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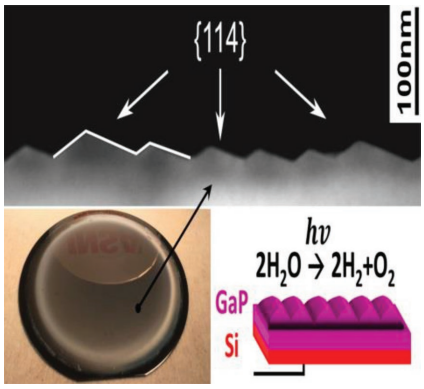
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A large-scale stress-free textured GaP template monolithically integrated on Si is by surface energy engineering, for water-splitting applications. The stability of GaP{114} facets is examined thermodynamically. The benefits of using a textured (114)A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

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

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

1. Introduction

Solar photoelectrochemical (PEC) water-splitting devices have attracted interest for decades with the ultimate objective to convert and store the solar energy into clean hydrogen fuel[1,2] at a lower production cost and environmental impact. Indeed, more than 90% of the hydrogen production is today made by steam methane reforming which releases carbon monoxide/dioxide and heat into the atmosphere while global warming is an issue.[3] The conversion of solar energy into hydrogen production through a water-splitting process assisted by photosemiconductor catalysts[4,5] is definitely the most promising technology for the near future with potentially plethora of hydrogen provided in a clean and sustainable manner. Many recent proposals deal with the use of the GaP semiconductor as a photoelectrode in PEC devices,[6] especially because its bandgap (2.26 eV) is larger than the 1.73 eV photopotential needed for water splitting.[7] Using this idea, demonstrations of GaP-based PEC devices[8–11] and descriptions of the physics/chemistry of the standard GaP surface,[12] its interaction with water[13,14] and hydrogen generation[15] were reported. To enhance conversion efficiency of GaP-based PEC devices, strategies like surface functionalization,[10] use of plasmon resonant nanostructures,[16] or integration of nanowires[17] were considered. Meanwhile, it was demonstrated recently that the texturation of surfaces at the electrode level greatly enhances the efficiency of $BiVO_4$ photoanodes in PEC devices.[18] Structuration of semiconductor surfaces can be performed by lithography techniques,[19] chemical processes,[20,21] nanowires, or by a self-organization during the epitaxial process of the material itself.[22] This last approach is usually driven by crystal strain-relief processes; it simplifies the postgrowth device processing but does not offer large degrees of freedom,

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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]

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

2. Results and Discussions

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

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

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

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



Ida Lucci received the B.Sc. and M.Sc. degrees in electrical engineering from University of Naples "Federico II," Italy, in 2012 and 2015, respectively. In 2015, she started studying the thermal management of integrated laser devices. She is now working toward the Ph.D. degree at FOTON Laboratory at INSA, Rennes, France. Her research focuses on the pseudomorphic integration of III–V semiconductors on silicon, understanding the impact of the silicon surface at the atomic scale on the crystal growth of III–V compounds.



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.

