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ARTICLE

Tuning the Proximity Effect through Interface Engineering in a Pb/Graphene/Pt Trilayer System

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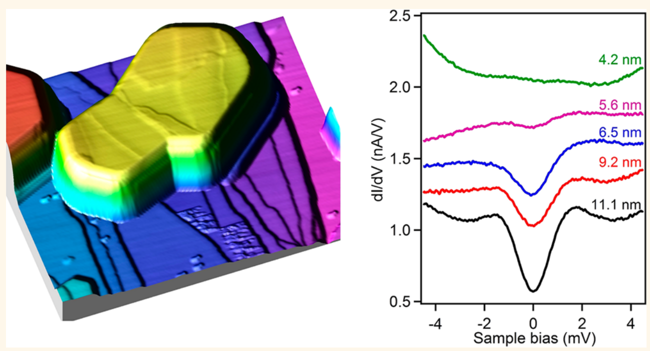
Supporting Information

ABSTRACT: The fate of superconductivity of a nanoscale superconducting film/island relies on the environment; for example, the proximity effect from the substrate plays a crucial role when the film thicknesses is much less than the coherent length. Here, we demonstrate that atomic-scale tuning of the proximity effects can be achieved by one atomically thin graphene layer inserted between the nanoscale Pb islands and the supporting Pt(111) substrate. By using scanning tunneling microscopy and spectroscopy, we show that the coupling between the electron in a normal metal and the Cooper pair in an adjacent superconductor is dampened by 1 order of magnitude *via* transmission through a single-atom-thick graphene. More interestingly, the superconductivity of the Pb islands is greatly affected by the moiré patterns of graphene, showing the intriguing influence of the graphene−substrate coupling on the superconducting properties of the overlayer.



KEYWORDS: *superconductivity, graphene, Pb, scanning tunneling microscopy*

Superconductivity in mesoscopic systems with spatial dimensions smaller than the superconducting coherence length is a subject of great scientific and technological importance and has attracted intense interest for decades. As prototype models, Pb films/islands have been epitaxially grown on various substrates with thickness in atomic precision, and their superconductivity has been studied *in situ* by low-temperature scanning tunneling microscopy and spectroscopy (LT-STM/STS) in recent years.[1−11] Superconducting order remains in atomically thin Pb films grown on Si(111).[3,4,6] In contrast, on bulk normal metal substrates, the superconductivity is suppressed due to the superconducting proximity effect,[12,13] thus the Pb film cannot show superconductivity until its thickness reaches the coherence length ξ (~80 nm). The different fate of superconductivity in these systems lies in the different substrate band structure (with or without band gap) in the vicinity of the Fermi level (E_F). These observations raise an interesting scenario: Can one tune the superconductivity by tuning the coupling between the superconductor thin films and the substrates? By inserting a single-layer graphene between the flat Pb thin islands and the supporting Pt substrate, we achieve atomic-scale tuning of the proximity effects between a superconducting thin film and the normal metal. We show that the graphene acts as a decoupling layer to reduce the proximity effect between Pb islands and Pt(111) substrate dramatically. At 4.3 K, the thickness threshold to exhibit a superconducting gap is reduced from 80 nm to 5 nm by inserting only *one atomic layer* of graphene between the substrate metal and the superconducting island. More interestingly, the superconductivity of the Pb islands is greatly affected by the moiré patterns of graphene, showing the intriguing influence of the graphene−substrate coupling on the superconducting properties of the overlayer.

RESULTS AND DISCUSSION

The as-grown single-layer graphene on Pt(111) exhibits various domains with different moiré superstructures, such as the rippled ones of $(\sqrt{37}\times\sqrt{37})R21°$, $(\sqrt{61}\times\sqrt{61})R26°$, and $(\sqrt{67}\times\sqrt{67})R12°$ and the unrippled ones of 2×2, 3×3, and 4×4 with respect to the graphene lattice, due to different

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rotation angles between the graphene and Pt lattices (see also the Supporting Information).[14−17] The different corrugation and interaction between the graphene moiré superstructures and the Pt substrate provides the epitaxial graphene as a desirable platform to engineer the superconductivity of the nanoscale Pb islands/films grown on it. Thermal deposition of Pb on the as-prepared graphene at room temperature leads to the formation of Pb islands, as shown in Figure 1a. The Pb

