Published in final edited form as:

ECS J Solid State Sci Technol. 2019 ; 8(6): . doi:10.1149/2.0311906jss.

Black GaAs with Sub-Wavelength Nanostructures Fabricated via Lithography-Free Metal-Assisted Chemical Etching

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Abstract

A practical nanofabrication process is detailed here for the generation of black GaAs. Discontinuous thin films of Au nanoparticles are electrodeposited onto GaAs substrates to catalyze site-specific etching in a solution of KMnO_4 and HF according to the metal-assisted chemical etching mechanism. This provides a solution-based and lithography-free method for fabricating sub-wavelength nanostructure arrays that exhibit solar-weighted reflectance approaching 4 %. This two-step benchtop process can be entirely performed at room-temperature without lithographic patterning or vacuum instrumentation, providing an alternative high-throughput nanotexturing approach for thin-film photovoltaics applications.

Introduction Text

Metal-assisted chemical etching (MacEtch) techniques are simple and cost-effective semiconductor nanofabrication methodologies whereby selective wet-chemical etching occurs in the presence of a metal catalyst (e.g., Au, Ag, etc.).^{1,2} First, a thin catalyst layer is deposited in direct contact with a semiconductor, followed by submersion in a solution consisting of an acid and an oxidant.³ MacEtch mechanisms may be interpreted based on a galvanic cell model, whereby the metal catalyzes the reduction of oxidant species within the solution, causing site-specific hole injection and localized oxidation of the substrate.^{4,5} The MacEtch solution is then tailored to preferentially dissolve the selectively oxidized substrate.^{5,6}

GaAs nanostructure fabrication can be realized through both wet- and dry-etch processing, each with a slew of advantages and limitations. For example, inductively-coupled plasma

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reactive-ion etching (ICP-RIE) often requires hazardous gases and high vacuum conditions.^{7,8} Moreover, most GaAs MacEtch processes involve high-vacuum metal deposition³ and/or nanoparticle catalyst formation via thermal agglomeration under annealing conditions approaching the substrate's congruent sublimation temperature.^{9,10}

Here, an entirely solution-based, lithography-free, and low-temperature nanofabrication process is presented for the generation of black GaAs with hemispherical solar-weighted reflectance (SWR) less than 5%. Specifically, electrodeposition and MacEtch are coupled such that every fabrication step may be performed in a conventional wet-bench without the need for elevated temperatures, hazardous process gases, or high vacuum instrumentation. This nanofabrication technique can be utilized as an efficient method to improve spectral absorbance for GaAs photovoltaics.

Experimental or Theoretical

All experiments were performed on semi-insulating GaAs(100) substrates. All wafers were cleaned with solvents prior to native-oxide removal in ammonium hydroxide. Au was deposited via electrodeposition using sulfite gold plating solution at 60 °C, and with constant current density of 50 mA/cm². Three samples, denoted A, B, and C, were prepared with different fabrication parameters. Electrodeposition times (t_{ED}) were 24 min for Sample A, and 12 min for Sample B and Sample C. All MacEtch experiments were performed at room temperature using a solution containing 14.07 mol/L hydrofluoric acid (HF) and 10.54 mmol/L potassium permanganate (KMnO₄). MacEtch times (t_{ME}) were 30 min for Sample A and Sample B, and 60 min for Sample C. Imaging was performed by scanning electron microscopy (SEM), and total (specular and diffuse) hemispherical reflectance spectra were measured using a spectrophotometer with an integrating sphere. Raman spectroscopy was performed using laser light at 532 nm, focused on the sample using a long-working-distance microscope objective with numerical aperture of 0.6 and 40× magnification. The incident power at the sample was 300 μW with a spot size diameter of 1 μm. The Raman scattered light was passed through a laser line filter into a monochromator and dispersed onto a 1340 × 100 pixel CCD array photodetector.

