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Novel Quantum Effect Devices realized by Fusion of Bio-template and Defect-Free Neutral Beam Etching

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Introduction

Recently, an all-silicon tandem solar cell comprising a quantum dot superlattice (QDSL) has attracted much attention due to its potential to breakthrough the Shockley-Queisser limit.[1,2] One of the advantages of the QDSL is that the required energy band gap for each cell can be engineered by changing the quantum dot size.[3] Reportedly, the maximum conversion efficiency can be improved up to 47.5% for three-cell tandem stacks.[4] However, not only the uniformity and control of QD size but also of the spacing between QDs are equivalently essential to generate the miniband in the QDSL for carrier transport.[5] The ideal spacing between QDs is approximately 2 nm or less in the SiO_2 matrix.[6] The technique widely used to fabricate the Si quantum dot superlattice is depositing alternately multiple layers of amorphous silicon-rich oxide (SiO_x, x<2) and stoichiometric silicon dioxide (SiO_2) by sputtering or plasma-enhanced chemical vapor deposition followed by annealing at a high temperature.[6,7] However, the results showed nonuniform dot size and dot spacing.

To address these problems, we have developed a sub-10nm-silicon-nano-disk (Si-ND) structure using the bio-template (□7-nm-etching-mask) and damage-free chlorine (Cl) neutral beam (NB) etching.[8] The fabricated ND had a quantum effect, i.e. Coulomb staircase, at room temperature (RT). Two geometrical parameters of thickness and diameter in Si-ND can be independently controlled. Interestingly, the quantum effect of a single Si-ND is strongly dependent on its thickness, while almost independent of its diameter.[8] In this study, a 2D Si ND array with a high-density and well-ordered arrangement could be fabricated by using bio-template and an etching process combined with nitrogen trifluoride (NF_3) gas/hydrogen radical treatment (NF_3 treatment) and Cl NB etching. In this structure, the controllable band gap energy (from 2.2eV to 1.4eV) and high photon absorption coefficient (>10^5 cm^{-1}) could be obtained at RT by controlling the Si-ND structure.

Fabrication of high-density 2D array of Si-ND

The fabrication of a 2D Si-ND array using the bio-template and damage-free NB etching[8] is schematically shown in Fig. 1(a). The steps are as follows: multilayer films of 1.4-nm SiO_2, several nm-thick poly-Si and 3-nm SiO_2 (the 3-nm SiO_2 was fabricated by our developed neutral beam oxidation at a low temperature of 300 ºC and is called NBO SiO_2 hereafter) were sequentially prepared on a Si wafer as shown in Fig.1(1), Fig.1(2), and Fig.1(3), respectively; (4) a 2D array of ferritin molecules (protein including iron oxide core (Fe-core) in the cavity) was placed through directed selforganization on the surface of NBO SiO_2; (5) ferritin protein shells were removed by heat treatment in oxygen atmosphere to obtain 2D Fe-core as a template; (6) etching was carried out using a NF_3 treatment and Cl NB etching to remove NBO SiO_2 and poly-Si, respectively; (7) and finally 2D Fe core was removed by using hydrochloric solution. The sample underwent NF_3 treatment for 30 min to remove NBO SiO_2 and NB etching for 90 seconds to remove 4-nm poly-Si. Figure 2 shows a SEM image of the top view of the sample after etching. We can see that the 2D Si-ND array has a high-density (>7×10^{11} cm^{-2}) and well-ordered arrangement. The 2D array is what remained after etching, proving that a good-quality 2D Si-ND array was successfully fabricated using the bio-template and Cl NB etching with NF_3 treatment. We performed NF_3 treatment to investigate the controllability of the ND diameter, i.e. the spacing between NDs. When the NF_3 treatment times were 15 and 30 min, the average gaps were about 1 and 3 nm (G_{ii} and G_{iii}), and the diameters were about 10 and 8 nm (D_{ii} and D_{iii}), respectively . These results suggest that the spacing between adjacent NDs can be controlled by changing the NF_3 treatment time, which also indicates that the formation of miniband in a 2D Si-ND array can be controlled. Although the spacing control by NF_3 treatment is accompanied by inevitable changes in diameter, as shown in Fig. 4, the diameter changes do not affect the quantum effect, which was proven in a previous work.[8]