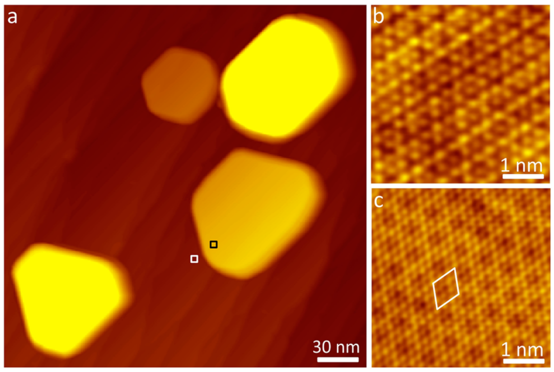

Figure 1. STM images of Pb islands grown on graphene/Pt(111). (a) Large-scale image showing the formation of Pb islands with straight edges and flat tops. (b) Atomic-resolution image acquired on a Pb island (the area marked with a black square in (a)) showing the modulation of the Pb lattice by the moiré pattern of graphene/Pt(111) underneath. (c) Atomic-resolution image acquired on the graphene (the area marked with a white square in (a)) near a Pb island showing a 3×3 moiré pattern with respect to the graphene lattice. The unit cell of the moiré superstructure is indicated by a white rhombus.

islands exhibit straight edges and truncated triangle or hexagonal shapes, indicating a (111)-faceted crystalline structure. The top of the Pb islands is very flat, even when these islands are extending over several terraces of graphene/Pt(111). An atomic-resolution STM image (Figure 1b) of such a Pb island with an average thickness of ∼5 nm reveals a hexagonal lattice with a lattice constant of 0.35 nm, in good agreement with that of bulk Pb(111). The bare area of graphene near this Pb island exhibits a 3×3 moiré pattern with respect to the graphene lattice, as shown in Figure 1c. It is noteworthy that the Pb atoms show inhomogeneous apparent heights, indicating significant influence of the graphene moiré pattern. These behaviors are very similar to those of Pb islands grown on graphene/Ru(0001).[18]

To eliminate the effect of lateral size on the superconductivity, we focus on the Pb islands with lateral sizes larger than the coherence length ξ (∼80 nm). Figure 2a shows a 6-nm-thick Pb island with a lateral size of ∼100 nm. A series of normalized differential conductance (dI/dV) spectra acquired on this Pb island at various temperatures are illustrated in Figure 2b. The spectrum measured at 0.45 K displays a clear superconducting energy gap and two sharp peaks corresponding to the quasi-particle excitation. These features are suppressed at elevated temperature and almost disappear at 6.26 K. These spectra can be fitted with the Bardeen−Cooper−Schrieffer (BCS)-like density of states (DOS) to extract a temperature-dependent superconducting gap $\Delta(T)$,[19] as shown in Figure 2c (see also the Supporting Information). Assuming a BCS temperature dependence of $\Delta(T)$,[20] we obtain a transition temperature (T_c) of ∼6.6 K and

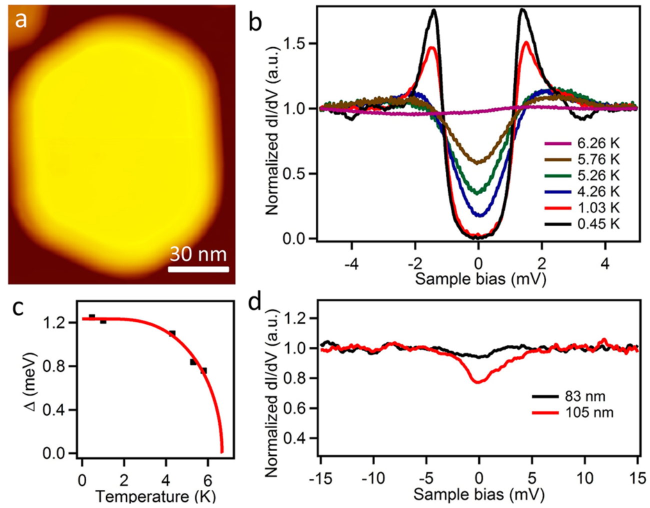

Figure 2. Superconductivity of the Pb islands grown on graphene/Pt(111). (a) STM image of a 6-nm-thick Pb island with a lateral size of ∼100 nm. (b) Normalized dI/dV spectra as a function of temperature acquired at the center of the Pb island shown in (a). (c) Temperature-dependent superconducting gap (Δ) (dark square) and the relevant fitting of the BCS gap function (red curve) for the Pb island shown in (a). (d) Normalized dI/dV spectra acquired on the Pb films grown on Cu(111) with a film thickness of 83 and 105 nm at 4.3 K.

