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Citation: Journal of Applied Physics 115, 194308 (2014); doi: 10.1063/1.4876753
View online: http://dx.doi.org/10.1063/1.4876753
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/115/19?ver=pdfcov

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Tailoring broadband light trapping of GaAs and Si substrates by self-organised nanopatterning

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(Received 2 April 2014; accepted 4 May 2014; published online 20 May 2014)

We report on the formation of high aspect ratio anisotropic nanopatterns on crystalline GaAs (100) and Si (100) substrates exploiting defocused Ion Beam Sputtering assisted by a sacrificial self-organised Au stencil mask. The tailored optical properties of the substrates are characterised in terms of total reflectivity and haze by means of integrating sphere measurements as a function of the morphological modification at increasing ion fluence. Refractive index grading from sub-wavelength surface features induces polarisation dependent anti-reflection behaviour in the visible-near infrared (VIS-NIR) range, while light scattering at off-specular angles from larger structures leads to very high values of the haze functions in reflection. The results, obtained for an important class of technologically relevant materials, are appealing in view of photovoltaic and photonic applications aiming at photon harvesting in ultrathin crystalline solar cells. © 2014 AIP Publishing LLC.

INTRODUCTION

It is well known that one of the main limitations to the cost reduction of the photovoltaic (PV) systems is related to the production of the active semiconductor materials. As an example, in market-leader crystalline silicon (c-Si) solar cells, the 200-300 μm thick active layer weighs for roughly the 50% on the total cost of the PV modules. Recent attempts have demonstrated that thinner c-Si solar cells, with semiconductor thickness reduced up to 14 μm, can reach photoconversion efficiencies close to 15% (Ref. 2) but still far from the record value of 25% of the bulk crystalline cells.3

A boost to the photoconversion efficiency of the thin crystalline devices could be achieved exploiting light trapping schemes, however those adopted in bulk cells cannot be employed since the typical sizes of the surface texture are in the 10 micrometer range, i.e., are bigger or comparable to the thickness of the ultrathin semiconductor layer in ultrathin crystalline solar cells.3 A large number of experimental and theoretical works has demonstrated that in the latter devices, efficient light trapping can be achieved by patterning the interfaces with dense arrays of high aspect ratio nanostructures, which allow to increase the fraction of photons scattered at large angles in the active layer of the devices thus increasing their effective optical path.5–11

Depending on the spatial and size distribution of the surface features, the optical functionality exhibited by the nanostructured surfaces can range from a reduction of the total reflected light to the enhancement of large-angle scattering in transmission and reflection. In so called bio-mimetic interfaces, the presence of surface features with sub-wavelength lateral dimension and periodicity and with a vertical amplitude comparable to a fraction of the light wavelength allows to gradually match the refractive index from the value of the external medium to that of the substrate.12 This kind of intrinsic index grading induces a broadband anti-reflective performance, often called the “moth-eye effect,” since the textured interface mimics the surface of the cornea of some nocturnal insects.12 On the other hand, large angle light scattering from nanostructured interfaces is promoted when the lateral size of the corrugations is increased up to a scale comparable with the wavelength of light, thus satisfying the diffraction condition.13

Intense research efforts are lately oriented at identifying the ideal morphologies, which enable broadband photon harvesting across the whole solar spectrum; and in this context, 1D-pseudo-random gratings appear to be a promising approach14 also because they can be addressed in simple simulations. Similar morphologies have in fact been addressed in view of efficient light trapping in thin film solar cells5,9,10,14 in photonic applications exploiting directional anti-reflection15 and phase-retardation properties,16 and with the aim of guiding the alignment of liquid crystals in electronic devices.17,18

In order to be suitable for large scale technological applications, surface nanostructuring needs to be performed by adopting techniques, which allow to control and define a pattern in a cost effective way over macroscopic areas and on a broad range of materials. Typical top-down processes require preparation of a primary mould in a resist, e.g., by direct e-beam writing or x-ray lithography. These techniques allow to synthesise well defined structures with a minimum feature size below 100 nm but cannot fulfil large scale production requirements because of limited throughput and costs. Conversely, in the context of the bottom-up approaches, the nanostructuring processes are typically cheap, the throughput is high but there are limitations related to the difficulty in extending the processes to all kind of substrates and to the poor control of the morphological evolution of the pattern.19

