

## Electronic Structure of Carbon Nanostripes

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Carbon nanostripes of graphene structure prepared on the stepped Ni(771) surface have been studied by angle-resolved photoemission. The electronic structure is anisotropic: parallel to the stripe direction, a graphite-type dispersion is measured, whereas the perpendicular direction displays two entangled band structures shifted in energy with respect to each other. These are experimentally identified as the microsurface-centered band structure and its umklapp scattered image caused by the superlattice.

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For a long time, surface science has dealt with the production of ideal surfaces and the behavior of electrons localized within the two dimensions given by the interface between solid and vacuum. The idea to place obstructions on a surface that are capable of reflecting electrons and can lead to their confinement has received increased attention since a remarkable visualization of these effects has been achieved by scanning tunneling spectroscopy (STS) [1,2]. STS is able to select atoms near a single step, and as it measures the local density of states, it can detect the presence of standing electron waves. In order to study the electronic interaction, the wave-vector-resolving methods of direct or inverse photoemission are required. Only with the help of these methods can one obtain answers to the question how an electron interacts with the step when it is moving parallel to it or when it moves towards it or away from it. Angle-resolved direct and inverse photoemission measure the global electronic structure and in order to obtain a sizable signal require a large number of identical and equally oriented steps. Experiments have shown that the presence of single or periodically repeated steps can cause in addition to the step-localized standing waves [1,2] certain superlattice effects [3–5] and a quantization [6] of the electronic spectrum. The experimental literature reports four different types of dispersion for surface states in the direction perpendicular to such step lattice: (i) a single parabola centered around the normal of the microsurface (terrace) [7], (ii) a single parabola, but arranged relative to the macrosurface normal [3,7], (iii) a repeated band dispersion related to the step periodicity [4,5], and (iv) quantum-well states with no dispersion [6].

It is astonishing that in spite of the principal difference between STS on the one hand and direct, two-photon, and inverse photoemission on the other hand, the states used so far to study steps at clean crystal surfaces are basically the same: Typically, the experiment picks a crystal-induced or image-potential induced surface state in order to probe the laterally structured surface. However, the

*L*-centered Shockley surface state, which has been used in all photoemission work to date, extends from  $E_F$  down to only 0.4 eV binding energy on Cu and Au. Our aim is to overcome this constraint and try to *impose the lateral superstructure of a stepped substrate onto the whole valence band of a monoatomic overlayer*. Therefore, we have prepared nanostripes of graphene (i.e., monolayer graphite), a material which has a truly two-dimensional electronic structure and allows us to probe a much larger *k*-space range and an energy range by almost 2 orders of magnitude wider than in previous photoemission work.

The graphene stripes were formed *in situ* on stepped Ni(771) by cracking of propylene at a partial pressure of  $1 \times 10^{-6}$  mbar and  $T = 500^\circ\text{C}$  sample temperature using a procedure elaborated previously for graphene on Ni(111) [8,9]. Propylene cracking is a self-limited reaction: as soon as the Ni surface is covered with a full graphene sheet, the reaction stops because it can take place only at a pure Ni surface. After additional annealing at  $450\text{--}500^\circ\text{C}$  in ultrahigh vacuum the system consists of graphene stripes along the Ni terraces with finite width in the perpendicular direction due to the limited size of the terraces. As shown by scanning tunneling microscopy [10], the Ni(771) surface is characterized by monoatomic steps with a height of 1.24 Å and Ni(110)-oriented terraces with a width of  $\approx 12.3$  Å which are conserved after graphitization. Low-energy electron diffraction (LEED) patterns measured *in situ* for the pure Ni(771) surface [Fig. 1(a)] and after graphene stripe preparation [Figs. 1(b) and 1(c)] display a well ordered structure. Besides the step-derived ( $7 \times 1$ ) superstructure, the LEED pattern from graphene/Ni(771) shows graphite rings [Fig. 1(c)] surrounding all principal spots of the Ni(110) structure. This is characteristic of graphene on top of surfaces with a nonhexagonal surface structure such as Ni(100) and Ni(110) [11]. Base pressure during experiment was in the upper  $10^{-11}$  mbar range.

