

A Stress-Free and Textured GaP Template on Silicon for Solar Water Splitting

Ida Lucci, Simon Charbonnier, Maxime Vallet, Pascal Turban, Yoan Léger, Tony Rohel, Nicolas Bertru, Antoine Létoublon, Jean-Baptiste Rodriguez, Laurent Cerutti, et al.

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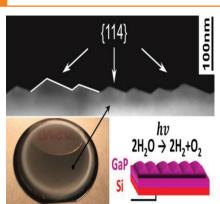
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FULL PAPERS

Water Splitting



A large-scale stress-free textured GaP template monolithically integrated on Si is by surface energy engineering, for water-splitting applications. The stability of GaP{114} facets is examined thermodynamically. The benefits of using $\frac{1}{7}$ a textured (114)A GaP/Si template for water-splitting applications, in terms of $\frac{\circ}{9}$ surface gain, band lineups, and ohmic 10 contacts are finally discussed.

FULL PAPER

Water Splitting

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A Stress-Free and Textured GaP Template on Silicon for Solar Water Splitting

Ida Lucci, Simon Charbonnier, Maxime Vallet, Pascal Turban, Yoan Léger, Tony Rohel, Nicolas Bertru, Antoine Létoublon, Jean-Baptiste Rodriguez, Laurent Cerutti, Eric Tournié, Anne Ponchet, Gilles Patriarche, Laurent Pedesseau,* and Charles Cornet*

13 This work shows that a large-scale textured GaP template monolithically inte-14 grated on Si can be developed by using surface energy engineering, for water-15 16 splitting applications. The stability of (114)A facets is first shown, based on 17 scanning tunneling microscopy images, transmission electron microscopy, 18 and atomic force microscopy. These observations are then discussed in terms 19 of thermodynamics through density functional theory calculations. A stress-20 free nanopatterned surface is obtained by molecular beam epitaxy, composed 21 22 of a regular array of GaP (114)A facets over a 2 in. vicinal Si substrate. The 23 advantages of such textured (114)A GaP/Si template in terms of surface gain, 24 band lineups, and ohmic contacts for water-splitting applications are finally 25 discussed. 26

29 30 **1. Introduction**

Solar photoelectrochemical (PEC) water-splitting devices have 31 32 attracted interest for decades with the ultimate objective to convert and store the solar energy into clean hydrogen fuel^[1,2] 33 34 at a lower production cost and environmental impact. Indeed, 35 more than 90% of the hydrogen production is today made by 36 steam methane reforming which releases carbon monoxide/ 37 dioxide and heat into the atmosphere while global warming is an issue.^[3] The conversion of solar energy into hydrogen 38 39 production through a water-splitting process assisted by 40

catalysts^[4,5] photosemiconductor is 13 definitely the most promising tech- 14 nology for the near future with potentially 15 plethora of hydrogen provided in a clean 16 and sustainable manner. Many recent 17 proposals deal with the use of the GaP 18 semiconductor as a photoelectrode in PEC 19 devices,^[6] especially because its bandgap 20 (2.26 eV) is larger than the 1.73 eV photo- 21 potential needed for water splitting.^[7] 22 Using this idea, demonstrations of GaP- 23 based PEC devices^[8-11] and descriptions of 24 the physics/chemistry of the standard GaP 25 surface.^[12] its interaction with water^[13,14] 26 and hydrogen generation^[15] were reported. 27 To enhance conversion efficiency of GaP-28

based PEC devices, strategies like surface functionalization,^[10] 29 use of plasmon resonant nanostructures,^[16] or integration of 30 nanowires^[17] were considered. Meanwhile, it was demonstrated 31 recently that the texturation of surfaces at the electrode level 32 greatly enhances the efficiency of BiVO₄ photoanodes in PEC 33 devices.^[18] Structuration of semiconductor surfaces can be per-34 formed by lithography techniques,^[19] chemical processes,^[20,21] 35 nanowires, or by a self-organization during the epitaxial process 36 of the material itself.^[22] This last approach is usually driven 37 by crystal strain-relief processes; it simplifies the postgrowth 38 device processing but does not offer large degrees of freedom, 39

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while keeping a crystal quality compatible with operating
devices. The need for a scalable PEC device, in view of its very
large-scale integration was also pointed out.^[23] In this regard,
GaP presents several advantages. Among them, its monolithic
integration on silicon leads to a high crystal quality, due to
the low lattice mismatch between GaP and Si (0.36% at room
temperature).^[24]

