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Dear editor:

We would like to submit an original paper titled as “Optical properties of nanocrystal-silicon thin films on silicon nanopillar arrays after thermal annealing” (Authors: Yonglei Li, Bo Qian*, Cong Li, Jun Xu, Chunping Jiang)” to *Applied Surface Science*.

In this paper, the optical properties of nanocrystal-silicon thin films on silicon nanopillar arrays after thermal annealing have been carefully studied. The results show the structure have great potential to the design of solar cell devices.

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Thank you very much for your help. It is greatly appreciated if you can give us the suggestions and comments as soon as possible.

Best wishes!

Sincerely yours,

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Highlights:

- A combined structure fabricated by conformally assembling nc-Si film on a periodic arranged silicon nanopillar array has been demonstrated.

- The reflectivity spectra of this combined structure have revealed a remarkable reduction and the minimum reflectivity has been demonstrated to be 0.7%.

- By tuning thermal annealing temperature, this structure shows a wide-range tunability of light emission efficiency of nc-Si, from big suppression to large enhancement, compared with the referential flat sample. The maximum emission suppression factor is 12.5 while the maximum enhancement factor is 8.8.
Optical properties of nanocrystal-silicon thin films on silicon nanopillar arrays after thermal annealing

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Abstract:

The optical properties of nanocrystal-silicon (nc-Si) thin films on silicon nanopillar arrays after thermal annealing treatments have been investigated in this paper. The structure was prepared by SiO\textsubscript{2} nanosphere lithography, reactive-ion etching, conformal deposition method and thermal annealing treatment, successively. The thickness of nc-Si thin film is about 100 nm, while the diameter, period and height of silicon nanopillar arrays are about 250 nm, 500 nm and 1 \(\mu\)m, respectively. By reflectivity and photoluminescence (PL) spectroscopy measurements in visible to near-infrared wavelength range, the minimum reflectivity of about 0.7\% has been demonstrated in such kind of structure, meanwhile, a large variation (from 12.5 times of suppression to 8.8 times of enhancement compared to the flat referential thin films) of the light emission efficiencies of the samples depending on the thermal annealing temperatures has been observed, which is due to the temperature dependent modification of optical constants of nc-Si thin films. By combining the nc-Si with
silicon nanopillar arrays, the structure will be very promising for the design of radial p-i-n junction solar cell devices.

**Keywords:** nanocrystal-silicon, nanopillar array, reflectivity, photoluminescence, solar cell.
1. Introduction

Silicon nanostructures, including silicon nanocrystals (nc-Si) [1-5] and nanowires (SiNWs) or nanopillars [6], are promising candidates for next generation solar cells with higher energy conversion efficiencies and lower cost. In nc-Si, it has been observed that there is carrier multiplication by generation of two or more electron-hole pairs following the absorption of a single photon [1]. This may lead to improved photovoltaic (PV) efficiencies, which is close to the energy conservation limit [2]. Meanwhile, SiNWs or nanopillar arrays are also very attractive for energy conversion for the new generation photovoltaic technology, since the structure’s extraordinary light-trapping path length enhancement factor is above the randomized scattering (Lambertian) limit [7-10] and is superior to other light trapping methods. Furthermore, the design of radial p-n junction structures on silicon nanopillars by conformal deposition method provide short travel distances of photo-excited minority carriers to the collection electrodes, leading to enhanced carrier-collection efficiency and minimum bulk recombination [11-13]. Another advantage of the radial geometry is the high tolerance of PVs for material defects, permitting the use of lower-quality Si with shorter minority-carrier diffusion lengths [6].

Therefore, it will be interesting to combining nc-Si and silicon nanopillar arrays to realize solar cell devices to achieve higher PV efficiencies [14], and the radial p-i-n junction geometry will be a suitable design [11]. Different from the previous work [11] on single SiNW, in this paper, a hybrid structure of nc-Si thin films and Si nanopillar arrays were prepared by conformal deposition method. The optical properties including reflectivity spectra and photoluminescence spectra of such structures with different thermal annealing temperatures have been investigated. This work will be a promising step to the design of nc-Si based photonics devices.
2. Experimental Details

The samples were fabricated by five steps as following: (I) Self-assembling of a close-packed 500 nm SiO$_2$ nanosphere monolayer was performed on a clean Si wafer by dip-coating method [7, 9]. The volume percent (V%) of SiO$_2$ nanospheres in ethyl alcohol is 3~5%. (II) Si nanopillar array was formed by nanosphere lithography technology [15] and an inductively coupled-plasma deep reactive-ion-etching (ICP-DRIE) process. The selective and anisotropic etching process was based on fluorine chemistry using a mixture gas of C$_4$F$_8$, SF$_6$ and O$_2$, with the flux ratio of 80sccm:70sccm:5sccm. (III) The remained nanospheres were selectively wiped off from the tips of the pillars by a buffered HF solution. (IV) 100 nm-thick Si-rich SiO$_x$ ($x<2$) film was deposited conformably upon the nanopillar array to construct the final combined structure by plasma enhanced chemical vapor deposition (PECVD) [16] with the reaction gas flux ratio here is SiH$_4$/N$_2$O/Ar=35sccm/710sccm/180sccm. Note that the same film was also deposited on flat Si wafer for reference. (V) To form nc-Si, all the samples were annealed at temperatures of 1100 °C, 1150°C, 1200°C, 1250 °C, respectively, for 30 min in N$_2$ protection, which is a usual way to prepare Si nanocrystals [17, 18].

