# Covalent Functionalization of GaP(110) Surfaces via a Staudinger-Type Reaction with Perfluorophenyl Azide

Miguel M. Ugeda,<sup>\*,†,‡,§,||</sup> Aaron J. Bradley,<sup>†</sup> Lucía Rodrigo,<sup> $\perp$ </sup> Min Yu,<sup>‡,#</sup> Wenjun Liu,<sup>‡, $\nabla$ </sup> Peter Doak,<sup>#, $\nabla$ </sup> Alexander Riss,<sup>†</sup> Jeffrey B. Neaton,<sup>†,#,O,•</sup> T. Don Tilley,<sup> $\nabla$ </sup> Rubén Pérez,<sup> $\perp$ ,¶</sup> and Michael F. Crommie<sup>\*,†,O,•</sup>

<sup>†</sup>Department of Physics and <sup>∇</sup>Department of Chemistry, University of California at Berkeley, Berkeley, California 94720, United States

<sup>‡</sup>Joint Center for Artificial Photosynthesis, <sup>#</sup>Molecular Foundry, and <sup>O</sup>Material Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

<sup>§</sup>CIC nanoGUNE, San Sebastián 20018, Spain

<sup>II</sup>Ikerbasque, Basque Foundation for Science, Bilbao 48011, Spain

<sup>⊥</sup>Departamento de Física Teórica de la Materia Condensada and <sup>¶</sup>Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, E-28049 Madrid, Spain

◆Kavli Energy Nanosciences Institute at Berkeley, Berkeley, California 94720, United States

**Supporting Information** 



**ABSTRACT:** Despite the markedly low chemical reactivity of the nonpolar (110) surfaces of III–V semiconductors, the covalent functionalization of GaP(110) surfaces with perfluorophenyl azide (PFPA) molecules by a Staudinger-type reaction occurs only slightly above room temperature (325 K). Scanning tunneling microscopy observations, combined with density functional theory calculations, support the formation of stable, covalent perfluorophenyl nitride (PFPN) molecule–surface bonds, which can be described as Lewis acidic Ga-stabilized phosphine imides.  $\pi-\pi$  stacking between aromatic, electron-deficient PFPN units results in compact, commensurate 2D molecular assembly at the surface. PFPA deposition on GaP(110) at room temperature with no additional annealing leads to an intermediate phase consistent with an alternating 1D array of physisorbed and chemisorbed molecular units. This work provides a new route for covalently bonding molecular linkages to the (110) surfaces of III–V semiconductors.

C hemical functionalization is widely used for tailoring the fundamental properties of semiconductor surfaces for a variety of applications.<sup>1-3</sup> For example, controlled covalent attachment of molecular species onto III–V semiconducting surfaces is being pursued in areas that include sensing,<sup>4</sup> electrooptical,<sup>5</sup> and catalytic<sup>1</sup> applications. For zinc-blende III–V semiconductors, the chemistry of the (100) and (111) surfaces is relatively well understood and a wealth of attachment strategies are known.<sup>4,6,7</sup> However, these strategies do not apply to the (110) surface and covalent functionalization of this surface has been much less successful. The most promising approach so far has involved organothiol surface

reactions,<sup>8–12</sup> but the structure of the resulting molecule– surface bonds remains elusive. Poor stability<sup>9,10,13</sup> and lack of long-range order<sup>11</sup> at room temperature for the thiol-derived layers obtained in this way limit the utility of this functionalization strategy.

The (110) surface is different from the more commonly studied crystal faces of zinc-blende III–V semiconductors in

Received:October 24, 2016Revised:October 27, 2016Published:October 31, 2016



**Figure 1.** (a) Sketch of the relaxed GaP(110) surface. The lone pair on the anion ( $P^-$ ) and the empty  $p_z$  orbital on the cation (Ga<sup>+</sup>) are depicted. (b) Staudinger reaction between a triaryl phosphine and an azide forming a phosphine imide. (c) Staudinger-type reaction on the GaP(110) surface with perfluorophenyl azide to form Lewis acidic surface Ga-stabilized phosphine imides. (d) Atomically resolved STM image of the bare GaP(110) surface before PFPA adsorption ( $V_s = +3$  V,  $I_t = 30$  pA, T = 7 K).

