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Random Surface Texturing of Silicon Dioxide Using Gold Agglomerates

by Kimberley A Olver

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by Kimberley A Olver
Sensors and Electron Devices Directorate, ARL

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1. Introduction

The US Army has been developing new types of photovoltaic (PV) devices—solar cells—for use in its efforts to more efficiently functionalize the Army warfighter. Gallium arsenide (GaAs) solar cells, as well as other III-V semiconductors, are currently being studied for their advantages over silicon solar cells. Because GaAs is a direct bandgap material, its conversion of light into power is more efficient than silicon. This gives GaAs solar cells the advantage in low-light conditions. Further, when designed with a multi-junction architecture, GaAs solar cells are able to respond to multiple wavelengths of light, respective of each P-N junction. Transmitted photons can pass through the different materials until they reach the layer in which they can be absorbed, thus increasing the solar cell's efficiency.

Solar cells work by converting sunlight (electromagnetic radiation) into electricity. Photon absorption needs to occur inside the solar cell's active region (near the bandgap; photon energy ≥ material bandgap) for a PV conversion to occur. However, due to energy losses, only a certain percentage of photons incident on the surface of the solar cell actually end up in the active region able to convert photon energy into electrical energy. Several mechanisms contribute to energy losses in solar cells, including heat loss, recombination loss, and reflective loss. Of those, reflection of incident light falling onto the surface of a solar cell is a major optical loss mechanism, which limits the efficiency of the PV.^{1,2}

One method of reducing the reflective loss and increasing the number of photons reaching the solar cell's active region is to attempt to confine the reflected light by creating a surface structure that internally reflects the light and sends it back into the device. This is sometimes referred to as light trapping. Light trapping is achieved by changing the angle by which the light travels back into the solar cell. The standard method for enhancing absorption in a solar cell is to employ front or back surface texturing that scatters light in the layer at multiple angles, thereby increasing its path length.³ The surface structure can be either a periodic or random pattern and can be a single layer on top of the solar cell or a top layer as part of a multilayer anti-reflective (AR) coating.

Because of its wide use in AR coatings, silicon dioxide (SiO₂) was chosen as the material for creating a random surface texture structure. In this study, the idea was to pattern the SiO₂ with a metal mask, then etch the oxide in a plasma etching tool for a given amount of time. For fabricating an irregular pattern into the SiO₂, evaporated gold was used as the dry etch mask material. A very thin film of gold, when deposited onto a clean SiO₂ surface, forms a discontinuous film. During the initial stages of nucleation on the surface, gold forms agglomerations consisting of

distinct island structures. These agglomerates are irregular in shape, but are regular in distribution. After forming the gold agglomerates, the SiO₂ can be dry etched to a depth that gives maximum enhancement to the solar cell. The gold can then be easily removed leaving only the SiO₂ surface structure.

2. Procedure

A fabrication process was designed for creating random surface texturing on SiO₂ using a thin film of evaporated gold. This textured surface would be used as a light-trapping structure on top of GaAs solar cells. A 3-inch silicon wafer with a 2-micron-thick cap layer of thermally grown SiO₂ was used as the test material. The wafer was first mechanically diced into 1 cm² samples. The samples were then cleaned by rinsing with acetone, then isopropyl, followed by deionized water (DiH₂O), and finally blown dry with nitrogen gas.

After cleaning, a sample was placed into a Thermionics vacuum electron beam deposition chamber. At the same time, a clean glass slide was also placed into the vacuum chamber in close proximity to the sample. The purpose of the glass slide was to act as a visual indicator of the formation of gold clusters on the SiO₂. The glass would make observing a color change in the gold film easier later in the fabrication process. The chamber was pumped down to a pressure of 1e⁻⁶ Torr. A timed evaporation of 110 Å of pure gold was performed at a constant rate of 1.3 Å/s. A Leybold-Heraeus Inficon crystal thickness monitor was used to measure the deposition rate.

After deposition, both the sample and the cover slide were simultaneously placed onto a preheated 340 °C hot plate. This thermal activation step reduced the oxide surface energy and aided in the agglomeration formation. The time needed on the hot plate was dependent upon the gold film changing from a green hue to a red hue, averaging less than 10 s. The color change seen on the glass slide was due to the agglomerates changing in size. Different sizes of particles resonate at specific frequencies. These frequencies equate to color changes in the film—in this case, the agglomerates becoming larger. This new gold film architecture would now be used as a metal mask in the SiO₂ etching process.

After the formation of the agglomerates, the SiO₂ sample was etched in a Unaxis VLR 700 Etcher with a plasma gas mixture of methane/tetrafluoride. After etching, the gold particles were removed. To remove the gold, the sample was sprayed with acetone, methanol and DiH₂O using a Paasche airbrush. The sample was then characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Figure 1 shows the details of the fabrication process.