Results and Discussion

Figure 1 shows top-view SEM images of pre-MacEtch samples wherein the catalyst geometry is modified using two Au electrodeposition times (t_{ED}). Figure 1a shows t_{ED} = 24 min and corresponds to Sample A with an average Au nanoparticle diameter of ~65 nm. Figure 1b shows t_{ED} = 12 min and represents Samples B and C with an average Au diameter of ~195 nm. Thus, a contiguous and porous Au film is formed after t_{ED} = 24 min, whereas only discrete particles are deposited after t_{ED} = 12 min. Deposition times longer than 24 min result in continuous Au film formation with increased overall substrate surface coverage, which is undesirable for the current MacEtch process.

MacEtch trials are performed over two different process periods, as seen in the tilted-view (top row) and cross-section (bottom row) SEM images in Figure 2. Sample A (Figure 2a,d) and Sample B (Figure 2b,e) show comparable etch depths, and both samples provide vertical

arrays of GaAs nanowires after $t_{ME} = 30$ min. Importantly, the discrete Au nanoparticles of Sample B are not observed to deviate from vertical etch directions (i.e., “detouring” effect) after a 30 min MacEtch step. However, the distinct catalyst size and substrate coverage on Samples A and B yield etched nanowires of disparate sizes (average nanowire diameters for Samples A and B are ~ 325 nm and ~ 170 nm, respectively). Although, Sample B and Sample C (Figure 2c,f) have equivalent Au size and coverage ($t_{ED} = 12$ min), they result in dramatically dissimilar nanostructure morphologies due to differing values of t_{ME} (30 and 60 min, respectively). In the case of Sample C, the longer MacEtch time results in exaggerated Au nanoparticle detouring and generation of non-vertical structures. Moreover, smaller dimension nanostructures (< 500 nm) are lost in the case of Sample C as catalyst etching paths begin to cross.

Figure 3 shows total hemispherical reflectance (i.e., specular and diffuse) spectra for bare GaAs (black curve) and MacEtched black GaAs Samples A, B, and C (red, cyan, and blue curves, respectively). The inset shows a photograph of side-by-side specular (pre-MacEtch, left) and matte (post-MacEtch, right) samples. The hemispherical SWR is calculated by weighing hemispherical reflectance with an appropriate solar irradiance spectrum⁹, in this case Air Mass 1.5. Bare GaAs is determined to have $35.87\% \pm 0.19\%$ SWR over the measured range of 280 nm to 800 nm, with the uncertainty representing the first standard deviation from the mean for at least three SWR measurements. The introduction of random nanostructures induces a graded refractive index and reduces Fresnel reflections, leading to SWR values of $5.21\% \pm 0.11\%$, $4.070\% \pm 0.059\%$, and $8.20\% \pm 0.13\%$ for Samples A, B, and C, respectively. Thus, Sample B exhibits an 89 % reduction in SWR compared to bare GaAs. Although Samples A and B have comparable overall etch depths, a more Lambertian surface results from shorter t_{ED} and smaller Au nanoparticles. At extended t_{ME} (Sample C), the light-absorbing quality of the surface is ultimately hindered, which is attributed to catalyst detouring and consequent exposure of non-vertical reflective surfaces. The ability to generate random features for improve light trapping is a critical strength of MacEtch over ICP-RIE. Reported reflectance values at 550 nm for GaAs nanowire arrays generated with ICP-RIE range from approximately 3.9% ⁷ to 6.7% ⁸ for nanowires of diameter 60 nm to 70 nm and 500 nm, respectively. In contrast, MacEtched GaAs reflectance values at 550 nm range from approximately 3 % at normal incidence for structures with diameter of 5 μm (reported by Lova et al.),⁵ to 3.8 % with sub-wavelength nanostructures (current study).

