Low Reflectance GaAs Nano-cones Fabricated by Colloidal Lithography for Solar Cells

Nan Liu, **Yu Hu**, **and Jian-Jun He**
State Key Laboratory of Modern Optical Instrumentation, Centre for Integrated Optoelectronics
Department of Optical Engineering, Zhejiang University, Hangzhou 310027, China

Abstract— In this paper, we demonstrate a new method of fabricating large-area well-ordered nano-cones using colloidal lithography and inductively coupled plasma (ICP) dry etching, and discuss the anti-reflectance performance. In the fabrication, we use SiO_2 nano-particles as the mask. Its selectivity in different reacting gases in ICP can result in different shapes of nanostructures. Before the etching, we use methanol-assisted self-assembly at the air/water interface to form the patterns. Different ICP etching recipes are used to form rod-shaped and cone-shaped nanowires with the same height and period. The resultant nano-cone structures are well-shaped with smooth side walls. After the fabrication, the anti-reflection performance is measured and compared, which shows that cone-shaped nanowires can reduce the surface reflection to lower than 4% over the wavelength range of 400–900 nm, while nano-rods can only keep this value at approximately 6%. Theoretical simulations are also carried out using Comsol, which confirm that nano-cones provide better anti-reflectance performance.

1. INTRODUCTION

Semiconductor nanostructures have attracted great attention for photovoltaic applications. Solar cells with surface modified by nanowires are demonstrated to have much lower reflectance, and thus higher absorption of photons. The improved light harvesting will result in a comparatively higher power conversion efficiency (PCE).

Abundant researches have been made on Si substrates. However, considering the promising application of GaAs nanowires for solar cells [1, 2], low cost and practical nanostructuring methods on III-V materials are in great demand. Generally, III-V compound semiconductor nanowires are fabricated via chemical vapor deposition (CVD), molecular beam epitaxy (MBE), and vapor-liquid-solid (VLS) mechanism [3, 4]. However, these methods require complex procedure and expensive equipment, which have prevented the technology from wide application and mass production. Colloidal lithography is a very appealing alternative choice for patterning nanostructures without using sophisticated equipment and is far less time consuming. In our earlier work, we succeeded in fabricating nano-rods on GaAs substrates using colloidal lithography and ICP dry etching [5]. However, in practical use, the cylindrical shape makes it difficult to fill the gaps between adjacent nano-rods with other materials to form electrodes [6] or p-n junctions [1, 2]. Hence, in this paper, a cone-shaped nanostructure is introduced to mitigate this problem. As for the patterning, we also present a new method of fabricating large-area well-ordered patterns using methanol-assisted self-assembly at the air/water interface instead of spin-coating. The fabricated patterns are uniformly-distributed and the area can be as large as $2 \times 2\,\mathrm{cm}^2$, or even larger. Lower reflection is obtained as compared to nano-rods with the same period and height.

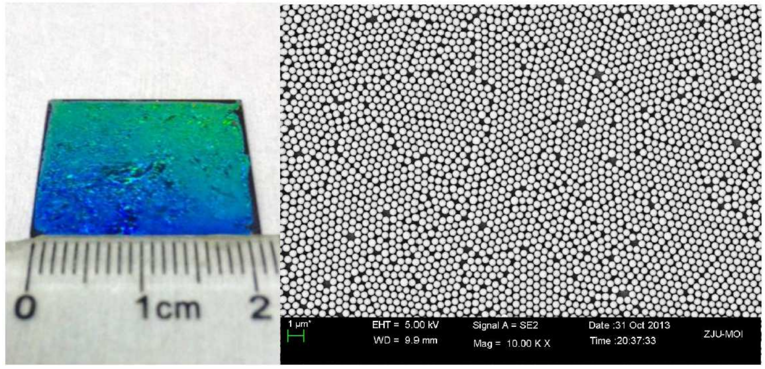
2. FABRECATION METHOD

We use methanol-assisted self-assembly [7, 8] to form a large-area uniformly-distributed SiO_2 nano-particle mask, as shown in Figure 1. First, we treat the cleaned GaAs substrate with oxygen plasma in ICP to improve its hydrophobicity. Then deionized water is dropped onto the wafer surface to form a 2 mm-thick water film, into which we continuously and slowly inject the well-mixed aqueous suspensions with SiO_2 nano-spheres. The methanol-water mixture carries the SiO_2 spheres to water film surface, which quickly disperse. After the sample is dried up, the nanoparticles are left self-assembled at the sample surface.

