# Image-potential states of graphene on noble-metal surfaces

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Time-, angle-, and energy-resolved two-photon photoelectron spectroscopy is used to study image-potential states of weakly bound monolayer graphene on the noble-metal surfaces Pt(111), Au/Ir(111), Au/Ni(111), and Ir(100). Binding energies are increased relative to the substrates, and lifetimes are similar for all systems under investigation. The properties of the image-potential states are mainly determined by the graphene layer with reduced influence of the substrate. Substrate-related occupied surface states close to the Fermi level are observed for graphene on fcc(111) substrates.

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# I. INTRODUCTION

Graphene forms a purely two-dimensional structure<sup>1</sup> and exhibits a high carrier mobility<sup>2,3</sup> due to ballistic carrier transport.<sup>4</sup> These properties make it a material of interest for basic research and application in devices like transparent electrodes.<sup>5</sup> As the original fabrication technique by mechanical exfoliation<sup>6</sup> is not scalable, the growth of graphene on metal films has been an objective of intensive work<sup>7,8</sup> as it is able to yield large-scale sheets in industrial dimensions.<sup>9,10</sup>

The electronic structure of weakly van der Waals-bound graphene on inert noble-metal surfaces closely resembles the one of the freestanding layer.<sup>11–14</sup> The system can therefore be used to study physics in a two-dimensional system. In the current study, image-potential states of graphene on several metal substrates were investigated. These states arise due to the 1/z potential that emerges when an electron at a distance z in front of a metallic surface is screened by the charge redistribution at the surface. The small binding energies  $E_n < 0.85 \,\mathrm{eV}/n^2$  of the *n*th image-potential state and their long lifetimes make these states a sensitive probe of surface properties. The charge delocalization and high carrier mobility of graphene may lead to an efficient screening of the external charge. If graphene provides perfect screening, differing underlying substrates are not expected to have a big influence on the image-potential state in front of the graphene layer. The decay of the image-potential state will preferentially go into substrate states because of the small density of states of graphene around the Fermi energy  $E_{\rm F}$  and the fact that decay into states near  $E_{\rm F}$  requires a large momentum transfer. Therefore, lifetime measurements provide information about the coupling between graphene and the substrate.

The existence of image-potential states on graphene was shown via field-emission resonances by scanning tunneling spectroscopy for Ru(0001)<sup>15,16</sup> and SiC substrates.<sup>17</sup> Two-photon photoemission (2PPE) directly observed the series of image-potential states for covalently bound monolayer graphene (Gr) on Ru(0001)<sup>18</sup> and van der Waals–bound Gr/Ir(111).<sup>19</sup> By time-resolved 2PPE the lifetimes of image-potential states were determined. The previous reports demonstrate the influence of periodic superstructures<sup>18</sup> and island size<sup>19</sup> on the energetics and dynamics of image-potential states. In this work we provide a systematic study of the influence of different substrates on the properties of image-potential

states. Many of the clean samples have intrinsic surface states, and the question of how the graphene layer modifies the surface states of the underlying substrate arises. In the case of Gr/Ru(0001), the interplay between image-potential states and the surface state dominates the surface electronic structure.<sup>18</sup> On the other hand, the surface state of Ir(111) is hardly affected by the deposition of graphene.<sup>19,20</sup> In the present work, image-potential states and surface states are studied by 2PPE and angle-resolved photoelectron spectroscopy (ARPES) as sketched in Fig. 1.

# **II. EXPERIMENT**

#### A. Sample preparation

Clean Pt(111) [Ni(111), Ir(100)] surfaces were prepared under ultrahigh vacuum (UHV) conditions (base pressure < $1 \times 10^{-8}$  Pa) by standard procedures. These include repeated cycles of argon-ion bombardment, subsequent annealing at 1280-1370 K (1280 K, 1500 K) and heating to 1180 K (580 K, 1250 K) in oxygen atmosphere to remove carbon impurities. In the case of Pt(111) and Ir(100), the oxygen pressure was  $6 \times 10^{-6}$  Pa in the UHV chamber but was locally enhanced by a factor of  $10^2$  to  $10^3$  by gas inlet through a capillary tube with its opening close to the surface (doser). In the case of Ni(111), oxygen was carefully dosed in order to prevent oxidation of the surface. Sample quality was monitored by low-energy electron diffraction (LEED) and ARPES to check the work function of the surface and in the case of nickel also the presence of surface states.<sup>21</sup> The preparation of the Ir(111) substrate and graphene layer followed Ref. 19.

Thermal decomposition of ethene (C<sub>2</sub>H<sub>4</sub>) was used to prepare graphene on the different substrates. The preparation procedure was slightly modified and optimized for each of the surfaces. Graphene formation on Pt(111) proceeded along the recipe given in Ref. 22: Ethene was adsorbed to saturation coverage at 90 K, and initial graphene islands were formed by subsequent heating to 1130–1170 K. At this temperature ethene was offered at a pressure of  $3 \times 10^{-5}$  Pa in order to reach monolayer coverage by chemical vapor deposition (CVD) growth. Due to the weak van der Waals bonding between graphene and platinum<sup>11,23</sup> different rotational orientations of the graphene layer on platinum are formed, as reported before.<sup>24</sup> Growth conditions were optimized to yield the most narrow contribution of rotational domains.