that it is neither strongly polar nor highly reactive. For example, while ethylene chemisorbs readily onto both Ga- and Asterminated GaAs(100) surfaces at room temperature,<sup>14</sup> it is unstable on the (110) surface of GaP except for very low temperatures.<sup>15</sup> (110) planes do develop a slight polar character upon reconstruction (see Figure 1a), but the partial polar character of the alternating nucleophilic (anionic lone pairs) and electrophilic (cationic with empty  $p_z$  orbitals) centers has not yet been exploited in chemical reactions. A possible chemical route is suggested by the fact that the P surface atoms of GaP(110) exist in environments resembling tertiary phosphines, which undergo the Staudinger reaction<sup>16</sup> with azide molecules to afford phosphine imides with loss of dinitrogen  $(N_2)$  (see Figure 1b). A heterogeneous version of the Staudinger reaction on the GaP(110) surface should then vield phosphine imide moieties containing P-N surfacemolecule bonds (see Figure 1c). Moreover, the Lewis acidic Ga atoms, adjacent to the P sites, might interact with the Lewis basic N atoms of the phosphine imide to form Ga-N bonds. Molecular examples of phosphine imides displaying such bonding interaction between Lewis basic N and certain Lewis acids, including a triaryl gallium, have been reported.<sup>17,18</sup>

Here we present combined scanning tunneling microscopy (STM) and density functional theory (DFT) of the thermally activated surface reaction between perfluorophenyl azides (C<sub>6</sub>F<sub>5</sub>N<sub>3</sub>, PFPA) and GaP(110). Our results provide strong evidence for the formation of covalent molecule–surface bonds in a three-membered-ring configuration (P–N–Ga) featuring both P–N and Ga–N interactions consistent with a Staudinger-type reaction at the GaP(110) surface. Interestingly, the noncovalent molecule–molecule  $\pi$  interaction between aromatic perfluorophenyl units (C<sub>6</sub>F<sub>5</sub><sup>-</sup>) also plays an important role in this surface reaction, by driving the formation of long-range, well-ordered supramolecular structures. We additionally find an intermediate state of this reaction at room temperature in which the molecular units form one-dimensional (1D) chains.

GaP(110) surfaces were obtained by mechanical cleavage under ultrahigh vacuum conditions at room temperature. This procedure yields high-quality flat surfaces with a low density of intrinsic defects<sup>15</sup> (see Figure 1d) that are ideal for chemical functionalization. PFPA molecules were subsequently deposited in situ onto the GaP(110) surfaces at room temperature. The STM image in Figure 2a shows the typical morphology of the



**Figure 2.** (a) Morphology of the GaP(110) surface after exposure to 0.7 L of PFPA at room temperature ( $V_s = -2.7$  V,  $I_t = 15$  pA, T = 7 K). High-resolution STM images (T = 7 K) of a 1D molecular chain are shown in (b) for occupied states ( $V_s = -3.2$  V,  $I_t = 100$  pA) and (c) for unoccupied states ( $V_s = +2.8$  V,  $I_t = 15$  pA).

GaP(110) surface after dosing with 0.7 langmuir (L) of PFPA at room temperature and cooling down to T = 7 K. The PFPA molecules are mobile at room temperature and diffuse along the surface to form 1D chains along two equivalent crystallographic directions that form an angle of 54° with respect to the [001] direction of the substrate. The molecular chains are typically composed of 2–10 repeating units and have a unit cell 9.2 Å long. Both the orientation and spacing observed in the chains can be described by a commensurate periodicity along  $\mathbf{A} = 2\mathbf{a} + \mathbf{b}$ , with the unit cell vectors  $\mathbf{a} =$  $(1\overline{10})$  and  $\mathbf{b} = (001)$  (see Supporting Information). The



**Figure 3.** (a) STM image of the GaP(110) surface after annealing the samples shown in Figure 2a at 325 K for 10 min ( $V_s = -3$  V,  $I_t = 30$  pA, T = 7 K). Close-up STM images (T = 7 K) of a 2D molecular island are shown in (b) for occupied states ( $V_s = -2.5$  V,  $I_t = 40$  pA) and (c) for unoccupied states ( $V_s = +2.4$  V,  $I_t = 40$  pA). Calculated STM images of the 1 × 1-PFPN/GaP(110) surface are shown in (d) for occupied states ( $V_s = -3$  V) and (e) for unoccupied states ( $V_s = +3.8$  V). f) Simulated relaxed structure for PFPN molecules on GaP(110). (g) Perspective view of the relaxed PFPN/GaP(110) surface showing the 1 × 1 close-packed stacking.

apparent height of the chains is approximately 5 Å, suggesting a vertical configuration for the molecules. This is further supported by comparison with the apparent height of only 1.3 Å for nearly flat-lying iodobenzene molecules ( $C_6H_5I$ ) on GaP(110) (see Supporting Information). Close-up views of the PFPA chains for both occupied and unoccupied states are presented in Figure 2b,c. Occupied-state STM images show two parallel sets of protrusions arranged in a 1D configuration (Figure 2b). At this bias polarity, both types of protrusions exhibit slightly different heights (5.5 Å vs 4.5 Å). Unoccupied-state STM images, however, show a single set of protrusions along the molecule chain (Figure 2c).