8 In this work, we show that a large-scale textured GaP template monolithically integrated on Si can be developed by using 9 surface energy engineering. We first evidence the remarkable 10 11 stability of (114)A GaP facets, based on scanning tunneling microscopy (STM) images, transmission electron microscopy 12 (TEM), and atomic force microscopy (AFM). Facets stabiliza-13 tion is also discussed in terms of thermodynamics through 14 density functional theory (DFT) calculations. We then demon-15 strate that a stress-free nanopatterned surface can be grown by 16 17 molecular beam epitaxy (MBE), composed of a regular array of 18 (114)A facets over a 2 in. vicinal Si substrate. We finally assess 19 the potentiality of the textured (114)A GaP/Si template toward 20 water-splitting applications.

21 22

$\frac{23}{24}$ 2. Results and Discussions

25 2.1. Textured GaP Surface on Si(001) 6°-off

26 27 To design efficiently a textured semiconductor surface, a good 28 knowledge of the non-(001) most stable surfaces is needed. Stable facets are easily identified in stress-induced nanostruc-29 30 tures, such as quantum dots.^[25] But it is also possible to use stress-free surface structures whose formation is highly cor-31 32 related to emerging defects, for instance, antiphase domains 33 (APDs) separated by emerging antiphase boundaries (APBs).^[26] 34 In this regard, a 10 nm thick GaP has been grown on a freshly 35 prepared HF-last Si(001) substrate. Before starting the GaP/ 36 Si(001) growth process, the silicon substrate has been annealed 37 at 800 °C in order to desorb the hydrogen. With this preparation (without Si buffer layer), the Si surface remains bi-domain. 38 39 After that, the GaP was grown at 350 °C by molecular beam epitaxy using migration enhanced epitaxy (see refs. [24,27,28] for 40 growth procedure and apparatus description). This layer was 41 42 further annealed at 500 °C. An amorphous As capping layer 43 was then deposited at cryogenic temperatures to avoid any air contamination during transfer to the STM ultrahigh vacuum 44 45 (UHV) chamber, as explained in refs. [25,29]

Figure 1a shows the STM image of the 10 nm thick GaP/ 46 Si surface. Two antiphase domains are observed. Each domain 47 48 is first characterized by a large (001) surface where the dimers 49 are aligned along the local [1-10] directions. Different facets can 50 be identified at the boundaries where the two domains coa-51 lesce. Among the different facets observed, {136}, {113}, and 52 (114)A and B are clearly identified by their angle and surface 53 reconstructions. Especially, as highlighted in Figure 1a, the 54 surface is quantitatively mainly covered by {114} and (001) 55 facets. The stability of GaAs{114}A or InGaAs {114}A facets was already widely discussed in the literature.^[30–32] The work 56 57 of Yamada et al., who performed STM investigations, showed low kink density and a highly uniform surface structure for the 58 59 GaAs{114}A facets. Márquez et al. also observed a well-ordered



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Laurent Pedesseau obtained his M.Sc. in condensed matter from the University of Montpellier in 2001. In 2004, he received his Ph.D. in physics from the University of Toulouse for atomistic empirical simulations applied to civil engineering materials. In 2013, he was appointed as assistant professor at FOTON Institute (INSA Rennes) to

work on III–V semiconductor nanostructures for silicon photonics, hybrid-perovskites for photovoltaics, and optoelectronic device simulations for optical telecommunication.



Charles Cornet received his Ph.D. degree in physics from Institut National des Sciences Appliquées, Rennes, France, in 2006 for his contribution to the understanding of electronic, optical, and dynamic properties of coupled self-assembled InAs/InP quantum dots. Since 2007, he is assistant professor Hab. at FOTON laboratory, specialist

of MBE material growth, structural and optical properties of III–V semiconductor nanostructures and devices, and their integration on silicon. Since 2017, he leads the "Optoelectronics, Heteroepitaxy and Materials" research group of the FOTON Institute.