Angle-resolved photoemission spectra have been measured at the undulator beam lines I311 at MAXlab and

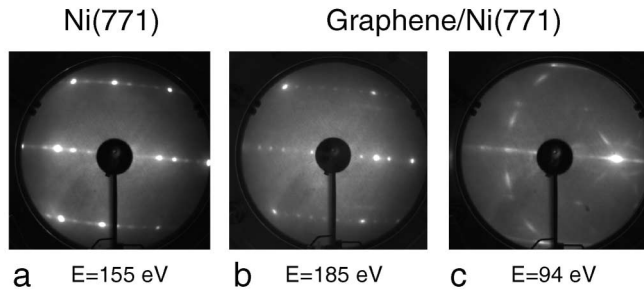


FIG. 1. Low-energy electron diffraction. The  $(7 \times 1)$  superstructure of the clean Ni(771) (a) is preserved after preparation of graphene nanostripes (b), which appear as circle sections (c). The steps and stripes run along  $[1\bar{1}0]$  which is close to the vertical direction in the figure.

U125/1-PGM at BESSY with linearly polarized light of 50 eV photon energy. Dispersions, i.e., polar angle scans of photoemission spectra, parallel and perpendicular to the step direction  $[1\bar{1}0]$ , have successively been measured from the same sample after azimuthal rotation by  $90^\circ$ .

Figures 2(a) and 2(b) show a typical series of photoemission spectra for graphene/Ni(771) where the electron emission angle is varied in the direction parallel (a) and perpendicular (b) to the graphene nanostripes. Spectra of clean Ni(771) (not shown) prove that practically all structures in the region 2 to 22 eV binding energy are graphene derived. The dispersions with the macrosurface-projected wave vector  $\mathbf{k}_{\parallel}$  corresponding to Fig. 2 are presented in Figs. 3 and 4, separately for  $\pi$ ,  $\sigma_{2,3}$ , and  $\sigma_1$  states. Figures 3 and 4 summarize data from four different preparations. Features with weak intensity are marked by crosses. The dispersions measured in the direction parallel to the nanostripes [Figs. 2(a) and 3] resemble almost fully the ones obtained from graphene on flat Ni(111) and can be assigned according to Refs. [9,12]. (The  $\sigma_{2,3}$  states near  $\bar{\Gamma}$  are too weak to be observed for present symmetry conditions.) Compared to monocrystalline bulk graphite, the  $\pi$  and  $\sigma$  branches are shifted towards higher binding energies due to strong  $C\pi$ -Ni $d$  interaction of the graphene sheet with the Ni substrate (similar to graphene/Ni(111) in Refs. [9,12]). Figure 3 shows a critical point appearing at about  $\mathbf{k}_{\parallel} = 1.55 \text{ \AA}^{-1}$ , a value which lies between the ones for  $M$  ( $1.4 \text{ \AA}^{-1}$ ) and  $K$  ( $1.7 \text{ \AA}^{-1}$ ) of graphite, indicating that the orientation of graphene hexagons relative to the steps is rotated in agreement with the LEED pattern of Fig. 1(c).

The dispersions observed perpendicular to the stripes, shown in Figs. 2(b) and 4, are very different. (i) *Two instead of one* graphene-type band structure can be recognized for  $\pi$  and  $\sigma$  states. Both band structures lead to photoemission peaks of high intensity with the left-hand one (in Fig. 4) somewhat more intense [see Fig. 2(b)]. The left-hand branches of  $\pi$  and  $\sigma$  states are shifted relative to the macrosurface normal  $[771]$  by  $-6^\circ$ . This value (which has been determined *in situ* from the parallel dispersion with the help of the azimuthal rotation) is identical to the miscut angle between the Ni(771) macro-