In order to test the stability and molecule–surface bonding properties of the 1D phase of PFPA/GaP(110), we gently annealed the PFPA/GaP(110) samples up to 325 K. Such annealing was enough to induce structural changes in the 1D phase and result in a new surface molecular arrangement, as seen in Figure 3a. Here the molecules are seen to rearrange into two-dimensional (2D) islands from the initial chain configuration. Similar to the case of the intermediate 1D phase, bias-dependent STM images of the 2D phase reveal different atomic-scale features (Figure 3). For occupied states the molecular islands in the STM images appear striped with straight rows running parallel to the atomic Ga–P rows along to  $\mathbf{a} = [1\overline{10}]$  (Figure 3b). These rows are offset from one another by 5.5 Å in the  $\mathbf{b} = [001]$  direction (perpendicular to  $\mathbf{a}$ ), a value equal to the surface unit cell length in that direction.

Unoccupied-state STM images (Figure 3c) further resolve the internal structure of the molecular rows to reveal elongated protrusions separated by 3.9 Å, a value equal to the surface unit cell length along **a**. These protrusions exhibit a long axis that is tilted by  $20 \pm 3^{\circ}$  from the [001] direction. This 2D island phase thus appears to be formed by molecular units in a highly packed (1 × 1) configuration.

To better understand the structure and chemical stability of these intermediate (Figure 2) and product (Figure 3) molecular phases on GaP(110), we simulated the system through DFT calculations using an exchange–correlation functional that includes van der Waals (vdW) interactions (see Supporting Information for further details). The highly packed molecular phase observed after annealing was modeled by positioning one PFPN ( $C_6F_5N$ ) molecule per surface unit cell (1 × 1). This is justified since phenyl azide releases N<sub>2</sub> upon thermal activation to form the highly reactive singlet phenyl nitrene.<sup>19</sup>

Figure 3f,g shows the energetically optimized structure for the simulated  $1 \times 1$ -PFPN/GaP(110) surface. This compact PFPN stacking is stable with the phenyl rings vertically oriented and bonded to the surface through the remaining N atom. The DFT–vdW binding energy (see Supporting Information) of a PFPN molecule in this  $1 \times 1$  phase is 1.98 eV. We estimate that vdW interactions account for ~55% of the total binding energy via both molecule–substrate and intermolecular bonding. Here each PFPN molecule is bonded to the surface via the formation of a three-membered Ga–P–N ring containing both P–N and

#### The Journal of Physical Chemistry C

Ga–N covalent bonds. Despite the dominant role of the covalent molecule–substrate interaction on the molecular assembly, intermolecular interactions cause the phenyl rings aligned parallel to the  $[1\overline{10}]$  direction to tilt by  $17^{\circ}$  from the [001] direction (see sketch in Figure 3e). This tilt results from a balance between attractive interactions that favor a parallel alignment of the molecular rings and steric repulsion that forces the molecules apart.

The calculated structure of the 2D molecular assembly that covalently functionalizes the GaP(110) surface is confirmed by comparing experimental STM images (Figure 3b,c) to simulated ones (Figure 3d,e) obtained within the Tersoff-Hamann approximation.<sup>20</sup> The occupied electronic state density (Figure 3d) arises primarily from the intermolecular hybridization of molecular orbitals (MOs) having p character that extend across the phenyl rings. Due to the parallel stacking of the phenyl rings, these MOs overlap and localize the charge density along the  $[1\overline{10}]$  direction. The calculated STM image for occupied states (Figure 3d) thus shows 1D chains of charge density along the stacking direction that are spaced by 5.5 Å, in good agreement with the corresponding experimental STM image (Figure 3b) (internal structure within the chains was not observed experimentally, likely due to the finite width of the tip). The simulated unoccupied-state STM image (Figure 3e) is dominated by PFPN MOs with s and p character that show two lobes localized within each phenyl ring. The simulated images are thus seen as elongated features tilted 20° from the [001] direction (Figure 3e). This simulated behavior is consistent with the experimental images for unoccupied states (Figure 3c), and allows us to identify the experimentally observed elongated protrusions with individual PFPN molecules. Since the optimized geometry of the simulation accurately reproduces both the experimentally observed molecular adsorption site and the main features of the STM images for both filled and empty states, we conclude that the adsorption and thermal activation of PFPA molecules lead to covalent functionalization of the GaP(110) surface with PFPN units.

