ni(771) [10,11]. Corresponding changes of intensities of the discussed above C-derived features (C 1s<sup>(1)</sup> and C 1s<sup>(2)</sup>) and that of the Ni 3p core-level signal upon increase of  $T_{\text{ann}}$  are shown in Fig. 1, b. From the analysis of the presented data we can conclude that after annealing at temperatures above 600–620 °C the graphite overlayer is almost completely destroyed, and a part of it is transformed into a carbide-like surface compound. The observed slight increase of the intensity of the Ni 3p signal supports the

above conclusion: at  $T_{\text{ann}} > 620$  °C the Ni atoms are not covered uniformly by the graphite layer anymore.

Similar conclusions can be derived from the analysis of intensities of the elastically reflected electron beam and an energy-loss peak ascribed to the longitudinal optical (LO) graphite-originating phonon mode measured by HREELS. The corresponding data for different annealing temperatures, which are strongly influenced by a degree of ordering of the graphite-derived surface and a presence of C atoms in the graphite phase at the surface, are presented in Fig. 2, a. As it was already shown by the PE measurements, after increase of the annealing temperature above 600–620 °C the graphite-derived features become suppressed also in the HREELS experiment. The LO graphite mode vanishes from the spectra, and all other graphite-derived energy-loss features decrease sharply. At the same time, a decrease of the signal of the elastically reflected peak is observed. Maximum intensity of the reflected beam and graphite-derived phonon modes (only results for the LO mode is shown in the figure) are reached in the range  $475 < T_{\text{ann}} < 590$  °C which demonstrates the formation of mostly ordered structures at these annealing temperatures.



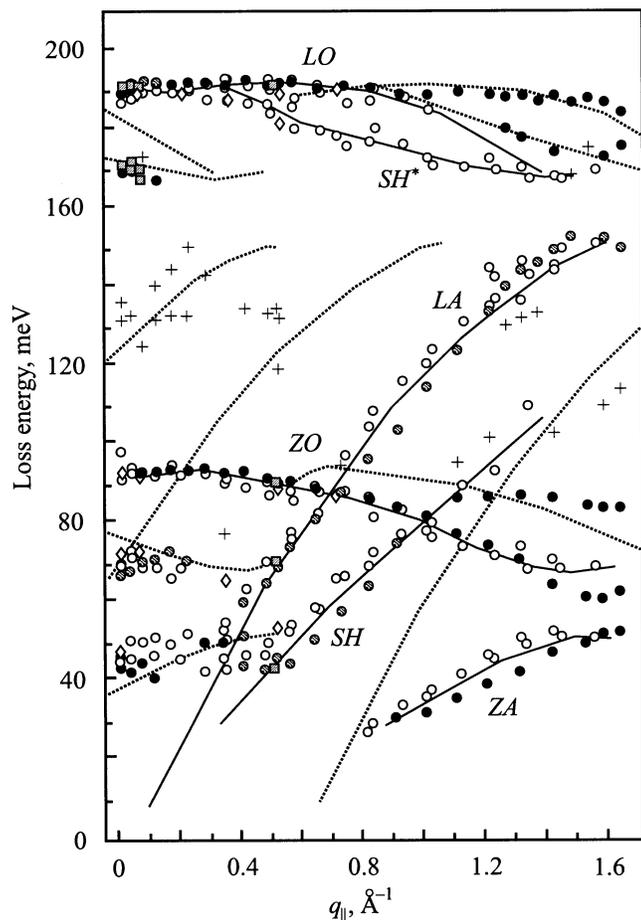
**Figure 2.** (a) HREELS intensity of elastically reflected beam (specular position, solid circles) and of the graphite-derived LO-phonon mode peak (energy loss  $E_{\text{loss}} \approx 190$  meV, open circles) depending on the annealing temperatures. (b) Polar-angle dependence of the reflected peak intensity measured in the directions parallel (open quadrates) and perpendicular (solid circles) to the Ni(771) steps.  $\theta_i$  is the primary electron incidence angle.