The samples’ surface morphologies and sizes were characterized by Hitachi S4800 scanning electron microscope (SEM) in the whole process. High-resolution transmission electron microscopy (HRTEM) was also performed to confirm the existence of nc-Si. To study the optical properties, room-temperature photoluminescence (PL) spectra of our samples, excited by a He-Cd 325nm laser and received by a CCD detector, were performed and analyzed with a grating monochromator. The reflectivity spectra of nc-Si films on flat Si wafers and on
nanopillar arrays were also measured. The refractive index of nc-Si films on flat referential substrates was measured by J.A.Woollam M-2000 ellipsometer.

3. Results and Discussion

Figure 1 gives the structure details in SEM images for each fabrication step. It can be confirmed in Fig. 1(a) that the large area, close-packed, hexagonal SiO$_2$ nanosphere monolayer has been produced by dip-coating. Although minority line and point defects exist, they are negligible compared to the whole area. After 4 minute ICP-DRIE process, the pattern of SiO$_2$ nanosphere monolayer was transformed into silicon nanopillar arrays as shown in Fig. 1(b). The size of SiO$_2$ nanospheres on nanopillars is reduced after etching. Following the nanosphere mask, the period of nanopillar arrays is about 500 nm. The pillar arrays after wiping off the SiO$_2$ nanospheres are presented in Fig. 1(c). The diameter and height of each nanopillar is about 250 nm and 1 µm respectively. From the inset of Fig. 1(c), the bottom of pillar array is observed relatively larger than the other part, just like a collar around it. This is probably due to the etching gas distribution between nanopillars. Fig. 1(d) shows the final structure after depositing 100 nm SiO$_x$ film on pillar array. The height of each pillar remains 1 µm while the diameter increases to about 330 nm, from which thickness of nc-Si film along the radial direction can be calculated to be about 40 nm, which means the lateral growth rate of the film is largely reduced. Note that the roughness of pillars is increased because of the conformal growth effect. However, such roughness has been proved to increase the electrical injection efficiency [6].

To study the basic structure and optical properties of nc-Si thin films, the TEM and ellipsometry measurement were performed with the referential nc-Si thin films on flat Si wafers. Fig. 2(a) presents a typical TEM picture of a nc-Si thin film sample, in
which nc-Si was obtained after 1200 °C thermal annealing. The average size of the nc-Si is about 3.5nm. Fig. 2(b) illustrates the evolution of refractive index for SiO$_x$ film on flat substrate annealed at different temperature. In the spectrum ranging from 350 nm to 1000 nm, it can be clearly observed that there is a monotonic decreasing of the refractive index when increasing the annealing temperature, which indicates increasingly widen of the optical band gap of the SiO$_x$ film [19-21]. This can be due to continuously decrease of the degree of disorder of the thin film, caused by the formation of nc-Si in it [22].

To demonstrate the extraordinary light trapping ability of Si nanopillar arrays [7-10], the reflectivity spectra of samples with the same nc-Si films on flat Si wafer and on nanopillar arrays at different annealing temperature were measured for comparison. Fig. 3(a) illustrated the results of the sample annealed at 1250°C. It can be observed that the main band in the reflectivity spectra of the nc-Si film on flat wafers is ranging from 300nm to 650nm, the maximum value is about 20.5% at around 375nm; for the wavelength longer than 650nm, the reflectivity is lower than 8%. For the samples on nanopillar arrays, the reflectivity band of flat samples vanishes and the reflectivity at 375nm is reduced to 1.4%, about 15 times reduction. The minimum reflectivity of the nanopillar samples is about 0.7% at about 550 nm, while the whole reflection spectra is lower than 3%. Fig. 3(b) shows the maximum and minimum reflectivity in all the reflectivity spectra for samples annealed at different temperatures. It can be observed that, for flat samples, the maximum of the reflectivity is increasing from 12.8% to 21.9% with improving annealing temperature, while the minimum of reflectivity is increasing from 2.4% to 4.3%. For nanopillar array samples, the maximum value of reflectivity is decreasing from 2.4% to 1.5%,
while the minimum reflectivity is, almost stay the same, lower than 1.0%. The results demonstrate such kind of structure on nanopillar arrays is very suitable for solar cell applications.

