

# 1 Black Phosphorus n-Type Doping by Cu: A Microscopic Surface 2 Investigation

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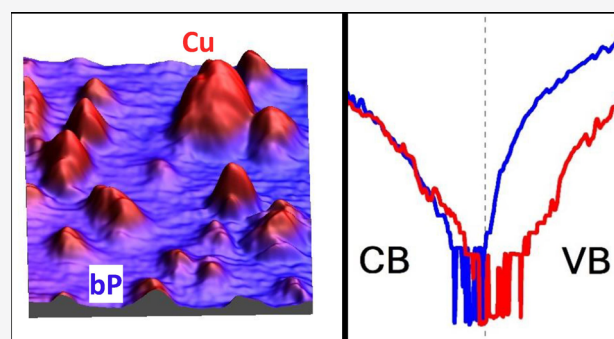


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Supporting Information

6 **ABSTRACT:** We study surface charge transfer doping of exfoliated  
 7 black phosphorus (bP) flakes by copper using scanning tunneling  
 8 microscopy (STM) and spectroscopy (STS) at room temperature.  
 9 The tunneling spectra reveal a gap in correspondence of Cu islands,  
 10 which is tentatively attributed to Coulomb blockade phenomena.  
 11 Moreover, using line spectroscopic measurements across small copper  
 12 islands, we exploit the potential of the local investigation, showing  
 13 that the n-type doping effect of copper on bP is short-ranged. These  
 14 experimental results are substantiated by first-principles simulations,  
 15 which quantify the role of cluster size for an effective n-type doping of  
 16 bP and show an electronic decoupling of the topmost bP layer from  
 17 the underlying layers driven by the copper cluster, consistent with the  
 18 Coulomb blockade interpretation. Our results provide novel under-  
 19 standing—difficult to retrieve by transport measurements—of the doping of bP by copper, which appears promising for the  
 20 implementation of ultrasharp p–n junctions in bP.



## 21 ■ INTRODUCTION

22 Black phosphorus (bP) is a semiconductor with a direct band  
 23 gap that ranges from  $\sim 0.3$  (bulk) to  $\sim 2.0$  eV (monolayer)  
 24 depending on layer thickness.<sup>1–3</sup> Among the van der Waals  
 25 elemental materials,<sup>4,5</sup> bP in its few-layer form attracted great  
 26 interest since its first exfoliation<sup>6,7</sup> because of the modulation  
 27 of the direct band gap,<sup>4,8</sup> the in-plane anisotropy,<sup>9–11</sup> and its  
 28 high charge-carrier mobility, up to  $5200 \text{ cm}^2/(\text{V s})$  at room  
 29 temperature,<sup>12</sup> appealing for possible device applications.<sup>13</sup>  
 30 The presence of phosphorus vacancies, as reported in a  
 31 recent scanning tunneling microscopy (STM) study,<sup>14</sup> makes  
 32 bP an intrinsically p-doped material.<sup>15,16</sup> N-type doping of bP  
 33 has been investigated in light of possible applications.<sup>17</sup> Several  
 34 strategies have been pursued, from the reversible doping by  
 35 field effect in transistors, where an ambipolar behavior was  
 36 obtained,<sup>1,18,19</sup> to exfoliation of bulk crystals obtained by  
 37 substitutional doping with Se<sup>20</sup> or Te.<sup>21</sup> A more promising  
 38 strategy for few-layer flakes could be surface charge transfer  
 39 doping, which has been implemented on several two-  
 40 dimensional materials such as graphene<sup>22,23</sup> and transition  
 41 metal dichalcogenides.<sup>24,25</sup> For bP, few studies report n-type  
 42 doping by surface charge transfer,<sup>26–34</sup> mostly for the case of  
 43 alkali metals.<sup>27,31,32</sup> Electrical transport measurements show n-  
 44 type behavior when bP is doped by the deposition of  
 45 copper.<sup>28,33</sup> However, no local spectroscopic investigation

has been performed so far to understand the effect of Cu on 46  
 the electronic properties of bP at the atomic level. 47

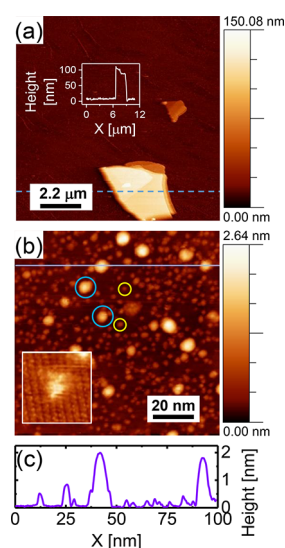
In this work, we performed an investigation of surface charge 48  
 transfer doping by copper deposition on exfoliated bP flakes, 49  
 combining STM and scanning tunneling spectroscopy (STS) 50  
 measurements with first-principles calculations based on 51  
 density functional theory (DFT). STS shows a gap in the 52  
 spectra measured on Cu islands that we attribute to Coulomb 53  
 blockade. The data also suggest that Cu induces an n-type 54  
 doping in bP. Line-spectroscopic measurements across copper 55  
 islands further show that the copper doping effect on bP is very 56  
 short-ranged. Theoretical simulations reveal that Cu clusters 57  
 efficiently decouple the topmost bP layer via charge local- 58  
 ization, which explains both the Coulomb blockade as well as 59  
 the local doping effect observed in experiments. 60

