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Effect of noble-metal contacts on doping and band gap of graphene

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Density-functional theory of graphene predicts that noble-metal contacts will provide doping but leave the Dirac crossing point intact. We use high-resolution angle-resolved photoemission and noble-metal intercalation to show that, instead, substantial band gaps open in proportion to the doping effect. Graphene on Au, however, remains gapless even during heavy electron doping by adsorbed Gd. A key role is assigned to quantum interference at the almost incommensurate graphene/Au interface.

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Graphene has been a subject of rapidly growing interest for half a decade.[1] Its specific atomic structure which is caused by sp^2 hybridization is that of a non-Bravais lattice consisting of two equivalent sublattices of triangular shape. This structure imparts unique properties to the graphene Hamiltonian resulting in the possibility of employing the relativistic Dirac equation for the description of quasiparticles which behave as massless Dirac fermions in the vicinity of the Fermi energy. The particular chirality in the graphene electronic structure leads to the absence of backward scattering[2] and to a half-integer quantum-Hall effect.[3,4]

Transport investigations have tried to confirm all of the novel phenomena but meet with difficulties when verifying, e.g., the universal minimum conductivity. Insufficient control over doping is believed to be the reason for it.[5] While clean isolated graphene has the Dirac point (E_D) with its vanishing density of states exactly at the Fermi energy (E_F), it was suggested that in real free-standing graphene, doped regions exist due to random charged impurities.[5] In these areas, the local Fermi energy is shifted by ΔE_F rendering the transport across these areas bipolar and subject to Klein tunneling.[6]

Even if the problem of random local shifts in E_F is abolished, an analogous effect is expected to occur where the free-standing graphene is contacted to the metal leads. Doping occurs there due to charge transfer from or to the metal, and this was found to affect the minimum conductivity in graphene as well,[7] in particular, so for two-point measurements.[8] The doping at the contacts means, on the other hand, that these contacts can be used to create from graphene a planar bipolar transistor, i.e., a graphene *p*-*n* junction, as has been studied in theory without considering metal interfaces.[9–11] The above-mentioned absence of backscattering can lead to ballistic transport across these devices[6,11] or, from another perspective, it means that an array of such one-dimensional *p*-*n* junctions becomes a superlattice without minigaps in the band structure.[12] Several groups have realized devices of planar graphene *p*-*n* junctions but metal contacts have not been considered so far.[13–16]

In contrast to a *p*-*n* junction in a bulk semiconductor with band-bending effects at length scales of 100 nm and thus far beyond the probing depth of photoelectrons, we can directly monitor the planar graphene transistor components by photoemission in a wave-vector resolved manner. The required single-crystalline systems can indeed be grown epitaxially in experiment and their band structure has been under investigation. Graphene on SiC(0001) displays the linear relativistic dispersion including the Dirac crossing point.[17] On this substrate, the graphene becomes electron doped with $\Delta E_F = -450$ meV (Ref. 17) which is attributed to dangling bonds at the interface. These dangling bonds are absent when graphene is grown on metals. In fact, several transition metals enable the epitaxial growth of graphene by surface segregation[18] or chemical-vapor deposition.[19,20] Moreover, epitaxial interfaces with metals on which graphene does not grow directly by either of the two methods, can be created by metal intercalation.[19] Noble metals belong to this class of materials. The system graphene/Au/Ni(111) has a Fermi level position similar to neutral graphite[21] and shows also the linear relativistic dispersion of free-standing graphene.[22] This is rather unexpected since Au, unlike SiC, is not a material that can decouple the graphene through an absolute band gap around E_F. The typical characteristics of the immediate interface of graphene with transition metals is instead a strong substrate interaction with closer substrate distance of ~ 2.0 Å.[23] [Exceptions have been reported for Pt (Ref. 23) and Ir.[24]] The most frequently studied example is that of graphene on Ni(111), where the strong interaction replaces the Dirac point by a large band gap of ~ 3 eV.[21,25] We show that the Au interlayer is unique in restoring the gapless state and unmatched also by Ag and Cu which provide substantial band gaps. The larger the doping, the larger becomes the band gap. Graphene on Au is only slightly *p* doped, and we will show that by using Gd, strong *n* doping can be achieved without opening a band gap in the graphene. The particular structure of the graphene/Au interface with its large unit cell is believed to minimize the effects of symmetry breaking.