Fig. 4(a) shows the schematics of the optical setup for PL measurements. The position of CCD detector is carefully adjusted to avoid the collection of input laser light, though at this condition it only can get part of the emission information. Following parts of Fig. 4 present the PL spectra of the nc-Si films on nanopillar arrays annealed at different temperatures meanwhile those of the same nc-Si films on flat Si substrates are also presented for references. From Fig. 4(b-e), two main emission bands centered around 430 nm and 790 nm can be observed in almost all of the samples, except the flat sample annealed at 1100℃ in Fig. 4(b). The peak at around 430 nm is commonly attributed to the recombination at an oxygen-related defect state (O-Si-O) [23, 24] related to nc-Si in SiO₂ matrices [18, 25-27]. The peak at around 790 nm in the near-infrared is generally assigned to the excitonic emission [28, 29] from Si=O state [30, 31] on the surface of nc-Si [18]. It should be noted that the peak shift in Fig. 4(b) from flat sample to the related nanopillar structure is probably due to the change of nc-Si size on the related combined structure at the lowest annealing temperature of 1100 ℃.

Interestingly, it can be observed in Fig. 4(b-e) that the combined nanopillar array structure shows a rather large tunability to the emission efficiency of nc-Si by controlling the annealing temperature. When annealed at 1100 ℃, as described in Fig. 4(b), the PL intensity of the combined structure shows a big suppression compared with the related flat sample, with the maximum suppression factor of 12.5 at 670 nm. It acts as a role of inhibiting or trapping light emission, just like the anti-reflection
surface for solar cells. At 1150 °C in Fig. 4(c), the structure increases a little bit of the emission intensity at around 430 nm, while oppositely decreases that at around 800 nm. When annealing temperature increases to 1200 °C in Fig. 4(d), the structure slightly reduces the intensity for both of the main emission bands above. At the highest annealing temperature of 1250 °C, comparison between the PL lineshapes of the both reveals that the structure possesses a tremendously large enhancement ability. For the emission band centered around 430 nm, emission intensity of this combined structure is about 8.8 times as tall as that of the flat sample, while for the band at around 800 nm, the enhancement factor is about 5.5.

As the monotonic decrease of refractive index of nc-Si films when increasing annealing temperature shown in Fig. 2(b), Tunable PL efficiency on this combined nanopillar structure in Fig. 4(b-e) is probably related to the dynamic optical periodic modification of our nanopillar array with nc-Si conformal film on it when annealed at different temperatures. The results are very important and helpful for the design of nc-Si based photonic devices [32].

4. Conclusion

We have demonstrated a combined structure fabricated by conformally assembling nc-Si film on a periodic arranged silicon nanopillar array. By tuning the thermal annealing temperature, photoluminescence behavior of such kind of structure shows a wide-range tunability of light emission efficiency of nc-Si, from big suppression to large enhancement, comparing with the referential flat sample. The maximum emission suppression factor is about 12.5 meanwhile the maximum enhancement factor is 8.8. The reflectivity spectra of this combined structure have revealed a remarkable reduction and the minimum reflectivity has been demonstrated
to be 0.7%, which shows a great potential application for the design of solar cell devices.

Acknowledgment

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References:


[16] Gong-Ru Lin, Chun-Jung Lin and Cheng-Tao Lin, Low-plasma and high-temperature PECVD grown silicon-rich SiOx film with enhanced carrier
tunneling and light emission, Nanotechnology 18 395202 (2007).


Captions:

Figure 1: Real-time monitoring of our combined structure by SEM images during the whole fabrication process. (a) Closely self-assembled nanosphere monolayer via dip-coating. (b) Nanopillar array with spheres on the tips after ICP-DRIE. (c) Nanopillar array after removal of the residual mask. (d) Final combined structure after depositing a layer of nc-Si film upon pillar array. The inset of each picture is the sectional view. Scale bar of the inset is 1 µm.

Figure 2: (a) High resolution TEM image of the nc-Si film annealed at 1200°C. The visible Silicon nanocrystals are highlighted by circles for clarity with average size about 3.5nm. (b) Curves of refractive index of nc-Si thin films deposited on flat Si wafers with different annealing temperatures.

Figure 3: (a) Reflectivity spectra of the nc-Si thin films on flat Si wafer (represented by squares) and on nanopillar array (represented by circles). Both the samples were annealed at 1250°C. (b) The maximum and minimum reflectivity of all the reflectivity spectra for samples annealed at different temperatures.

Figure 4: Schematic diagram of PL testing (Fig. (a)) & Comparison of PL lineshapes between the same nc-Si film deposited on flat Si wafer and our nanopillar array. Films were annealed at (b) 1100°C, (c) 1150°C, (d) 1200°C and (e) 1250°C, respectively.
Figure 3

(a) Reflectivity of nc-Si film on flat Si wafer and nc-Si film on nanopillar array as a function of wavelength.

(b) Reflectivity of nc-Si film on flat wafer and nc-Si film on nanopillar array as a function of annealing temperature.
Figure 4

(c) Annealed at 1150°C
- nc-Si on flat wafer
- nc-Si on nanopillar array

(d) Annealed at 1200°C
- nc-Si on flat wafer
- nc-Si on nanopillar array

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Figure 4

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