Manipulation of photonic crystal nanostructures based on nanosphere lithography

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Abstract

In this paper, we investigate optical absorption characteristic of highly ordered subwavelength 2D nanocone arrays which are fabricated by single-step deep reactive ion etching with nanosphere lithography. By changing reactive gas content, we successfully achieved various sidewall profiles which determine absorption characteristic of 2D nanocone array. Our total absorption measurement results show that the absorption of crystalline Si is improved from 68% to ~95% over a broad wavelength range of 400nm to 900nm with Si nanocone array.

1. Introduction

After first demonstration of solar cell, many researchers have been strived to improve photovoltaic efficiency and an economical rationality. Due to the innate high refractive index value of silicon (Si) material, Si based solar cell suffer from a low absorption of the solar energy. Therefore the cost reduction and absorption enhancement become a major interest in photovoltaic technology. The surface texturing (such as inverted pyramid etc.) developed for an enhanced light trapping in bulk Si over broad spectral range and wide incident angle. This could be a better solution than the quarter-wavelength antireflection coating which can only improve the absorption of a specific wavelength range and limited angle of incident solar energy. However, due to the thickness limitation, this strategy cannot directly compatible with thin film Si solar cell, which is about two order of magnitude thinner and cheaper than bulk Si solar cell. Recently, new strategy of enhanced light absorption based on nanostructure, such as Si nanocone (SiNC) [1] and Si nanowire (SiNW) [2] is proposed. These nanostructures can provide a gradually increased nanoscale refractive index structure and minimize reflection arising from refractive index difference at the Si and air interface.[3] Therefore, it is necessary to investigate the correlation between absorption characteristic and geometry of Si nanostructure. In this paper, we have fabricated aligned Si nanocone array with various sidewall profile by using nanosphere lithography and single-step deep reactive ion etching. And we have investigated total (spectral and diffused) absorption and reflection property of nanostructures on crystalline Si substrate based on UV/VIS spectrometer with integrating sphere.

2. Sample preparation

Our approach to highly ordered Si nanostructure using self-assembled nanosphere lithography is composed of two steps. The first step is deposition of polystyrene (PS) nanosphere mask. And the second step is inductively coupled plasma (ICP) etching. Before the deposition, p-type (1 0 0) crystalline silicon substrates were cut in to pieces of 20mm \times 20mm. Every pieces were cleaned with standard RCA I process (kept in a solution of NH₄OH (25%), $H_2O_2(30\%)$, and water at 80°C for 15min) to make hydrophilic Si surface.

The deposition of PS sphere (dia. = 500nm), purchased from Thermo Scientific, begins from introducing of a nanosphere mixture solution on the surface of deionized water (18 M Ω ·cm) in a large petri dish (dia. = 20cm). The mixture solution consists of ethanol and nanosphere water suspension (10% w/v) with proper ratio. As you can see the inset of Fig. 1(a), only when we make the suitable mixture concentration, we can see the iridescent colour from a monolayer of highly ordered 2D close packed PS nanosphere on the water. Subsequently, the deionized water is drained and evaporated. Finally, the monolayer of nanosphere was slowly transferred onto the silicon substrate located beneath the petri dish. [4]

The pattern of PS sphere mask was transferred to the Si substrate via ICP etching. The reactive gas SF_6 and C_4F_8 , and O_2 were used to remove the substrate and control the sidewall profile of Si nanostructure. The conventional 'Bosch' time-multiplexed reactive ion etching(or deep reactive ion etching (DRIE)) process consist of alternated etching cycle of SF_6 based Si etch and C_4F_8 based deposition of fluorinated polymer for sidewall passivation. For the convenience of fabrication, we choose the single-step DRIE (ICP etching with of SF_6 and C_4F_8 reactive plasma gas).[5] Due to a vertical side wall and high Si etch rate, these two reactive gases are popular for nanostructure fabrication.

During the ICP etching, relatively low etching selectivity of the plasma gases to PS sphere mask makes a Si nanocone via simultaneous removal of PS sphere mask and Si substrate.[3] And we show that the side wall profile of nanocone can changed by adjusting a small amount of additional O_2 plasma gas (about 10sccm). Therefore, we can achieve the fabrication of Si nanocone without the time-multiplexed step as shown in Fig. 1.



