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Nanofabrication for Quantum Dot Solar Cell with High Conversion Efficiency

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Abstract. Quantum dot solar cells attract much attention worldwide because of their potential of high power conversion efficiency. Uniform size and highly ordered array of quantum dots are of great importance for the improvement of their power conversion efficiency. In this work, a fabrication technology of uniform and ordered quantum dots based on electron beam lithography and reactive etching was proposed. The influence of the thickness of the tunneling layer on the characteristics was investigated using the fabricated multilayer n-i-p Si simple solar cells. The uniform and ordered Si dots were successfully fabricated using the 2-step etching method. It was exhibited that this nanofabrication technology to obtain high-quality quantum dots could be very useful and possible to greatly improve the power conversion efficiency of quantum dot solar cells.

1. Introduction

Fossil fuel exhaustion and global warming have been concerned in recent years. One of solutions is to use low-cost and high-efficiency photovoltaic technology [1]. Currently Si-based solar cells are most widely used but their cost remains a big problem. In recent years, some new materials and structures are proposed to improve the power conversion efficiency (PCE) [2-5]. Quantum dot solar cell is one of the most researched solar cells as a next generation solar cell because it can have a much higher PCE than current Si solar cells in theory. Using detailed thermodynamic calculations, NREL has shown that quantum dot solar cells operating under concentrated sunlight can have maximum theoretical PCE twice that achievable by conventional solar cells—up to 66%, compared to 31% for present-day first- and second-generation solar cells. How to fabricate the high-quality quantum dots for application to solar cells is a critical problem. Most researchers are focusing on the colloidal quantum dots since they are fabricated from a solution based synthetic methods and they have easily tunable optoelectronic properties [6-9]. However, the arrangement of synthetic quantum dots is difficult to control although a narrow size distribution is possible. When these disordered quantum dots are used for solar cells, recombination of holes and electrons often occurs. This usually results in low PCEs (mostly less than 10%) of these colloidal quantum dot solar cells [10]. The PCE is much less than the current Si-based solar cells. As a result, in order to greatly improve the PCE of quantum dot solar cells, some new methods to fabricate high-quality quantum dots should be insensitively investigated. In this work, a novel fabrication method to obtain a highly ordered quantum dots for solar cells is proposed and some fundamental experimental results are reported in this paper.

2. Quantum dot solar cell

Figure 1(a) shows a conventional p-n junction solar cell and its major losses are schematically shown in Fig. 1(b). There are 6 intrinsic losses for solar cells: the optical loss, the below E_g loss, the thermalization loss, the emission loss, the Carnot loss and the angle mismatch loss [11]. The below E_g loss and thermalization loss are the major losses for the single junction solar cells. When the cell is exposed to the solar spectrum, a photon that has an energy less than the bandgap E_g makes no contribution to the cell output. This loss caused by mismatch between the broad solar spectrum and the mono-energetic absorption of a single bandgap is called below E_g loss [12]. The thermalization loss originates from the fraction of the photons transmitting into the cells that have the energy larger than the bandgap. The free carriers excited by these photons release their energy E in excess of the bandgap (E-E_g) to the phonons, contributing to heat generation.

Schematic of a quantum dot solar cell is shown in Fig. 1(c). There exist quantum dots between n and p semiconductors. As described in the introduction section, quantum dot solar cells are expected to reduce the losses mentioned above. In bulk materials the bandgap is fixed by the choice of material. Quantum dots have band gaps that are tunable across a wide range of energy levels by changing the dots' size. Quantum dots are semiconducting particles that have been reduced below the size of the Exciton Bohr radius and due to quantum mechanics considerations, the electron energies that can exist within them become finite [13]. As a result, the structural configuration of quantum dots leads to formation of an intermediate-band. Mismatch between bandgap and energy of photons can be greatly reduced [14]. Besides this, recombination can be also suppressed in quantum dot solar cells.