Self-organised defocused ion beam sputtering (IBS) has been successfully employed to pattern substrates over macroscopic areas in a cheap and time saving way.20–22 Unfortunately, direct bombardment of a substrate does not result in the formation of a self-organised pattern for all kinds of materials due to the complex interplay of...
material-dependent roughening and ion-induced smoothing terms.25 Recently, we demonstrated that it is possible to overcome this limitation in the case of substrates of relevance for photonic applications, as glass.26 These experiments demonstrate that by IBS, it is possible to prepare a self-organised nanowire stencil mask from an initially flat polycrystalline metal film; subsequent ion erosion through the sacrificial mask guides and speeds up the self-organized formation of high aspect ratio 1-dimensional quasi-periodic nanostructures even on substrates, which are not prone to develop roughening instabilities during ion irradiation due to enhanced ion-induced smoothing.27,28

The second aim will be to demonstrate that the light trapping approaches, which have successfully been demonstrated in thin film amorphous Si solar cells grown on patterned glass superstrates, can be extended to materials of relevance in ultrathin crystalline solar cells.29 In particular, following the approach described in Ref. 28 for glass substrates, we will exploit the possibility to produce high aspect ratio nano-patterns also on GaAs and Si substrates of relevance in photovoltaic and photonic applications exploiting defocused IBS assisted by a sacrificial self-organised stencil mask. One of the main advantages of this approach is related to the possibility to develop an anisotropic 1-dimensional morphology over macroscopic portions of the substrate material, tailoring the amplitude, and periodicity of the pattern in a self-organised fashion. We will then study the correlation between the morphology of the textured substrates and their haze and optical reflectivity as a function of ion fluence, exploiting the moth-eye anti-reflection functionality coupled to the high scattering efficiency of the surface patterns.

**EXPERIMENTAL**

The sacrificial metal mask employed for the pattern transfer process is formed from a 150 nm polycrystalline Au film which has been deposited on polished GaAs (100) and Si (100) substrates by thermal evaporation from an alumina crucible at a constant flux of 6 nm/min calibrated by means of a quartz microbalance.

The samples have been exposed to defocused ion beam irradiation from a gridded multi-aperture Ar⁺ source (Tectra instruments) under grazing incidence conditions (θ = 82°) at a constant flux of 4.0 × 10¹⁵ ions/cm⁻² s⁻¹ (measured in a plane orthogonal to the beam direction) and an energy of 800 eV. A biased tungsten filament (V bias = −13 V), providing electrons via thermionic emission, was placed close to the extraction grid in order to compensate surface charging effects due to ion irradiation. During irradiation of the Au films, a periodic ripple undulation develops at the metal-vacuum interface;30,31 the ripple amplitude increases with ion dose while the residual thickness of the Au film decreases until the bottom of the ripple valleys reach the glass and a disconnected array of nanowires is formed. From this ion fluence onwards the nanowire array acts as a stencil mask, which guides selective etching of the underlying substrate in correspondence to the disconnected gaps. The samples have been further exposed to the ion beam until complete removal of the gold stencil mask is achieved with the aim of texturing the substrate with high aspect ratio anisotropic patterns.

The morphology of the sample was investigated ex-situ by means of atomic force microscopy (AFM) operating in intermittent-contact mode (Nanosurf Mobile S) equipped with a high aspect ratio Si tip (ACLA by AppNano). The topography images have been processed by using WSxM software in order to evaluate root-mean-square (rms) roughness σ, height-height correlation functions H(r), and the other statistical parameters of the patterns.

Finally, the optical characterization of the textured substrates has been performed with the aim of assessing the interplay between surface morphology and reflectance under diffuse or specular conditions. Integrated reflectance measurements were made by means of a compensated deuterium-halogen lamp (DH-2000-BAL, Mikropak) coupled through an optical fiber system to an integrating sphere (Ocean Optics ISP-50-8-R) whose output was processed by a PC controlled high resolution solid state spectrometer (HR4000, Ocean Optics). The integrating sphere was endowed with an optical trap in order to exclude the specularly reflected beam from the collected signal.