 $GaAs(114)A\alpha 2(2 \times 1)$ reconstruction, discussing its relative stability with respect to the $GaAs(001)A\beta 2(2 \times 4)$ one with ab initio calculations. 57

To promote $\{114\}A$ surface texturation, we need thermodynamic conditions where the energy of the $\{114\}A$ faceted 59



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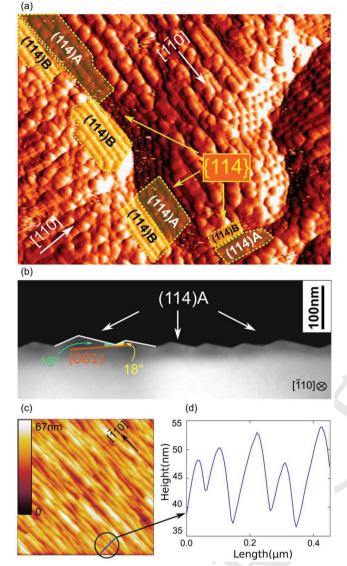


Figure 1. a) $25 \times 30 \text{ nm}^2$ STM image of a bi-domain 10 nm thick GaP on Si(001) evidencing the presence of numerous (114)A and B facets at the antiphase boundaries edges. b) TEM image of 1 µm thick GaP on Si 6°-off. c) 3 µm × 3 µm AFM image of the surface of the same sample as (b). (d) A profile taken by small region of the AFM image. TEM and AFM observations show the (114)A faceting of the GaP surface.

surface is lower than the {001} one, that is, by developing a surface energy engineering approach. To this aim, a 1 µm thick GaP sample was grown on a vicinal Si (001)-6°-off substrate. Corresponding TEM and AFM images and profiles are shown in Figure 1a,c,d. In this sample, most of the antiphase domains (APDs) were annihilated within the first 20 nm, by using AlGaP filtering layers, as demonstrated in the TEM image of ref. [24] The remaining GaP is grown at 580 °C, with an intermediate beam equivalent pressure (BEP) V/III ratio of 4. The crystal growth was monitored in situ using reflection high-energy electron diffraction (RHEED) experiments. The 1 µm thickness is well above the critical thickness, and X-ray diffraction experi-58 ments (not shown here) reveal an overall full relaxation of the 59 GaP crystal. Figure 1b shows the (110) cross-sectional TEM

image of the sample. The surface presents a saw-tooth profile 1 along the lateral (110) direction. All facets have an angle with 2 the (001) plane between 18° and 20° , close to the theoretical 3 angle calculated for the {114} facets, that is, $\theta = 19.48^{\circ}$. The 4 average distance between two maxima is 100 nm with a disper- 5 sion of 40%. In the TEM image, left-oriented and right-oriented 6 (114)A facets present different widths. The saw-tooth asym-7 metry allows compensating the 6°-miscut of the silicon sub- 8 strate. It is important to note that (001) facets are completely 9 missing. We also point out that (114) facets are parallel to the 10 step edges direction of the vicinal silicon substrate, suggesting 11 that the direction of the substrate miscut determines the domi-12 nant polarity of the grown GaP. We also note that emerging dis-13 location density remains low on this relaxed sample, because of 14 15 the low lattice mismatch.

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Interestingly, these facets were also observed by RHEED. 16 During the growth a thin and streaky pattern, orientated with 17 a 15°-20° angle from the conventional (001) usual RHEED 18 diffraction direction was observed. Even if the RHEED appa- 19 ratus used in this study does not allow to determine precisely 20 the observed reconstruction, diffraction lines were found to 21 be remarkably thin as compared to the usual (2×4) (001) GaP 22 ones, suggesting a good planarity of the facets. We also note 23 here that similar observations were done on more than ten dif-24 ferent samples, grown in the same conditions, showing the 25 reproducibility of the process. 26

The resulting surface pattern is also highlighted in Figure 1c 27 where a plan-view AFM image is shown. The corresponding saw-28 tooth profile is also given in Figure 1d. Here, the measured pro-29 file is smoother than the one obtained with TEM measurements, 30 because of AFM tip convolution effects. A strong anisotropy of the 31 surface structuration is revealed. The typical length of one facet is 32 larger than 2 µm, to be compared to the 100 nm average distance 33 between saw-tooth profile. This confirms that antiphase domains 34 have been well annihilated, over the observed $3 \times 3 \text{ } \text{um}^2$ sur-35 face. The morphologies observed by TEM and AFM thus clearly 36 show that in these conditions the (001) GaP surface is unstable 37 against (114)A faceting. It experimentally suggests that the 38 energy surface of the (114)A surface over $\cos(\theta)$ is here lower 39 than the (001) surface energy. Interestingly, it is worth men- 40 tioning that a similar growth on the GaP native substrate does 41 not lead to any {114} surface structuration indicating that growth 42 on the vicinal silicon substrate impacts the surface properties. 43