Lastly, we address the nature of the 1D nanostructures observed as an intermediate state (before annealing) of the reaction of PFPA on GaP(110). Our bias-dependent STM imaging of these 1D chains (Figure 2b,c) indicates a more complex molecular structure than a simple 1D  $\pi$ - $\pi$  stacking of molecules as previously reported for phenyl group functionalization of silicon surfaces.<sup>21,22</sup> We calculated several possible configurations of PFPA and PFPN molecules consistent with the observed orientation of the molecular chains on the GaP(110) surface. Of these, just one structure was compatible with our bias-dependent STM images. This structure contains one PFPA molecule and one PFPN molecule per unit cell, with a DFT-vdW binding energy of 3.81 eV. This implies a lower average binding energy per molecule (1.91 eV) compared to the annealed phase (1.98 eV), as expected for a less stable intermediate configuration. Calculated images of this structure show good qualitative agreement with our STM chain images (see Supporting Information). The coexistence of PFPA and PFPN molecules in this intermediate phase is compatible with two experimental observations: (i) the necessity of thermal activation to form the covalent close-packed PFPN phase (Figure 3) and (ii) the relatively small energy barrier to inducing N2 detachment from PFPA and subsequent full PFPN passivation of GaP(110). The formation of 1D chains shows the large role played by molecule-molecule interactions in the early stage of the reaction.

In conclusion, we have demonstrated the reaction of perfluorophenyl azide on the (110) surface of GaP, a prototypical III–V semiconductor. This heterogeneous surface reaction, derived from a Staudinger reaction, leads to stable molecular functionalization of the surface that is stable at room temperature. Molecule–molecule interactions are seen to promote ordered molecular organization into long-range, close-packed 2D structures. Considering the wide range of azide molecules available, this novel functionalization strategy creates a new opportunity for modifying III–V semiconductor (110) surfaces for different purposes.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b10691.

Experimental section, materials and DFT details; morphology of GaP(110) surface after PFPA deposition; apparent height of phenyl-based nanostructures on GaP(110); DFT model of intermediate state; evolution of reaction from intermediate to product state (PDF)

#### AUTHOR INFORMATION

#### **Corresponding Authors**

\*E-mail: mmugeda@nanogune.eu. Tel.: +34 943 574 046. \*E-mail: crommie@berkeley.edu. Tel.: (510) 642-9392.

12-mail: cromme(aberkeley.edu. 1ei.: (510) 042-9392.

## Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This research was supported by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award No. DE-SC0004993 (PFPA chemical synthesis and theory) and by the DOE Nanomachine program Award no. DE-ACO2-05CH11231 (PFPA/GaP surface functionalization and STM imaging). L.R. and R.P. acknowledge the financial support of MINECO (projects CSD2010-00024, MAT2011-23627 and MAT2014-54484-P). Computer time was provided by the Lawrence Berkeley National Laboratory facilities and the Spanish Supercomputing Network (RES). Experimental and simulated STM images were rendered using WSxM software.<sup>23</sup>

#### REFERENCES

(1) Lewis, N. S. Chemical Control of Charge Transfer and Recombination at Semiconductor Photoelectrode Surfaces. *Inorg. Chem.* **2005**, *44*, 6900–6911.

(2) Liu, L. H.; Yan, M. D. Perfluorophenyl Azides: New Applications in Surface Functionalization and Nanomaterial Synthesis. *Acc. Chem. Res.* **2010**, *43*, 1434–1443.

(3) Somorjai, G. A.; Li, Y. M. Impact of Surface Chemistry. Proc. Natl. Acad. Sci. U. S. A. 2011, 108, 917–924.

(4) Seker, F.; Meeker, K.; Kuech, T. F.; Ellis, A. B. Surface Chemistry of Prototypical Bulk II-VI and III-V Semiconductors and Implications for Chemical Sensing. *Chem. Rev.* **2000**, *100*, 2505–2536.

(5) Mokkapati, S.; Jagadish, C. III-V Compound SC for Optoelectronic Devices. *Mater. Today* **2009**, *12*, 22–32.

(6) Lebedev, M. V. Surface Modification of III-V Semiconductors: Chemical Processes and Electronic Properties. *Prog. Surf. Sci.* 2002, *70*, 153–186.

(7) Richards, D.; Luce, P.; Zemlyanov, D.; Ivanisevic, A. Quantitative Analysis of the Functionalization of Gallium Phosphide with Organic Azides. *Scanning* **2012**, *34*, 332–340.