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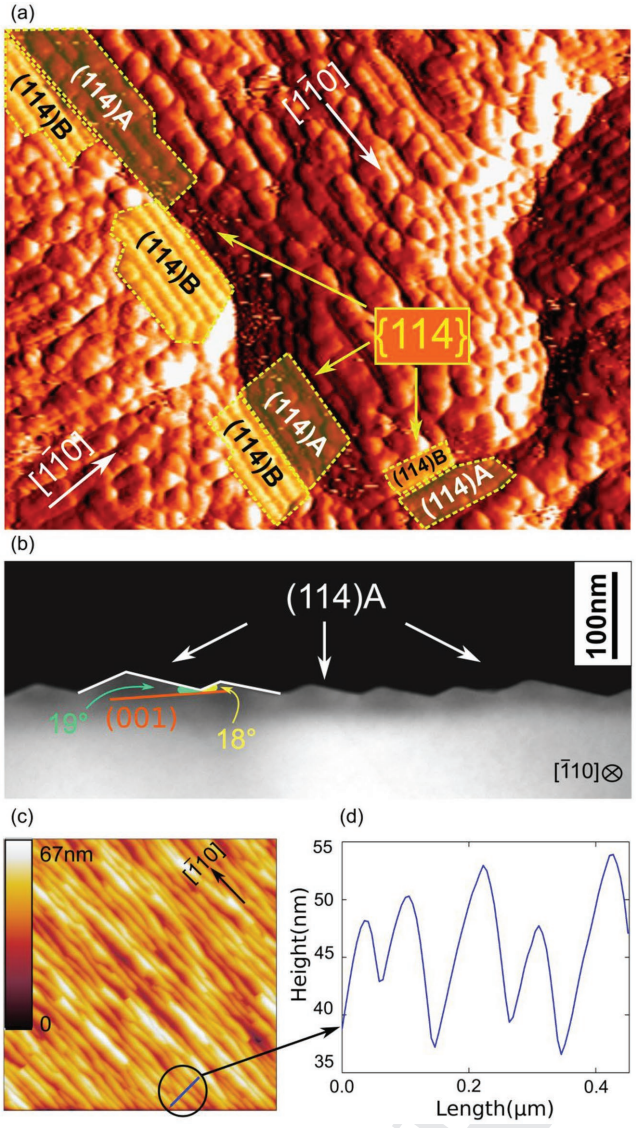


Figure 1. a) 25 × 30 nm^2 STM image of a bi-domain 10 nm thick GaP on Si(001) evidencing the presence of numerous (114)A and B facets at the antiphase boundaries edges. b) TEM image of 1 µm thick GaP on Si 6°-off. c) 3 µm × 3 µm AFM image of the surface of the same sample as (b). (d) A profile taken 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 experiments (not shown here) reveal an overall full relaxation of the GaP crystal. Figure 1b shows the ⟨110⟩ cross-sectional TEM image of the sample. The surface presents a saw-tooth profile along the lateral ⟨110⟩ direction. All facets have an angle with the (001) plane between 18° and 20°, close to the theoretical angle calculated for the {114} facets, that is, $\theta = 19.48°$. The average distance between two maxima is 100 nm with a dispersion of 40%. In the TEM image, left-oriented and right-oriented (114)A facets present different widths. The saw-tooth asymmetry allows compensating the 6°-miscut of the silicon substrate. It is important to note that (001) facets are completely missing. We also point out that (114) facets are parallel to the step edges direction of the vicinal silicon substrate, suggesting that the direction of the substrate miscut determines the dominant polarity of the grown GaP. We also note that emerging dislocation density remains low on this relaxed sample, because of the low lattice mismatch.

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

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

Beyond the use of a vicinal substrate, we have also observed that changing group-V atmosphere above the surface on a nominal GaP substrate, can be another strategy for surface energy engineering promoting a textured-surface formation on GaP. Indeed, the textured behavior was obtained by simply exposing the GaP surface under Sb atmosphere (Figure S1, Supporting Information). Besides III–Vs systems, a similar surface energy engineering strategy has also been developed to control the growth morphology by promoting a 2D–3D transition for growing self-assembled II–VI and nitride quantum dots (QDs).[33–35] Indeed, in both the cases, the SK transition was interpreted as a surface energy change due to a saturation of the dangling bonds by changing the species exposure. Nevertheless, all the present observations demonstrate that there is a real competition between the growth of a (001) surface and the (114)A faceting.

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2.2. Surface Energies Computed by DFT

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

For the polar GaP(114) surfaces, two types of (2×1) reconstructions have been simulated: the Ga-rich GaP(114)A-$\alpha 2(2 \times 1)$ 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] While simple subtraction methods can be used to compute surface energies of nonpolar surfaces such as the GaP(001) ones, fictitious hydrogen methods have to be used to compute A and B polar surfaces independently with a good accuracy (see the Supporting Information for a detailed surface structures description). In the case of nonstoichiometric surfaces such as the (001) surfaces considered here, surface atoms are in equilibrium with a reservoir, therefore the computed surface energy strongly depends on the chemical potential μ and the surface stoichiometry $\Delta N = N_P - N_{Ga}$.[45]