FIG. 1. (Color online) Two-photon photoemission process from a surface state via image-potential states into free-electron states and direct photoemission from the surface state. Using the same total photon energy ensures that the same initial and final states are probed by both photoemission techniques.

On Ni(111) [Ir(100)] graphene growth was achieved by a single CVD step for 5 min (2 min) at 980 K (1450 K) under  $10^{-6}$  Pa ethene atmosphere using the doser. Due to the covalent bonding between nickel and carbon and because of the small lattice mismatch, graphene grows aligned with the Ni(111) surface in a 1 × 1 structure.<sup>25</sup> Gr/Au/Ni(111) was established by intercalation of gold between graphene and nickel.<sup>26</sup> For this purpose, one monolayer of gold, referring to Au(111), was thermally evaporated onto the Gr/Ni(111) surface. The same intercalation procedure was used for Gr/Au/Ir(111).

#### B. Photoelectron spectroscopy

Sample preparation and photoemission experiments were performed in two similar experimental setups with different photoelectron analyzers, leading to consistent results for all systems under investigation. Both setups consist of a UHV chamber (base pressure  $< 1 \times 10^{-8}$  Pa) holding the equipment for sample preparation including LEED optics. Both laser systems<sup>27,28</sup> are based on 76-MHz Ti:sapphire oscillators providing infrared laser pulses (IR) of hv = 1.55 eV photon energy. The 2PPE experiments used the fundamental laser output as well as its third harmonic, which was generated in nonlinear crystals. An additional crystal was used to generate the fourth harmonic for ARPES measurements. All experiments used *p*-polarized beams.

The data presented from Pt(111) and Ir(100) were recorded using an Omicron EA 125 HR hemispherical analyzer with an energy resolution of 35 meV and an angular resolution of  $1.6^{\circ}$ . A detailed description of the setup is given in Ref. 28. Data from graphene prepared on Ni(111) as well as timeresolved measurements for graphene on Ir(100) were recorded using an ellipsoidal display-type analyzer which records twodimensional momentum distribution patterns at a given energy. For details see Ref. 29. The acceptance cone covers  $88^{\circ}$ ; energy and angular resolution are 50 meV and  $3^{\circ}$ , respectively. As the dispersion of the observed surface states and image-potential states is isotropic within the experimental resolution, data were averaged along the azimuthal direction in order to yield better statistics.

Work functions were determined from the low-energy cutoff of 2PPE or ARPES spectra.

## **III. RESULTS**

#### A. Graphene/Pt(111)

LEED patterns of Gr/Pt(111) are shown in Figs. 2(a) and 2(b). In addition to the hexagonal unit mesh of the Pt(111) surface, diffraction intensity appears along a ring

# (a) Graphene/Pt(111) (b)



FIG. 2. (Color online) (a) LEED pattern of Gr/Pt(111) showing graphene spots  $\pm 23^{\circ}$  away from the six substrate spots. (b) A different preparation showed additional spots aligned with the substrate spots. (c) The 2PPE data measured with photon energies of 4.66 eV (pump) and 1.55 eV (probe) for the single- and two-domain sample preparations (lower and upper curves, respectively). (d) The 2PPE intensity map for the two-domain sample shown in (b). ARPES data taken with a photon energy of 6.22 eV (e) as measured and (f) normalized to the Fermi function for the two-domain sample.

corresponding to the reciprocal lattice constant of graphene. The intensity distribution indicates graphene domains of various orientations relative to the Pt(111) lattice. In Fig. 2(a) the intensity maxima are  $\pm 23^{\circ}$  away from the substrate spots, as observed before.<sup>30,31</sup> A different preparation additionally shows diffraction from graphene domains aligned with the substrate [Fig. 2(b)]. In the following we refer to these two preparations as single- and two-domain samples. The double-diffraction features around the substrate spots similar to Ref. 32 indicate a well-ordered graphene layer with large domains. Various orientations between  $0^\circ$  and  $6^\circ$  have been reported.<sup>11,24,30,32</sup> Under the preparation conditions used in this work domains rotated by  $\sim 15^{\circ}$  (Refs. 11,24, and 33) were not observed. The absence of an energetically favored single orientation is attributed to the weak van der Waals-type bonding between graphene and the substrate.<sup>11,24,33</sup>