## 61 ■ RESULTS AND DISCUSSION

Figure 1 reports an STM analysis of copper deposited on bP 62 fl  
 flakes supported by a graphene-on-SiC substrate, which acts as 63

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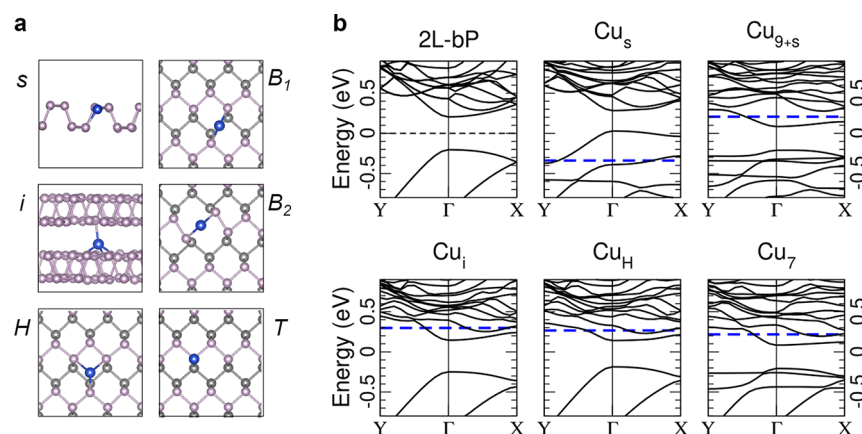
**Figure 1.** (a)  $11\ \mu\text{m} \times 11\ \mu\text{m}$  STM image showing two bP flakes on a graphene substrate after 20 min of copper deposition. Scan parameters:  $(-3.0\ \text{V}, 0.33\ \text{nA})$ . Inset: height profile across the larger flake along the dashed blue line. The flake has two plateaus; the higher region (top part of the flake) is  $93\ \text{nm}$  high, the lower (bottom part)  $80\ \text{nm}$ . All measurements presented in the following panels were performed on the lower plateau. (b)  $100\ \text{nm} \times 100\ \text{nm}$  STM image on the larger flake, showing copper islands on bP. Some of the smaller and larger copper islands are identified by yellow and blue circles, respectively. Inset:  $5\ \text{nm} \times 5\ \text{nm}$  STM image obtained upon further zoom-in, showing a copper island on top of the atomically resolved bP surface. Scan parameters for both images:  $(-1.0\ \text{V}, 0.33\ \text{nA})$ . (c) Height profile along the violet line in panel b.

64 a conductive ground electrode.<sup>35</sup> A comparison of bP surfaces  
65 before and after copper deposition is shown in the Supporting  
66 Information (Figure S2), where the pristine bP surface appears  
67 clean and flat at this magnification, with some defects related  
68 to intrinsic phosphorus vacancies, consistent with previous  
69 reports.<sup>14,35,36</sup> Figure 1a shows two representative bP flakes on  
70 which copper was deposited for 20 min. A zoom-in on the  
71 larger flake (Figure 1b) shows bright features on the surface

that appear only after copper deposition and are therefore 72  
identified as copper islands, indicative of a Volmer–Weber 73  
growth mode. Copper islands of two different sizes can be 74  
seen, indicated by blue (larger islands, diameter  $7.84 \pm 1.08$  75  
 $\text{nm}$ , height  $1.91 \pm 0.31\ \text{nm}$ ) and yellow circles (smaller islands, 76  
diameter  $3.75 \pm 0.51\ \text{nm}$ , height  $0.63 \pm 0.11\ \text{nm}$ ). From a 77  
statistical analysis of several different spots on the flake, we 78  
compute a coverage of  $0.80 \pm 0.11\ \text{ML}$  of copper on the bP 79  
surface.<sup>37</sup> We underline that these islands are rather different 80  
from the chiral Cu structures that were recently reported and 81  
were obtained upon heating of Cu nanoparticles on bP flakes 82  
at  $300\ ^\circ\text{C}$ .<sup>38</sup> 83