The general equation used to determine the surface energies is

$$\gamma_{surface} A = E_{slab} - \sum_i \mu_i N_i \quad (1)$$

where $\gamma_{surface}$ is the surface energy, A the surface area, E_{slab} is the slab energy calculated by DFT, μ_i is the chemical potential of the species i (where i is Ga or P), and N_i is the number of particles of the species i of the slab. The temperature dependence is ignored because the contributions tend to cancel for free-energy differences as claimed for the GaAs material in a previous study.[46]

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

The slope of the P-rich GaP(001)(2×4) and Ga-rich GaP(001)md(2×4) surface energy curves (the green and blue one, respectively) is inherent to their stoichiometry. Indeed, both GaP(001)(2×4) surfaces are nonstoichiometric, that is, $N_P \neq N_{Ga}$. In particular, we find $\Delta N = 16$ for the P-rich GaP(001) (2×4) case while $\Delta N = 8$ for the Ga-rich GaP(001)md(2×4) one. Instead, the GaP(114)A-$\alpha 2(2 \times 1)$ and the GaP(114)B-$\alpha 2(2 \times 1)$ surfaces are stoichiometric ($\Delta N = 0$). Consequently, their surface energies (the pink and brown curve, respectively) are constant with the chemical potential. Their values are about 59.9 and 67.3 meV Å^{-2}, respectively.

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

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

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

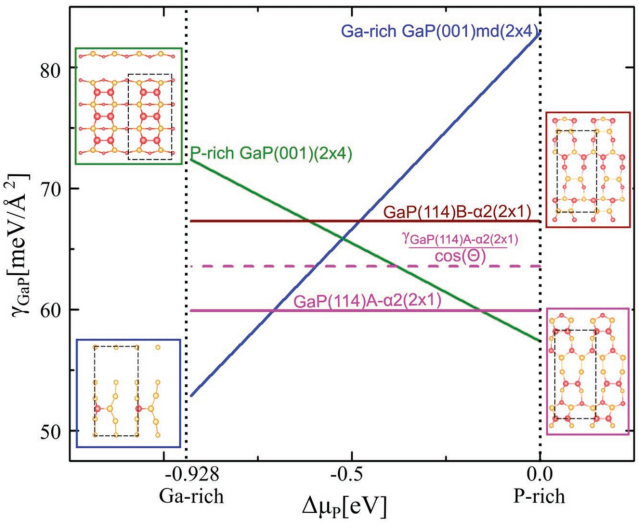


Figure 2. GaP surface energies γ versus the phosphorus chemical potential variation $\Delta\mu_P = \mu_P - \mu_P^{P-bulk}$. The dashed black lines represent the thermodynamic boundaries allowed for $\Delta\mu_P$: ΔH_f(GaP)[= −0.928 eV] $< \Delta\mu_P < 0$.

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

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

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

To study the sample optical properties, we used as a reference object a metal box, labeled "INSA" (see **Figure 3**a,b). Then, the reflection/diffusion properties of light coming from this object are observed at the center of the sample surface. Ambient lightning is added, on the right side of the picture. Two pictures of the experiment performed exactly in the same conditions are given in Figure 3a,b. The same sample has been used in both figures, but the sample has been simply rotated by 90°. An arrow gives the Si [110] direction of the sample on both images. Two distinct areas are observed on this sample: (i) the central area of the sample that corresponds to nearly 90% of the total sample surface, starting from the center, and (ii) the crown area, corresponding to the edges of the sample (10% of the total sample surface on the outskirts of the sample). In the central area of the surface sample in Figure 3a, the edge of the metal box and the INSA logo are well and precisely reflected indicating that diffusion does not occur significantly. The sample appears mirror-like. If the sample azimuth is rotated by 90° (Figure 3b), a "milky" surface behavior appears indicating important contribution of light diffusion. These results suggest a strong and homogeneous anisotropy of surface texturation over 90% of the 2 in. sample. We then conclude that the central area of the sample is perfectly monodomain, and that {114}A textured surface has been obtained homogeneously over nearly 2 in.