(8) Ohno, H.; Motomatsu, M.; Mizutani, W.; Tokumoto, H. AFM Observation of Self-Assembled Monolayer Films on GaAs(110). *Jpn. J. Appl. Phys.* **1995**, *34*, 1381–1386.

(9) Camillone, N.; Khan, K. A.; Osgood, R. M. The Thermal Chemistry of Model Organosulfur Compounds on Gallium Arsenide (110). *Surf. Sci.* **2000**, *453*, 83–102.

(10) Rodriguez, L. M.; Gayone, J. E.; Sanchez, E. A.; Grizzi, O.; Blum, B.; Salvarezza, R. C.; Xi, L.; Lau, W. M. Gas Phase Formation of Dense Alkanethiol Layers on GaAs(110). *J. Am. Chem. Soc.* **2007**, *129*, 7807–7813.

(11) McGuiness, C. L.; Diehl, G. A.; Blasini, D.; Smilgies, D. M.; Zhu, M.; Samarth, N.; Weidner, T.; Ballav, N.; Zharnikov, M.; Allara, D. L. Molecular Self-Assembly at Bare Semiconductor Surfaces: Cooperative Substrate Molecule Effects in Octadecanethiolate Mono Layer Assemblies on GaAs(111), (110), and (100). ACS Nano 2010, 4, 3447–3465.

(12) Rodriguez, L. M.; Cristina, L. J.; Alarcon, L. S.; Blum, B.; Salvarezza, R. C.; Xi, L.; Lau, W. M.; Sanchez, E. A.; Gayone, J. E.; Grizzi, O. Adsorption and Thermal Stability of Alkanethiol Films on GaAs(110): A Comparative Study by TOF-DRS and TOF-SIMS. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2011**, *269*, 924–931.

(13) Donev, S.; Brack, N.; Paris, N. J.; Pigram, P. J.; Singh, N. K.; Usher, B. F. Surface Reactions of 1-Propanethiol on GaAs(100). *Langmuir* **2005**, *21*, 1866–1874.

(14) Chen, Y.; Barnard, J. C.; Siller, L.; Schmidt, J.; Palmer, R. E. Adsorption and Decomposition of Ethylene  $(C_2H_4)$  on GaAs(100). *Surf. Sci.* **1999**, 441, 192–198.

(15) Ugeda, M. M.; Yu, M.; Bradley, A. J.; Doak, P.; Liu, W. J.; Moore, G. F.; Sharp, I. D.; Tilley, T. D.; Neaton, J. B.; Crommie, M. F. Adsorption and Stability of  $\pi$ -Bonded Ethylene on GaP(110). *J. Phys. Chem.* C **2013**, *117*, 26091–26096.

(16) Staudinger, H.; Meyer, J. On New Organic Phosphorus Bonding. *Helv. Chim. Acta* 1919, 2, 612–618.

(17) Wei, P. R.; Chan, K. T. K.; Stephan, D. W. Metallated Triphenylphosphinimine Complexes. *Dalton Trans.* **2003**, 3804–3810.

(18) Kano, N.; Yanaizumi, K.; Meng, X. T.; Kawashima, T. Control of Reactivity of Phosphine Imides by Intramolecular Coordination with an Organoboryl Group. *Heteroat. Chem.* **2012**, *23*, 429–434.

(19) Poe, R.; Schnapp, K.; Young, M. J. T.; Grayzar, J.; Platz, M. S. Chemistry and Kinetics of Singlet (Pentafluorophenyl)Nitrene. *J. Am. Chem. Soc.* **1992**, *114*, 5054–5067.

(20) Tersoff, J.; Hamann, D. R. Theory of the Scanning Tunneling Microscope. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1985**, 31, 805–813.

(21) Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. Self-Directed Growth of Molecular Nanostructures on Silicon. *Nature* 2000, 406, 48–51.

(22) Hossain, M. Z.; Kato, H. S.; Kawai, M. Competing Forward and Reversed Chain Reactions in One-Dimensional Molecular Line Growth on the Si(100)-( $2 \times 1$ )-H Surface. *J. Am. Chem. Soc.* **2007**, 129, 3328–3332.

(23) Horcas, I.; Fernández, R.; Gómez-Rodríguez, J. M.; Colchero, J.; Gómez-Herrero, J.; Baró, A. M. WSxM: A Software for Scanning Probe Microscopy and a Tool for Nanotechnology. *Rev. Sci. Instrum.* **2007**, 78, 013705.