Photoemission measurements were performed with a Scienta SES100 spectrometer installed at the beamline UE112-lowE-PGM at BESSY II. A parallel angular detection mode and a six-axes automated cryomanipulator were used. Scanning tunneling microscopy (STM) was performed with an Omicron VT STM microscope at room temperature. The Ni(111) surface was prepared as a 15–20 monolayer (ML) thick film on W(110) and graphene was synthesized by cracking of propylene at the Ni(111) surface held at $T \sim 800$ K. Because the surface reactivity drops drastically with graphene, this procedure results in exactly one graphene monolayer.[25] Intercalation of monolayers of Cu,[26] Ag,[27] and

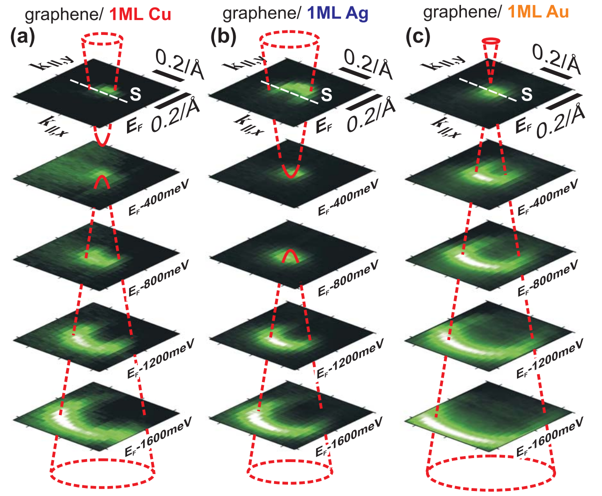

FIG. 1. (Color online) Constant-energy surfaces of the π band near the Dirac point in graphene on monolayers of (a) Cu, (b) Ag, and (c) Au by angle-resolved photoemission. It is seen that only Au leads to neutral graphene while Cu and Ag cause heavy electron doping.

Au (Ref. 21) was achieved by deposition on the graphene followed by brief annealing at 700 K. Adsorption of alkali (K) and rare-earth (Gd) atoms as well as subsequent photoemission measurements were done at $T=30$ K. The Gd deposition rate was calibrated by a quartz-crystal microbalance, and the K was deposited until the same ΔE_F as with Gd was reached. Overall energy (electrons and photons) and angular resolution of the experiments were 5 meV and 0.2°, respectively, at a probing area of ~ 0.01 mm^2. The base pressure was $1-2\times 10^{-10}$ mbar.

Figure 1 shows the graphene π band in the vicinity of the Fermi energy after intercalation of monolayers of Cu, Ag, and Au. Photoemission measurements of constant-energy surfaces at E_F, i.e., the Fermi surface, and stepwise down to 1.6 eV binding energy are displayed. These scans in two **k**-space dimensions guarantee that the measurement does not miss the Dirac point since alignment is a very critical factor.[28] *Only for Au is the Dirac point close to the Fermi energy.* The interfaces with Cu and Ag lead, instead, to strong downward shifts of the Dirac energy, i.e., heavy electron doping. This is confirmed in Fig. 2 by measurements passing precisely through the $\bar{K}$ point along direction "S" (mark in Fig. 1) with an alignment accuracy of ±0.1° corresponding to ± 0.007 Å^{-1}. A quantitative analysis of Fig. 2 reveals a shift of the Dirac crossing point in graphene/Cu by $\Delta E_F=-310$ meV and in graphene/Ag by -560 meV, where ΔE_F is defined as the difference between the Fermi energy and the middle of the gap. For Au, where the Fermi edge visibly cuts through the dispersion near E_F, the fit reveals a very small hole doping ($\Delta E_F=+100\pm 20$ meV). If we compare these values to the work functions[29] of (111) surfaces of Cu (5.22 eV), Ag (4.92 eV), and Au (5.54 eV), we find an excellent relative agreement (Fig. 3). The work function of graphene is, however, 4.6 eV (Ref. 25) so that we may expect graphene/Ag to be the closest to neutral and not the farthest.

