Spin-Orbit Coupling Induced Gap in Graphene on Pt(111) with Intercalated Pb Monolayer

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Abstract

Graphene is one of the most promising materials for nanoelectronics owing to its unique Dirac cone-like dispersion of the electronic state and high mobility of the charge carriers. However, to facilitate the implementation of the graphene-based devices, an essential change of its electronic structure, a creation of the band gap should controllably be done.

Brought about by two fundamentally different mechanisms, a sublattice symmetry breaking or an induced strong spin-orbit interaction, the band gap appearance can drive graphene into a narrow-gap semiconductor or a 2D topological insulator phase, respectively, both cases being technologically relevant. The later case, characterized by a *spin-orbit gap* between the valence and conduction bands, can give rise to the spin-polarized topologically protected edge states. Here, we study the effect of the spin-orbit interaction enhancement in graphene placed in contact with a lead monolayer. By means of angle-resolved photoemission spectroscopy we show that intercalation of Pb interlayer between the graphene sheet and Pt(111) surface leads to formation of a gap of about 200 meV at the Dirac point of graphene. Spin-resolved measurements confirm the splitting to be of a spin-orbit nature, and the measured near-gap spin structure resembles that of the quantum spin Hall state in graphene, proposed by Kane and Mele [Phys. Rev. Lett. 95, 226801 (2005)]. With a bandstructure tuned in this way,

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graphene acquires a functionality going beyond its intrinsic properties and becomes more attractive for possible spintronic applications.

Discovery of a quantum state of matter, called topological insulator (TI), probably is one of the most important breakthroughs in the solid state physics of the last decade.¹⁻³ A material is said to be in a topologically-nontrivial state, when a sufficiently strong spin-orbit interaction (SOI) inverts its bulk band gap, topologically distinguishing it from the trivial insulators that have no band inversion. The most prominent manifestation of the nontrivial topology of the bulk bands appears, however, at the border between a topological and a trivial insulator, in particular, at that with a vacuum. There, at the interface between the two materials with the distinct band topologies, a topological phase transition occurs through developing of the gapless interface state that cannot disappear until the time-reversal symmetry is preserved. In this way, the three- and two-dimensional TIs are respectively characterized by the topological surface and edge states, showing a spin-momentum locking and a Dirac cone-like dispersion.³⁻⁶ Such a peculiar electronic structure makes the topological state electrons immune to the elastic backscattering, in principle allowing to create spintronic and quantum computing devices on the basis of these materials.^{7,8}

Historically, the first system predicted to have the non-trivial topology was graphene. Haldane⁹ considered a graphene honeycomb lattice with periodic local magnetic field and showed that in this case a gap between valence and conduction band opens and a quantum Hall phase appears without net magnetic flux. A quantization of the resulting density of states guarantees a topological protection and the stability of the system against weak disorder. Then, Kane and Mele¹⁰ presented a model for generation of the quantum Hall phase in graphene using SOI as a key ingredient that does not require time-reversal symmetry breaking. The predicted phenomenon was called the quantum spin Hall effect (QSHE), corresponding to a 2D topological insulator phase, which had later been observed experimentally in the systems with

strong SOI – HgTe/CdTe quantum wells.¹¹ Due to its weak SOI, the formation of a topological insulator phase in graphene still represents an open problem whose solution would enable the special ways of graphene's use in electronics, particularly, in spin-orbitronics.¹²⁻¹⁴

According to the Kane-Mele model,¹⁰ spin-orbit interaction in graphene can be described by two additional terms in Hamiltonian. The first one, a so-called intrinsic SOI, takes the form,

$$H_i = \lambda_i \psi^\dagger \sigma_z \tau_z s_z \psi, \quad (1)$$

where σ are the Pauli matrices acting on the pseudospin space with $\sigma_z = \pm 1$ describing states on the A(B) sublattice and $\tau_z = \pm 1$ – those at the $K(K')$ points. According to the effective mass model, the electronic wavefunctions are obtained by the product of basic states and the envelope function ψ . The real spin is presented by the Pauli matrices s and λ_i is the strength of the intrinsic SOI. The second SOI term is called extrinsic or Rashba term, which reads as

$$H_R = \lambda_R \psi^\dagger (\sigma_x \tau_z s_y - \sigma_y s_x) \psi, \quad (2)$$

where λ_R quantifies the strength of the Rashba SOI. If $|\lambda_i|$ is larger than $|\lambda_R|$, a non-trivial energy gap with a magnitude of $2(|\lambda_i| - |\lambda_R|)$ appears in the graphene Dirac point, giving rise to the topologically protected spin-polarized edge states in the case of graphene strip.

