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Optical Characteristics of Two-dimensional Array of Si Nano-disks Fabricated by Defect-free Neutral Beam Etching with Bio-template

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1. Introduction

An all-Si tandem solar cell comprised of quantum dots (QDs) has attracted much attention due to its potential to breakthrough the Shockley-Queisser limit and compatibility with current Si technology.[1)] QDs provide the opportunity to control the energy of carrier states by adjusting the confinement in all three spatial dimensions for various absorption ranges of the solar spectrum. With close-packed QDs embedded in a dielectric matrix, such as SiO_x, SiN_x or SiC, minibands would result from the overlap of the wave functions of adjacent QDs for carrier transport. However, not only the uniformity and control of QD size but also of the spacing between QDs are essential for generating minibands in a close-packed structure for carrier transport. The ideal spacing between QDs is approximately 2 nm or less in a SiO_2 matrix.[2)] The technique widely used to fabricate the Si quantum dot superlattice is alternately depositing multiple layers of amorphous silicon-rich oxide (SiO_x, x<2) and stoichiometric silicon dioxide (SiO_2) using sputtering or plasma-enhanced chemical vapor deposition followed by annealing at a high temperature (usually at 1100 ºC).[2)] However, the results showed nonuniform dot size and dot spacing, which indicates that the minibands would be very difficult to control.

To overcome these issues, we have developed a sub-10-nm-silicon-nano-disk (Si-ND) structure using a bio-template ϕ7-nm etching mask) and damage-free neutral beam (NB) etching.[3)] The fabricated ND shows a quantum effect, i.e. Coulomb staircase, at room temperature (RT). The Si-ND has two geometrical parameters of thickness and diameter, which 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.[3)] We fabricated a 2D Si-ND array with a high-density and well-ordered arrangement using the bio-template and an etching process combined with nitrogen trifluoride (NF_3) gas/hydrogen radical treatment (NF_3 treatment) and Cl NB etching. We investigated the optical characteristics of a 2D Si-ND.

2. Experiment Method

We began the fabrication of a 2D Si-ND array using the bio-template and damage-free NB etching[3)] with (1) deposition of several nm-thick poly-Si thin film on a quartz substrate; (2) formation of a 3-nm SiO_2 film on the poly-Si thin film (the 3-nm SiO_2 film was fabricated using our developed neutral beam oxidation (NBO) process at a low temperature of 300ºC (hereafter, the film is called NBO SiO_2); (3) a 2D array of ferritin molecules (protein including an iron oxide core (Fe-core) in the cavity of ferritin molecule) was placed through directed self-assembly on the surface of the NBO SiO_2; (4) ferritin protein shells were removed using heat treatment in oxygen atmosphere to obtain a 2D Fe-core with a hexagonally close-packed array as a template; (5) etching was carried out using NF_3 treatment and NB etching to remove the NBO SiO_2 and poly-Si, respectively; (6) and finally the 2D Fe core was removed using hydrochloric solution to obtain a 2D Si-ND array. Optical absorption of the 2D Si-ND array and poly-Si thin film were recorded using a JASCO ultra violet visible-near infrared (UV-vis-NIR) spectrophotometer (Model: V-570) with normal incidence light at room temperature. Photoluminescence (PL) of the 2D Si-ND array was measured with an excitation wavelength of 532 nm and excitation power of 10 W/cm^2 at 100 K.

3. Results and Discussions

Figure 1 shows a top view SEM image of a sample after etching of NF_3 treatment for 30 min to remove the NBO SiO_2 and NB etching for 90 seconds to remove the 4-nm poly-Si thin film. We can see that the 2D Si-ND array has a high-density (>7 × 10^{11} cm^{-2}) and well-ordered arrangement (diameter: 10 nm, gap: 2 nm). 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 NB etching with NF_3 treatment.

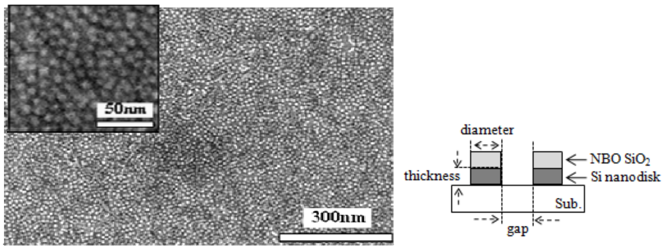
The absorption properties of the structure were studied by measuring the transmission of samples using an UV-vis-NIR spectrophotometer. The absorption coefficient was calculated based on the following equation[4)]

$$\ln (I_0/I) = \alpha d,$$

where α is the absorption coefficient, d is the total thickness of the ND thickness, and I_0 and I are the intensities of incident and transmitted light, respectively. Figure 2 shows the results of an absorption coefficient of the 2D Si-ND array and poly-Si thin film as a function of ND thickness and film thickness, respectively. We found that the absorption spectra of the poly-Si thin film slightly depend on the thin film thickness, and the absorption edge is blue-shifted when the thin film thickness decreases. On the other hand, the absorption spectra of the 2D Si-ND array strongly depend on the ND thickness and show a blue-shift as well. To determine the optical band gap energies of the 2D Si-ND array and poly-Si thin film, we used the Tauc formula:

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

where A is a constant, h is Planck's constant, ν 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 intercept of the linear fitting line at zero absorption in the Tauc plot gives E_g. Figure 3 shows the results of E_g as a function of thin film and ND thicknesses. When the poly-Si thin film thickness changes from 2 to 6 nm, E_g varies from 1.6 to 1.2 eV, which is very close to E_g of bulk Si. For the 2D Si-ND array, E_g can be controlled from 2.2 to 1.4 eV when the ND thickness changes from 2 to 12 nm. This wide controllable range of E_g is suitable for developing all-Si tandem solar cells. For the 3 cells of all-Si tandem solar cell, the E_g of the top cell requires 2 eV. We compared the absorption coefficient when E_g is around 1.4 eV, i.e., ND thickness of 10 nm and thin film thickness of 4 nm. The absorption coefficient of the 2D Si-ND array is compensated by area ratio of 2.5 because around 40% of the measured area is occupied by Si-NDs. Figure 4 shows the results of the absorption coefficient comparison. We found that the absorption coefficient of an 2D Si-ND array is comparable to that of poly-Si thin film. This result suggests that our 2D Si-ND array can achieve a high photon absorption coefficient because of the high in-plane density of NDs. Figure 5 shows the PL spectra of the 2D Si-ND array with ND thicknesses of 4, 6 and 8 nm. When the ND thickness decreases, the PL peaks observed



(a) (b)

Figure 1. (a) SEM images of 2D Si-ND array fabricated using bio-template and neutral beam etching with NF_3 treatment and (b) schematic of cross-sectional 2D Si-ND array (diameter: 10 nm, gap: 2 nm)

(a)

(b)

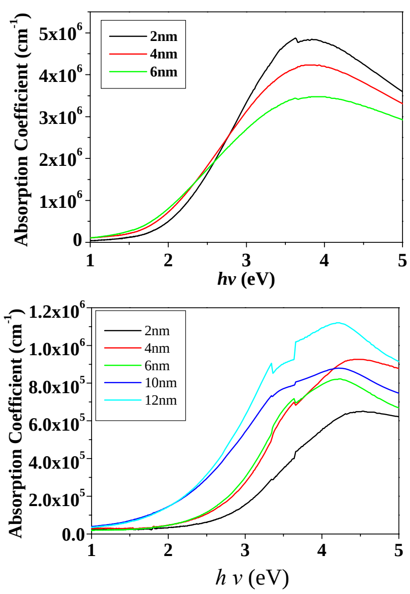


Figure 2. Absorption coefficient of (a) poly-Si thin film with different thicknesses from 2 to 6 nm (b) 2D Si-ND array with different ND thicknesses from 2 to 12 nm.

are also blue-shifted and change from 2.1 to 1.9 eV, which corresponds to E_g measured using the UV-vis-NIR spectrophotometer. From these results, we found that E_g could be controlled by simply changing the ND thickness with thin-film deposition in our proposed fabrication process.

4. Conclusions

We created a 2D Si-ND array with a high-density and well-ordered arrangement using a bio-template and an advanced etching process that included NF_3 treatment and damage-free NB etching. The controllable range of E_g is much wider than poly-Si thin film, which is suitable for developing all-Si tandem solar cells. The E_g and PL emission peaks can be easily controlled by changing the ND thickness during thin film deposition. In our previous study, we had demonstrated stacked NDs, which is for incorporating NDs into the 3rd dimension. Therefore, 3D Si-NDs could be fabricated using a combination of processes of a 2D Si-ND array and stacked NDs, and has great potential for the fabrication of all-Si tandem solar cells.

References

1) M. A. Green et al., 20th EU-PVSEC (2005), 1AP.1.1.
2) E. C. Cho et al., Nanotechnology. **19** (2008) 245201.
3) S. Samukawa et. al., Appl. Phys. Express 1 (2008) 074002.
4) B. Pejova et al., Mater. Chem. Phys. 90 (2005) 35.

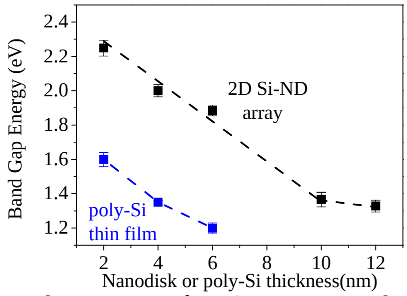


Figure 3. Band gap energy of 2D Si-ND array and poly-Si thin film

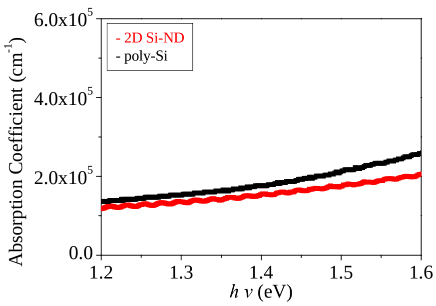


Figure 4. Absorption coefficient comparison between 2D Si-ND array (thickness: 10 nm) and poly-Si thin film (thickness: 4 nm) around the band gap energy of 1.4 eV

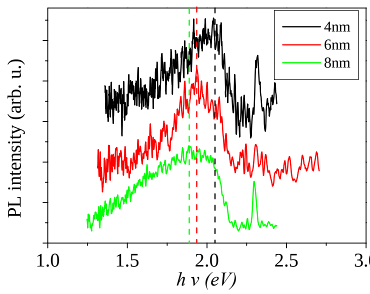


Figure 5. Photoluminescence spectra of 2D Si-ND array with ND thicknesses of 4, 6, and 8 nm at 100 K (excitation wavelength: 532 nm, excitation power: 10 W/cm^2)