A further zoom-in on the flake is shown in the inset of 84  
Figure 1b. The surface shows the zigzag pattern characteristic 85  
of the  $[100]$  direction of bP<sup>35</sup> and a copper island on top of it. 86  
This observation allows us to exclude an intercalation of the 87  
Cu here since in that case the typical lattice structure of bP 88  
should be visible also on top of the intercalated copper, as 89  
observed in similar systems such as lithium-intercalated 90  
graphene.<sup>39</sup> The fact that the edges of the copper island 91  
appear fuzzy when imaged at high resolution is a sign of 92  
thermally activated motion of copper atoms at room 93  
temperature.<sup>40</sup> Despite this motion, however, the copper 94  
islands are stable, since their relative positions remain 95  
unchanged in multiple scans of the same location (Figure 96  
S3). This excludes any tip-induced effects and is in contrast to 97  
other reports, where motion or modification of islands on the 98  
substrate was induced by the tip of an STM.<sup>41,42</sup> 99

This structural microscopic investigation by STM is coupled 100  
to DFT-based ab initio simulations addressing the formation 101  
energies of the main Cu point defects and adatoms on few- 102  
layer bP slabs, together with adsorbed clusters of increasing 103  
size. Figure 2a illustrates the single Cu impurities investigated 104  
here: substitutional ( $\text{Cu}_s$ ), interstitial ( $\text{Cu}_i$ ), and adsorbed 105  
copper in four different adsorption sites, i.e., hollow ( $\text{Cu}_H$ ), top 106  
( $\text{Cu}_T$ ), and two bridge sites ( $\text{Cu}_{B_1}$  and  $\text{Cu}_{B_2}$ , bridging atoms on 107  
adjacent zigzag rows and adjacent atoms on the same zigzag 108  
row, respectively). According to the values reported in Table 1, 109  
 $\text{Cu}_s$  saturating P vacancies is the most stable point defect, 110



**Figure 2.** (a) Ball-and-stick models for single Cu impurities (blue spheres) in bP. The interstitial, *i*, and substitutional, *s*, sites are shown as side views. For adsorbed Cu atoms, several sites were considered, that is hollow (*H*), top (*T*) and two different bridge positions ( $B_1$  and  $B_2$ ), shown as top views. For the top views, the bottom phosphorus layer is represented in gray, in order to make the figures clearer. (b) Band structure of the three lowest energy Cu impurities and two representative Cu clusters. The band structure of pristine 2L-bP is reported for comparison, the midgap of which is set as the zero energy reference for all band structures. The Fermi level of the different Cu configurations is highlighted by dashed blue lines. The high-symmetry points X and Y indicate the zone-center along the zigzag and armchair direction, respectively.

111 followed by  $\text{Cu}_i$ , while single Cu adatoms are preferentially  
112 adsorbed in a hollow position ( $\text{Cu}_H$ ).

**Table 1. Formation Energy ( $\Delta E$ ) of Cu Single Impurities (Left) and Cu Clusters (Right) on bP at  $T = 0 \text{ K}$ <sup>a</sup>**

site	$\Delta E$ (eV)	cluster	$\Delta E/N_{\text{Cu}}$ (eV)	$\delta E/N_{\text{Cu}_{\text{ads}}}$ (eV)
s	-4.47	$\text{Cu}_{1+s}$	-4.01	-0.87
i	-3.46	$\text{Cu}_{3+i}$	-3.56	-0.58
H	-2.68	$\text{Cu}_{7+H}$	-3.36	-0.51
B <sub>1</sub>	-2.55	$\text{Cu}_{9+s}$	-3.42	-0.62
B <sub>2</sub>	-1.61	$\text{Cu}_3$	-2.85	-0.08
T	-1.51	$\text{Cu}_7$	-3.03	-0.35

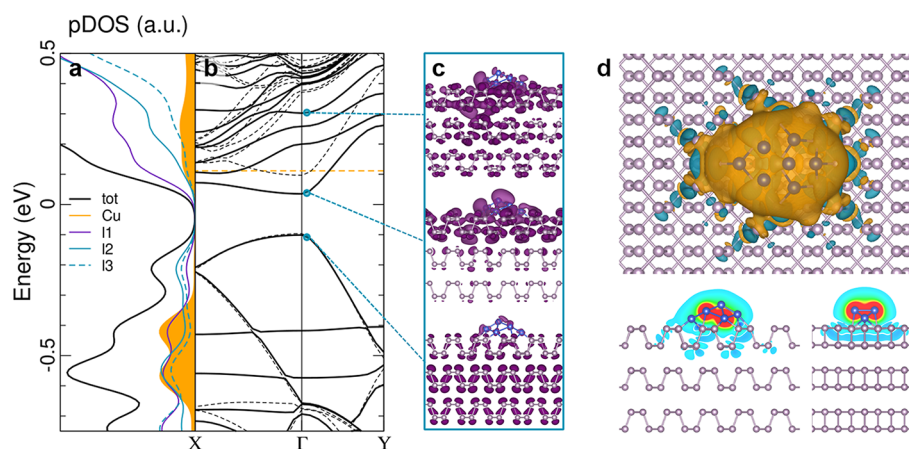
<sup>a</sup>For Cu adatoms, several sites were considered, that is hollow (H), top (T), and two different bridge positions (B<sub>1</sub> and B<sub>2</sub>). The formation energy of adsorbed Cu clusters of increasing size is reported per Cu atom, while the energy gain with respect to the single impurities is per Cu adsorbed atom. Clusters are labeled as  $\text{Cu}_{n+s}$  ( $n$  Cu atoms added to the  $\text{Cu}_s$  impurity) and  $\text{Cu}_n$  ( $n$  adsorbed Cu atoms including the initial  $\text{Cu}_H$ ).