**RESULT AND DISCUSSION**

In this work, we used GaAs (and Si) substrates due to their relevance in the production of high efficiency solar devices and to their primary importance in the field of electronics and optics. Up to now, only few experimental works report the formation of nanostructures on GaAs surfaces employing defocused ion bombardment of heavy Cs⁺ or reactive O₂⁻ (Ref. 33) and high energy Ar⁺ (60 keV).34 In the low energy regime (0.7–1 keV), the formation of dense arrays of dots has been reported after high temperature and normal incidence irradiation of substrates with argon ions.35

It is worth to notice that under the experimental conditions adopted in our experiments (i.e., grazing incidence Ar⁺ irradiation at 800 eV at room temperature) in absence of the stencil mask, the vertical amplification of the GaAs surface pattern is insufficient to confer optical functionality to the interface. In order to promote the vertical amplification of the nanoscale pattern, we thus tested the performance of a self-organised metal stencil mask, which was so far only employed on glass substrates.26 A 150 nm thick polycrystalline gold film was thus deposited on the GaAs substrates of the surface prior to defocused Ar⁺ bombardment at grazing incidence (θ = 82°). Following ion irradiation, at the surface of the metal film, a rippled morphology develops with ridges running parallel to the beam projection.30 By increasing ion fluence, the valleys of the ripple modulation reach the substrate so that the ripple pattern decomposes into a well disconnected array of metal nanowires. In Fig. 1(a), we show a 6 μm × 6 μm AFM topography of the Au surface at a fluence Fₗ = 33 × 10¹⁷ ions/cm², which clearly evidences the formation of a nanowire array pattern elongated along the ion beam direction (black arrow). As reported in Refs. 27 and 28, using Secondary Neutral Mass Spectroscopy (SNMS), it is possible to determine the threshold ion dose at which the deepest grooves of the metal ripple reach for the first time
the semiconductor substrate (disconnection of the metallic ripple pattern) thus exposing the substrate to the ion beam; beyond this ion fluence, the SNMS signal originating from the substrate atoms becomes observable, while the Au signal exhibits a concurrent decrease. Prolonging further ion irradiation, the pattern of the stencil mask is transferred to the GaAs substrate by selective etching in correspondence to the gaps, which separate the nanowires until, at fluence $F_{III} = 49 \times 10^{17}$ ions/cm$^2$, the metallic mask is completely eroded, Fig. 1(b). In Fig. 1(c), we finally show the evolution of the GaAs surface morphology after further irradiation up to fluence $F_{III} = 349 \times 10^{17}$ ions/cm$^2$.

In agreement with results reported in Ref. 27 for glass substrates, an extraordinary vertical amplification of the GaAs surface corrugations is observed with respect to those of the Au stencil mask. This is made clear performing a quantitative analysis of the statistical parameters of the AFM images. At first, we can notice that the rms roughness, $\sigma$, for the sample sputtered at fluence $F_{II} = 49 \times 10^{17}$ ions/cm$^2$, is almost four times higher than that of the rippled metal film ($\sigma \sim 12$ nm). The increase of the interface width is a consequence of the different ion beam erosion velocities of (i) the GaAs substrate exposed in correspondence to the gaps of the stencil mask and of (ii) the residual gold nanowire. During this process, the GaAs system is forced into a strongly out of equilibrium morphology by the Au stencil mask, so that the evolution of the surface pattern is the result of the competition between the local erosive action of the ion beam, imposed by the anisotropic stencil mask, and of efficient relaxation of GaAs mobile species, either thermally activated or ion induced.

After exposing the system up to fluence $F_{III}$, a dramatic drop of $\sigma$ to $\sim 16$ nm is observed: once the perturbing action of metallic mask has been removed, the GaAs surface relaxes towards a less corrugated configuration indicating that smoothing mechanisms prevail over ion induced roughening; this is plausibly related to enhanced Ga mobility in presence of preferential Ga enrichment, as well as to thermal and ion-enhanced diffusion.