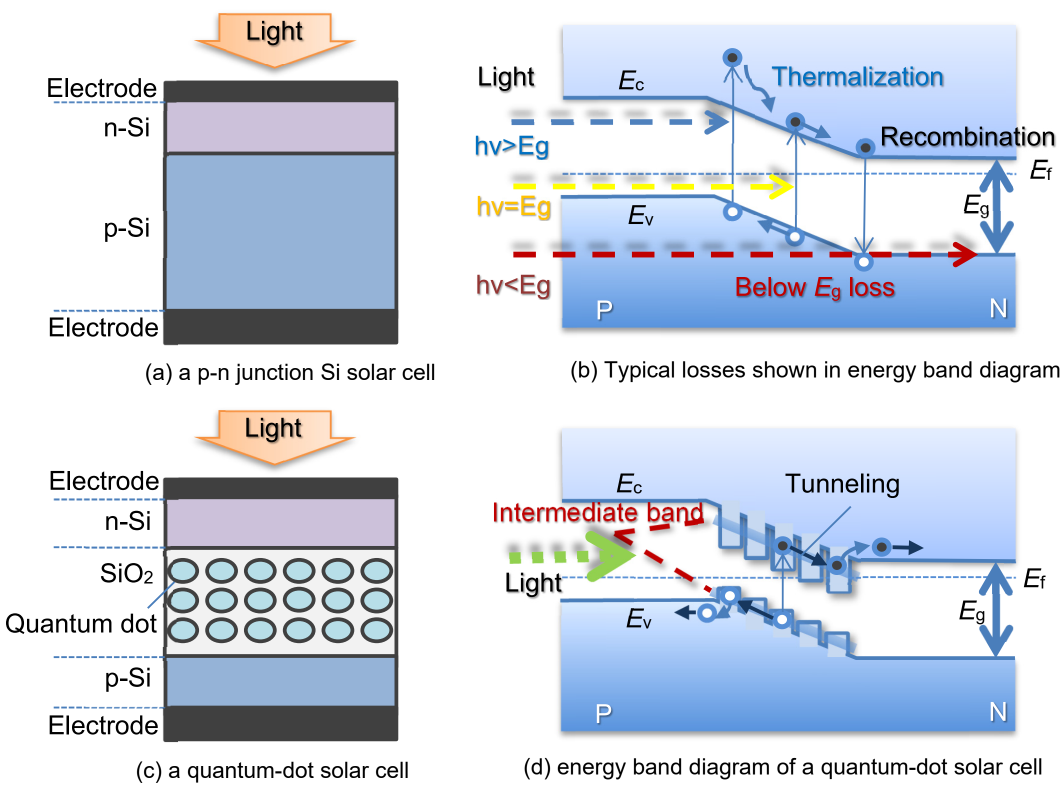


Fig. 1. (a) Schematic diagram of a p-n junction Si solar cell. (b) Typical losses shown in energy band diagram. (c) Schematic diagram of a quantum-dot solar cell. (d) Schematic of energy band diagram of a quantum-dot solar cell.

3. Proposal of a novel quantum dot solar cell

There many methods to fabricate quantum dots for solar cells. Most popular fabrication technique of quantum dots is to take advantage of spontaneous self-assembly or self-organization of coherent 3D islands in lattice mismatched heteroeptaxy in a colloidal solution, molecular beam epitaxy or metalorganic vapour phase epitaxy [14]. However, these quantum dots exhibited random arrangements, which is the main reason why the current quantum dot solar cells have very low PCEs.

In this study, a novel quantum dot solar cell with uniform and ordered quantum dots is proposed. The fabrication processes are shown in Fig. 2. Firstly, SiO_2, intrinsic Si (i-Si) and n-type Si nanolayers are deposited by chemical vapor deposition. Secondly, a layer of electron-beam (EB) resist is spin coated on the top of n-Si layer. Thirdly, dot pattern is formed by EB drawing. Fourthly, the pattern was transferred by etching. Fifthly, electrodes are formed as shown in Fig. 2(e). EB drawing results in uniform and ordered quantum dots and the etching process makes vertical order possible. Figure 2(f) shows the diagram of the measurement of the fabricated solar cell.