Fig. 1 Sample preparation and investigation procedure (a) transferred PS sphere (Dia.=500nm) monolayer mask on Si substrate ($20 \times 20 \text{ mm}$) (b) SEM image of transferred PS sphere (normal view) (c) SEM image of Si substrate and PS sphere mask during the nanocone fabrication via ICP etching (d) Side wall profile investigation method with SEM of dual beam focused ion beam (FIB)

3. Experimental result

To evaluate optical property of our Si nanostructure, we measure the total (spectral and diffuse) reflection and transmission from 250nm to 900nm with Shimadz UV-VIS-NIR spectrophotometer (model. UV3600) and 60mm integrating sphere (MPC-3100). The spectrophotometer can support the total re-

flection and transmission at 8° without leaning the sample. From the energy conservation, we can assume that the total incident light energy to be transmitted, reflected, or absorbed, that is, A = 1 - R - T.[6] After measure the transmission and reflection, we can evaluate the absorption.



Fig. 2 Side wall profile (cross sectional SEM image) from dual focused ion beam (FIB) with different taper angle (a) Si nanocone 1 (SF₆:C₄F₈=45:35 sccm) (b) Si nanocone 2 (SF₆:C₄F₈:O₂=45:35:10 sccm)
(c) Absorbance data of Si nanocones and bare Si substrate at 8° incident angle (also transmission data of Si)

As shown in Fig. 2, we compare two different Si nanocone structure. The Si nanocone1 (Fig. 2(a)) has a sharp tip with height of ~500nm and taper angle 110°. And the Si nanocone2 (Fig. 2(b)) has a round tip with height of ~600nm and taper angle 95°. The absorption of Si substrate is significantly improved from 68% to ~95% with the nanocone structures in Fig. 2.

4. Conclusion

In this paper, we fabricated highly ordered subwavelength 2D nanocone array with controllable sidewall profile via single-step deep reactive ion ething and nanosphere lithography. Based on measurement of total reflection and transmission with UV/VIS/NIR spectrometer, we have investigated absorption characteristic of 2D nanocone array. Our experimental results show that the absorption of crystalline Si is improved from 68% to ~95% over a broad wavelength range of 400nm to 900nm with an optimized Si nanocone array.

Acknowledgments

This work has been supported by the Low Observable Technology Research Center program of Defense Acquisition Program Administration and Agency for Defence Development.

References

- J. Zhu, Z. Yu, G. F. Burkhard, C. Hsu, S. T. Connor, Y. Xu, Q. Wang, M. McGehee, S. Fan, and Y. Cui, "Optical Absorption Enhancement in Amorphous Silicon Nanowire and Nanocone Arrays", Nano Lett., vol.9, pp.279-282, 2009.
- [2] K. Peng, Y. Xu, Y. Wu, Y. Yan, S, Lee, and J, Zhu, "Aligned Single-Crystalline Si Nanowire Arrays for Photovoltaic Applications", small, vol. 1, pp.1062-1067, 2005.
- [3] S. Chuang, H. Chen, J. Shieh, C. Lin, C. Cheng, H. Liu, and C. Yu, "Nanoscale of biomimetic moth eye structures exhibiting inverse polarization phenomena at the Brewster angle", Nanoscale, vol.2 pp.799-805, 2010.
- [4] A. Kosiorek, W. Kandulski, H. Glaczynska, and M. Giersig, "Fabrication of Nanoscale Rings, Dots, and Rods by Combining Shadow Nanosphere Lithography and Annealed Polystyrene Nanosphere Masks", Small, vol. 1, pp.439-444, 2005.
- [5] Y. Hung, S. Lee, and L. A. Coldren, "Deep and tapered silicon photonic crystals for achieving antireflection and enhanced absorption", Optics Express, vol.18, pp.6841-6852, 2010.
- [6] Z. Yang,L.Ci, J. A. Bur,S. Lin, and P. M. Ajayan, "Experimental Observation of an Extremely Dark Material Made By a Low-Density Nanotube Array", Nano Lett. vol. 8 pp.446-451, 2008.