Although the intrinsic SO coupling is extremely weak for carbon it can be enhanced by a contact with heavy metal atoms. Theoretically, two mechanisms for increasing the intrinsic SOI and creating the spin-orbit gap in graphene with adatoms were proposed by Weeks *et al.*¹⁵ and Hu *et al.*¹⁶ The first one is based on the tunnelling of an electron from graphene to a heavy p -adatom and “feeling” a strong SOI. In this way a formation of the QSH phase in graphene with Tl or In adatoms has been predicted.¹⁵ The second method relies on a strong hybridization of the $5d$ -metal atoms states with graphene Dirac cone, when such a hybrid band experiences a strong spin-orbit splitting.¹⁶ Using this strategy, graphene with adsorbed Os and Ir atoms,¹⁶

as well as intercalated by Re,^{17,18} has also been predicted to feature a nontrivial spin-orbit gap.

Nevertheless, the first experimental data obtained for graphene contacting with Au and Ir show only the increase of the Rashba spin splitting of the electronic states.^{19–22} In these systems, spin-dependent hybridization of the graphene π and a metal $5d$ states takes place in the regions far from the Dirac point. However, in the case of graphene contacting with Pt it was shown that the spin structure is characterized by a non-Rashba behavior near the Fermi level.^{23,24} Unfortunately, p -doping of graphene does not allow to measure the spin-resolved spectra near the Dirac point in these systems. As far as the heavy p -elements are concerned, it has recently been shown that the π states spin splitting of the graphene on Ni(111) with intercalated Bi monolayer does not exceed 10 meV, while the formation of the Dirac point gap observed has been attributed to the breaking of the A-B sublattice symmetry.²⁵ On the other hand, a remarkable result has been reported by Calleja *et al.*²⁶ for graphene on Ir(111) with one atom thick Pb islands intercalated in between (intercalation ratio of $\sim 20\%$). By means of STS, an appearance of the quasi-Landau levels without external magnetic field has been revealed for the islands with a lateral size of about 10 nm. The authors have concluded, that the Pb interlayer induces a strong SOI in graphene that is spatially modulated near the Pb islands edges, acting as a pseudo magnetic field. Enhancement of spin-orbit interaction in graphene with Pb adsorbates has also theoretically been studied in Refs.,^{27,28} the latter work predicting the opening of the spin-orbit gap in the Dirac cone at certain conditions. However no photoemission studies of the electronic and spin structure of graphene contacted with Pb have been reported so far and the experimental realization of the spin-orbit gap in graphene system is still a pending problem.

In this work, using angle-resolved photoemission spectroscopy (ARPES), we study the electronic and spin structure of graphene on Pt(111) intercalated by a full Pb monolayer. By employing a low energy electron diffraction (LEED) technique we show the graphene lattice

to be commensurate with that of the underlying Pb/Pt(111) substrate, characterized by the formation of the ordered Pb $c(4\times 2)$ superstructure. The observed commensurability favors the enhancement of an intrinsic spin-orbit coupling in graphene and leads to an opening of a wide band gap between its valence and conduction bands. By means of spin-resolved ARPES measurements we show that the spin-splitting of the formed band gap edges corresponds to the case of $|\lambda_i| > |\lambda_R|$, allowing to conclude that the observed band gap is induced by spin-orbit coupling.