a superconducting gap $\Delta(0)$ of ∼1.24 meV for this Pb island. The dimensionless ratio $2\Delta/k_BT_c$ = 4.36 indicates that the Pb island on graphene/Pt(111) is in the strong-coupling limit. In contrast, for Pb film grown on Cu(111), the superconducting gap is not observable at 4.3 K until the thickness exceeds 80 nm, as shown in Figure 2d. Similar behavior is expected for Pb film grown on Pt(111), but all efforts to obtain a clean Pt(111) surface failed after the growth of graphene on it. This dramatic contrast highlights the intriguing influence of the single-layer graphene at the interface. Presumably this single-layer graphene acts as a decoupling layer, suppressing the transmission of the Cooper pair into the metallic substrate. The superconductivity is still not as robust as that of Pb grown on a Si substrate, implying that a residual proximity effect still remains. Nevertheless, it is remarkable that with only a single layer of graphene the thickness threshold to observe a significant superconducting gap is reduced by more than 1 order of magnitude. Notably, we exclusively assign the gaps around the Fermi level to the superconducting energy gaps, as the graphene layer in our work is distinct from the insulating buffer layers (*e.g.*, hBN and NaCl) that were adopted in previous reports.[21,22] It had been shown that the presence of an hBN or NaCl layer between the Pb islands and the bulk metal substrate can lead to a nonohmic contact and the arising of the Coulomb block effect, which may contribute to the dips/peaks around the Fermi level in dI/dV spectra,[21,22] in particular for the Pb islands with lateral sizes significantly smaller than 80 nm. In contrast, in our case of Pb islands on graphene/Pt, the weak but nontrivial coupling between the graphene layer and the Pt substrate results in a slightly p-doped feature (the Dirac point of the graphene layer is upward shifted by ∼30 meV) and a finite density of states around the Fermi level in graphene.[15] Thus, the graphene layer is metallic and electrically in good contact with the Pt substrate, which indicates that our Pb/graphene/Pt system is essentially different from the Pb/NaCl/Ag, Pb/hBN/Ni, Pb/HOPG, Pb/Si, Al/Si, and In/Si systems in

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the literature, and the Coulomb block effect is negligible.[21−23] Moreover, the observation of strong coherent peaks and typical BCS line shapes of dI/dV spectra and the $\Delta(T)$ curve (Figure 2c) indicate that no pseudogap has been observed in our STS investigations.[24]

We have collected dI/dV spectra on a variety of nanoscale Pb islands grown on graphene/Pt(111). In spite of different island shapes and moiré superstructures of graphene/Pt(111) underneath, we find that a minimum thickness of ∼5 nm is required for the Pb islands grown on graphene/Pt(111) to exhibit superconductivity at 4.3 K, which is different from previous reports of Pb islands/films grown on various substrates. For example, it has been shown that Pb film grown on Si(111) can hold a robust T_c in the ultrathin regime.[1,4,6,25] In contrast, for Pb films grown on bulk normal metal, *e.g.*, Ag and Cu, their superconductivity is quenched drastically when the thickness is less than the coherent length ξ (∼80 nm).[5,11,13] The different fate of superconductivity of Pb films grown on semiconductor and normal metal substrates can be easily explained by the superconducting proximity effect. For Pb films grown on Si, the Cooper pairs of Pb can survive even for the thinnest Pb films, as Si is a semiconductor, which is an effective insulator. In contrast, Ag and Cu are normal metals, and their free electrons can propagate into the Pb films and break the Cooper pairs of Pb, leading to the suppression of superconductivity of the Pb films with thickness < 80 nm.[11] In the present case of Pb islands grown on graphene/Pt, the Pt substrate is covered by a graphene sheet. Thus, the propagation of free electron from the Pt substrate to the Pb islands is significantly reduced due to the graphene sheet, leading to a much less critical thickness of Pb islands to exhibit superconductivity than that of Pb films/islands grown on Pt(111). Assuming that the density distribution of the free electrons propagated from the Pt(111) substrate to the Pb islands follows the one-dimensional diffusion equation in both cases of Pb/graphene/Pt and Pb/Pt, we estimate that the transmission factor of free electrons from the Pt substrate to the Pb islands is reduced by an order of magnitude by a single-layer graphene, in line with previous reports that the carrier concentration in multilayer epitaxial graphene on SiC decreases by about an order of magnitude for each adjacent layer due to the interlayer electronic screening.[26,27]