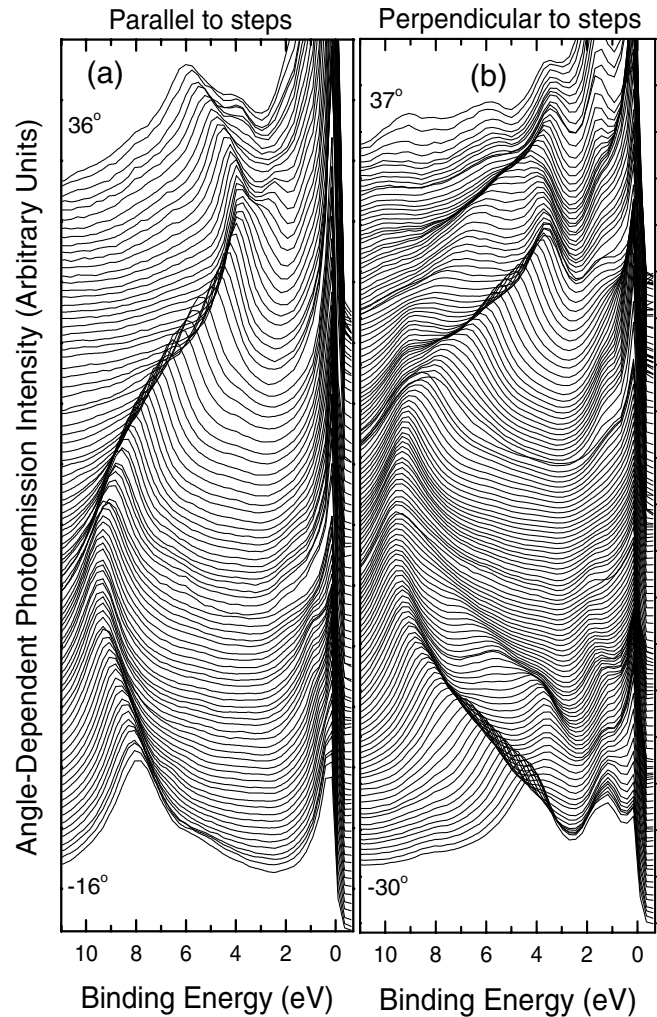


FIG. 2. Photoemission spectra at  $h\nu = 50 \text{ eV}$  for  $\mathbf{k}_{\parallel}$  parallel (a) and perpendicular (b) to the nanostripe direction.

surface and the Ni(110) terraces [10] and allows us to ascribe the left-hand branches to  $(110)$ -microsurface-centered states. Moreover, (ii) the right-hand band structure shows *pronounced gaps* for the  $\pi$ ,  $\sigma_2$ , and  $\sigma_1$  states, which have no counterpart in the parallel dispersion data [Figs. 2(a) and 3] or for graphene on flat Ni(111) or bulk graphite [9,12]. The most pronounced gap in our data appears at  $\mathbf{k}_{\parallel} \approx 1.0 \text{ \AA}^{-1}$  in Fig. 4. (iii) Our data are compatible with further gaps appearing at  $\mathbf{k}_{\parallel} = 0$  (flat band at 9.2 eV binding energy),  $\approx 1.5 \text{ \AA}^{-1}$  (between 4.3 and 5 eV), and  $\approx 2.05 \text{ \AA}^{-1}$  (between 8.1 and 8.8 eV). (iv) A weak band between about 5 and 8 eV binding energy appears periodic characteristic of back-folding into the repeated Brillouin zone scheme of the superlattice which could possibly be described by a one-dimensional Kronig-Penney model for electrons on a stepped surface [13].

The appearance of two band structures is an astonishing, unprecedented observation. The assumption of a second phase due to artifacts such as sputtering defects or faceting is at variance with the STM characterization [10]. It should be kept in mind that, in view of the