The AFM images of Fig. 1 make clear that the self-organized ripple pattern on the GaAs surface is similar to that of the metal stencil mask, nevertheless changes (coarsening) are evident in the lateral dimension of the corrugations. A quantitative evaluation of the morphological changes can be achieved by calculating the height-height correlation function, $H(r) = \langle [h(x + r) - h(x)]^2 \rangle$, where $h(x)$ and $h(x + r)$ are, respectively, the one-dimensional height profile of the surface along the fast AFM scan direction, $x$ (chosen orthogonal to the ripple axis) and the height profile of the surface shifted by the displacement variable $r$. In Fig. 2(a) (black solid squares), it is worth to notice that they are in quantitative agreement with the trend discussed previously and based on the direct evaluation of $\sigma$ from the AFM topographies since the two methods provide values which overlap within the uncertainty of the symbol size. The red triangles instead, refer to the roughness exponent, $x$, obtained through linear fits of the functions in the

![Fig. 1](image1.png)

**FIG. 1.** AFM topography images of (a) Au film sputtered at $\theta = 82^\circ$ and fluence $F_1 = 33 \times 10^{17}$ ions/cm$^2$, (b) GaAs surface after the complete erosion of the Au mask, fluence $F_{II} = 49 \times 10^{17}$ ions/cm$^2$, and (c) GaAs surface over-exposed up to a fluence $F_{III} = 349 \times 10^{17}$ ions/cm$^2$. Black arrows indicate the projection of the ion beam directions on the substrate plane. (d) Log-Log plot of the height-height correlation functions $H(r)$ from the AFM images of panel: (a) blue open triangles, (b) red solid circles, and (c) black open circles. Black arrow represents the interception between the linear and the saturation regime of $H(r)$ and has been used to evaluate the lateral correlation length, $T$.

![Fig. 2](image2.png)

**FIG. 2.** Statistical parameters of the surface patterns shown in Figs. 1(a)–1(c) as a function of the ion fluence. (a) Solid black squares: rms roughness, $\sigma$. Solid red triangles: roughness exponent, $x$. (b) Solid black squares: correlation length, $T$. Solid red triangles: mean slope, $\beta$, of the surface ripple facets.
range of small $r$. One can observe that for all sputtered GaAs substrates $z$, ranges around 0.8–0.9; while on the contrary, the value observed for the Au stencil mask is reduced to about 0.65. Another important parameter which can be derived from the $H(r)$ functions is the characteristic lateral correlation length $T$ of the system, i.e., the maximum lateral separation for which the surface morphological features present a statistically relevant correlation.

We evaluated $T$ as the lateral shift $r$ value for which a break appears in the linear trend (see arrow in Fig. 1(d)). The evolution of $T$, solid black square in Fig. 2(b), reveals a monotonic increase with ion fluence: at fluence $F_I$ (disconnection stage of the stencil mask), $T$ reads around 70 nm; it reaches 120 nm for the GaAs substrate sputtered at fluence $F_H$ and significantly increases to 550 nm when the substrate is overexposed up to fluence $F_{HI}$. Combining together the $T$, $z$, and $F$ parameters, we can also estimate the average slope of the surface ripples, $\psi$, through the relation $\psi = \sigma^{1/3} / T$.57 The average slope, solid red triangles in Fig. 2(b), remains relatively stable during the early stages of the pattern transfer process (fluence $F_I$ and $F_H$) in which it reads around $30^\circ$. This means that the increase in height of the nanostructures takes place in parallel with an amplification of their lateral size as revealed by the concurrent increase of the correlation length. For the overexposed sample (fluence $F_{HI}$), surface smoothing dominates and $\psi$ drops to around $4^\circ$ in agreement with the observed decrease of the roughness and with the increase of the correlation length. The AFM investigations on the GaAs substrates allow to confirm that at low ion fluence ($F_{HI}$) the pattern transfer process is effective in sculpting surface features with subwavelength lateral dimensions and amplified vertical size; it is also worth to notice that the morphological parameters of the sputtered GaAs sample are comparable to those of standard textured substrates employed for light trapping applications in thin film solar cells. In order to make a comparison we can refer to the Asahi-U-type substrate, a commercial fluorine-doped tin oxide (SnO:F), which is employed as superstrate for thin film solar cells. In order to make a comparison we can refer to the Asahi-U-type substrate, a commercial fluorine-doped tin oxide (SnO:F), which is employed as superstrate for thin film solar cells featuring enhanced light trapping, since it is endowed with pyramidal surface features with lateral correlation length in the range 150–200 nm and rms roughness of about 40 nm.38