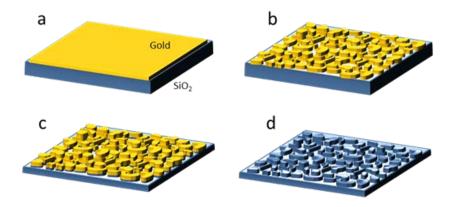


Fig. 1 a) E-beam deposited thin gold layer the SiO_2 surface, b) gold agglomerates on the SiO_2 surface, c) agglomerates used as the etch mask, and d) irregular pattern etched into the SiO_2 surface

3. Results and Discussion

The goal of this study was to create a surface texturing technique that would be used in the fabrication of a light-trapping structure on the surface of a solar cell. Photons that are lost due to reflection are not absorbed in the active region of the solar cell (the bandgap), and therefore do not generate power. This textured surface would reduce reflections from the surface of the solar cell, redirecting the light (photons) back into the active region of the device, thus increasing the number of mobile charge carriers, and therefore increasing the efficiency of the solar cell.

Gold was used as the mask material for fabricating the light-trapping structure. When gold is deposited as a very thin layer onto an oxide, it coalesces and forms irregular islands on the surface. This is known as the Volmer-Weber growth mechanism or "complete islanding",⁴ in which the deposited metal (in this case, gold) immediately forms islands on the oxide surface during the initial stages of nucleation. These islands form as an even distribution of small irregular shapes. When heat is applied the metal-oxide bond is weakened, further facilitating the islanding.

Creating an irregular surface in the SiO₂ top layer of the solar cell was accomplished by first depositing a very thin film of gold metal onto the oxide surface and then placing the sample onto a pre-heated hot plate. The gold almost immediately formed agglomerates on the surface of the oxide. This new gold morphology was then used as a gold etching mask for the SiO₂ film underneath. SEM and AFM were the primary characterization techniques used to evaluate the resulting surfaces, before and after etching, and after removing the gold (Figs. 2 and 3).

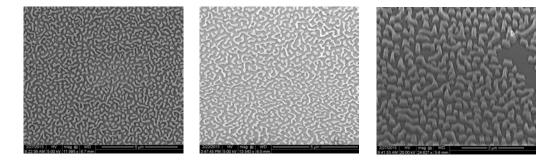


Fig. 2 $\,$ a) SEM images of gold agglomerates on the surface of the SiO₂, b) after etching, and c) after gold removal

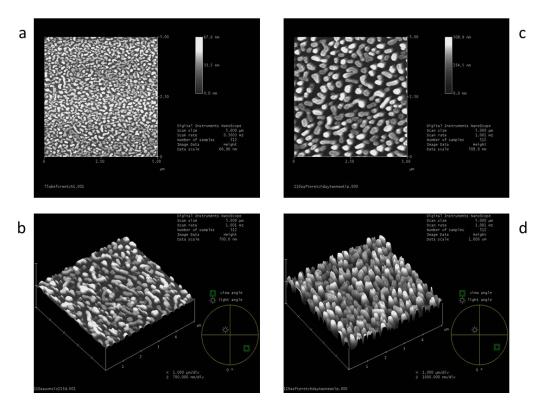


Fig. 3 AFM images (a, b) before and (c, d) after etching the SiO₂

Both the SEM images in Fig. 2 and the AFM images in Fig. 3 show the gold agglomerations on the surface of the SiO_2 film and the fabricated surface structure. As seen in the images, the deposited gold layer formed an even distribution of small, irregular shapes on the surface of the oxide. Figures 2c, 3c, and 3d show the resulting textured SiO_2 film.

4. Conclusion

In conclusion, a fabrication process for the formation of a textured structure for use in AR coatings has been demonstrated. The nucleation of a deposited thin gold film on the surface of SiO_2 was observed. Heating the film further coalesced the gold into discreet islands forming irregular agglomerates on the oxide surface. These agglomerates formed the pattern of gold used as a metal mask for the SiO_2 dry etch process. By varying the thickness of the film and the annealing time and temperature, it may be possible to design a more specific pattern of agglomeration on the oxide surface.

Using SiO₂ as the top layer in an AR coating and creating this surface structure would be the best way of testing the effectiveness of this surface structure in reducing the reflective losses in GaAs solar cells.

5. References

- 1. Honsberg C, Bowden S. PVCDROM [accessed 2015]. www.pveducation.org.
- 2. Chhajed S, Schubert MF, Kim JK, Schubert EF. Nanostructured multilayer graded-index antireflection coating for Si solar cells with broadband and omnidirectional characteristics. Applied Phys Let. 2008;93.25:251108.
- 3. Ferry VE, Munday JN, Atwater HA. Design considerations for plasmonic photovoltaics. Adv Mat. 2010;22.43:4794–4808.
- 4. Feldman LC, Mayer JW. Fundamentals of surface and thin film analysis. New York: North-Holland; 1986.

Bibliography

NanoComposix. plasmonic nanoparticles [accessed 2015]. http://nanocomposix.com/pages/plasmonics.

Paulson G, Friedberg A. coalescence and agglomeration of gold films. Thin Solid Films. 1970;5:47–52.

List of Symbols, Abbreviations, and Acronyms

AFM atomic force microscopy

AR anti-reflective

DiH₂O deionized water

GaAs gallium arsenide

PV photovoltaic

SEM scanning electron microscopy

SiO₂ silicon dioxide

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- 2 US ARMY RSRCH LAB (PDF) IMAL HRA MAIL & RECORDS MGMT RDRL CIO L TECHL LIB
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