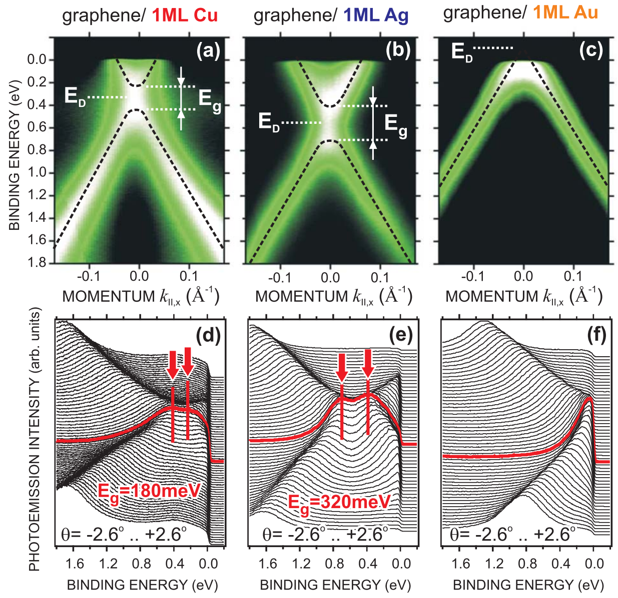

FIG. 2. (Color online) $E(k)$ dispersions of Dirac fermions in graphene on monolayers of [(a) and (d)] Cu, [(b) and (e)] Ag, and [(c) and (f)] Au. The momentum scan (line S in Fig. 1) cuts precisely through the $\bar{K}$ point of the graphene Brillouin zone. Cu and Ag interlayers open substantial band gaps destroying the Dirac point in graphene.

The doping effect of epitaxial noble-metal contacts on graphene has recently been studied by first-principles calculations for fcc(111) interfaces.[23] These are the ideal model systems for the present experiments because the work function is determined by the atomic layer at the top and a single intercalated noble-metal (Cu) monolayer is theoretically sufficient to restore the Dirac crossing in graphene/Ni(111).[31] Reference 23 finds $\Delta E_F=-0.17$ eV, -0.32 eV, and $+0.19$ eV for graphene on Cu, Ag, and Au, respectively, with very similar results when the adsorption geometry at the interface is modified.[32]

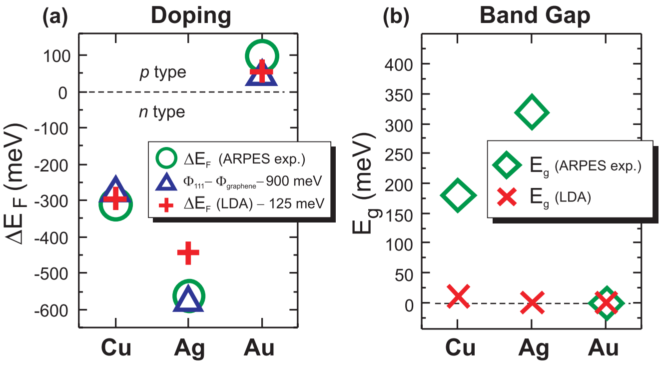

FIG. 3. (Color online) (a) The doping measured in photoemission as ΔE_F (○) is tied to the difference of the work functions Φ of the noble metal and graphene minus a constant offset of 900 meV (△). The offset needed to reconcile the experiment with local-density theory (Ref. 23) is much smaller (125 meV) but still overestimates hole doping (+). (b) The tendency for gap formation is strongly underestimated by local-density theory (×) (Refs. 23 and 30) as the comparison with our experimental gap values E_g (◇) shows.