Total reflected and diffused light spectra have been collected in the visible-near infrared (VIS-NIR) range by means of an integrating sphere setup in order to evidence the correlation between the morphological parameters of the nanostructured GaAs interfaces and (i) their anti-reflective behaviour and/or (ii) their performance with respect to light scattering at off-normal angles. In addition, we also performed some simple calculations in order to characterize the optical response of the nanostructured substrates in terms of the response of a 1-dimensional grating whose parameters are statistically equivalent to those of the observed surface morphology. When dealing with random rough surfaces, a typical approach is given by the scalar scattering theory in which the statistical parameters of the nano-textured interfaces are used to solve Kirchoff’s diffraction integrals.1,19 alternatively, a powerful method is the Rigorous Coupled Wave Analysis (RCWA) in which the equations of the electromagnetic problem are coupled together in a matrix form and numerically solved in each of the strata into which the interface is arbitrary divided in order to simplify the description.40 Here, we performed RCWA calculations by using the software package GD-CALC (grating diffraction calculator) implemented in MATLAB environment.41 For the refractive index of GaAs, we used the values calculated by coupling un-polarized normal incidence reflectivity measurements, performed on flat substrates by means of an optical fiber probe setup, with Fresnel coefficient equation derived in the same condition of the experimental ones.42 In order to maintain the model as simple as possible, following the approach of Refs. 26, 39, and 43, we describe the optical response of the sputtered samples as that of 1-dimensional sinusoidal gratings of period, $P$, amplitude $a$ (half peak-to-valley amplitude), respectively related to the correlation length $T$, and rms roughness $\sigma$, of the samples through the relations: $h = \sigma 2$ and $P = \pi T \sigma 2$.26,39,43 In order to take into account the dispersion of the morphological parameters of the self-organised patterns, we averaged the optical response of five gratings whose correlation lengths are distributed in a range of 10% around the central value provided by the AFM analysis.

Illumination with a monochromatic linearly polarized plane wave takes place at an incidence angle of $8^\circ$ with respect to the substrate normal (this choice reproduces the experimental geometrical condition employed for the measurements with the integrating sphere). The total reflected intensity is obtained by summing over all the reflected diffraction orders calculated for incident light in the wavelength range 400–900 nm, either with TE polarization (electric field parallel to the grating lines) or with TM polarization (electric field orthogonal to the grating lines).