The clean Pt(111) surface has a work function of 5.97 eV, as reported before.<sup>34</sup> With graphene this value is drastically reduced to  $4.85 \pm 0.03$  and  $4.81 \pm 0.03$  eV for the singleand two-domain samples, respectively. Photoemission from inhomogeneous surfaces measures the average work function from the different patches. We estimate a work function of 4.77 eV for the domains aligned with the substrate assuming an equal distribution of  $0^{\circ}$  and  $23^{\circ}$  orientations for the two-domain sample. This estimate is based on the roughly equal intensity of both orientations in the LEED image of Fig. 2(b). Further support comes from the 2PPE data, which are shown in Fig. 2(c). The n = 1 image-potential state from the single-domain sample (bottom curve) shows a single narrow peak. For the two-domain sample (top curve) two peaks with roughly equal integrated intensity (dashed curves) are needed to describe the spectrum. The narrower peak matches in energetic position and width the peak observed for the singledomain surface. It is therefore assigned to the image-potential state on domains with 23° orientation and has a binding energy of  $E_1 = 0.87 \pm 0.02$  eV with respect to the vacuum level. The broader peak at lower energy for the two-domain sample is then assigned to the domains aligned with the substrate. The binding energy is  $0.83 \pm 0.02$  eV relative to the vacuum level of the domains with the lower local work function. The binding energies of the n = 2 image-potential states are  $0.23 \pm 0.02$  and  $0.22 \pm 0.02$  eV for the rotated and aligned domains, respectively. The effective mass of the n = 1 state is, for both samples, close to the free-electron mass, as can be seen from the dispersion shown in Fig. 2(d) for the two-domain sample. All binding energies are significantly larger than the ones reported for bare Pt(111), which are  $E_1 = 0.65$  eV and  $E_2 = 0.16 \text{ eV.}^{34}$ 

The intensity of the first image-potential state in Fig. 2(d) has a maximum between 0.05 and 0.10 Å<sup>-1</sup>, pointing to resonant optical excitation of the state by the pump pulse. This resonance is observed only for the two-domain sample and must therefore arise from the aligned domains. The situation is similar to Gr/Ir(111), where the graphene is aligned with the substrate. There a resonance between the image-potential states and a downward-dispersing Rashba-split Shockley-type surface state occurs.<sup>19</sup> In order to clarify the nature of the initial states involved for Gr/Pt(111), ARPES measurements at a photon energy of 6.22 eV were performed. Results are



FIG. 3. (Color online) (a) LEED pattern from Gr/Au/Ir(111) with 5 ML of gold intercalated. Crosses mark the substrate spots derived from LEED observations at higher energies. (b) Angle-resolved 2PPE data taken with photon energies of 4.65 eV (pump) and 1.55 eV (probe).

shown in Fig. 2(e). In Fig. 2(f) the data were normalized to the Fermi function to obtain additional information in the energy range slightly above  $E_{\rm F}$ . The 2PPE data show that between 0.05 and 0.10 Å<sup>-1</sup> the n = 1 state is resonantly pumped from the initial states around -0.65 eV observed in ARPES. The downward-dispersing band observed in ARPES at lower energy fits the resonance condition reasonably well, in contrast to the downward-dispersing band at higher energy [Figs. 2(e) and 2(f)]. Details of the surface electronic structure must be responsible for the quenching of the resonance between the Shockley-type surface state and the image-potential states upon graphene adsorption in rotated orientation.

## B. Graphene/Au/Ir(111)

The growth of graphene on Au(111) requires high pressures for  $\text{CVD}^{35}$  or deposition of carbon by an electron beam evaporator.<sup>36,37</sup> Intercalation of gold on a graphene-covered substrate provides an alternative.<sup>26,38</sup> We chose the Ir(111) surface as a substrate because of the small lattice mismatch between Ir and Au and the low solubility of Au in Ir.<sup>39</sup> Figure 3(a) shows the LEED pattern for 5 monolayers (ML) of Au intercalated after annealing to 870 K on graphene on Ir(111). The diffraction spots show a well-ordered graphene layer. The substrate spots are not visible at this electron energy and are marked by crosses. At higher energies the substrate spots clearly indicate that the orientation of the substrate is assumed by the intercalated gold layer and kept by the graphene layer.

The work function of the 5-ML intercalated sample is  $4.88 \pm 0.02$  eV compared to  $5.53 \pm 0.03$  eV for 5 ML of Au deposited directly on the Ir(111) substrate. The latter value agrees well with the work function of 5.55 eV for Au(111).<sup>40</sup> Angle-resolved ultraviolet photoemission spectroscopy and 2PPE results have converged at a thickness of 5 ML, which is therefore representative for a Au(111) substrate.

The two-photon photoemission data [Fig. 3(b)] show two image-potential bands with effective masses close to the free-electron mass. For  $k_{\parallel} = 0$  the energies of the n = 1 and 2 image-potential states are  $3.84 \pm 0.01$  and  $4.48 \pm 0.01$  eV, respectively. With a work function of 4.88 eV

this would give binding energies larger than allowed by the equation

$$E_n = \frac{0.85 \text{ eV}}{(n+a)^2}, \quad n = 1, 2...,$$
 (1)

for quantum defects 0 < a < 0.5. The energetic difference between the two image-potential states can be determined to  $0.64 \pm 0.01$  eV, which would be obtained from Eq. (1) for a =0. Using this value, we can extrapolate the work function to 4.69 eV, which is considerably smaller than the measured value of 4.88 eV. To resolve this discrepancy we assume that some areas of the surface have a higher work function than the areas where we observe the image-potential states. Gold remaining on the graphene after the annealing step for intercalation could explain the observed behavior. Scanning tunneling microscopy would be needed to confirm this conjecture. Measurements for 1 and 2 ML of Au intercalated showed very similar results. They are not reported here in detail because coverage and intercalation process could not be controlled with sufficient accuracy. For 5 ML the precise coverage is of minor importance because all observed properties have converged at this coverage.

