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# Fabrication of three-dimensional GaAs antireflective structures by metal-assisted chemical etching

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ABSTRACT

Antireflective GaAs subwavelength structures (SWSs) were fabricated by Au-assisted chemical etching. Thermally agglomerated Au nanoparticles caused catalytic reactions with the GaAs substrates in $KMnO_4$ and HF etchant. Various features of the Au nanoparticles agglomerated after heat treatment of Au thin films. The reflectance of GaAs strongly depended on the three-dimensional features of the GaAs SWSs, which were controlled by Au agglomeration and chemical etching. GaAs SWSs dramatically reduced the total reflectance to 4.5% in a wavelength rage of 200–850 nm up to the incident angle of 50°. Solar-weighted total reflectance values quantitatively confirmed the highly efficient antireflective coating fabricated by metal assisted chemical etching on GaAs SWSs. To our knowledge, this is the first report that fabricates GaAs SWSs using metal-assisted chemical etching with thermally agglomerated metal catalyst. This technique is a viable alternative to conventional reactive ion etching and nano-lithography for fabricating antireflective SWSs for III–V solar cells.



## 1. Introduction

Surface antireflection techniques are widely used to improve the performance of optical devices such as solar cells [1–3], optical sensors [4,5], and light-emitting diodes [6,7] by eliminating unwanted surface reflection. Various types of antireflective coatings have been used to reduce surface reflection; however, these coatings are only effective over a limited spectral range and suffer from issues such as thermal mismatch, poor adhesion and stability [8,9]. On the other hand, subwavelength structures (SWSs), which were inspired by the moth eye [10], have been shown to be highly effective. SWSs have surface nanostructures with smaller dimensions than the wavelength of incident light. Their reflectance is low over a wide spectral range, producing the same effects as a stack of thin films with antireflective coatings due to a graded drop in the effective refractive index from air to the device [11]. In addition, because SWSs are fabricated by surface texturing, the absence of foreign materials enhances the long-term stability of optical devices, without material issues regarding mechanical and thermal stability. For high efficiency solar cell applications, a broadband wide-angle antireflective layer is required. Many studies have investigated whether applying SWSs to Si-based solar cells improves device performance [12–15].

Gallium arsenide (GaAs) is a crucial semiconductor material in high efficiency solar cell applications, especially in single junction solar cells, because it has the optimum bandgap energy according to the Shockley–Queisser theoretical efficiency limit. However, SWSs of GaAs have not been investigated intensively. Addition of SWSs to GaAs solar cells is expected to suppress surface reflection and significantly improve quantum efficiency [16,17].

Common fabrication methods for SWSs are based on reactive ion etching of nano-scale etch mask patterns formed by e-beam or nanoimprint lithography [18,19]. However, these nanolithography processes are expensive and complex. In addition, reactive ion etching is not suitable for III–V semiconductor materials such as GaAs because high-energy plasma ions induce incurable surface charging and damage the crystal structure, resulting in the formation of minority carrier recombination sites [20].

In this work, we perform metal-assisted chemical etching using thermally agglomerated Au nanoparticles to fabricate subwavelength GaAs surface structures. A thermal agglomeration and sputtering methodology of metal thin films are of great interest for forming nanopatterns because they allows simple and low cost fabrication over a large area [21–23] as compared with conventional lithography techniques. Thermally agglomerated Au nanoparticles act as etch catalysts during metal-assisted chemical etching, providing SWSs with antireflective properties. Metal-assisted chemical etching is a simple wet-based anisotropic etch process based on a metal catalyst and redox solution [24–26]. Electronic holes generated by catalytic reactions move into the

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semiconductor and cause oxidization. Subsequently, the oxidized semiconductor is etched by an acid solution. The continual repetition of oxidation and removing cycle submerges the metal layer in the semiconductor. It has been reported to be a viable alternative to conventional etching techniques for high aspect ratio 3-D semiconductor architectures with limited damage [27–30].

Antireflective characteristics of SWSs depend strongly on their dimensions and heights. We adjusted the dimension of SWSs by controlling the thickness of Au films and the thermal temperature. The height of SWSs was controlled by etch time. We systematically investigated the antireflection properties of GaAs SWSs, and determined their weighted reflectance for the standard solar spectrum. Reflectance was analyzed quantitatively to determine the optimal antireflection structures for solar cell applications.

## 2. Experiments details

Si-doped n-GaAs (100) substrates with resistivity in the range of 2.4–3.3 $\times 10^{-3}\,\Omega$ cm were pre-cleaned with conventional solvent and rinsed in deionized (DI) water. Au thin films that were 3, 5, and 10 nm thick were thermally evaporated on GaAs substrates at a 0.3 Å/s deposition rate under a pressure of $10^{-6}$ Torr. Prior to evaporation, native oxides were removed using a dilute HCl solution ($HCl:H_2O=1:1$), and substrates were thoroughly cleaned by rinsing with DI water. To form Au nanoparticles, samples were treated thermally by rapid thermal annealing (RTA) at temperatures of 500, 600, and 700 °C for 100 s in a nitrogen environment. Au nanoparticles were used as catalysts for metal-assisted chemical etching. An etch solution was prepared by dissolving potassium permanganate ($KMnO_4$) in DI water by stirring for 30 min. Then $KMnO_4$ solution was mixed with hydrofluoric acid (HF). Samples were dipped in the solution for designated durations of 3, 6, 9, or 12 min at 50 °C. During this metal-assisted chemical etching process, Au nanoparticles sank into the GaAs substrate through chemical reaction between the metal catalyst and redox solution, resulting in the formation of subwavelength nanohole structures. The thermally agglomerated Au nanopatterns and etched profiles, depths, and surface morphologies of GaAs SWSs were characterized by Field emission scanning electron microscopy (FE-SEM). The average sizes of Au nanoparticles and etched nanoholes were quantified using ImageJ (NIH, http://imagej.nih.gov/ij/). To evaluate the reflectance of GaAs SWSs, total reflectance and variable angle specular reflectance at angles of 7°, 20°, 30°, 40°, 50°, 60°, and 70° were measured using an UV–vis–NIR spectrophotometer.