Beyond the use of a vicinal substrate, we have also observed 44 that changing group-V atmosphere above the surface on a 45 nominal GaP substrate, can be another strategy for surface 46 energy engineering promoting a textured-surface formation 47 on GaP. Indeed, the textured behavior was obtained by simply 48 exposing the GaP surface under Sb atmosphere (Figure S1, 49 Supporting Information). Besides III-Vs systems, a similar 50 surface energy engineering strategy has also been developed to 51 control the growth morphology by promoting a 2D-3D transi-52 tion for growing self-assembled II-VI and nitride quantum 53 dots (QDs).^[33-35] Indeed, in both the cases, the SK transition 54 was interpreted as a surface energy change due to a saturation 55 of the dangling bonds by changing the species exposure. Never- 56 theless, all the present observations demonstrate that there is a 57 real competition between the growth of a (001) surface and the 58 (114)A faceting. 59

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2.2. Surface Energies Computed by DFT

3 The stability of the {114} facets is discussed thermodynami-4 cally in the following. The DFT is used to estimate the surface 5 energy of the (001) polar GaP surface and the (114) A and B polar GaP surfaces. Every surface considered in this work ful-6 7 fills the electron counting model (ECM).^[36] For both (001) and 8 {114} facets, P-rich and Ga-rich reconstructions are considered. 9 In the case of the nonpolar GaP(001) surface, two different (2×4) reconstructions are computed. For the Ga-rich GaP(001) 10 surface, the GaP(001)md(2×4)^[37,38] reconstruction (where md 11 stands for mixed dimers) is assumed. This reconstruction is 12 often considered for Ga-rich conditions in the literature.^[12,14,39] 13 For the P-rich GaP(001) surface, different stable structures were 14 proposed^[40] and H-passivated reconstructions were consid-15 ered for metal-organic chemical vapor deposition growth or in 16 17 the context of water-splitting applications.^[14,41,42] In this study 18 where samples are grown by MBE, we use a simple anion (P)-19 rich GaP(001) surface that fulfills the ECM criteria as proposed for GaAs.^[36] We believe that any change of this reconstruction 20 21 does not qualitatively affect the main conclusions of the study.

22 For the polar GaP(114) surfaces, two types of (2×1) recon-23 structions have been simulated: the Ga-rich GaP(114)A- $\alpha 2(2 \times 1)$ 24 and the P-rich GaP(114)B- $\alpha 2(2 \times 1)$ which are similar to the ones already thoroughly investigated for the GaAs(114).[31,43,44] 25 26 While simple subtraction methods can be used to compute surface energies of nonpolar surfaces such as the GaP(001) ones, 27 28 fictitious hydrogen methods have to be used to compute A 29 and B polar surfaces independently with a good accuracy (see the Supporting Information for a detailed surface structures 30 31 description). In the case of nonstoichiometric surfaces such as the (001) surfaces considered here, surface atoms are in equi-32 librium with a reservoir, therefore the computed surface energy 33 34 strongly depends on the chemical potential μ and the surface 35 stoichiometry $\Delta N = N_{\rm P} - N_{\rm Ga}$.^[45]

36 The general equation used to determine the surface energies is

$$\begin{array}{l} 38 \quad \gamma_{\text{surface}} A = E_{\text{slab}} - \sum_{i} \mu_{i} N_{i} \end{array} \tag{1}$$

40 where γ_{surface} is the surface energy, *A* the surface area, *E*_{slab} is 41 the slab energy calculated by DFT, μ_i is the chemical potential 42 of the species *i* (where *i* is Ga or P), and N_i is the number of 43 particles of the species *i* of the slab. The temperature depend-44 ence is ignored because the contributions tend to cancel for 45 free-energy differences as claimed for the GaAs material in a 46 previous study.^[46]

In Figure 2, the surface energies versus the chemical potentialvariations are shown for GaP(001) and GaP(114) surfaces.