113 The formation of clusters on the bP surface is also  
114 investigated, as shown in Table 1, starting from the most  
115 stable single Cu impurities decorating the surface, i.e.,  $\text{Cu}_s$  and  
116  $\text{Cu}_H$ . In particular, we considered two series of clusters as  
117 obtained by using either a surface substitutional  $\text{Cu}_s$  or a single  
118 adsorbed  $\text{Cu}_H$  atom as nucleus and adding further Cu atoms to  
119 build clusters of increasing size. The two series are hereafter  
120 labeled as  $\text{Cu}_{n+s}$  ( $n$  Cu atoms added to the  $\text{Cu}_s$  impurity) and  
121  $\text{Cu}_n$  ( $n$  adsorbed Cu atoms including the initial  $\text{Cu}_H$ ). In  
122 addition to the formation energy per Cu atom, Table 1 reports  
123 also the energy gain for the clusters with respect to the isolated  
124 impurities per adsorbed Cu atom (last column): this value  
125 indicates that cluster formation is always favored, in overall  
126 agreement with experimental observations, which do not  
127 evidence single Cu atoms on the surface at room temperature.  
128 More specifically, we find that cluster nucleation around  $\text{Cu}_s$   
129 sites is the (thermodynamically) most favorable process.

For a better understanding of the electronic properties of Cu  
on bP, we report in Figure 2b the computed DFT band  
structure for the three lowest-energy isolated Cu impurities  
discussed above, i.e.,  $\text{Cu}_s$ ,  $\text{Cu}_i$ , and  $\text{Cu}_H$ , together with the band  
structure of selected adsorbed clusters. The band structure of  
pristine 2-layer (2L-) bP is shown as a reference. Starting with  
the single Cu impurities, we notice that  $\text{Cu}_i$  and  $\text{Cu}_H$  behave as  
n-type dopants whereas substitutional copper leads to a p-  
doping of bP. While for the n-doped systems ( $\text{Cu}_i$  and  $\text{Cu}_H$ )  
the valence band is very similar to the pristine one, the p-  
doped system ( $\text{Cu}_s$ ) has a markedly different valence-band  
structure. In all cases, the band gap is either reduced (by up to  
150 meV for  $\text{Cu}_s$ ) or almost unchanged ( $\text{Cu}_i$ )<sup>43</sup> in the  
presence of Cu atoms, as previously observed for other TM  
adatoms.<sup>44,45</sup>

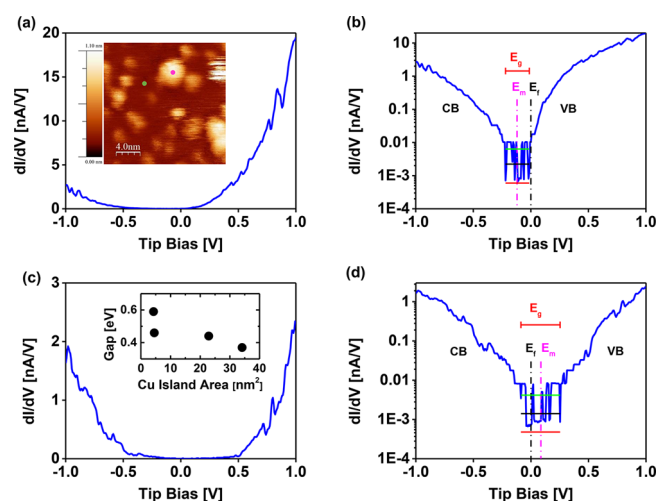
Considering now the clusters, the doping effect for  $\text{Cu}_7$ ,  
which is adsorbed on the pristine surface, is very similar to that  
of a single Cu adatom ( $\text{Cu}_H$ ), i.e., n-type, and shows only some  
additional nondispersive Cu states in the region close to the  
band gap. In the case of clusters building on a substitutional  
 $\text{Cu}_s$  seed ( $\text{Cu}_{n+s}$ ), the n-type doping effect of the cluster tends  
to overcome the p-type doping character of the  $\text{Cu}_s$  seed for  
sufficiently large clusters, resulting in a band structure similar  
to that of the adsorbed clusters without seed, as can be seen by  
comparing  $\text{Cu}_{9+s}$  and  $\text{Cu}_7$ . This points to the existence of a  
critical size at which all Cu clusters would behave the same, i.e.,  
n-doping and band gap reduction, irrespective of the presence  
of a substitutional seed.

