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 breach the Shockley-Queisser limit.\textsuperscript{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.\textsuperscript{3) Reportedly, the maximum conversion efficiency can be improved up to 47.5\% for three-cell tandem stacks.\textsuperscript{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.\textsuperscript{3) The ideal spacing between QDs is approximately 2 nm or less in the SiO\textsubscript{2} matrix.\textsuperscript{5) The technique widely used to fabricate the Si quantum dot superlattice is depositing alternately multiple layers of amorphous silicon-rich oxide (SiO\textsubscript{x}, x<2) and stoichiometric silicon dioxide (SiO\textsubscript{2}) by sputtering or plasma-enhanced chemical vapor deposition followed by annealing at a high temperature.\textsuperscript{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.\textsuperscript{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.\textsuperscript{9) In this study, a 2D Si ND array with a high-density and well-ordered arrangement could be fabricated by using bio-template and Cl NB etching.\textsuperscript{8) The fabricated ND layers of amorphous silicon-rich oxide (SiO\textsubscript{x}, x<2) and stoichiometric silicon dioxide (SiO\textsubscript{2}) were sequentially prepared on a Si wafer as shown in Fig. 1(a). The steps are as follows: multilayer films of 1.4-nm SiO\textsubscript{2}, several nm-thick poly-Si and 3-nm SiO\textsubscript{2} (the 3-nm SiO\textsubscript{2} was fabricated by our developed neutral beam oxidation at a low temperature of 300 °C and is called NBO SiO\textsubscript{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\textsubscript{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\textsubscript{3} treatment and Cl NB etching to remove NBO SiO\textsubscript{2} and poly-Si, respectively; (7) and finally 2D Fe core was removed by using hydrochloric solution. The sample underwent NF\textsubscript{3} treatment for 30 min to remove NBO SiO\textsubscript{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\textsuperscript{11} cm\textsuperscript{-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\textsubscript{3} treatment. We performed NF\textsubscript{3} treatment to investigate the controllability of the ND diameter, i.e. the spacing between NDs. When the NF\textsubscript{3} treatment times were 15 and 30 min, the average gaps were about 1 and 3 nm (G\textsubscript{ii} and G\textsubscript{iii}), and the diameters were about 10 and 8 nm (D\textsubscript{ii} and D\textsubscript{iii}), respectively. These results suggest that the spacing between adjacent NDs can be controlled by changing the NF\textsubscript{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\textsubscript{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.\textsuperscript{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\textsuperscript{9)}

\[ T=e^{-\alpha d} \]

\( \alpha \) 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\textsuperscript{5} cm\textsuperscript{-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 3\textsuperscript{rd} dimension. To determine the optical band gap energy of the structure, the Tauc formula was used:

\[ (a\nu)^{2/3}=A(h\nu-E_g) \]

where \( A \) is a constant, \( h \) is Planck’s constant, \( \nu \) 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 1.4 eV 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

2) M. A. Green et al, 20th EU-PVSEC (2005), 1AP.1.1.

![Figure 1: Fabrication flow of 2 dimensional Si nano-disk array by bio-template and chlorine neutral beam etching.](image1)

![Figure 2: SEM images of 2 dimensional Si nano-disk array fabricated by Cl neutral beam etching with bio-template.](image2)

![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.](image3)

![Figure 4: Band gap energy ($E_g$) of nano-disk with different Si nano-disk thicknesses by using UV-vis-NIR.](image4)

![Figure 5: Scheme of all-silicon tandem solar cell assembled with 3 dimensional Si nano-disk array.](image5)