In Fig. 3(a), we plot the total reflectance spectra of the GaAs sample obtained by sputtering up to fluence $F_H$. Compared to a flat GaAs substrate (black trace + “Flat” tag, for which no noticeable difference is found between TE and TM polarizations), the TE spectrum of the textured sample (red trace + “TE” tag) shows a uniform decrease (about 10%) over the whole spectral range. The reduction of the reflected intensity is much more evident for TM polarization (blue trace + “TM” tag) and is more pronounced at short wavelengths: the total reflectivity shifts down from 40% to 20% at $\lambda = 400$ nm and from 30% to 20% at $\lambda = 800$ nm. It is thus clear that the presence of sub-wavelength anisotropic surface corrugations is responsible for the occurrence of an anti-reflective “moth eye” behaviour with a strong dependence on incident polarization (dichroism). Reflection losses are thus reduced by the index grading effect associated with the nanostructures created at the air/GaAs interface, characterised by a periodicity $T = 120$ nm and statistical roughness $\sigma = 45$ nm. The calculated reflectance (red solid triangles for TE polarization and blue open triangles for TM) has been derived for sinusoidal gratings whose central period and amplitude have been determined from the experimental values according to Refs. 26, 39, and 43; the RCWA calculations appear to be in good agreement with the measurements and in particular reproduce the dichroic anti-reflective behaviour of the surface and
FIG. 3. (a) Total reflectance of initial GaAs (100) flat substrate for TE and TM polarization (black trace + tag). Total reflectance spectra of sample sputtered at fluence $F_{III}$; red trace + “TE” tag corresponds to incident light TE-polarized, blue trace + “TM” tag to light TM-polarized. Red solid and blue open triangles correspond to RCWA calculations, respectively, for TE and TM polarizations. (b) Sample sputtered at fluence $F_{II}$: the TE (red trace) and TM (not shown) total reflectance spectra are indistinguishable from the spectra of the initial GaAs (100) flat substrate (black trace). Red solid and blue open triangles correspond to RCWA calculation, respectively, for TE and TM polarizations. All spectra have been normalized to the total reflectance of the standard RS2-Avantes mirror (Al + MgF coating). Normalised diffuse reflectance (Haze) of flat GaAs substrate (black line + tag) and for TE polarization (red line + tag) and TM (blue line + tag) for sample obtained at fluence: (c) $F_{II}$ and (d) $F_{III}$.

the wavelength dependence of the TM response. For the over-exposed sample (fluence $F_{III}$, periodicity $T = 550$ nm, roughness $\sigma = 16$ nm), the optical spectra are reported in Fig. 3(b); in this case, no reduction of the reflected intensity is observed and the TE (red trace) and TM (not shown) spectra overlap in good agreement with those of the flat reference substrate (black trace) and with the calculations (triangles) for the statistically equivalent sinusoidal grating. A quantitative analysis of the morphology of this sample shows that overexposing the substrate at higher ion fluencies results in a decay of the smaller spatial components so that the only corrugations, which survive, though strongly reduced in amplitude, are those of larger lateral size, i.e., those comparable or larger than light wavelengths. For this reason, from the optical point of view, the sample behaves similarly to an untreated flat GaAs substrate.

In order to highlight the light trapping potential of the nanostructured substrates, we are also interested in determining their diffuse scattering efficiency; therefore, we have measured the spectrally resolved haze functions, defined as the ratio of reflected diffusely to total reflected light. Measurements of the diffuse light spectra have been performed by means of the integrating sphere, either trapping or integrating the specular component of the reflected beam. In Fig. 3(c), we plot the haze functions for the sample obtained at fluence $F_{II}$; the data indicate that off-specular light scattering is strongly dependent on incident light polarization; and in particular, it is more effective for light polarized perpendicular to the ripple ridges (TM polarization). If one considers an array of nanostructures with sub-wavelength (non-diffracting) periodicity, the system can be described as an effective medium in which the refractive index is graded vertically. The negligible lateral modulation of the effective refractive index corresponds to negligible light scattering for the considered wavelength range. For this reason in our case, the measured light scattering intensity is mostly related to Fourier components of the pattern with periodicity comparable or larger to the light wavelength. In fact, only for these spatial modulations, the diffraction condition is fulfilled and the intensity of the diffracted orders contributes to the measured haze function. The polarization dependence of the haze function can thus be interpreted in terms of the morphological anisotropy derived from the AFM topographies. The power spectrum of the Fourier spatial components (data not shown) evaluated for line profiles parallel to the long axis (TE polarization) is smaller than for line profiles orthogonal to the long axis (TM polarization) and thus, in the considered range of optical wavelengths (400–900 nm), diffraction is more pronounced for the latter polarization. Normalized diffuse reflectance (haze) is strongly enhanced (above 50%), with respect to the flat case for both polarizations, at wavelengths shorter than 600 nm. In the long wavelength region, haze rapidly decreases towards the value of the flat case remaining however higher than 20%. For the flat reference GaAs substrate (black trace + “Flat” tag), throughout the considered wavelength range the haze function remains around 5%, a value which can be considered as a reference threshold, due to incomplete trapping of the specularly reflected beam. Finally, for the sample overexposed to high ion fluencies $F_{III}$, the data shown in Fig. 3(d) demonstrate that the light scattering turns out to be not very different with respect to a flat substrate both for TE and TM polarized lights throughout the whole wavelength range. This conclusion could have been derived also considering the reduction in sample roughness and aspect ratio, as well as the increase of the relevant lateral size of the surface features.