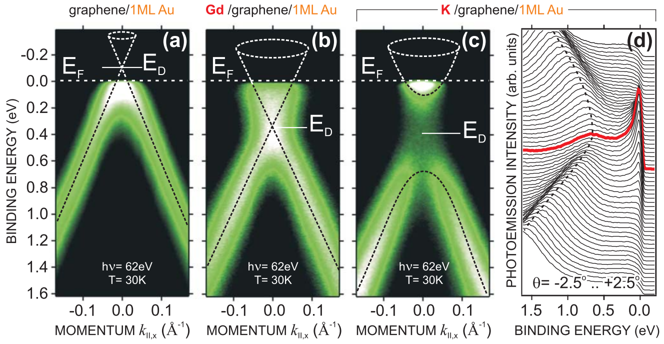

FIG. 4. (Color online) Graphene/Au (a) before and after extra *n* doping by (b) Gd and [(c) and (d)] K. It is seen that electron doping by K opens a large gap while Gd demonstrates that graphene is gapless also above the Dirac point.

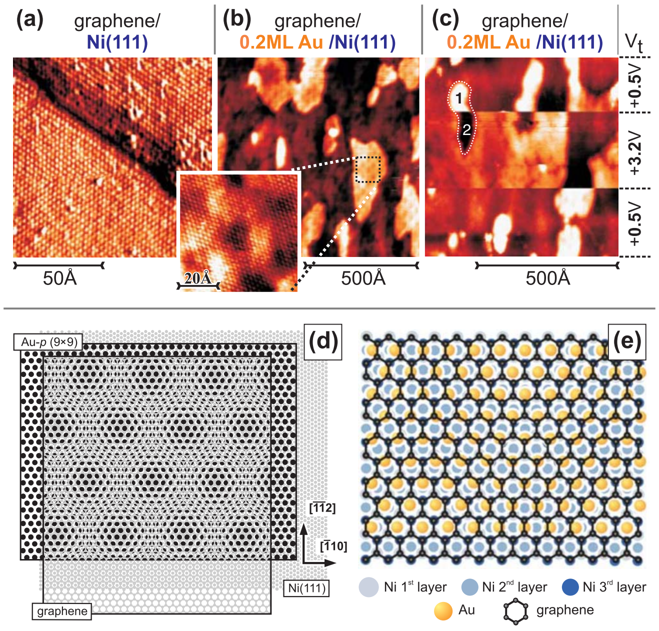

FIG. 5. (Color online) STM (a) before and (b) after intercalation of 0.2 ML Au. Bright regions in (b) are with the intercalated Au monolayer and dark areas are without. (c) This contrast is electronic because it reverses with bias. (d) Model for the Moiré pattern based on the atomically resolved experiment [zoom in (b)]. It suggests that Au forms a $p(9\times9)$ superstructure under graphene. This results in (e) a very large commensuration cell of the graphene with the Au monolayer which amplifies the electronic decoupling of graphene from the metal substrate.

Figure 3 compares our experimental results with the theoretical findings.[23] The improved agreement with experiment beyond the work-function argument can be reached if one accounts for chemical interaction: the quantum-mechanical terms allow for energy differences of up to 0.9 eV in the graphene-metal systems.[23] As seen in Fig. 3(a), their consideration by means of the local-density approximation[23] reduces the deviation from the experimental results from 900 to 125 meV in average. Figure 3(b) shows, however, that the substantial energy gaps in graphene/Cu ($E_g=180$ meV) and graphene/Ag (320 meV) are strongly underestimated by *ab initio* calculations.[23] They predict weak substrate interactions and band gaps vanishing[23] or small against room temperature [11 meV for Cu (Ref. 30)]. In order to find out whether a similar gap lurks in the unoccupied states of graphene/Au/Ni(111), we deposited K which is a donor for graphene/SiC.[17] Figure 4(c) shows that graphene is easily doped but that also a band gap opens. The gap is best seen from the stacked spectra of Fig. 4(d). In Fig. 4(b) we doped instead by Gd deposition: the linear dispersion of the π band remains largely intact and no band gap opens. A quantitative analysis gives 20 meV as upper limit for a gap. Keeping transport applications of neutral graphene in mind, we consider the Dirac point as restored when the gap is smaller than 26 meV, i.e., room temperature. *This means that Au behaves differently from Ag and Cu not only when it comes to charge neutrality but also to preserving the gapless state.* As there is no apparent electronic reason for K to affect the graphene more than Gd does, it must be due to different adsorption geometries. Note that the seemingly opposite effect which intercalated K has on graphite, i.e., that of re-establishing the linear π dispersion, is simply explained by changing the graphite layer stacking from a-b to a-a which enhances the symmetry of the graphene layers.[33]