The intensity distribution in Fig. 3(b) shows enhanced intensity on the n = 2 band for  $k_{\parallel} \approx 0.08$  Å<sup>-1</sup>. This is attributed to a resonant transition from the Shockley surface state of Au(111) which persists upon graphene adsorption. ARPES results showed this state clearly after intercalating 2 ML of gold. Resonant transitions between surface states and image-potential states have been observed for graphene on Pt(111) (Sec. III A) and Ir(111).<sup>19</sup>

## C. Graphene/Au/Ni(111)

The prerequisite for graphene on gold on Ni(111) is the preparation of the Ni(111) substrate followed by the CVD growth of a graphene monolayer. Gold is then intercalated between graphene and the Ni(111) substrate. LEED patterns for graphene-covered Ni(111) are shown in Fig. 4(a). Only one set of LEED spots is observed due to the small lattice mismatch and strong bonding between graphene and Ni(111). The clean Ni(111) surface exhibits a work function of  $5.37 \pm 0.04 \text{ eV}$ , in agreement with previously reported values, <sup>41,42</sup> and two surface states of Ni(111) are observed, consistent with Refs. 21 and 43–46. After graphene growth, the work function





FIG. 5. (Color online) (a) LEED pattern from Gr/Au/Ni(111). (b) Angle-resolved 2PPE data taken with photon energies of 4.65 eV (pump) and 1.55 eV (probe).

drops to  $4.06 \pm 0.07$  eV, in agreement with Ref. 47. In the ARPES data in Fig. 4(b) two prominent bands at energies of -0.20 and -0.69 eV and effective masses of  $m^*/m_0 = 0.77$  and -0.32 are visible. These bands were not resolved in previous experiments<sup>12,26,48–51</sup> and were partly identified in calculations.<sup>52–54</sup> The Ni(111)-derived surface states still exist at the Gr/Ni(111) system in spite of the small distance between graphene and the substrate.<sup>52</sup> A similar observation has been made also for Gr/Ir(111) with a larger distance.<sup>19</sup> The low work function of Gr/Ni(111) made 2PPE experiments difficult with the available laser systems. Since graphene is also strongly bound to Ni(111), we did not pursue this system any further and focused on weakly bound graphene on noble-metal surfaces.

After gold intercalation and annealing to 630 K on Gr/Ni(111) the LEED pattern in Fig. 5(a) shows a weak moiré superstructure with a periodicity of  $\approx 10 \times 10$ , in agreement with scanning tunneling microscopy (STM) images.<sup>12</sup> It indicates that gold is intercalated, forming a hexagonal layer with a larger lattice constant than graphene and Ni(111). The lattice constant of the intercalated gold layer is slightly compressed compared to the value for bulk Au. The work function is measured to  $4.56 \pm 0.09$  eV. This value is between the work functions of the Ni(111) substrate (5.37 eV) and Gr/Ni(111) (4.06 eV) and close to the value obtained for Gr/Au/Ir(111) (4.69 eV, Sec. III B) and the number calculated for graphene on Au(111) (4.74 eV).<sup>55</sup> The lowest members of the series of image-potential states are clearly resolved in the 2PPE data, as shown in Fig. 5(b). The binding energy of the first image-potential state amounts to  $E_1 = 0.74$  eV, and its effective mass is close to the free-electron mass. The uniform intensity distribution along the image-potential bands indicates the absence of resonance effects from initial states. This is in accordance with ARPES measurements (not shown), which show no clear surface states, in agreement with previous reports.12,56

## D. Graphene/Ir(100)

While graphene growth on Ir(111) is well studied and known to lead to almost defect-free monolayer graphene,<sup>14,57,58</sup> only a little work has been performed for graphene grown on the square Ir(100) surface.<sup>59</sup> Figure 6(a)



FIG. 6. (Color online) (a) LEED pattern from Gr/Ir(100). (b) Angle-resolved 2PPE data taken with photon energies of 4.65 eV (pump) and 1.55 eV (probe). (c) Energy distribution curves from the first image-potential state of Gr/Ir(100) recorded at photon energies of 4.89 eV (pump) and 1.63 eV (probe). (d) Results from fits to the spectra. The spot size of the low-energy component indicates the intensity relative to the main peak.

shows the LEED image for Gr/Ir(100). The  $5 \times 1$  reconstruction of the bare substrate has disappeared, and the  $1 \times 1$  spots remain. The graphene LEED pattern shows a ring dominated by domains rotated by  $\pm 15^{\circ}$  relative to the square substrate. The situation is very similar to the case of Gr/Pt(100).<sup>60</sup>

The 2PPE data of Fig. 6(b) show two image-potential bands with a rather broad intensity distribution of the n = 1 state. The energy distribution curves in Fig. 6(c) show the first imagepotential state of graphene on Ir(100) at different polar angles  $\Theta$ . In contrast to the case of Gr/Pt(111) and Gr/Au/Ni(111), the line shape is asymmetric, with a low-energy shoulder. As the fit curves demonstrate, this line shape is well reproduced by a superposition of two Voigt functions with an energy spacing of 140 meV almost independent of  $k_{\parallel}$ , as shown in Fig. 6(d). The two components can be explained by an inhomogeneous surface covered by two different structures. STM topographs show regions of flat graphene beside areas with a stripelike linear moiré that has a periodicity of 22 Å and an apparent corrugation of several angstroms.<sup>59</sup> We interpret the two observed states as a consequence of the two different structures exhibiting different work functions. As the recorded LEED patterns do not show a pronounced moiré structure, it seems plausible to assign the prominent high-energy component to flat graphene.