We further investigate the band gap modification and doping  
induced by copper clusters by focusing on  $\text{Cu}_7$  and consider a  
larger supercell ( $5 \times 5$ ) and a thicker bP slab (3-layer, 3L)  
to minimize the effect due to periodic replicas. The results are  
shown in Figure 3. A similar analysis for the case of  $\text{Cu}_{7+s}$  is  
reported in the Supporting Information (Figure S4). Figure 3a  
shows the projected density of states (pDOS) of  $\text{Cu}_7$  on 3L-bP  
separated into the contribution of Cu atomic orbitals (orange  
curve) and the atomic orbitals of each bP layer (violet and light  
blue). Panel b shows the band structure computed for the



**Figure 3.** Electronic properties of adsorbed  $\text{Cu}_7$  on 3L-bP. (a) The total density of states (black line) is split into the contribution of the Cu cluster (orange curve) and bP first (11), second (12), and third layers (13) by using atomic projections. (b) The band structure in the presence of the adsorbed Cu cluster (solid black line) is compared to that of pristine 3L-bP (dashed line). The Fermi level of the doped system is also reported (orange dashed line), with the midgap of the pristine 3L-bP set as the zero energy reference. (c) A few relevant Kohn–Sham squared wave functions are displayed, with purple (blue) balls denoting P (Cu) atoms. The isosurface amplitude is  $7 \times 10^{-5}$  a.u. (d) Top-view of the charge density difference with an isosurface amplitude of  $3 \times 10^{-4}$  a.u. (top panel, orange (blue) is the positive (negative) isosurface), together with two sections of the isosurface along armchair and zigzag directions (bottom panel). For the sections, we use a RGB color scale with red and blue corresponding to +0.03 and -0.008, respectively.

168 Cu<sub>7</sub>/3L-bP case, as compared to the band structure of pristine  
 169 3L-bP (black dashed lines). While the band structure  
 170 highlights the same qualitative features described above for  
 171 Cu<sub>7</sub>/2L-bP (see Figure 2), the pDOS shows that the copper  
 172 affects mainly the topmost bP layer, which presents Cu-derived  
 173 peaks at about -0.4 and +0.15 eV (I1, violet line). At these  
 174 energies, the contributions from the bottom bP layers (I2 and  
 175 I3, light blue) are instead significantly smaller. This suggests  
 176 that the Cu levels around the band gap region hybridize mainly  
 177 with states localized in the topmost bP layer and are essentially  
 178 decoupled from the layers underneath. In contrast, deeper Cu-  
 179 originating states hybridize with states from all three bP layers.  
 180 This is confirmed by the plot of the Kohn–Sham orbitals for  
 181 selected states (Figure 3c). Indeed, the orbitals at the bottom  
 182 of the conduction band are spatially localized at the topmost  
 183 bP layer. Only at higher energies, the wave functions are  
 184 distributed over the entire system (i.e., similar to those of  
 185 pristine bP). Deeper insight into the charge-density redistri-  
 186 bution upon Cu doping can be obtained by plotting the  
 187 charge-density difference for the Cu<sub>7</sub>/3L-bP system, obtained  
 188 by subtracting the charge computed for the pristine substrate  
 189 from the total charge of the doped system (see Figure 3d).  
 190 From both the top view of the isosurface plot (top panel) and  
 191 the isosurface sections along the zigzag and armchair directions  
 192 (bottom panels), we note that (i) the Cu charge transferred to  
 193 bP remains mostly localized on the topmost layer and (ii) the  
 194 charge shows a strong localization in the bP plane around the  
 195 cluster, with an abrupt decay within a few lattice units. In  
 196 addition, the charge rearrangement in the stacking direction  
 197 reveals the origin of the spatial localization of the frontier  
 198 orbitals described above as a result of the local field generated  
 199 at the interface, reminiscent of what is found in the presence of  
 200 an applied external electric field.<sup>46,47</sup> This finds a correspond-  
 201 ence in the potential energy difference (or workfunction  
 202 difference) between the top (i.e., doped side) and bottom of  
 203 the Cu-decorated bP slab, which is positive for the n-type  
 204 doped Cu<sub>7</sub>/3L-bP system and amounts to 98 meV.  
 205 Taking advantage of the DFT analysis, we next move to local  
 206 spectroscopy by STS, both on flat bP surface areas and on  
 207 copper islands. Typical differential-conductance curves are  
 208 shown in Figure 4, where both linear and logarithmic plots are  
 209 displayed for an analysis of spectral shape and identification of  
 210 the gap region, respectively. The shape of the spectra recorded  
 211 off the copper islands (Figure 4a), with a larger amplitude at  
 212 positive tip bias, very much resembles that of pristine bP.<sup>14,48</sup>  
 213 On the contrary, the spectra measured on copper islands  
 214 (Figure 4c) display similar spectral amplitude at ±1 V and thus  
 215 a more symmetric shape. We can exclude that the shape of the  
 216 spectra is affected by thermal drift of the STM tip in z-  
 217 direction, since we have checked that for all spectra the  
 218 forward and backward sweeps were coinciding (as shown in  
 219 the Supporting Information).  
 220 From more than 40 spectra measured in several spots on the  
 221 flake, we obtain a gap value of 0.25 ± 0.10 eV for the flat bP  
 222 areas, consistent with the reported band gap value of pristine  
 223 bP.<sup>14,15,36,48</sup> As shown in Figure 4b, the position of the Fermi  
 224 level (at zero bias, vertical black dot-dash line) is lying close to  
 225 the valence-band edge, which implies p-type doping, consistent  
 226 with the literature for pristine bP.<sup>14</sup> Thus, the spectra  
 227 measured on the flat bP surface away from Cu islands can  
 228 be attributed to pristine bP. The same analysis for spectra  
 229 recorded on copper islands gives a gap value of 0.46 ± 0.20 eV.