Results and discussion

Structural and electronic properties of the system. Experimental dispersion relations of graphene on Pt(111) measured by means of ARPES are presented in Fig. 1a. The first derivative of the ARPES data is presented for better visibility of the main spectral features. The spectra were obtained at a photon energy of 62 eV at room temperature in the $\bar{\Gamma}\bar{K}$ direction of the 2D Brillouin zone (BZ) (hereinafter $\bar{K}$ stands for the $\bar{K}$ -point of the graphene BZ, $k_{\parallel}=1.7 \text{ \AA}^{-1}$). According to previous studies,^{29–32} graphene grown on top of Pt(111) features various rotational domains. Most of them are incommensurate with the substrate and have Moiré patterns of different periodicities. The photoemission signal coming from the π states of at least three different graphene domains can be seen in Fig. 1a, as highlighted by blue dashed lines. Nevertheless, the signal from the graphene domains commensurate with the Pt substrate can be distinguished by a linear dispersion near the Fermi level. In Ref.²³ we had shown that such domains have a $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity and the position of the Dirac point energy for them was estimated as 150 meV above the Fermi level. Furthermore, a spin-dependent hybridization of graphene and spin-orbit split Pt $5d$ states was observed near the Fermi level, resulting in the spin splitting of the graphene π states of more than 100 meV. Indeed, as we can see from Fig. 1a, Pt $5d$ states hybridize with the π state of graphene at the binding energy of ~ 1 eV and at the Fermi level. The enhancement of the intrinsic SOI, that could lead to the spin-orbit gap

Figure 1: First derivative of the ARPES data measured in the $\bar{\Gamma}\bar{K}$ direction of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domain for (a) graphene/Pt(111) and (b) graphene/Pb/Pt(111) using of a photon energy of 62 eV. Blue dashed lines highlight the spectral features originating from graphene rotational domains with periodicities different from $(\sqrt{3} \times \sqrt{3})R30^\circ$. (c, left) LEED pattern of graphene/Pb/Pt(111) taken at $E_p=150$ eV. Blue circles mark the reflexes coming from different rotational domains of graphene with respect to Pt(111). (c, right) 2D reciprocal lattices of graphene $(\sqrt{3} \times \sqrt{3})R30^\circ$, Pb $c(4 \times 2)$ (with three equivalent rotational domains of Pb relative to Pt(111), see the text and Supplementary Note 2) and Pt(111) (1×1) shown in black, yellow and violet, respectively. (d) Sketch of the graphene/Pb/Pt(111) atomic structure deduced from the LEED measurements with black, yellow and grey balls showing carbon, lead and platinum atoms, respectively.

opening, has been theoretically predicted for this system,²³ but owing to the *p*-doping of the graphene bands, the experimental confirmation of the prediction was hindered.

As it has been mentioned above, an appearance of spin-orbit gap can also be anticipated in graphene contacted with Pb, but contrary to the graphene on Pt, the Dirac cone is expected to be *n*-doped²⁶ enabling direct inspection of the near Dirac point energy region by ARPES. To this end, a Pb interlayer had been intercalated in between graphene and the Pt(111) substrate. The intercalation process was verified by x-ray photoemission spectroscopy (XPS) measurements of Pt, C and Pb core levels, see Fig. S1 in Supporting Information. Detailed quantitative analysis, based on different probing depth for various emission angles, allows to conclude that the $(\sqrt{3} \times \sqrt{3})R30^\circ$ graphene/Pt(111) domain is fully intercalated with an atom-thick Pb layer (Supplementary Note 1).

In Ref.,²⁶ where, aside from the partially Pb-intercalated graphene/Ir(111), the almost fully intercalated one was also considered for a structure characterization purpose, the $c(4 \times 2)$ Pb superstructure commensurate with Ir(111) was observed. Iridium and platinum have the similar structural properties and in the graphene/Pt(111) case the intercalated Pb layer expectedly forms the same $c(4 \times 2)$ superstructure as is evidenced by the system's LEED pattern shown in Fig. 1c, left. The spots inside the graphene hexagon represent three $c(4 \times 2)$ rotational domains of Pb with respect to Pt(111) [not to be confused with the rotational domains of graphene/Pt(111)], as shown of the right side of Fig. 1c. The $c(4 \times 2)$ superstructure is defined by the interaction of Pb with Pt(111), while its three rotational domains (each commensurate with the substrate underneath) arise from the combination of the hexagonal and rectangular lattices of Pt(111) and Pb, respectively (see Supplementary Note 2). Possible arrangement of graphene, Pb and Pt layers for one of the Pb rotational domains is schematically shown in Fig. 1d as deduced from the LEED measurements. One can see that Pb atoms are located in the equivalent positions

relative to the graphene's A and B sublattices, thus preserving the A-B sublattice symmetry (see Supplementary Note 3 for details).