Attempts to prepare a pure phase with only one n = 1 image-potential state were not successful. Depending on sample preparation, average work functions vary from 4.75 to 4.92 eV, with an average of 4.83 eV. This suggests slightly different compositions of the surface which could not be

identified in LEED. Nevertheless, energies referred to the Fermi level as well as the asymmetric line shape are reproducible for different sample preparations. The energies of the n = 1(2) image-potential state (main peak) are  $E_{\rm F}$  + 4.00(4.54) eV. Using the simple quantum defect model [Eq. (1)], a work function of 4.74 eV can be extrapolated. The resulting binding energies would be 0.74(0.20) eV. The measured work functions  $\ge 4.75$  eV indicate areas of higher local work function because the measured value is the weighted average of the values of areas of different local work functions.<sup>61</sup> The areas of higher local work function might be attributed to patches of the Ir(100) substrate. They cannot be the home of the second n = 1 image-potential state which is located 0.14 eV below the main component. Its binding energy would then be at least 0.9 eV, well above the limiting value of 0.85 eV. We can only speculate on the possible existence of additional areas with a lower work function than 4.74 eV. These could be the areas with the large corrugation.<sup>59</sup> Based on the available information a final assignment for the second component of the n = 1 image-potential state is not possible.

## E. Dynamics of image-potential states

Time-resolved spectra of the first two image-potential states are shown in Fig. 7. Lifetimes of the n = 1 image-potential state are shorter than the width of the cross-correlation trace in our experiments. The latter amounts to 69 fs for the hemispherical analyzer setup used in the case of Gr/Pt(111) and Gr/Au/Ir(111). For Gr/Au/Ni(111) and Gr/Ir(100) the



FIG. 7. (Color online) Time-resolved 2PPE spectra from the first two image-potential states of the systems under investigation. Data for Gr/Pt(111) and Gr/Au/Ir(111) were taken with the hemispherical analyzer setup and are plotted on a semilogarithmic scale. For the other samples the display-type analyzer was used, providing a lower dynamical range. These data are shown on a linear scale normalized to the same peak height.

time resolution was 140 and 220 fs, respectively. Therefore, cross-correlation traces of the n = 1 image-potential state are symmetrically Gaussian shaped, but a shift of the peak maximum relative to time-delay zero occurs.<sup>62</sup> For the second image-potential state, an exponential decay is observed directly in the spectra. Data were modeled using optical Bloch equations including a single decay channel.<sup>28</sup> In the case of Gr/Ir(100) an additional component accounting for IR-pumped transitions was added. This contribution is attributed to the *sp* bands above  $E_{\rm F}$  in the (100) direction, which can be excited by IR photons and emitted by UV photons.<sup>63</sup> On the (111) surfaces these *sp* bands are not available above  $E_{\rm F}$  around  $\overline{\Gamma}$ .

The lifetimes  $\tau_n$  of the n = 1 (2) image-potential state are 30 (79) fs for Gr/Pt(111), 30 (115) fs for Gr/Au/Ir(111), 23 (75) fs for Gr/Au/Ni(111), and 19 (65) fs for Gr/Ir(100). The longest lifetimes are found for Gr/Au/Ir(111), which also shows the sharpest LEED pattern of the four systems. The high-quality-growth system Gr/Ir(111) has only slightly higher lifetimes of 35 (114) fs.<sup>19</sup>

Lifetimes are sensitive to the coupling of the imagepotential states with decay channels for electron-hole creation, which are provided mainly by substrate states because of the low density of states of graphene near  $E_{\rm F}$ . Furthermore, the states near  $E_{\rm F}$  are located near the Brillouin zone boundary around the K point, and the decay of image-potential states around the  $\overline{\Gamma}$  point requires a large momentum transfer, which reduces the phase space of possible inelastic scattering processes. Samples of lower quality have more defects or domain boundaries from which the image-potential electrons are scattered elastically.<sup>64</sup> The elastic scattering increases the measured linewidth. For long delay times the corresponding scattering or dephasing rate can be obtained independent of the decay rate measured by the lifetime.<sup>28,65</sup> Figure 8(a) shows 2PPE spectra for Gr/Pt(111), demonstrating the linewidth narrowing at long delays. Note the almost equal intensity of the n = 1 and 2 states at long delays due to the shorter lifetime of the n = 1 image-potential state. For the n = 1image-potential state on Gr/Pt(111) a dephasing rate of 10 meV