**Figure 4.** Differential conductance ( $dI/dV$ ) spectra (a) for pristine bP and (c) for Cu on bP. The green and the pink spots in the STM image shown as an inset to panel a indicate where the spectra in panels a and c, respectively, were recorded. The same spectra as in panels a and c are plotted on a logarithmic scale in panels b and d for pristine bP and Cu on bP, respectively. The inset to panel c shows how the gap measured on Cu islands changes with island area. Scan parameters of the STM image in panel a and STS set point for all spectra (on bP and Cu islands): (-1.0 V, 0.33 nA). The bias is applied to the tip.

To determine the gap values, we followed the procedure  
 described in ref 14.

Even though the increase in the band gap and the symmetry  
 of the differential-conductance curves in the presence of the  
 Cu islands are in apparent contradiction with the DFT results  
 described above, the results can be consistently understood if  
 we invoke a Coulomb blockade for the Cu islands. Similar  
 effects have already been observed in the single-electron  
 tunneling spectra of ultrasmall metal islands at room  
 temperature.<sup>49–51</sup> Here, DFT calculations show that close to  
 the Fermi level, the localized frontier states do not hybridize  
 with the lower bP layers, thus creating a tunnel barrier between  
 the Cu islands and the bP bulk. In this situation, the electron  
 charge on the Cu islands can be quantized if two conditions are  
 met:<sup>49,52</sup> (i) The capacitance  $C$  of the islands is sufficiently  
 small such that the charging energy  $e^2/2C$  exceeds the thermal  
 energy  $k_B T$ . Here, applying a parallel plate capacitor model,<sup>53</sup>  
 we estimate  $C \approx 10^{-18}$  F, which leads to  $e^2/2C \approx 100$  meV,  
 larger than  $k_B T$  ( $\sim 25$  meV at room temperature). (ii) The  
 tunneling resistance  $R_T$  between STM tip and Cu island is  
 much larger than the resistance quantum  $R_K = h/e^2 \approx 25.8$  k $\Omega$ .  
 From Figure 4d, we get  $R_T > 10$  G $\Omega$  for  $V_{\text{tip}} < \pm 0.5$  V. Being  
 in a situation in which these two conditions are met, it is  
 reasonable to conclude that the experimentally observed gap  
 might be due to Coulomb blockade. Consistently, a Coulomb  
 gap of 0.45 eV ( $= e/C$ )<sup>53</sup> corresponds to a capacitance  $C = 4 \times$   
 $10^{-19}$  F, in good agreement with the estimate based on the  
 parallel plate capacitor model. A further evidence of Coulomb  
 blockade effect is given by the gap dependence with the island  
 dimension. As shown in the inset to Figure 4c, the  
 experimentally observed gap decreases with increasing island  
 area, as expected for Coulomb blockade,<sup>54</sup> approaching the  
 value of the bP band gap for the largest island measured.