Intensities of the reflected peak measured at different polar angles relative to the elastic peak direction in the directions parallel and perpendicular to Ni(771) steps are shown in Fig. 2, b. The results are plotted as functions of the parallel momentum transfer,  $q_{\parallel}$ . For the measurements in the direction parallel to the steps, a monotonic decrease of the intensity of the reflected peak is monitored in the whole region of the presented values of the momentum transfer. In contrast to that, in the direction perpendicular to the steps, a rather sharp peak is observed at a polar angle corresponding to  $q_{\parallel} \approx 0.52 \text{ \AA}^{-1}$  in the scattering geometry used in this experiment. Assuming diffraction origin of this peak, we can find a value of the corresponding period in real space to be equal to  $12.1 \text{ \AA}$ , which is very close to the width of terraces periodically arranged on the stepped Ni(771). Hence, the presented HREELS results provide a convincing evidence that the grown graphite overlayer on Ni(771) forms stripes of the certain fixed width located on top of vicinal terraces.

Dispersion of the graphite-derived phonon modes in the MGS/Ni(771) system after annealing between 530 and 590°C, which were measured in the directions parallel (open symbols) and perpendicular (solid symbols) to the steps, are presented in Fig. 3. Corresponding angle-resolved phonon spectra can be found in [14]. Crosses in Fig. 3 denote features characterized by weak signal-to-noise ratio

in the spectra measured in the direction perpendicular to the steps. Solid lines correspond to the averaged data for phonon modes measured in the direction parallel to the steps. The measured phonon spectra and the corresponding phonon dispersions in the direction parallel to the steps are very similar to those observed for natural monocrystalline graphite [15] and the graphite monolayer on top of Ni(111) [5,8,9]. As for the MG/Ni(111) structure, the corresponding phonon modes in the MGS/Ni(771) system are shifted toward the region of lower energy losses as compared to their positions in monocrystalline graphite due to the interaction with Ni substrate [5,8,9].

In the case of measurements in the direction perpendicular to the steps, the phonon spectra are characterized by a number of additional features. These features are mainly observed for large values of the parallel momentum transfer and are situated in the loss energy regions of about 90 and 200 meV. On the basis of the data presented in Fig. 3, we attempted to interpret these features by a series of unmodified graphite-derived phonon modes measured in the direction parallel to the steps and shifted relative to the initial ones by values of  $q_{\parallel}$  multiple of  $0.52 \text{ \AA}^{-1}$ . These curves are shown by dotted lines in Fig. 3. Analyzing the presented data one can conclude that in first approximation, almost all additional features can be assigned to these dotted curves.



**Figure 3.** Dispersions of graphite-derived phonon modes in the directions parallel (open symbols) and perpendicular (solid symbols) to the steps for the MGS/Ni(771) system after annealing at temperatures between 530 and 590°C. Dotted lines denote dispersion curves shifted by  $q_{\parallel}$ -value multiple of  $0.52 \text{ \AA}^{-1}$  relative to the original ones characteristic for the directions parallel to steps (solid lines).

The observed differences in the phonon dispersions in the directions perpendicular and parallel to the steps reveal certain size-limited effects in the system graphite stripes on Ni(771). Detailed analysis of the nature of these phenomena will be given in a forthcoming publication [16].

In summary, graphite stripes on the Ni(771) substrate were grown by cracking of propylene followed by annealing at optimal temperatures in the region between 450 and 590°C. The C 1s spectra in this temperature region reveal dominant graphite-like character. The binding energy of the C 1s peak is shifted, however, relative to its position in bulk monocrystalline graphite due to the interaction of graphite stripes with the Ni substrate. The elastically reflected beam in the HREELS experiment has maximum intensity for these annealing temperatures that testifies the formation of mostly structurally ordered system. The

phonon spectra measured in the direction parallel and perpendicular to the Ni(771) steps reveal certain differences, which can be explained on the basis of size-limited effects.

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