Intercalation of the Pb layer underneath graphene leads to significant modifications of electronic structure of the graphene/Pt(111) system. Fig. 1b represents the resulting ARPES dispersion relations of graphene/Pb/Pt(111), measured under the same experimental conditions as graphene/Pt(111) (Fig. 1a). One can clearly see that after Pb intercalation graphene states shift to higher binding energies by about 350 meV. Such a behavior correlates with the relative electronegativities of Pb and Pt and can be explained by the charge transfer from Pb interlayer to graphene. Similar *n*-doping was observed by means of STS for the Pb intercalated graphene on Ir(111).²⁶ Furthermore, it is seen that the avoided-crossing effects between the graphene π and Pt 5*d* states become less pronounced, meaning the weakening of the graphene interaction with the substrate. The decoupling of graphene from the substrate by Pb intercalation has also been reported in Ref.³³

Owing to the charge transfer from Pb atoms, the graphene π^* state becomes occupied and can be seen in ARPES (Fig. 1b) near the $\bar{K}$ point ($k_{\parallel}=1.75 \text{ \AA}^{-1}$) slightly below the Fermi level. The set of raw ARPES spectra can be found in Fig. S4b of Supporting Information. Therefore, the Dirac point is expected to be located at the binding energy of 200 meV. However, as one can see the π and π^* states do not touch each other, featuring a local gap in the electronic structure. To get further insight into the nature of the observed gap the spin-resolved ARPES measurements have been performed.

Spin structure of the Dirac cone. As it is mentioned in the introduction, spin-orbit interaction in graphene splits into an intrinsic and extrinsic (Rashba-like) contribution. According to Refs.^{34,35} the eigenvalues of the overall Hamiltonian near the $\bar{K}$ -point take the form

$$E_{\mu,\nu} = \epsilon_{2p} + \mu\lambda_R + \nu\sqrt{(\hbar v_F k)^2 + (\lambda_R - \mu\lambda_i)^2}, \quad (3)$$

where $\nu = \pm 1$ corresponds to valence and

conduction bands, $\mu = \pm 1$ to different spin-chiral states, and ϵ_{2p} stands for the orbital energies of the $2p$ electrons, *i.e.* position of the Dirac point. The wave vector k is given relative to the $\bar{K}$ point. It is clearly seen that in the absence of any SO contribution, the spectrum becomes degenerate and shows a linear, Dirac cone-like dispersion. However, this situation changes drastically in the presence of a strong SOI.

If one breaks the inversion symmetry and introduces only the Rashba term in the Hamiltonian the degeneracy of the spectrum lifts and the π states become spin split, the spin vector lying in the xy plane and directed normally to the wave vector. At that, the value of the splitting near the $\bar{K}$ point remains constant with the increase of $k_{\parallel}$. Nevertheless, the spectrum is gapless in this case. Such a behavior has been observed in graphene on Ni(111) with intercalated Au monolayer^{19,20} with the value of splitting up to 100 meV. A value of 50 meV has been revealed for graphene on Ir(111).²¹ Noteworthy, if an intrinsic SO coupling, which is always present in any real material, is also taken into account, the spectrum of the graphene states shows no significant differences until $|\lambda_i| < |\lambda_R|$. We now apply this model for a graphene on Pt(111) first.

Recently it has been shown in Ref.²³ that the spin structure of the π states of graphene on Pt(111) is quite complex owing to hybridization with the Pt $5d$ states at the $\bar{K}$ point. Strictly speaking, it cannot be described as the one with simple Rashba-type spin splitting. However, the p -doping of graphene does not allow to measure this near the expected position of the Dirac point using ARPES. We therefore cannot reliably quantify an intrinsic SOI contribution to this system from the experimental data, which nevertheless allow us to estimate the value of the Rashba splitting as being approximately equal to 150 meV. The band structure obtained using Eq. (3) for λ_i and λ_R equal to 0 and 150 meV, respectively, is shown in Fig. 2c. One can see the Rashba-type spin splitting of the π states and the absence of the gap at the Dirac point. The electronic structure is characterized by the linearly dispersing

π states near the Fermi level in this case. Corresponding to the situation shown in Fig. 2c ARPES image is shown in Fig. 2a. As distinct from that shown in Fig. 1a, the spectrum has been taken along the cut through the $\bar{K}$ point in the direction perpendicular to the $\bar{\Gamma}\bar{K}$ line for graphene on Pt(111).