The STS data in Figure 4d, which was measured on a Cu  
 island, shows that the position of the Fermi level does not

265 coincide with the midgap position but is shifted toward the  
 266 conduction band edge. According to the orthodox theory of  
 267 tunneling through a double junction, which applies here,<sup>54</sup> the  
 268 asymmetric gap observed in Figure 4d is due to the fractional  
 269 residual charge  $Q_0$  on the Cu island.<sup>55</sup> According to Hanna and  
 270 Tinkham,<sup>55</sup>  $Q_0$  originates from the difference in work function,  
 271 or the contact potential, across the junctions.  $Q_0$  is then  
 272 obtained from

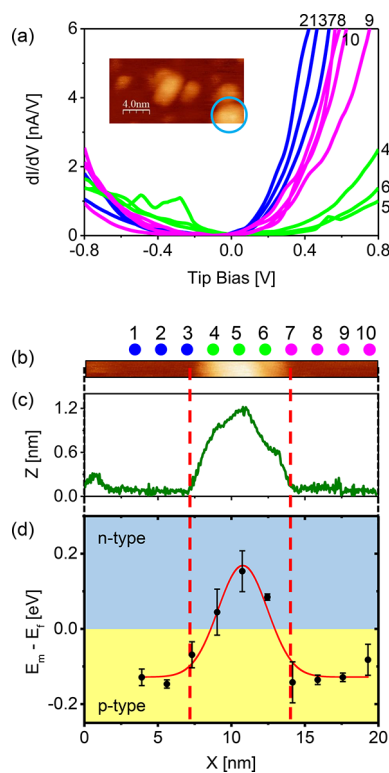
$$Q_0 = \frac{1}{e} [C_1 \Delta\Phi_1 - C_2 \Delta\Phi_2] \quad (1)$$

274 with  $C_i$  the capacitance of junction  $i$  and  $\Delta\Phi_i$  the difference in  
 275 work function across junction  $i$ ;  $i = 1$  indicates the tip-island  
 276 junction and  $i = 2$  the island-substrate junction. Here, we  
 277 observe a positive  $Q_0 > 0$ , and thus a positive value of the  
 278 contact potential, which indicates an n-type doping of the bP,  
 279 in agreement with our DFT calculations and literature.<sup>28,33</sup>

280 To corroborate these results and determine experimentally  
 281 the length scale of the electronic effect driven by copper, we  
 282 performed line-spectroscopic measurements across copper  
 283 islands, as shown in Figure 5. We measured in total five  
 284 different copper islands, and we see line spectra showing  
 285 consistent behavior. Figure 5 shows a series of tunneling  
 286 spectra laterally separated from each other by  $\sim 2$  nm. The  
 287 measurement spots follow a path across a copper island, as  
 288 shown in Figure 5b. The individual spots are color-coded, from  
 289 blue, the starting point of the path, to pink, the end point of  
 290 the path, both of which lie on the flat bP surface. The copper  
 291 island lies in between, with the corresponding green spots. For  
 292 each spot, six spectra were recorded, and the resulting averages  
 293 are shown in Figure 5a, using the same colors. The blue and  
 294 pink curves, corresponding to the data from bP, are clearly  
 295 different from the green curves measured on the copper island.  
 296 These observations are consistent with the spectra shown in  
 297 Figure 4 and thus demonstrate how reproducible these spectral  
 298 features are, and indicate a negligible drift of the tip during the  
 299 line STS measurement.

300 A height profile across the Cu island is reported in Figure 5c,  
 301 with two vertical dashed red lines marking the extremes of the  
 302 island. Figures 5b–d have the same  $x$ -axis, corresponding to  
 303 the scan size of the STM image. The midgap values obtained  
 304 from the spectra shown in Figure 5a are plotted versus lateral  
 305 position in Figure 5d. A clear transition from p-type (n-type)  
 306 to n-type (p-type) behavior can be seen in correspondence of  
 307 the extremes of the Cu island. The data points of Figure 5d are  
 308 well fitted with a Gaussian curve, centered at  $10.78 \pm 0.17$  nm  
 309 with a fwhm of  $3.96 \pm 0.47$  nm, in excellent agreement with  
 310 the center of the copper island. Our experimental observations  
 311 are in good agreement with the results shown in Figure 3d and  
 312 consistent with a strong quantum confinement of charge  
 313 transfer from copper to bP. Using the same technique of line-  
 314 spectroscopic measurements, similar short-ranged spectral  
 315 features have been previously reported for N-doped  
 316 graphene<sup>56</sup> and P-vacancies in bP.<sup>14</sup>

317 Our local investigation of bP doping induced by copper  
 318 islands shows that only the regions of bP lying in close  
 319 proximity to copper islands are significantly n-type doped,  
 320 while the regions of bP few nanometers away from the copper  
 321 islands still retain their intrinsic p-type doping. Thus, the  
 322 presence of isolated Cu-islands on bP implies the formation of  
 323 localized n-doped regions surrounded by intrinsic bP p-doped  
 324 regions. We anticipate that decreasing the copper island size  
 325 and increasing their density will result in homogeneously