49 The slope of the P-rich GaP(001)(2 \times 4) and Ga-rich 50 GaP(001)md(2×4) surface energy curves (the green and blue 51 one, respectively) is inherent to their stoichiometry. Indeed, 52 both GaP(001)(2×4) surfaces are nonstoichiometric, that is, 53 $N_{\rm P} \neq N_{\rm Ga}$. In particular, we find $\Delta N = 16$ for the P-rich GaP(001) 54 (2×4) case while $\Delta N = 8$ for the Ga-rich GaP(001)md(2 × 4) one. 55 Instead, the GaP(114)A- α 2(2 × 1) and the GaP(114)B- α 2(2 × 1) 56 surfaces are stoichiometric ($\Delta N = 0$). Consequently, their sur-57 face energies (the pink and brown curve, respectively) are con-58 stant with the chemical potential. Their values are about 59.9 and 67.3 meV Å⁻², respectively. 59

The chemical potential μ_i has to vary between two extremes 1 thermodynamic conditions: Ga-rich limit (i.e., bulk Ga will 2 form preferentially) and P-rich limit (bulk P will form pref-3 erentially). In particular, the P-rich limit is when $\mu_{\rm P} = \mu_{\rm P}^{\rm P-bulk}$ 4 while the Ga-rich limit corresponds to case when $\Delta \mu_{\rm P}$ is equal 5 to the GaP heat of formation (ΔH_f (GaP) = -0.928 eV) which 6 has been calculated with the black phosphorus phase and the 7 orthorhombic & Ga phase.^[47,48] A detailed explanation of the 8 computational part is presented in the Supporting Information. 9

For the Ga-rich limit, the most stable reconstruction is the 10 Ga-rich GaP(001)md(2 × 4) with a value of 52.9 meV Å⁻² while 11 in the P-rich limit the most stable one is the P-rich GaP(001) 12 (2×4) with a value of 57.4 meV Å⁻². The GaP(114)A- $\alpha 2(2 \times 1)$ 13 surface is thermodynamically more stable than the GaP(114) 14 B- $\alpha 2(2 \times 1)$ surface, as already reported in previous works for 15 the GaAs material. The GaAs(114)A surface energy was found to 16 lie 3 meV Å⁻² below the GaAs(114)B.^[44] In the interval from Ga-17 rich up to $\Delta \mu_{\rm P} = -0.70$ eV, then from -0.70 eV $< \Delta \mu_{\rm P} < -0.16$ eV 18 and finally from $\Delta \mu_{\rm P} = -0.16$ eV to P-rich conditions, the lowest 19 surface energies are the ones of Ga-rich GaP(001)md(2×4), 20 GaP(114)A- $\alpha 2(2 \times 1)$, and P-rich GaP(001)(2 × 4), respectively. 21 Overall, the surface energy of the GaP(114)A- α 2(2 × 1) is the 22 lowest over a wide $\Delta \mu_{\rm P}$ intermediate range (almost 60% of the 23 full $\Delta \mu_{\rm P}$ range) as compared to the GaP(001) surface energies. 24 However, to predict the possible destabilization of the (001) sur-25 face by (114)A faceting, one should consider $\gamma_{GaP(114)A-\alpha 2(2\,\times\,1)}/$ 26 $\cos(\theta)$ (dashed pink line in Figure 2), where $\Theta = 19.48^{\circ}$ is the 27 angle between the GaP(114) and the GaP(001) surfaces. We 28 can see that this corrected surface energy is still lower than the 29 GaP (001) ones in almost 30% of the full $\Delta \mu_{\rm p}$ range (-0.60 eV < 30 $\Delta \mu_{\rm P}$ < -0.36 eV), traducing a destabilization of the (001) sur-31 face by GaP(114)A- α 2(2 × 1) faceting. In contrast, the GaP(114) 32 B- $\alpha 2(2 \times 1)$ surface obviously cannot destabilize the (001) sur-33 face, in agreement with experimental observations. 34

We note that although the destabilization of the (001) GaP surface by (114)A faceting is predicted by DFT in homoepitaxy, it 36

Ga-rich GaP(001)md(2x4

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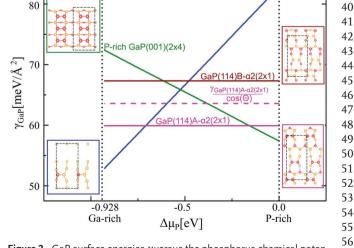