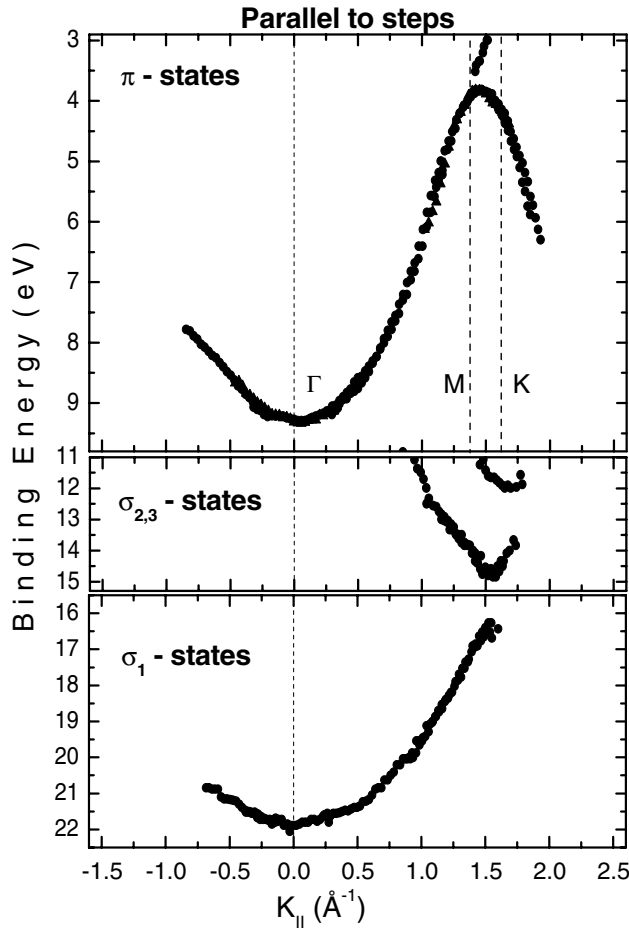


FIG. 3.  $E$  vs  $k_{\parallel}$  dispersion for the macrosurface-projected wave vector  $\mathbf{k}_{\parallel}$  parallel to the nanostripe direction.

comparable photoemission intensity of the two branches, any such artifact would have to involve a large portion of the sample surface which does not reconcile with the characterization of the macrosurface as (771) [14]. We consider the two bands and additional parallel branches an intrinsic property of the photoemission from a single phase of graphene nanostripes.

In order to assign the band structures, we varied the photon energy and plotted the dependence on the angle [Fig. 5(a)] and the parallel wave vector relative to the microsurface normal [Fig. 5(b)]. The coincidence of the left-hand branch for all photon energies confirms the assignment as microsurface-centered branch. The right-hand branches also coincide and together with a third branch (see  $h\nu = 90$  eV) are shifted by a constant value of  $\mathbf{G}$  and  $2\mathbf{G}$ , respectively, where  $\mathbf{G} = 2\pi/L$  and  $L = 12.3$  Å is the terrace width. For each band structure shifted by  $\mathbf{G}$  we are dealing with the first Brillouin zone branch only since graphite suppresses second-Brillouin-zone emission [15]. In a superlattice as well as in a simple lattice geometry, distinction of a periodic band dispersion from umklapp effects during excitation is usually difficult. The present data, however, give two reasons why the right-hand branch cannot be assigned to

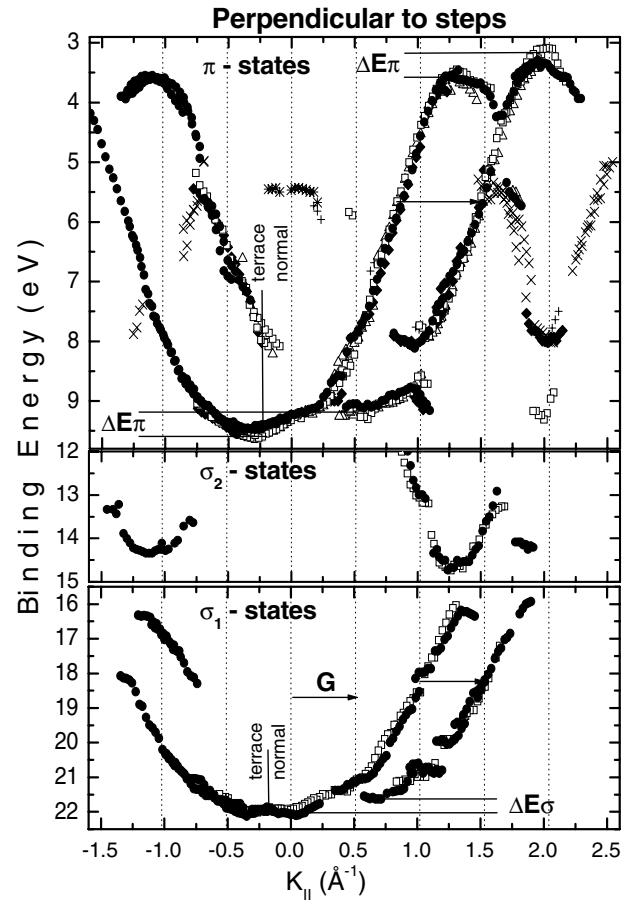


FIG. 4. Same as Fig. 3 but for  $\mathbf{k}_{\parallel}$  perpendicular to the nanostripe direction.  $\mathbf{k}_{\parallel}$  is again defined relative to the macrosurface normal. Each symbol represents a new nanostripe preparation. Note that gaps are more or less pronounced depending on the sample preparation (temperature and duration of propylene cracking). Vertical lines mark multiples of the wave vector  $\mathbf{G}$  corresponding to the step periodicity.