It has been recently reported that the 3-ML-thick Pb islands grown on graphene/SiC(0001) show a T_c of 5.8 K, which is similar to free-standing calculations.[7] This indicates that due to the single atomic layer thickness of graphene and its finite DOS near E_F (natural doping) the epitaxial graphene on SiC(0001) plays a negligible role in damping of superconductivity. In our case, the nearly free-standing nature of the graphene layer grown on Pt(111) is similar to that grown on SiC.[14,15] However, the superconductivity of on-top Pb islands in our studies is entirely different with either the free-standing (graphene/SiC), half-free-standing (Si(111)), or highly quenched case (bulk normal metal). In fact, the graphene layer plays a role in engineering the interface between the normal metal (Pt) and the superconductor (Pb islands).

The superconductivity of the nanoscale Pb islands grown on graphene/Pt(111) is also influenced by several other factors, *e.g.*, island thickness and the moiré superstructure of graphene/Pt(111) underneath. Figure 3 displays the raw dI/dV spectra acquired at 4.3 K on a selected set of unrippled Pb islands, each with a lateral size of ∼100 nm but with different thickness. The spectra exhibit significant asymmetrical line shapes, due to the

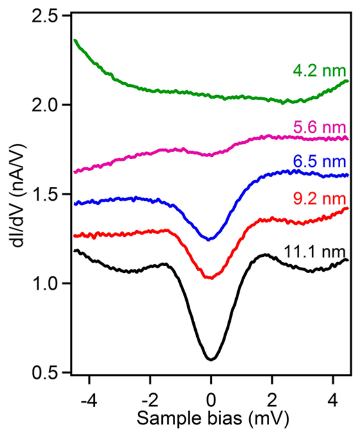

Figure 3. Thickness-dependent superconductivity of the Pb islands grown on graphene/Pt(111). Raw dI/dV spectra acquired at 4.3 K on a selected set of Pb islands, each with a lateral size of ∼100 nm but with different thickness. The curves, except the black one, are offset vertically by 0.15 nA/V with respect to their neighbors for clarity.

quantum-well states of the Pb islands and the nonconstant DOS of the graphene/Pt(111) substrate.[1,3,7,28] Nevertheless, these spectra display a clear superconducting gap decreasing with reducing island thickness. The superconducting gap and quasi-particle excitation peaks are completely suppressed for the Pb island with a thickness of ∼4.2 nm at 4.3 K. It has been shown that the quantum confinement in the ultrathin Pb films grown on Si can cause T_c oscillations.[1,29] However, the oscillation amplitude is rather small (∼0.1 K) and quickly damped out when the thickness is larger than 10 ML. This effect is thus ignored in our discussion.

More intriguingly, other than the thickness dependency of T_c, we observed that the moiré superstructure of graphene/Pt(111) underneath can also significantly affect the superconductivity of on-top Pb islands. Figure 4a shows a three-dimensional (3D) STM topography of a Pb island with a lateral

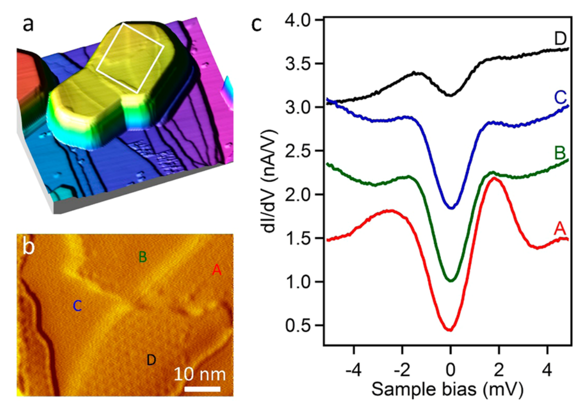

Figure 4. Superconductivity of the Pb islands influenced by the moiré pattern of graphene/Pt(111). (a) 3D STM image of a Pb island extending across several terraces of graphene/Pt(111). Scan area 150 nm × 120 nm. (b) Zoom-in (the area marked with a white rectangle in (a)) showing that the Pb island extends across several domains and terraces of graphene/Pt(111) with different moiré patterns. (c) Raw dI/dV spectra acquired on different areas (indicated with dots in (b)) of the Pb island. The curves, except the red one, are offset vertically by 0.7 nA/V with respect to their neighbors for clarity.