Figure 2. GaP surface energies γ versus the phosphorus chemical potential variation $\Delta \mu_{\rm P} = \mu_{\rm P} - \mu_{\rm P}^{\rm p-bulk}$. The dashed black lines represent the thermodynamic boundaries allowed for $\Delta \mu_{\rm P}$: $\Delta H_{\rm f}({\rm GaP})[= -0.928 \text{ eV}]$ $< \Delta \mu_{\rm P} < 0.$

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has not been experimentally observed on GaP substrate yet. This 1 2 shows that the heteroepitaxial growth on the silicon substrate 3 changes the surface energies balance. Note that a small shift of about +2 or $-2 \text{ meV} \text{ }^{-2}$ in the surface energy of the (114) 4 5 A or (001) surfaces, respectively, would be sufficient to inhibit the destabilization in the DFT prediction. This suggests that the 6 7 destabilization regime is highly sensitive to small variations of 8 surface properties. Although the relaxation degree of the GaP 9 layer on Si is very high, a small residual stress induced by the 10 heteroepitaxy cannot be ruled out and could explain why the destabilization was observed on Si and not on GaP substrates. 11 An eventual anisotropic effect induced by vicinal Si substrates 12 13 should be further investigated by comparisons of growth on vicinal and nominal substrates. We also point out that the GaP(001)-14 oriented surfaces on vicinal Si substrates were already obtained 15 16 in previous works with different growth conditions.^[26,49,50] 17

19 2.3. Textured GaP Surface over 2 in. Wafer and Its Benefits 20 in the Water-Splitting Application

22 Even if a stress-free and textured GaP template on Si substrate 23 has been obtained, the question of sample homogeneity is still 24 raised, in the general context of a very large-scale integration. 25 In order to check the homogeneity of the anisotropic surface 26 texturation over a 2 in. wafer, optical surface control is the most 27 efficient approach. For this aim, a 3 µm GaP/Si was grown in 28 the same conditions as the 1 µm thick GaP/Si sample. Sim-29 ilar RHEED observations (streaky misoriented RHEED pat-30 tern) were obtained during the growth. The average distance 31 between the ridges significantly increased, as compared to the 32 1 µm GaP/Si and reached 400 nm. Therefore, the pattern 33 dimension becomes of the same order of magnitude that of the 34 visible light wavelength.

35 To study the sample optical properties, we used as a reference 36 object a metal box, labeled "INSA" (see Figure 3a,b). Then, the

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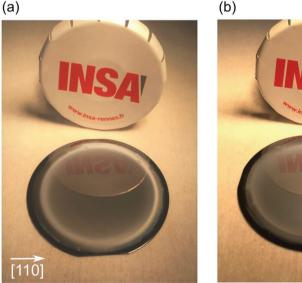
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58 Figure 3. a,b) Study of light reflection on the 2 in. wafer of GaP(114)/Si 6°-off surface rotated by 90° with respect to (b).



reflection/diffusion properties of light coming from this object 1 are observed at the center of the sample surface. Ambient light- 2 ning is added, on the right side of the picture. Two pictures of 3 the experiment performed exactly in the same conditions are 4 given in Figure 3a,b. The same sample has been used in both 5 figures, but the sample has been simply rotated by 90°. An 6 arrow gives the Si [110] direction of the sample on both images. 7 Two distinct areas are observed on this sample: (i) the central 8 area of the sample that corresponds to nearly 90% of the total 9 sample surface, starting from the center, and (ii) the crown 10 area, corresponding to the edges of the sample (10% of the total 11 sample surface on the outskirts of the sample). In the central 12 area of the surface sample in Figure 3a, the edge of the metal 13 box and the INSA logo are well and precisely reflected indicating 14 that diffusion does not occur significantly. The sample appears 15 mirror-like. If the sample azimuth is rotated by 90° (Figure 3b), 16 a "milky" surface behavior appears indicating important con- 17 tribution of light diffusion. These results suggest a strong and 18 homogeneous anisotropy of surface texturation over 90% of 19 the 2 in. sample. We then conclude that the central area of the 20 sample is perfectly monodomain, and that {114}A textured sur- 21