At this point, we want to stress the main results obtained with GaAs substrates before attempting to generalize their validity to the Si case. At first, we demonstrated that by using an ion projection lithography approach through a self-organised metal stencil mask, it is possible to create high aspect ratio nanostructures on a substrate which is otherwise not prone to develop roughness under ion irradiation conditions. This is specifically the case of GaAs, one of the relevant materials for photonic and photovoltaic applications. We also demonstrated that interrupting ion bombardment at a fluence $F_{II}$ corresponding to the complete removal of the metallic mask, self-organized nanostructures with maximum vertical amplification and correlation length below 200 nm can be produced. The surface exhibits interesting optical properties in terms of anti-reflection and diffuse scattering, which are strongly dependent on incident light polarization as a consequence of the anisotropic pattern. The long term evolution of the irradiated surface, evaluated at fluence $F_{III}$, shows a decay of the small scale roughness components of the pattern, which is reflected in the decrease of diffuse reflectance towards the values observed for the untreated flat substrate.

In order to demonstrate the general validity of the results obtained for GaAs, we decided to perform the same experiments using a Si (001) substrate, which is another reference
material for opto-electronic and photovoltaic devices. Employing the same kind of self-organised Au stencil mask and irradiating up to ion fluence \( F_{II} \) (equivalent to the GaAs case), a nanoscale pattern was defined on the Si surface as shown in the AFM topography of Fig. 4(a), which is quantitatively described by the corresponding height-height correlation function of Fig. 4(b). The rms roughness of the surface corrugations amounts to 40 nm and confirms that also in this case, at the early stage of the process, the pattern is transferred to the substrate with a vertical dynamic, which is amplified with respect to the metal stencil mask. When comparing Si to the GaAs at equivalent ion fluence, we observe an increase of the lateral correlation length that reads about 150 nm and a decrease of the mean slope of the surface features to 25°.

In this case, the optical spectra were measured employing an unpolarized light beam; the occurrence of an anti-reflective behaviour in the VIS-NIR spectral range is made clear by comparing the total reflectance of the sample (blue trace + “Sputtered” tag reported in Fig. 4(c)) to that of a flat Si substrate (black line + “Flat” tag); the reflection losses are reduced by about 20% over the whole spectral range. The haze function shown in Fig. 4(d) (blue line + “Sputtered” tag) confirms that, at short wavelengths, light is more effectively scattered at off-specular angles; while at large wavelengths, haze is still 20% higher than the flat case (black trace + “Flat” tag). The results are quantitatively described in Fig. 4(c) by the RCWA calculation (triangles) performed analogously to the GaAs case.

Since the formation of the self-organised Au stencil mask is independent from the supporting substrate, we can use the morphological and optical analysis of GaAs and Si samples, sputtered under the same experimental conditions, to draw some conclusions on the generality of the pattern transfer process. In both cases, we observe an increase of the lateral correlation length of the transferred pattern with respect to the gold stencil mask as demonstrated by the GaAs sample overexposed at fluence \( F_{III} \). This indicates that due to enhanced mass transport (either thermally activated or ion induced), surface relaxation is more effective in inducing the decay of the smaller features; while in order to observe a significant decay of the larger structures, much higher irradiation dose is needed. Despite the same sputtering conditions for Si substrates with respect to GaAs, a 25% increase of \( T \) and a 10% decrease of \( \sigma \) are observed in the AFM investigations, indicating that the relaxation mechanism are more effective for the former material. The morphological differences of the two patterns are strictly related to the optical response summarized in Fig. 5 under un-polarized illumination conditions. The total reflectance spectra reported in Fig. 5(a) are normalized to the respective flat reference substrates and show that the anti-reflection behaviour is more pronounced for GaAs (black trace + “GaAs” tag) with respect to Si (red trace + “Si” tag): the reduction of reflectivity is about 30% across the whole wavelength range for the former sample, and about 20% for the latter, reflecting the morphological difference of the two samples.