Figure 2: ARPES spectra acquired with a photon energy of 40 eV for (a) graphene/Pt(111) and (b) graphene/Pb/Pt(111). The direction of measurements is indicated in panel (a). Shown on the right side of (b) is the $\bar{K}$ -point energy distribution curve (EDC) for graphene/Pb/Pt(111). The linear background is subtracted in ARPES spectra in panel (b). (c, d) The model band structures obtained using Eq. (3) for $\lambda_i=0$ and $\lambda_R=150$ meV (c) and $\lambda_i=-150$ and $\lambda_R=50$ meV (d). Red and blue lines correspond to $\mu=+1$ and $\mu=-1$, respectively (see text for more details).

A drastically different result is obtained after the Pb intercalation underneath graphene. As shown in Fig. 2b, a clear n -type doping is observed by ARPES for graphene/Pb/Pt(111), leading to a partial occupation of the π^* state. Moreover, judging by the intensity dip seen just below the Fermi level in the EDC taken at the $\bar{K}$ -point, one can recognize a formation of a band gap of about 200 meV that separates the

π and π^* states (full 2D mapping in two orthogonal directions near the $\bar{K}$ -point can be found in Fig.S4a of the Supporting Information). As it was shown in Ref.¹⁰ such a structure can be obtained if an intrinsic SO coupling is stronger than a Rashba-like one. This situation is illustrated in Fig. 2d, showing the bandstructure that Eq. (3) yields if $\lambda_i = -150$ meV and $\lambda_R = 50$ meV. One can clearly see the spin-orbit gap between the bonding and antibonding states. Furthermore, the spin splitting for the valence band (π state) is marginal, which is due to subtraction of the SO terms in Eq. (3) ($\nu = -1$). On the other hand, the π^* state shows a higher splitting, because in this case the SO contributions are summed ($\nu = +1$). For the $\lambda_i > 0$, this situation reverses and the higher (lower) splitting is seen for the π (π^*) state. As we show below, it is the choice of the negative λ_i that provides qualitative agreement of the model spectra with the result of the spin-resolved measurement. Note, that the sign of λ_i does not affect the gap value, it only determines which of the two states, π or π^* , is split stronger (in the case of Rashba SOI presence). As it is seen in Fig. 2d, $\lambda_i < 0$ leads to a strong (negligible) splitting of the π^* (π) state, which indeed can occur for certain adsorption geometries of the heavy p atoms on graphene.^{15,28}

The spin structure shown in Fig. 2d can be verified directly by means of spin-resolved ARPES measurements. Spin-resolved spectra of the graphene/Pb/Pt(111) system obtained using a Mott detector are shown in Fig. 3a for the two emission angles, corresponding to $k_{\parallel}=1.65 \text{ \AA}^{-1}$ (left) and $k_{\parallel}=1.75 \text{ \AA}^{-1}$ (right). It is appropriate to recall here, that along the $\bar{\Gamma}\bar{K}\bar{M}$ direction in photoemission one of the dispersion lines is missing due to the matrix elements selection rules³⁶ (which also means that the spins polarization of this dispersion line does not contribute to the spin -resolved data). Indeed, as it is seen in the inset to Fig. 3a, where the ARPES map near the $\bar{K}$ -point is shown, the π state intensity is high along $\bar{\Gamma}\bar{K}$, but is below the noise level along $\bar{K}\bar{M}$, supporting the suggestion that the gap formed is not caused by the A-B sublattice symmetry breaking.³⁷

Therefore, one can clearly distinguish be-

tween the π and π^* states by measuring in the first (at $k_{\parallel}=1.65 \text{ \AA}^{-1}$) and the second (at $k_{\parallel}=1.75 \text{ \AA}^{-1}$) BZs, respectively. Note, that the contribution of the Pt 5d states to the spectra may not be negligibly small (see the discussion below), but as it is seen from the spin-integrated data (see Fig.S4b in Supporting Information) the π states of graphene are easily resolved in the vicinity of the $\bar{K}$ -point. Thus, the spectrum on the left(right)-hand side has been obtained for $k_{\parallel}=1.65 \text{ \AA}^{-1}$ ($k_{\parallel}=1.75 \text{ \AA}^{-1}$), to probe the spin structure of the lower (upper) cone, *i.e.* of the bonding π (antibonding π^*) state. Raw asymmetry analysis and fitting of the EDC after the background subtraction by the Voigt functions shows that the spin splitting of the π states is below the experimental resolution (10 meV). In stark contrast, a pronounced spin asymmetry is seen for the upper cone (Fig. 3a, right) with the spin splitting near the Fermi level of more than 100 meV. Precise determination of the splitting value is complicated due to the angular integration of the spin-resolved spectra and the low intensity of the ARPES signal for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ graphene domain. Thus, one can see that the spin splitting of the bonding π states of graphene/Pb/Pt(111) is practically absent, while for the antibonding π^* band it is more than 100 meV. Such a spin texture corresponds to the proposed model with $|\lambda_i| > |\lambda_R|$ and negative λ_i shown in Fig. 2d.