an initial-state superlattice effect: First is the obvious shift to lower binding energy by 0.4–0.5 eV and 0.3–0.4 eV for  $\pi$  and  $\sigma_1$  branches, respectively. Second is the fact that the band gap (we refer to  $\approx 1.0$  Å<sup>-1</sup> in Fig. 4) is not a property of the initial-state band structure of the superlattice since it does not appear at constant  $\mathbf{k}_{\parallel}$  as seen from Fig. 5(b). The right-hand branch must therefore be due to umklapp scattering with wave-vector transfer of  $\Delta\mathbf{k} = 2\pi/L$  characteristic of the superlattice structure. Umklapp scattering depends on the availability of final states and this likely introduces the photon-energy dependence of the band gap. For bulk graphite, umklapp scattering contributes substantially to photoemission and its dependence on photon energy has been measured [16]. During umklapp scattering the wave-vector difference is transferred to collective excitations, usually phonons. It is interesting to note in this context that the phonon dispersion of graphite nanostripes on Ni(771) as measured by electron energy loss spectroscopy has indeed displayed strong superlattice effects in the first study of its kind [8]. We caution, however, that a

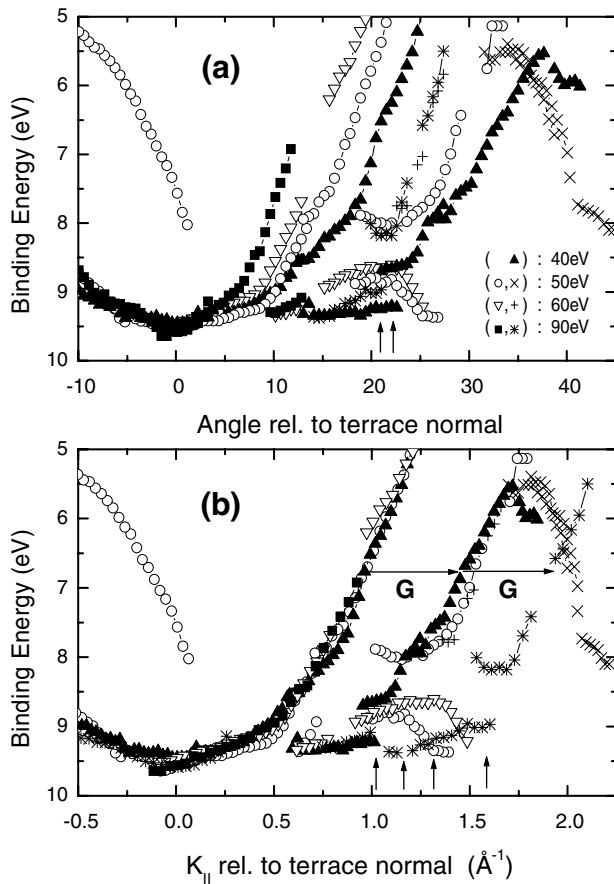


FIG. 5. Photon-energy dependence perpendicular to the stripe direction versus electron emission angle (a) and  $k_{||}$  relative to the microsurface normal (b).  $G$  indicates a reciprocal superlattice vector, and vertical arrows mark band gap positions for various photon energies.

simple identification of phonon excitation with the energy shift measured in this work fails due to the different energy scale and that further research efforts need to be undertaken in this new and exciting field.

In summary, we prepared a regular array of carbon nanostripes and observe an anisotropic dispersion with two band structures in the direction perpendicular to the stripes: a gapped and a microsurface-centered one. We showed that umklapp scattering in the excited state caused by the superlattice instead of a conventional superlattice effect of the ground state is the origin of this behavior.

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