Figure 3a,b also shows a more intriguing feature with this patterned surface. Indeed, for light parallel to [110], the central area appears mirror-like and the crown appears with a white "milky" behavior. On the opposite, when the light direction is along the [−110], the central area appears "milky," the crown appears mirror-like. This shows that a {114}A textured surface has also been obtained in the crown area, but its orientation is turned by 90°, as compared to the central area. These opposite light effects, at the center and at the edge of the sample, suggest that the majority domains developed in these two areas are different. These two areas are therefore in antiphase one for the other. A giant antiphase boundary is therefore expected at the separation between the central area and the crown area.

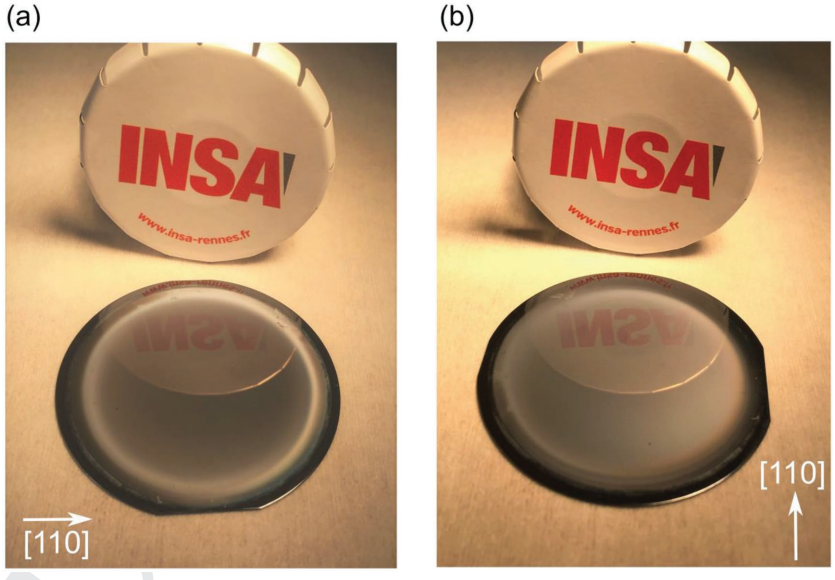


Figure 3. a,b) Study of light reflection on the 2 in. wafer of GaP(114)/Si 6°-off surface rotated by 90° with respect to (b).

We assume that the formation of these two different domains could be due to the inhomogeneity of growth temperatures and fluxes in the central area and in the crown area during the sample growth. Further works will be needed to clarify this finding. Nevertheless, a large-scale {114}A textured GaP surface has been successfully obtained in this work on a silicon substrate. We now discuss the relevance of GaP(114)A surfaces for water-splitting applications. Indeed, beyond the high thermal stability and the benefit of the free postprocessing aspect, there are other advantages in terms of optical and electrical devices properties inherent to the GaP material. First, the electric device properties can benefit from the GaP direct growth on Si substrate where the ohmic contact can be realized easily to connect an external circuit. Indeed, the realization of ohmic contacts on the GaP remains very challenging because of its large bandgap,[51] while for the Si substrate it is a well-known process which

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

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

3. Conclusions

A large-scale textured surface was achieved by growing micrometer-thick GaP layers on vicinal Si(001) substrates, thanks to the instability of the (001) GaP surface against (114)A faceting. This destabilization is also predicted by DFT calculations of GaP(001)(2 × 4), GaP(001)md(2 × 4), and GaP(114)A-α2(2 × 1) surface energies. We propose to use this surface energy engineering to develop large-scale textured GaP templates monolithically integrated on Si, for water-splitting applications. We believe that this nanopatterning approach could also benefit to various other applications, such as window layers in photovoltaic solar cells, nanofluidic applications, surface nanofunctionalization, or biologic sensors.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

GaP/Si, nanopatterning, self-organization, textured surfaces, water splitting

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