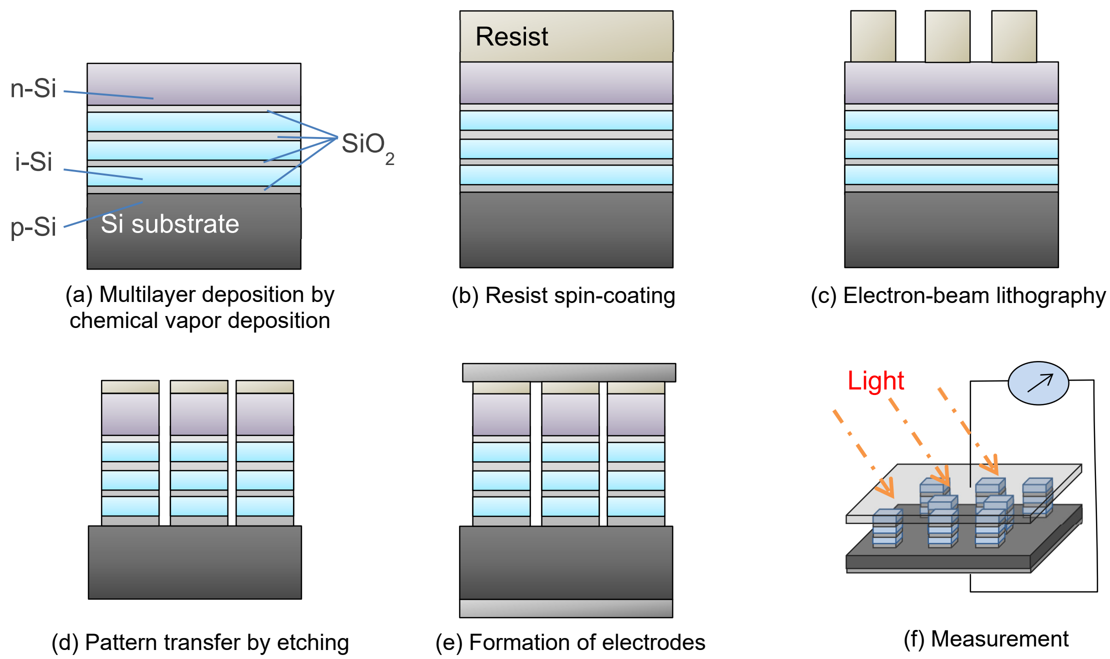


Fig. 2. Schematic of processes of fabrication and measurement of a quantum dot solar

4. Experimental results

4.1 The influence of the tunneling thickness on the characteristics

The schematic diagram of simple solar cells were shown in Fig. 3(a). A SiO_2 layer with a thickness $th_{ox\text{-}p}$ of 1 or 2 nm was thermally grown on the p-type Si substrate. Then a 10-nm-thick amorphous Si layer was deposited using low pressure chemical vapor deposition (LPCVD) and annealed to be poly-Si in N_2 atmosphere. After that, SiO_2 layer with a thickness $th_{ox\text{-}n}$ of 0, 1, 2, or 5 nm was deposited using LPCVD. Finally, a layer of 50-nm-thick poly-Si was deposited using LPCVD and doped P to be a n-type Si.

The *I-V* characteristics of these solar cells with Ag paste electrodes when they were illuminated are shown in Fig. 3(b). All of these simple solar cells showed *I-V* characteristics shifted from that of a typical diode although there existed tunneling layers in the solar cells. It is obvious that the short-circuit current decreased with increasing the thickness $th_{ox\text{-}n}$. The resistances of solar cells are shown in Fig. 3(c). The thicker the SiO_2 layer, the larger the resistance. This should result from the decrease in tunneling possibility for the thicker one. Fig. 3(d) shows the maximum power of the solar cells. High output power could be obtained for solar cells with thin tunneling SiO_2 layers. Based on the *I-V* characteristics of the solar cells, therefore, it can be concluded that 1-nm-thick tunneling SiO_2 layer should be suitable for the quantum dot solar cells.