Figure 4 shows the Raman scattering spectrum for Sample C (blue curve), while the inset shows a comparison with bare GaAs (black curve). The position and full-width at half-maximum (FWHM) of Raman peaks are determined using Lorentzian fitting of the deconvolved spectra (inset, grey curves). Crystal orientation determines which mode(s) are excited within bulk samples, based on selection rules.⁶ Bare zinc-blende GaAs(100) exhibits a strong longitudinal optical (LO) peak at 292.3 cm^{-1} with a FWHM of 3.1 cm^{-1} (inset, black curve), as expected for the bulk substrate.¹¹ However, the anisotropic nature of MacEtch-generated nanostructures modulates modal angular dependencies and permits orthogonal polarization scattering that is forbidden by bulk selection rules.¹² Consequently, distinct transverse optical (TO) phonon modes are observed in the MacEtched sample (blue curve). Additionally, phonons that are confined along the free surfaces of nanowires induce

an additional surface optical (SO) phonon mode in the Raman spectrum of the MacEtched sample. Thus, Sample C shows TO, SO, and LO peaks centered at 268.8 cm^{-1} , 288.4 cm^{-1} , and 291.1 cm^{-1} , respectively, with corresponding FWHM values of 3.3 cm^{-1} , 6.5 cm^{-1} , and 3.1 cm^{-1} . All values are in agreement with previously published theoretical and experimental values reported for top-down GaAs nanowires.¹³ Unlike prior reports of GaAs nanowires fabricated by MacEtch using similar solutions,⁶ no broadening or redshift in the LO peak is observed here, and a significant amount of TO and SO scattering is found in post-MacEtch GaAs. This can be explained by the disparity in structural orientation (e.g., ordered and random arrays) and morphology (e.g., diameter and height). Lastly, the current black GaAs samples do not show substantial formation of $\beta\text{-Ga}_2\text{O}_3$, crystalline As (c-As), or amorphous As ($\alpha\text{-As}$) phases, which is in contrast to previously reported GaAs nanowires after MacEtch under similar conditions⁶ and ICP-RIE-fabricated GaAs nanowires after photo-thermal excitation.¹³ The absence of such parasitic phases holds promise for integration of MacEtch-fabricated black GaAs in thin-film and flexible membrane photovoltaic devices.

Summary

An entirely solution-based and lithography-free nanofabrication process has been described using a two-step method involving electrodeposition and MacEtch. The generation of black GaAs with hemispherical solar-weighted reflectance of 4.07% was demonstrated, which represents an 89% reduction compared with bare GaAs. This approach has potential as a straightforward and cost-efficient means of engineering nanotextured solar cell surfaces.

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Figure 1. Top-view SEM images showing pre-MacEtch GaAs after Au electrodeposition for (a) $t_{ED} = 24$ min (Sample A) and (b) $t_{ED} = 12$ min (Samples B and C). Scale bars represent 1 μm .

Figure 2.

Tilted-view (top row) and cross-sectional (bottom row) SEM images showing (a,d) Sample A after $t_{ED} = 24$ min and $t_{ME} = 30$ min, (b,e) Sample B after $t_{ED} = 12$ min and $t_{ME} = 30$ min, and (c,f) Sample C after $t_{ED} = 12$ min and $t_{ME} = 60$ min. Scale bars in (a-c) represent $3\ \mu\text{m}$, and in (d-f) represent $1\ \mu\text{m}$.

Figure 3.

Total hemispherical reflectance for bare GaAs and MacEtched GaAs (Samples A – C). Corresponding hemispherical SWR values are shown in the legend. Inset: photograph of specular pre-MacEtch (left; fluorescent lamp reflection visible) and matte post-MacEtch (right) samples.

Figure 4. Post-MacEtch Raman spectrum for Sample C (blue curve) with only trace amounts of β -Ga₂O₃ and α -As phases. The inset shows spectral deconvolution and Lorentzian fitting (grey curves) of Sample C to determine frequency and FWHM of TO, SO, and LO peaks. The red dashed curve shows the cumulative fit. The inset also shows the bare GaAs(100) Raman spectrum (black curve) for comparison.