FIG. 8. (Color online) (a) 2PPE spectra of the image-potential states for Gr/Pt(111) normalized to the same maximum height, showing a linewidth narrowing with increasing delay. (b) Lorentzian linewidth of the n = 1 image-potential state for Gr/Ir(111) as a function of time delay (dots) compared to calculations for different dephasing rates.<sup>65</sup> Open symbols show additional data points from the Gr/Pt(111) spectra shown in (a) and from the Gr/Au/Ir(111) sample.

is obtained. The same value is found for Gr/Ir(111) from Fig. 8(b), where linewidth data are compared to calculations for different dephasing rates.<sup>65</sup> The data points for Gr/Pt(111) and Gr/Au/Ir(111) agree with the ones for Ir(111). This shows that the three systems have the same dephasing rate (10 meV) and lifetime (30–35 fs). Note that the decay rates  $\hbar/\tau_1$  are about a factor of 2 larger than the dephasing rates. The second component at lower energy found for Gr/Pt(111) has a linewidth of 100 meV, in agreement with the lifetime of ~10 fs. The lower resolution of the hemispherical analyzer did not allow us to determine the intrinsic linewidth for Gr/Au/Ni(111). The double-peak structure observed for Gr/Ir(100) also hampered a reliable determination of the dephasing rate.

# **IV. DISCUSSION**

The measured data of image-potential states for graphene on various metal substrates are compiled in Table I. Results for  $Ir(111)^{19}$  and  $Ru(0001)^{18}$  are added to extend the database. For comparison results for the clean substrates and for the work function are included. For inhomogeneous surfaces the extrapolated work function is given.

# A. Work function

The work function for the various graphene-covered surfaces varies between 4.06 eV for Gr/Ni(111) and 4.85 eV for Gr/Pt(111). The lowest values are found for Ni(111) and Ru(0001), which are known to be strongly coupled and have short graphene-substrate distances. Within the noble-metal systems Gr/Au/Ni(111) has the lowest work function of 4.56 eV, which might indicate some remaining influence of the Ni(111) substrate. While the graphene work functions span a range of 0.29 eV, the difference of the work function between graphene and substrate varies from 0.64 to 1.20 eV. The large work function changes indicate a large charge transfer between substrate and graphene layer of about 0.01 electron per unit cell.<sup>55</sup>

#### **B.** Surface states

For graphene-covered surfaces the main focus has been on the region around the  $\overline{K}$  point. Therefore, high-resolution photoemission studies around the  $\overline{\Gamma}$  point are scarce. Theoretical work has been hampered by the large unit cells of the surfaces with moiré superstructures. An exception is the lattice-matched Gr/Ni(111) surface, for which several calculations are available.<sup>53,54</sup> Therefore, we compare our results for graphene-covered noble-metal surfaces to the information available for the clean surfaces. This yields additional information on the electronic interaction and distance between graphene and the substrate.

The close-packed fcc(111) surfaces of Cu, Ag, and Au are known for their upward-dispersing Shockley-type surface states.<sup>70</sup> For Ir(111) this state shows a Rashba-type splitting and disperses downward because the lower *sp*-band edge disperses downward close to  $\overline{\Gamma}$ , in contrast to the other surfaces.<sup>19,20</sup> For Pt(111) the band structure around  $\overline{\Gamma}$  is similar to Ir(111), and one might expect also a downward-dispersing surface state. Calculations<sup>71–73</sup> find an upward dispersing

TABLE I. Work function  $\Phi$ , binding energies  $E_n$ , effective mass  $m_1^*$ , and lifetimes  $\tau_n$  of image-potential states for various graphene-covered and clean substrates. Extrapolated work functions for inhomogeneous surfaces are given in italics. For the graphene-covered surfaces the phase shift  $\phi_{Gr}$  by the graphene layer is given.