In order to obtain a well-ordered monolayer of nano-spheres, it is essential to inject an appropriate amount of the suspension liquid. The SiO_2 nano-sphere number n in unit volume of suspension liquid is given by

$$n = 6w/\left(\pi Q D^3\right) \tag{1}$$

where w is the SiO_2 sphere content (in weight) in unit volume, and Q and D are the density and diameter of the SiO_2 spheres, respectively. The needed volume V of the suspension liquid should



(a) (b)

Figure 1: (a) Photo of a self-assembled SiO_2 nano-spheres sample showing iridescent color, and (b) the top view by SEM.

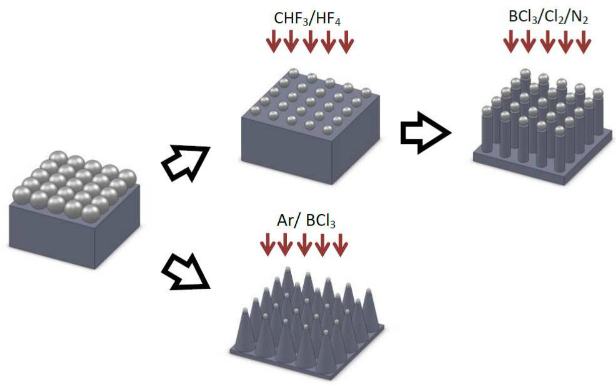


Figure 2: Different procedure of fabricating nano-rods and nano-cones.

satisfy

$$\frac{\pi SQD}{6w} < V < \frac{2SQD}{3w} \tag{2}$$

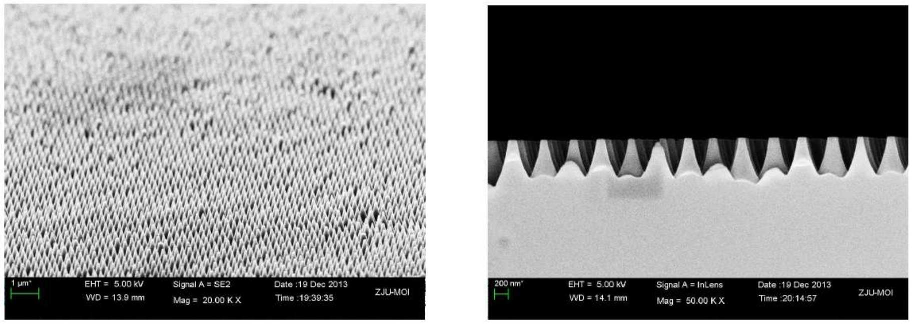
where S is the area of the wafer.

After the self-assembly process, etching of GaAs is performed by ICP (Oxford Plasmalab System 100) using Ar/ BCl_3 chemistry. BCl_3 is the main reactive gas for etching GaAs, while the accelerated Ar plasma provides a non-selective etching on both SiO_2 and GaAs. The two gases, with a ratio of 1 : 3, result in the cone-shaped nanostructure, as shown in Figure 2.

Figure 3 shows the SEM images of the fabricated nano-cones. For nano-rods, we use a $BCl_3/Cl_2/N_2$ chemistry instead to obtain vertical side walls. BCl_3 and Cl_2 provide high selectivity in etching GaAs under SiO_2 mask, while N_2 generates a passivation layer to improve smoothness and verticality [9].