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size of ~100 nm. This Pb island extends across several domains and terraces of graphene/Pt(111) with different moiré patterns, as seen in the zoom-in shown in Figure 4b. In addition, the flat morphology of the Pb areas grown on the A, B, and C domains indicates that the graphene of the A, B, and C domains is unrippled, in contrast to the rippled graphene of the D domain exhibiting a moiré superstructure of $(\sqrt{67}\times\sqrt{67})R12°$ with respect to the graphene lattice. Line profile analysis reveals that the Pb areas on the A, B, C, and D graphene domains are 10.66, 10.29, 9.83, and 10.29 nm in thickness, respectively. Figure 4c displays a set of dI/dV spectra acquired on different Pb areas at 4.3 K. Notably, the dI/dV spectra collected on the same domains are essentially the same, despite being taken at different sites. By the same fitting procedure as we have shown above, the superconducting gaps at 4.3 K can be extracted as 1.15, 1.06, 1.00, and 0.92 meV for the A, B, C, and D areas, respectively. The superconducting gap of the A, B, and C areas deceases with the sequence of A > B > C, in line with the decreasing thickness of these areas. However, the superconducting gap of the D area is much smaller than that of the B area, despite their identical thickness and similar lateral domain sizes. The main difference is the unrippled *vs* rippled graphene structures underneath the B and D areas, respectively, indicating that the superconductivity of the Pb islands is affected by the graphene moiré superstructure underneath. The variation of the periodicity and the rotation angle between the graphene and Pt lattices for different graphene moiré superstructures results in distinct separation and interfacial coupling between the graphene moiré superstructure and the Pt substrate. Thus, the energy barrier for the free electrons to propagate from the Pt substrate to the Pb islands is tuned by the graphene moiré superstructure, leading to the modulation of the superconductivity of the Pb islands by the graphene moiré superstructure underneath.

CONCLUSIONS

In summary, we have studied the superconductivity of nanoscale Pb islands grown on epitaxial graphene on Pt(111) by LT-STM/STS. We find that the graphene acts as a decoupling layer to reduce the proximity effect between the Pb islands and the Pt(111) substrate. Without this decoupling layer, a superconducting gap cannot be observed at 4.3 K until the Pb island is thicker than 80 nm. On the other hand, with this decoupling layer, the Pb islands exhibit superconductivity at 4.3 K at a thickness of ~5 nm, which is an order of magnitude thinner. More interestingly, we find that the superconductivity of the Pb islands is greatly affected by the moiré patterns of graphene, showing the intriguing influence of the graphene−substrate coupling on the superconducting properties of the overlayer, which might be very helpful for the fabrication of novel devices based on graphene−superconductor heterostructures.

METHODS

The experiments were conducted in an ultrahigh vacuum (base pressure $<1 \times 10^{-10}$ mbar) LT-STM (Unisoku), equipped with standard surface processing facilities. A low-temperature of 0.4 K is achieved by means of a single-shot ^{3}He cryostat. The Pt(111) surface was prepared by repeated cycles of sputtering with argon ions and annealing to 800 °C. Graphene was grown *via* pyrolysis of ethylene on a Pt(111) substrate that was held at 600 °C, as described elsewhere.[14−16] Pb was deposited *via* vacuum sublimation from a homemade Knudsen-type evaporator at ~500 °C, while the graphene/Pt(111) substrate was held at room temperature. The typical deposition rate was ~0.01 monolayer (ML)/min (1 ML = 9.4 × 10^{14} atoms/cm^2, corresponding to a single layer of bulk Pb(111)), as calibrated by LT-STM. STM images were acquired in the constant-current mode, and all given voltages refer to the sample. Differential conductance spectra were collected using a lock-in technique with a 50 μV_{rms} sinusoidal modulation at a frequency of 973 Hz. All measurements were performed with electrochemically etched tungsten tips. Measurements of local spectroscopy were electronically calibrated by performing dI/dV measurements on clean graphene/Pt(111) before and after measurements on Pb islands, based on the well-known V-shaped DOS of graphene/Pt(111).[14,15,17]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.6b00298.

STM images of various moiré patterns of graphene/Pt(111) with respect to the graphene lattice and fitting of the collected dI/dV spectra with the BCS-like DOS (PDF)

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Notes

The authors declare no competing financial interest.

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