	Φ (eV)	$E_1$ (eV)	$E_2$ (eV)	$\tau_1$ (fs)	$\tau_2$ (fs)	$\phi_{ m Gr}/\pi$
Gr/Pt(111) (0°) Gr/Pt(111) (23°) Pt(111) <sup>a</sup>	$4.77 \pm 0.04$ $4.85 \pm 0.03$ $5.97 \pm 0.03$	$\begin{array}{c} 0.83 \pm 0.03 \\ 0.87 \pm 0.02 \\ 0.65 \pm 0.05 \end{array}$	$\begin{array}{c} 0.22 \pm 0.03 \\ 0.23 \pm 0.02 \\ 0.16 \pm 0.05 \end{array}$	$30 \pm 3$ $33 \pm 3$ $26 \pm 7$	$79 \pm 6$ $62 \pm 7$	$0.22 \pm 0.02$ $0.24 \pm 0.02$
Gr/Au/Ir(111) Au(111) <sup>b</sup>	$4.69 \pm 0.02$ $5.55 \pm 0.05$	$\begin{array}{c} 0.85 \pm 0.02 \\ 0.80 \pm 0.03 \end{array}$	$0.21\pm0.02$	$30 \pm 3$	$115\pm5$	$0.29 \pm 0.03$
Gr/Au/Ni(111) Ni(111) <sup>c</sup>	$\begin{array}{c} 4.56 \pm 0.09 \\ 5.20 \pm 0.03 \end{array}$	$0.74 \pm 0.03$ $0.80 \pm 0.03$	$\begin{array}{c} 0.15 \pm 0.06 \\ 0.25 \pm 0.05 \end{array}$	$\begin{array}{c} 23\pm5\\7\pm3\end{array}$	$75\pm5$	$0.28\pm0.03$
Gr/Ir(100) Ir(100) <sup>d</sup>	$4.74 \pm 0.03$ $5.85 \pm 0.03$	$0.74 \pm 0.03$ $0.73 \pm 0.03$	$0.20\pm0.03$	$19\pm 6$	$65 \pm 11$	$0.32\pm0.03$
Gr/Ir(111) <sup>e</sup> Ir(111) <sup>e</sup>	$\begin{array}{c} 4.65 \pm 0.10 \\ 5.79 \pm 0.10 \end{array}$	$0.83\pm0.02$	$0.19\pm0.02$	$35 \pm 3$	$114\pm 6$	$0.28 \pm 0.02^{f}$
Gr/Ru(0001) <sup>g</sup> Ru(0001) <sup>h</sup>	$4.24 \pm 0.10$ $5.40 \pm 0.02$	$\begin{array}{c} 0.80 \pm 0.05 \\ 0.66 \pm 0.02 \end{array}$	$\begin{array}{c} 0.18 \pm 0.07 \\ 0.19 \pm 0.02 \end{array}$	$\begin{array}{c} 11\pm8\\ 11\pm2 \end{array}$	$\begin{array}{c} 85\pm13\\ 57\pm5\end{array}$	$0.43\pm0.05$

<sup>a</sup>Reference 34.

<sup>b</sup>Reference 40.

<sup>c</sup>References 66 and 67.

<sup>d</sup>Work function for the metastable Ir(100)(1×1) surface, which is the substrate for graphene. The binding energy  $E_1$  refers to the thermodynamically stable 5 × 1 reconstructed surface with  $\Phi = 5.54$  eV.<sup>68</sup>

<sup>e</sup>Reference 19.

<sup>f</sup>In Ref. 19 a value of 0.18 has been reported using a crude approximation for the barrier phase shift.

<sup>g</sup>Reference 18.

<sup>h</sup>Reference 69.

surface state 0.3 eV above  $E_F$ , in agreement with STM results.<sup>71</sup> However, some states below  $E_F$  with high probability density around  $\overline{\Gamma}$  have also been calculated,<sup>71</sup> in agreement with photoemission data.<sup>74</sup> The ARPES results for Pt(111) [see Figs. 2(e) and 2(f)] and Ir(111)<sup>19</sup> are overlaid in Fig. 9 on the corresponding spectral functions.<sup>73</sup> The agreement for Pt(111) is excellent. For Ir(111) the experimental data lie  $\approx 0.3$  eV below the calculation, while the Rashba splitting matches. This discrepancy can be resolved in photoemission calculations.<sup>75,76</sup> The energetic shift could also be attributed to the change of the surface potential due to the graphene layer. However, a slight upward shift of  $\approx 0.1$  eV has been observed for the graphene-covered surface.<sup>14,19,20,77</sup>



The ferromagnetic Ni(111) surface has upward- and downward-dispersing surface states for majority- and minority-spin electrons.<sup>21,43–46,78</sup> The main spectral weight is carried by the upward-dispersing majority-spin state and the downward-dispersing minority-spin state.<sup>78</sup> Our ARPES data for Gr/Ni(111) (see Fig. 4) show two bands with similar dispersion as observed in high-resolution studies on the clean surface.<sup>21,43–46</sup> Previous ARPES studies used higher photon energies<sup>12,26,48–51</sup> and did not resolve these two bands. The photoemission cross section for the *sp* surface states decreases with increasing photon energy.<sup>79</sup> Theoretical calculations for Gr/Ni(111) show similar surface states as for the substrate.<sup>52–54</sup>

After gold intercalation on Ni(111) the surface states disappear, and we observe some intensity below  $E_{\rm F}$  with no discernible dispersion, in qualitative agreement with previous work.<sup>26,50,51</sup> Calculations predict a surface state with weak downward dispersion.<sup>53</sup> Apparently, the intercalated Au layer has a drastic influence on the surface electronic structure, as evidenced also by photoemission results.<sup>50,56</sup> Similar observations have been reported for Ru(0001), where the surface electronic structure for the graphene-covered surfaces around  $\overline{\Gamma}$  changes drastically after gold intercalation.<sup>80</sup> For gold intercalation on Ir(111) the upward-dispersing Au(111) Shockley surface state appears from 2 ML on.