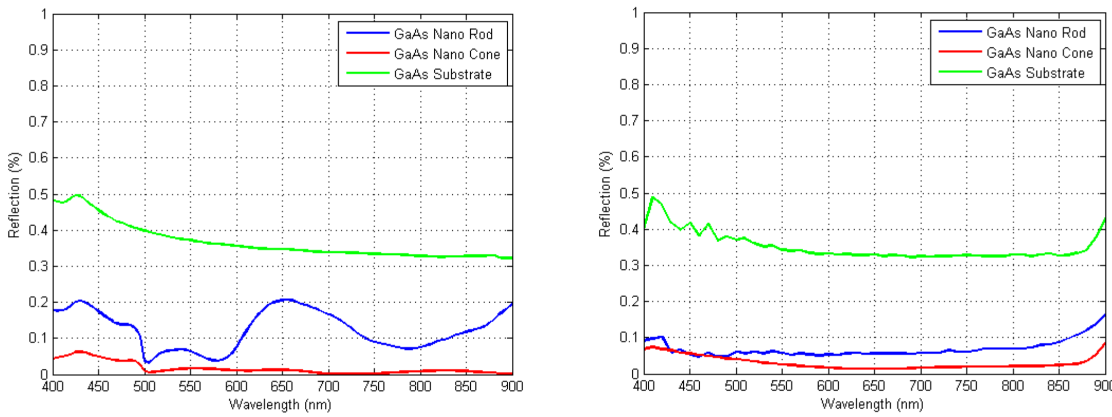
3. RESULTS AND DISCUSSIONS

Figure 4 shows the simulated and measured reflectance of the nano-cone sample, compared with those of a nanorode sample and a GaAs substrate. For comparison, the etched nano-rods have the same period and height as the nano-cones. The simulation was performed using the finite element method [10]. Both the simulation and experimental results show that the nano-cone sample has lower reflectance compared to the nano-rod sample, while both exhibit significantly lower reflection compared to the GaAs substrate. The valleys of both nano-rod and nano-cone curves at 500 nm in the calculated spectra are due to the grating effect resulted from the assumption of perfect periodicity, which are absent in the measured spectra. The oscillations in the nano-rod reflection spectra are due to Fabry-Perot effect inside the cylindrical structure, with a flat top playing the role as the cavity mirror. The fact that the nano-cones exhibit better anti-reflectance performance than nano-rods can thus be attributed to the non-reflective sharp tips. In the measured spectra of



(a) (b)

Figure 3: (a) Top view and (b) side view of fabricated nano-cones by SEM.



(a) (b)

Figure 4: (a) Simulated and (b) measured reflectance of nano-cone and nano-rod modified surfaces.

Fig. 4(b), the reflectance increases after 870 nm, for which the substrates become transparent, are due to artifact of back reflection from the sample holder.

4. CONCLUSION

In conclusion, we fabricated a large-area uniformly-distributed GaAs nano-cones by colloidal lithography and ICP dry etching. The nano-cone structure has smooth side walls and provides anti-reflectance performance better than that of nano-rod structure.

ACKNOWLEDGMENT

The authors thank R. R. LaPierre of McMaster University for helpful discussions. This work was supported by the Ministry of Science and Technology of China (Grant No. 2010DFA61370).

REFERENCES

1. Bi, H. and R. R. LaPierre, "A GaAs nanowire/P3HT hybrid photovoltaic device," *Nanotechnology*, Vol. 20, No. 46, 465205, 2009.
2. Chao, J.-J., S.-C. Shiu, S.-C. Hung, and C.-F. Lin, "GaAs nanowire/poly (3,4-ethylenedioxythiophene): poly(styrenesulfonate) hybrid solar cells," *Nanotechnology*, Vol. 21, No. 28, 285203, 2010.
3. Mohseni, P. K., C. Maunders, G. A. Botton, and R. R. LaPierre, "GaP/GaAsP/GaP core-multishell nanowire heterostructures on (111) silicon," *Nanotechnology*, Vol. 18, No. 44, 445304, 2007.
4. Asoh, H., A. Uehara, and S. Ono, "Nanopatterning of Si substrate using nanospheres as a mask for localized anodization," *Japanese Journal of Applied Physics*, Vol. 43, Part 1, No. 8A, 5667, 2004.

5. Chen, K., M. Li, J.-J. He, and R. LaPierre, "GaAs nanowires fabricated using colloidal lithography and dry etching," *IEEE Asia Communications and Photonics Conference and Exhibition*, 2011.
6. Liang, D., Y. Kang, Y. Huo, Y. Chen, Y. Cui, and J. S. Harris, "High-efficiency nanostructured window GaAs solar cells," *Nano Letters,* Vol. 13, No. 10, 4850–4856, 2013.
7. Ngo, H. T., H. N. Wang, A. M. Fales, and T. Vo-Dinh, "Label-free DNA biosensor based on SERS molecular sentinel on nanowave chip," *Analytical Chemistry,* Vol. 85, No. 13, 6378–6383, 2013.
8. Dai, Z., Y. Li, G. Duan, L. Jia, and W. Cai, "Phase diagram, design of monolayer binary colloidal crystals, and their fabrication based on ethanol-assisted self-assembly at the air/water interface," *ACS Nano*, Vol. 6, No. 8, 6706–6716, 2012.
9. Volatier, M., D. Duchesne, and R. Morandotti, "Extremely high aspect ratio GaAs and GaAs/AlGaAs nanowave-guides fabricated using chlorine ICP etching with N2-promoted passivation," *Nanotechnology,* Vol. 21, No. 13, 134014, 2010.
10. Hu, Y., R. R. LaPierre, M. Li, K. Chen, and J.-J. He, "Optical characteristics of GaAs nanowire solar cells," *Journal of Applied Physics,* Vol. 112, No. 10, 104311, 2012.