We investigated the adsorption of graphene/Au also microscopically. Figure 5(b) shows an atomically resolved STM image (tip bias voltage $V_t=+20-30$ mV, current 16–25 nA). The symmetry is threefold as it was before Au intercalation [Fig. 5(a)]. [Note that for $p(1\times1)$ graphene/Ni(111) with lattice mismatch (tensile) of 1.2% (Refs. 18 and 20) the threefold symmetry is due to "on top" adsorption, where every other carbon atom has no Ni neighbor underneath and A-B symmetry in graphene is maximally broken.] In addition, a Moiré pattern is seen which forms only after intercalation. The Au monolayer on Ni(111) grows itself in a 9×9 structure.[34] Figure 5(d) shows a simulation of the Moiré pattern based on this 9×9 structure and an equilibrium graphene lattice with lattice constant $a=2.46$ Å.

The threefold symmetry seen in STM means that A-B symmetry of graphene is broken in the local stacking geometry also after Au intercalation. It appears, however, that more important to the free-standing electronic structure is the formation of the Moiré pattern. It is known that graphene bilayers grown on SiC($000\bar{1}$) contain a high density of twist boundary faults and a relative rotation between bilayer constituents shall lead to an effective decoupling of the electronic structures.[35,36] The dispersion changes from quadratic to linear already upon a small twist[37,38] which makes the interface between otherwise identical graphene layers highly incommensurate. One can explain this effect generally by quantum interference at the boundary.[39] Considering the atomic structure of graphene on $p(9\times9)$ Au/Ni(111) in detail [Fig. 5(e)], one notes that less than ~20% of graphene hexagons are in registry with this Au superstructure. The huge lattice mismatch between graphene and Au leads to this very large commensuration cell and decouples graphene from the Au, similarly to the case of twisted bilayers. Cu grows $p(1\times1)$ on Ni(111) which leads to maximum breaking of the A-B symmetry in the graphene. We assume that for the Ag, the interface potential gradient, which is largest among the systems considered here, causes the opening of the gap via symmetry breaking. Returning to the example of the twisted bilayer graphene, it was recently studied how an extra electric field affects its perfect Dirac cone: the dispersions shift against each other but they do not become rounded off at the Dirac point as they do for the bilayers with graphite-type stacking.[40] We estimate that in Au, only the combination of the Moiré and the neutrality suffices to preserve the Dirac point in the graphene.

It is remarkable that A-B symmetry breaking has no influence on the Dirac point in local-density calculations of graphene/Au.[23] This holds for R-$(\sqrt{3}\times\sqrt{3})$ graphene/Au(111).[23] Even on top $p(1\times1)$ graphene/Cu(111) with maximum symmetry breaking preserves the Dirac point opening a gap of only 11 meV.[30] The theory apparently underestimates the tendency for substrate interaction and band-gap formation. A reason could be van der Waals contributions which become important for weak Coulomb interactions at large graphene-metal separations and are not included in the calculations. Differently from predictions by density-functional theory, we suggest that only the combination of (i) absence of substrate electronic states at the Dirac point, (ii) absence of charge transfer from or to the metal substrate, and (iii) a very large commensuration cell is able to restore the Dirac cone for graphene at a metal contact. It appears that quantum interference at the interface is the common denominator in restoring ideal graphene behavior in few-layer graphene and in graphene on metals. The results demonstrate constant doping over macroscopic areas and show that p-n junctions may be created without any additional doping by selective deposition of different noble metals and subsequent intercalation. Such junctions could be employed for investigating implications of Klein tunneling in graphene.

Note added in proof. A band gap was most recently reported in the systems K/graphene/Au/Ru(0001) (Ref. 41) and K/graphene/Au/Ni(111) (Ref. 42) but ascribed to the effect of the intercalated Au monolayer.

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