It should be noted that the Kane-Mele model does not include the hybridization of the graphene and substrate states. Approximate (and probably somewhat overestimated) contribution of the Pt 5d states to the graphene/Pb/Pt(111) spin-resolved spectrum shown in Fig. 3a can be obtained by measuring the spin polarization coming directly from the Pt(111) substrate through the non-intercalated graphene-on-Pt(111) sheet. As we show in the Supplementary Note 4, the Pt 5d states spin polarization is, in fact, opposite to that measured for Pb-intercalated graphene and therefore its subtraction only enhances the spin splitting observed in Fig. 3a, right. On the other hand, the role of the Pt substrate in the formation of the spin-orbit gap observed is fundamental and graphene cannot

be completely decoupled from it by the intercalated Pb layer. Indeed, graphene, whose π - and π^* -states are mostly hybridized with Pb, is slightly hybridized with Pt as well *via* Pb states hybridized with Pt (see Supplementary Note 4). In this sense the contribution of the Pb/Pt(111) substrate spin-polarization is unavoidable in the graphene/Pb/Pt(111) system. However, the hybridization between graphene and Pb is the strongest because the Pb layer is adjacent to the graphene sheet. It is noteworthy, that this hybridization and the charge transfer to graphene strongly affect the electronic properties of Pb layer as well.

The most exciting effect arising from SOI in graphene is the QSHE,¹⁰ that can be realized if the graphene's sublattice symmetry is not broken and the intrinsic SOI is stronger than the Rashba one. In this work we infer that the graphene/Pb system satisfies these conditions, and, if grown on the insulating substrate, may exhibit the 2D TI phase. As it has been theoretically shown recently,²⁸ the spin-orbit gap is efficiently created in graphene when the Pb atoms are located in the hollow sites of the honeycomb lattice, when only the intrinsic contribution to the SOI is present. The on-top location of the Pb atoms features both Rashba-like and intrinsic contributions, the latter having the opposite sign to that of the hollow site. In the case of Pb array, the latter results in enhancement (suppression) of the intrinsic-like SOI in graphene if the lead atoms occupy adsorption positions of only one type (several types). Therefore, graphene/Pb/Ir(111), studied in Ref.,²⁶ is expected to feature only the Rashba-type SOI, due to occupation of many different locations of Pb atoms relative to graphene.

In the graphene/Pb/Pt(111) system studied here, several atomic configurations satisfying the LEED pattern shown in Fig. 1c are possible. Importantly, the A-B sublattice symmetry is conserved for all of these configurations (see Supporting Note 3 for details). The one shown in Fig. 1d reveals such an interface structure that the lead atoms take the equivalent positions relative to graphene lattice. For such a structure, an intrinsic SO contribution is expected to enhance owing to the same sign for

all Pb atoms. If the intrinsic SOI turns out to be stronger than the Rashba one, the electronic bands of graphene are predicted to show the spin-orbit gap at the $\bar{K}$ point, with a different spin splitting of the bonding and antibonding states, that depends on the λ_i sign. For the negative λ_i , the dispersion relation obtained from Eq. (3) is shown in the three-dimensional representation in Fig. 3c.

Detailed experimental dispersion relations obtained at 17 K and shown in Fig. 3b clearly exhibit the gap between the valence and conduction bands in Pb intercalated graphene on Pt(111). This spectrum is measured along the $\bar{\Gamma}\bar{K}\bar{M}$ direction and exhibits the uniform intensity distribution in 1st and 2nd BZs owing to the summing of the ARPES images taken with *p* and *s* polarizations of synchrotron radiation. Noteworthy, the metallic substrate used in the present study would mask the edge states in graphene and the use of an insulating or a semiconducting substrate is required to realize pure QSH phase. Therefore, further studies performed on the electronic and spin structures of graphene/Pb systems grown on different insulating substrate are very welcome.