face has been obtained homogeneously over nearly 2 in. 22 Figure 3a,b also shows a more intriguing feature with this 23 patterned surface. Indeed, for light parallel to [110], the cen-24 tral area appears mirror-like and the crown appears with a 25 white "milky" behavior. On the opposite, when the light direc-26 tion is along the [-110], the central area appears "milky," the 27 crown appears mirror-like. This shows that a {114}A textured 28 surface has also been obtained in the crown area, but its ori- 29 entation is turned by 90°, as compared to the central area. 30 These opposite light effects, at the center and at the edge of 31 the sample, suggest that the majority domains developed in 32 these two areas are different. These two areas are therefore 33 in antiphase one for the other. A giant antiphase boundary is 34 therefore expected at the separation between the central area 35 and the crown area. 36

We assume that the formation of these two 37 different domains could be due to the inho-38 mogeneity of growth temperatures and fluxes 39 in the central area and in the crown area 40 during the sample growth. Further works 41 will be needed to clarify this finding. Nev-42 ertheless, a large-scale {114}A textured GaP 43 surface has been successfully obtained in 44 this work on a silicon substrate. We now dis-45 cuss the relevance of GaP(114)A surfaces for 46 water-splitting applications. Indeed, beyond 47 the high thermal stability and the benefit 48 of the free postprocessing aspect, there are 49 other advantages in terms of optical and elec-50 trical devices properties inherent to the GaP 51 material. First, the electric device properties 52 can benefit from the GaP direct growth on 53 Si substrate where the ohmic contact can 54 be realized easily to connect an external cir- 55 cuit. Indeed, the realization of ohmic con- 56 tacts on the GaP remains very challenging 57 because of its large bandgap,^[51] while for the 58 Si substrate it is a well-known process which 59



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1 simplifies the device fabrication. Moreover, the band lineup of the 2 GaP/Si heterointerface is another advantage. Indeed, GaP and 3 Si have a large bandgap difference ($E_g^{Si} = 1.12 \text{ eV}, E_g^{GaP} = 2.26 \text{ eV}$ 4 at 300 K) and their bandgap alignment is of type I favoring the 5 extraction of the photogenerated carriers in the GaP photocata-6 lyst through the Si substrate, when a potential is applied. We 7 also point out that if GaP naturally fits photocathode requirements, quasi lattice-matched AlGaP^[52] can also be grown on Si 8 9 that lowers the alloy valence band to reach photoanode adapted 10 band lineups.^[53]

11 Finally, in the water-splitting reaction, the catalyst surface 12 area plays an important role since it constitutes the main part where the oxidation occurs. It means that a stable and high cat-13 14 alyst surface area is beneficial for the water-splitting efficiency providing more active sites for the photocatalytic reaction.^[40-43] 15 Here, thanks to the surface texturation, a larger surface area 16 17 has also been gained with respect to the planar one. The gain 18 can be easily quantified since we know the GaP{114}A facets angle. The GaP (001) and GaP (114)A surface areas are linked 19 20 with $S_{\text{GaP}(001)} = \cos \theta S_{\text{GaP}(114)}$, where $\cos \theta \approx 0.94$. Consequently, 21 we expect a surface gain of 6%. Moreover, the textured surface may enable a more efficient light trapping into the material, 22 23 where the direct expected consequence is an increase of light 24 absorption which enhances the photogenerated carrier density. 25

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27 3. Conclusions 28

29 A large-scale textured surface was achieved by growing micrometer-thick GaP layers on vicinal Si(001) substrates, thanks to 30 31 the instability of the (001) GaP surface against (114)A faceting. This destabilization is also predicted by DFT calculations of 32 33 $GaP(001)(2 \times 4)$, $GaP(001)md(2 \times 4)$, and $GaP(114)A-\alpha 2(2 \times 1)$ 34 surface energies. We propose to use this surface energy engi-35 neering to develop large-scale textured GaP templates mono-36 lithically integrated on Si, for water-splitting applications. We 37 believe that this nanopatterning approach could also benefit 38 to various other applications, such as window layers in photo-39 voltaic solar cells, nanofluidic applications, surface nanofunc-40 tionalization, or biologic sensors.

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43 Supporting Information 44

Supporting Information is available from the Wiley Online Library or 45 from the author. 46

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56

57 **Conflict of Interest** 58

59 The authors declare no conflict of interest.

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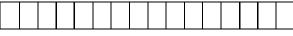
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