## 3. Results and discussion

Fig. 1 shows the top-view SEM images of Au nanopatterns after RTA at 600 °C for (A) 3 nm-, (B) 5 nm- and (C) 10 nm-thick Au films, and after RTA at (D) 500 °C and (E) 700 °C for 3 nm-thick Au film. During the RTA process, Au films agglomerated into nano-sized particles due to the interplay between thermodynamics and kinetics. The geometry of Au nanopatterns was strongly dependent on the initial thickness of the Au films and subsequent temperature. When the Au films became thicker at 600 °C (A, B, C), the Au nanoparticles became, on average, larger. The Au nanoparticles were $67.1 \pm 47.0$ nm, $94.2 \pm 63.2$ nm, and $125.9 \pm 101.7$ nm for the 3, 5, and 10 nm-thick Au films, respectively. For thicker Au films, agglomeration was not complete. Because the thermal energy provided was not sufficient, the nanoparticles had a non-uniform size distribution with a large deviation. For the fixed Au film thickness of 3 nm (A, D, E), the size of Au nanoparticles gradually increased from $36.8 \pm 17.5$ nm to $93.4 \pm 70.7$ nm as the temperature increased from 500 °C to 700 °C. We attributed this to an increase in the agglomeration rate at a higher thermal temperature because of the relatively high surface free energy. Clearly, catalyst size, which is an important determinant of the dimensions of SWSs, could be adjusted by controlling the thickness of the Au films and the thermal temperature. However, at the temperature of 700 °C, as shown in Fig. 1E, surface morphology changed and circular craters with diameters of 200–400 nm and depths of 5–16 nm were formed. This was due to reaction between Au and Ga at this high temperature, resulting in production of $AuGa_2$. Fig. 1F shows XRD profiles before (as-dep.) and after (A, E) thermal annealing of RTA at 600 and 700 °C for Au films of 3 nm in diffraction angle ($2\theta$) of 20–50°. $AuGa_2$ peaks appeared after annealing at 700 °C. The reaction of Au with Ga degrades the catalytic activity of the Au nanoparticles for etching and negatively affects the reflectance characteristics. This point will be discussed in more detail below.

Thermally agglomerated Au nanoparticles were used as catalysts for metal-assisted chemical etching. During the etching, the continual cycles of oxidation and removal force the Au

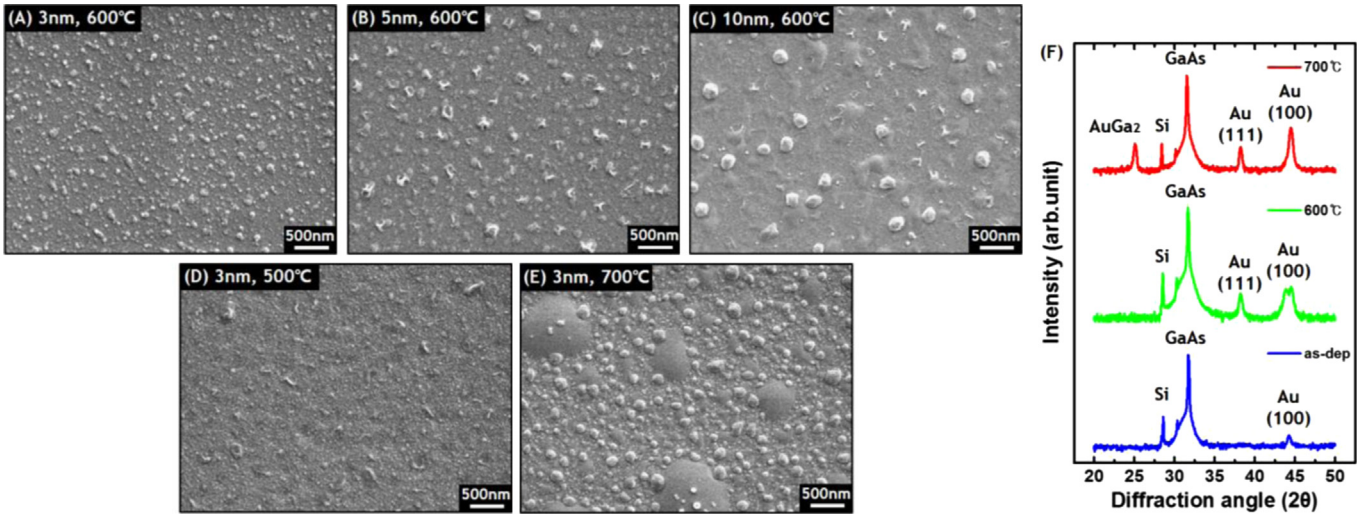


**Fig. 1.** Top view SEM images of the Au nanopatterns on GaAs substrates after RTA at 600 °C for (A) 3 nm-, (B) 5 nm-, and (C) 10 nm-thick Au film and after RTA at (D) 500 °C and (E) 700 °C for 3 nm-thick Au film. The RTA time was fixed at 100 s. (F) XRD profiles before (as-dep.) and after (A, E) thermal annealing of RTA at 600 and 700 °C for Au films of 3 nm in diffraction angle ($2\theta$) of 20–50°.