While a decrease of the reflectivity is surely an important factor in order to increase the number of photons harvested by a thin film photovoltaic device, several examples have demonstrated that even more important can be the increase of the effective photon path length induced by textured interfaces through total internal reflection at large scattering angles. A measurement of diffuse optical scattering (haze) thus provides an important indication of the quality of the textured surfaces for light trapping applications, especially in the photovoltaic field. We have summarized haze measurements on patterned GaAs and Si substrates in Fig. 5(b): it is confirmed that analogously to total reflectance GaAs (black trace + “GaAs” tag) is about twice effective.
than Si (red trace + “Si” tag) across the whole spectral range, and that for short wavelengths diffuse scattering (haze) reaches the 60%–80% of the total. This difference in the optical response of the two substrates is a consequence of the morphological differences of the materials patterned under the same ion irradiation conditions: at fixed light wavelength, the haze function in fact increases monotonically with the rms roughness and decreases with the lateral correlation length. As demonstrated by recent works, the introduction of a nano-textured front-contact interface, characterised by high haze (>50%) in reflection, leads to a significant improvement of the external quantum efficiency of a thin film solar cell with respect to a reference one grown on flat substrate. In the cited examples, the cells were grown on transparent conductive oxide (TCO) layers pre-patterned with random 2-dimensional textures by wet etching. In other examples, back contacts textured with 1-dimensional patterns have been addressed with success. Naqavi et al. found that photon absorption can be enhanced if a 1-dimensional periodic texture is adopted at the back reflector, due to resonant coupling of scattered light into wave-guided modes confined in the high index silicon layer; in particular, an enhancement of the photocurrent up to 20% (depending on the polarization state of the illuminating light) can be reached by preparing 1D-sinusoidal gratings of optimised amplitude and periodicity. The controlled modification of periodicity and amplitude of the undulated pattern thus represents one of the fundamental issues for the optical functionalization of these technologically relevant interfaces.

The present nanostructuring approach based on the use of self-organised stencil masks thus appears suitable for broadband light trapping applications in which a high degree of light scattering (haze) is achieved exploiting a sub-micrometer band light trapping applications in which a high degree of self-organised stencil masks thus appears suitable for broad-functionalization of these technologically relevant interfaces.

CONCLUSION

In this work, we have explored the possibility to form nanostructured surfaces with controlled and tunable light scattering performance over a broad spectral range spanning the VIS-NIR range on an important class of materials relevant in photonic and photovoltaic applications, such as Si and GaAs. Recurring to ion beam sputtering, a self-organised metal nanowire stencil mask is sacrificed in order to project its pattern on the underlying semiconductor substrate. We have investigated the morphological evolution of the surface of GaAs and Si substrates as a function of the ion fluence by means of AFM measurements and we have characterised their optical properties in terms of total reflectivity and haze. The optical measurements demonstrate the occurrence of a polarization dependent anti-reflection behaviour in the VIS-NIR range induced by the presence of sub-wavelength surface features; at the same time the presence of larger structures induces light scattering at off-spectacular angles as confirmed by the high values of the haze functions in reflection. Validation of the optical measurements has been done through the RCWA algorithm implemented in the GD-CALC software by simply modelling the patterned substrates with sinusoidal gratings of period and amplitude correlated with the morphological parameters obtained by the AFM investigations. In conclusion, we have demonstrated that ion nanostructuring with a self-organised stencil mask is effective in patterning macroscopic areas of a broad range of materials in a cheap and time saving way. The general validity of the approach, demonstrated for a broad class of materials, opens to the realization of textured interfaces of relevance for photon harvesting applications in ultrathin crystalline solar cells.

ACKNOWLEDGMENTS

We acknowledge partial support by MSE in the framework of the Operating Agreement with ENEA for Research on the Electric System, by MAE in the framework of the Italia-Polonia bilateral program, and by Compagnia di San Paolo. Technical assistance by E. Vigo is acknowledged.

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