# C. Image-potential states

The binding energies of the n = 1 image-potential state for graphene-covered surfaces in Table I vary between 0.74 and 0.87 eV. The binding energies are 0.06–0.22 eV larger than the values for the clean substrates, with the exception

FIG. 9. (Color online) Bloch spectral functions for surface atoms of (a) Pt(111) and (b) Ir(111) from Ref. 73. The dispersion of the measured surface states from Fig. 2 and Ref. 19 is marked by orange dots.

of Ir(100), where the binding energy was determined on a reconstructed clean surface. The lowering of the work function by graphene shifts the image-potential state downward in the projected bulk band gap, and a reduction instead of an increase of the binding energy should occur.<sup>81</sup> For Gr/Ru(0001) the values in Table I for image-potential states assigned to the high areas on the corrugated surface were used.<sup>18</sup> An additional n = 1 state with lower binding energy has been observed and is assigned to the low areas. On the other noble-metal systems no indications for additional states with energy between the n = 1 and 2 image-potential states have been found. This supports the interpretation of the additional states of the low areas of the strongly corrugated Gr/Ru(0001) surface<sup>18</sup> and contradicts an assignment to image-potential states of odd symmetry with respect to the graphene layer.<sup>17,82</sup>

Surface states can also be calculated using a phase-shift model.<sup>83</sup> The phase shift  $\phi_{Gr}$  for the electron traversing the graphene layer has been calculated following Ref. 19. The corresponding values are listed in the last column of Table I. The values for the (111) surfaces are almost identical, indicating that the phase shift model describes the substrate and barrier phase shift for the graphene system reasonably well. The significantly larger phase shift calculated for Ru(0001) might be attributed to the lower binding distance and large corrugation of graphene on this surface.

## D. Electron dynamics

The lifetimes of the n = 1 and n = 2 image-potential states for all graphene-covered surfaces range from 11 to 35 fs and from 62 to 115 fs, respectively (see Table I). The largest values are found for the noble-metal (111) substrates of Pt and Ir. As far as data from the clean metal substrate are available, increased lifetimes are observed for graphenecovered surfaces. The slightly increased lifetimes for graphene relative to the bare substrate are consistent with a reduced overlap of the image-potential-state wave function located in front of the graphene layer<sup>82</sup> with the substrate states. In addition, the work function reduction by the graphene pushes the energy of the image-potential states further toward the center of the projected bulk band gap. This leads to a reduced penetration of the wave function into the substrate and in turn to a longer lifetime.<sup>81</sup> This effect is seen clearly for Au(111), where a surface resonance with a linewidth corresponding to a lifetime of 4 fs is observed on the clean surface. With graphene the energy of the n = 1 image-potential state is pushed into the band gap, and the lifetime increases to 30 fs. The lifetimes of the graphene-covered surfaces are comparable to other surfaces like Cu(100).<sup>70</sup> This indicates a significant interaction with the electrons of the substrate because a decay within the graphene layer is reduced due to the small density of states near  $E_{\rm F}$  and the limited phase space of possible inelastic scattering processes.

A well-ordered surface provides no defects for quasielastic scattering of image-potential-state electrons. For wellprepared Cu(100) surfaces the dephasing rate of the n = 1image-potential state is  $\approx 2 \text{ meV}$  at the limit of the experimental accuracy.<sup>65</sup> Large perfectly ordered areas are found for Gr/Ir(111);<sup>22</sup> however, the dephasing rate is a factor of 5 larger than for Cu(100). In addition, quantum beats<sup>84</sup> are not observed for the n = 3 image-potential state and are only weakly seen for n = 4 [see Fig. 7(b)] for Gr/Ir(111). For Cu(100) strong quantum beat patterns are observed.<sup>64,84</sup> The graphene layer on Ir(111) is well ordered but slightly corrugated due to the moiré structure. This periodic superstructure should lead to back-folded bands, as observed for image-potential states on stepped Cu surfaces.<sup>85</sup> No evidence for back-folded bands is found for Gr/Ir(111).<sup>19</sup> The main difference between Cu(100) and Gr/Ir(111) is the moiré structure on the latter surface. The moiré structure leads to a corrugation of the potential and local work function as known from the heavily corrugated Gr/Ru(0001) surface, where additional imagepotential states are observed.<sup>18</sup> A smaller potential modulation would lead to a broadening affecting the linewidth of the n = 1 image-potential state. This contribution to the linewidth corresponds to the observed dephasing rate of 10 meV. Farther away from the surface the potential corrugation is weaker because the potential has to converge to the limiting value of the macroscopic global work function. For the higher image-potential states with their probability density farther away from the surface the determination of the linewidth is difficult due to the longer lifetimes and the overlap between neighboring states. However, the quasielastic scattering by the corrugated, although weak, potential still influences the phase of the wave functions. This destroys the phase coherence between neighboring image-potential states, in agreement with the observed absence of quantum beats for the n = 3image-potential state.

## **V. CONCLUSIONS**

In summary, image-potential states of graphene on Pt(111), Au/Ir(111), Au/Ni(111), and Ir(100) were observed. Binding energies, lifetimes, and the dispersion of the first members of the series of image-potential states were determined. In all systems under study, the binding energy of the first imagepotential state is increased by graphene deposition compared to the bare substrate. This indicates that the substrate is screened significantly by the graphene layer and has a reduced influence on the external charge in the image-potential states. Similar lifetimes of image-potential states are observed for all systems and are increased relative to the values for the clean substrates. This indicates some overlap of the image-potential states with the states of the substrates. The moiré structure provides a corrugated potential which leads to an increased linewidth and to the absence of quantum beats due to scattering destroying the phase coherence.

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