**Figure 5.** Line STS across a single copper island. (a) Average spectra recorded along a line across a copper island, numbered corresponding to lateral spots shown in panels b. The copper island is shown in the 20 nm  $\times$  10 nm STM image in the inset (indicated by the blue circle). (b) 20 nm  $\times$  1 nm STM image of the copper island on bP on which the line STS measurement was performed. Spots of individual measurements are indicated by blue, green, and pink dots. (c) Height profile across the island. (d) Midgap value of individual spectra with respect to the Fermi level, plotted as a function of lateral position. The plot field is colored with yellow and blue to indicate p-type and n-type doping regions, respectively. The  $x$ -axes in panels b–d are the same. Two vertical dashed red lines show the position of the edges of the copper island. Scan parameters of the STM images in panels a and b and STS set point for all spectra: (–1.0 V, 0.33 nA). Between the spectra taken at various points along the line, the feedback loop was engaged.

doped n-type bP samples. Technically, this could be achieved  
 326 by sputter-deposition of Cu, as already demonstrated by  
 327 Koenig et al.<sup>28</sup> An alternative approach could be based on our  
 328 result that Cu clusters preferentially nucleate at Cu<sub>i</sub> sites. Thus,  
 329 one might influence the distribution of Cu by a defect  
 330 engineering of the P vacancies, for example by an ion  
 331 bombardment of the bP surface prior to Cu deposition. 332

In summary, our study provides a combined experimental  
 333 and theoretical in-depth understanding of the doping behavior  
 334 of Cu on bP at the nanoscale. STS measurements suggest  
 335 Coulomb blockade in the Cu islands and an n-type doping in  
 336 bP after Cu deposition, consistent with DFT predictions. The  
 337 DFT analysis also shows a decoupling of the topmost bP layer  
 338 in the presence of copper. Line-spectroscopy measurements  
 339 finally highlight that the doping effect of Cu on bP is short  
 340 ranged, in good agreement with the results of our DFT  
 341 calculations. This first STM investigation of Cu-doped bP at  
 342 the nanoscale is of significant importance both for a  
 343 fundamental understanding of the doping mechanisms and in  
 344 view of potential applications of this material in electronics.  
 345 Our results indicate a route toward ultrasharp p–n junctions in 346

347 bP, which would be exciting to explore in transport  
348 measurements on high-mobility bP and might enable  
349 observation of electro-optical effects in this material.<sup>57</sup>

## 350 ■ METHODS

351 Thin flakes of bP were prepared using the scotch tape  
352 exfoliation method. The exfoliated bP flakes were transferred  
353 onto monolayer graphene grown epitaxially on silicon carbide.  
354 This graphene film was used as a substrate and connected to  
355 ground potential. Details of sample preparation are reported  
356 elsewhere.<sup>35</sup> Typical dimensions of the bP flakes are area  $2.7 \pm$   
357  $3.2 \mu\text{m}^2$  and thickness  $37.5 \pm 22.4$  nm. All measurements  
358 presented here were performed on a flake 80 nm-thick. Copper  
359 was then deposited in situ via thermal evaporation using an  
360 EFM-3S e-beam evaporator, and surface investigations were  
361 performed at room temperature using an Omicron LT-STM.  
362 Theoretical investigation of both stability and electronic  
363 properties of Cu-doped bP was carried out by using a first-  
364 principles plane-wave pseudopotential implementation of  
365 density functional theory (DFT), as available in the Quantum  
366 ESPRESSO package.<sup>58,59</sup> The Perdew–Burke–Ernzerhof  
367 (PBE) generalized gradient approximation for the exchange-  
368 correlation functional was used,<sup>60</sup> and dispersion corrections  
369 were included within the semiempirical method developed by  
370 Grimme (DFT-D2).<sup>61</sup> Ultrasoft pseudopotentials were em-  
371 ployed as available in the SSSP Library.<sup>62</sup> Further details on  
372 experiment and theory are reported in the [Supporting](#)  
373 [Information](#).

## 374 ■ ASSOCIATED CONTENT

### 375 ■ Supporting Information

376 The Supporting Information is available free of charge at  
377 <https://pubs.acs.org/doi/10.1021/acs.jpcc.1c03531>.

378 Extended experimental methods, Raman spectroscopy  
379 measurements, STM images of bP surfaces before and  
380 after Cu deposition, stability of Cu islands, numerical  
381 details of DFT simulations, and complementary data  
382 ([PDF](#))

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## Notes

The authors declare no competing financial interest.

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559 number, we used 8.96 g/cm<sup>3</sup> as the copper density,  $1.055 \times 10^{-22}$  g as  
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