Conclusions

In summary, we have experimentally demonstrated the spin-orbit gap opening in the Dirac point of graphene contacted with lead interlayer. Crucially for the gap observation by means of spin- and angle-resolved photoemission spectroscopy, the Pb monolayer intercalation between graphene layer and a Pt(111) substrate changes the Dirac cone doping character from *p* to *n* leading to the partial occupation of the π^* state. Analysis of the system's low-energy spectrum has revealed the gap of about 200 meV, separating the graphene π states, that show a marginal spin splitting, from the π^* states, that are split by more than 100 meV. According to previous theoretical predictions, such a bandstructure corresponds to enhancement of the intrinsic spin-orbit interaction in graphene that results in the spin-orbit gap formation and satisfies the conditions of the quantum spin Hall phase onset.

Methods

The experiments were carried out at

Figure 3: (a) Spin-resolved photoemission spectra of the graphene/Pb/Pt(111) system taken in the $\bar{\Gamma}\bar{K}\bar{M}$ direction at the two different emission angles, corresponding to $k_{\parallel}=1.65 \text{ \AA}^{-1}$ (left panel) and $k_{\parallel}=1.75 \text{ \AA}^{-1}$ (right panel). Quantization axis of the spin vector is in-plane, perpendicular to the momentum. The inset to (a) shows ARPES data near the $\bar{K}$ point, where the green lines mark the emission angles, for which the spin-resolved spectra were obtained. Also presented in (a), is the spin polarization calculated as the raw asymmetry $(I_{up} - I_{down})/(I_{up} + I_{down})$ multiplied by the Sherman function $S_{eff}=0.12$. (b) ARPES image of graphene/Pb/Pt(111) obtained by summing the intensity of the spectra taken at the temperature of 17 K with p and s polarizations of synchrotron radiation. (c) Schematic spin structure of the graphene states in the case of $|\lambda_i| > |\lambda_R|$ near the $\bar{K}$ point.

Helmholtz-Zentrum Berlin (BESSY II) at the UE112-SGM and U125/2-SGM beamlines, at Research Resource Center of Saint Petersburg State University “Physical methods of surface investigation” with a Scienta R4000 energy analyzer, and at BaDElPh beamline of the Elettra synchrotron in Trieste (Italy).³⁸ The spin-resolved photoemission spectra were measured using a Mott spin detector operated at 26 keV. Total energy resolution during experiments was 50 meV. The Spin ARPES measurements were carried out with the angular resolution of 1° , that corresponds to a momentum resolution of $0.07 \text{ \AA}^{-1}$ at a photon energy of 62 eV. The measurable spin splitting is not limited by the energy resolution, but rather by the acquired statistics. Our estimations of the splitting between the resolved features in photoemission spectra were derived from the fitting of the spectrum features and from the procedures described in Ref.²¹ The spin asymmetry can be calculated as $A = \frac{N_L - N_R}{N_L + N_R}$, where N_L and N_R are the number of electrons counted in the detec-

tors. The background offsets were obtained by measuring of reference magnetic sample upon reversal in-plane magnetization. The resulting asymmetry yields the spin resolved intensity spectra

$$I_{up,down} = (1 \pm A/S)I_s/2, \quad (4)$$

where $I_s = N_L + N_R$ and S is the so-called Sherman function.

Clean surface of Pt(111) was prepared by repeated cycles of Ar sputtering and annealing at 1300 K. The crystalline order and purity of the surface were verified by low energy electron diffraction (LEED) and X-ray photoemission spectroscopy (XPS). The graphene monolayer was synthesized on Pt(111) by cracking of the propylene (C_3H_6) at a pressure of 1×10^{-7} mbar. We keep the temperature of the sample at 1150 K during the cracking, in order to grow the $(\sqrt{3} \times \sqrt{3})R30^\circ$ graphene domain. Intercalation of 1 ML of Pb was achieved by deposition of ≈ 3 ML of Pb on graphene followed by brief annealing at 820 K, with evaporation of

the residual Pb atoms. The calibration of the Pb coverage for deposition was performed using quartz microbalance and XPS measurements.

Supporting information

XPS measurements, raw ARPES spectra in two directions, additional spin-resolved measurements of the system and scheme of the experiment are presented. This material is available free of charge *via* the Internet at <http://pubs.acs.org>

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Graphical TOC Entry