Optical Properties of 2D Si-ND array

The absorption properties of the structure were studied by measuring the transmission for samples by UV-vis-NIR. The absorption coefficient has been calculated in accordance with the equation below[9]

$$T=e^{-\alpha d}$$

α being the absorption coefficient, *d* the total thickness of the ND thickness and surface oxide thickness (3-nm thick), and *T* the transmittance of light passing through the structure. Figure 3(a) shows the results of an absorption coefficient of the structure as a function of ND thickness. We found that the absorption spectra strongly depend on the ND thickness and the absorption edge is blue-shifted when the ND thickness decreases due to the quantum size effect. Additionally, the absorption coefficient (>10^5 cm^{-1}) of 2D Si-ND array is extremely high, and therefore it is possible to obtain sufficient absorption if the NDs can be integrated into the 3rd dimension. To determine the optical band gap energy of the structure, the Tauc formula was used:

$$(\alpha h\nu)^{1/2}=A(h\nu-E_g),$$

where *A* is a constant, *h* is Planck/s constant, *v* is frequency, E_g is the band gap energy, and *n* is 1/2 in the case of indirect allowed and forbidden electronic transitions. The Tauc

formulation as a function of ND thickness is plotted in Fig. 3(b). As the ND thickness changes from 2 to 12 nm, the E_g could be controlled from 2.2 to 1.4eV as shown in Fig. 4. From these results, we found that E_g could be certainly controlled by simply changing ND thickness by thin-film deposition in our proposed fabrication Based on the processes, all-Si tandem solar cells assembled with 3D ND array fabricated by stacking 2D Si-ND array as schematically shown in Fig. 5 could be constructed.

Conclusions

We created a 2D Si-ND array with a high-density and well-ordered arrangement using bio-template and an advanced etching process that included NF_3 treatment and damage-free Cl NB etching. The spacing between Si NDs can be controlled in the structure by changing NF_3 treatment time. The E_g can be easily controlled by changing the ND thickness during thin film deposition. The absorption coefficient of single layer 2D Si-ND is comparable to that of 3D QDSL. Our proposed processes for 2D Si-ND array and stacked ND are very feasible for the all-Si tandem solar cells comprising QDSL.

References

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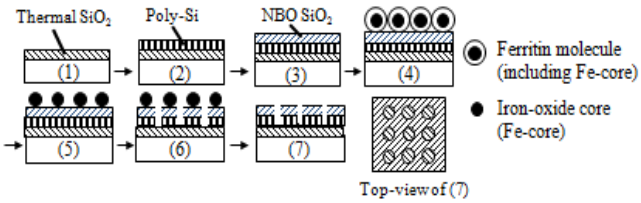

Figure 1. Fabrication flow of 2 dimensional Si nano-disk array by bio-template and chlorine neutral beam etching.

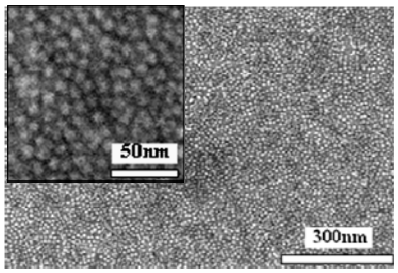

Figure 2. SEM images of 2 dimensional Si nano-disk array fabricated by Cl neutral beam etching with bio-template.

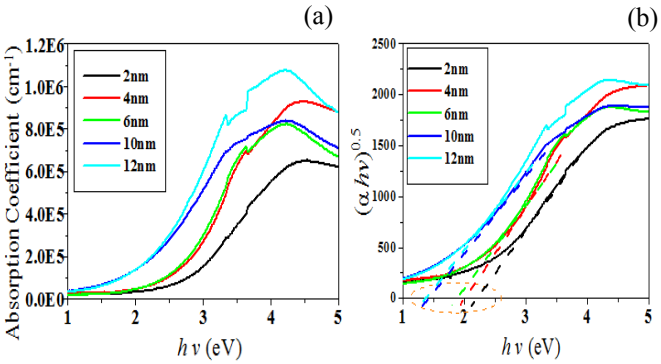

Figure 3. (a) Absorption coefficient (b) Tauc plot of 2 dimensional Si nano-disk array with different nano-disk thicknesses from 2 nm to 12 nm..

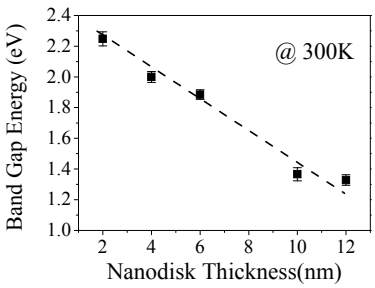

Figure 4. Band gap energy (E_g) of nano-disk with different Si nano-disk thicknesses by using UV-vis-NIR.

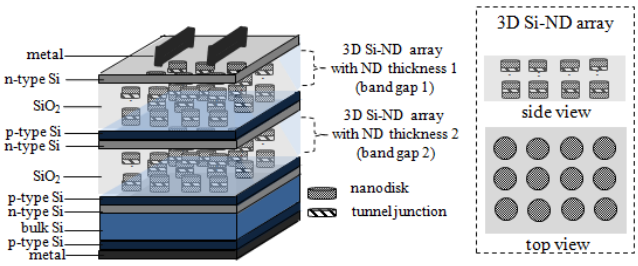

Figure 5. Scheme of all-silicon tandem solar cell assembled with 3 dimensional Si nano-disk array.