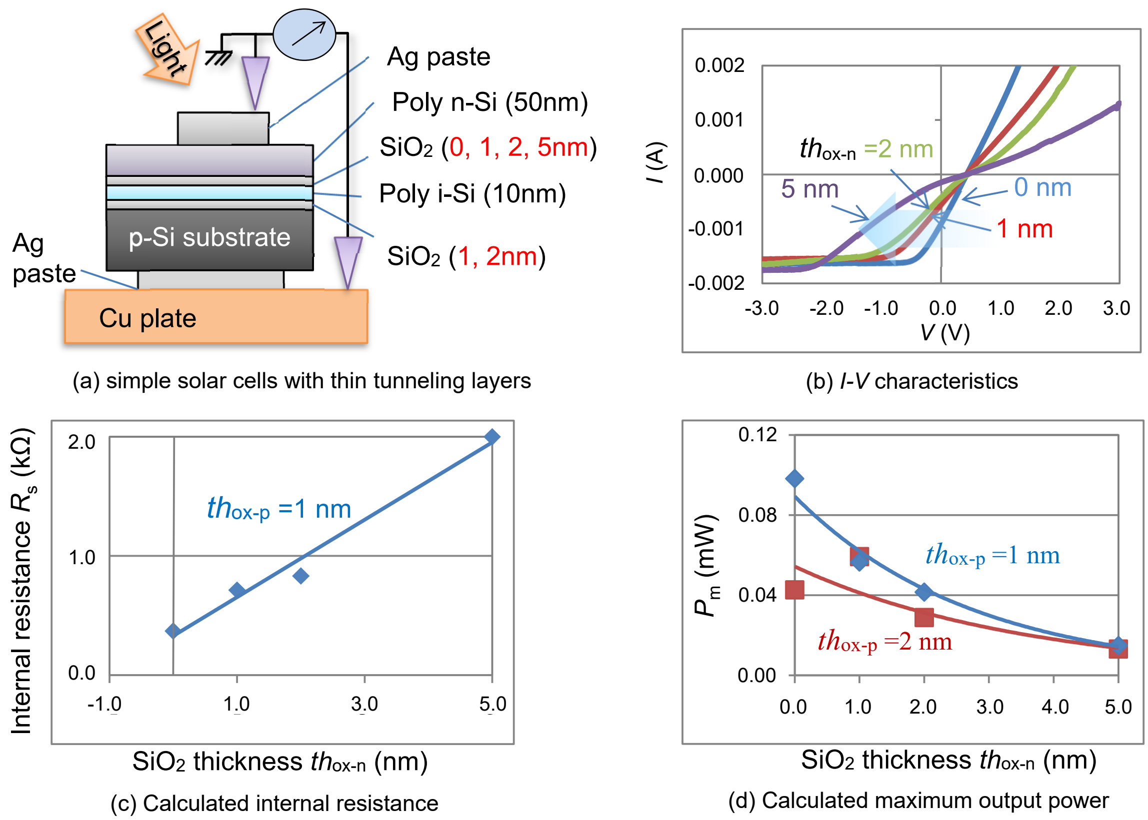


Fig. 3. (a) Schematic of simple solar cells with thin tunneling layers. (b) *I*-*V* characteristics of solar cells with a thickness $th_{ox\text{-}p}$ of 1 nm. (c) Calculated internal resistance as a function of SiO_2 thickness $th_{ox\text{-}n}$. (d) Calculated maximum output power P_m as a function of SiO_2

4.2 Fabrication of quantum dots for solar cell

In this work, a two-step etching method was used for pattern transfer after nano dots were formed. It is not possible to directly transfer the pattern from the resist layer to multilayer Si substrate since the selectivity is not high enough. The processes to form Si quantum dots are illustrated in Fig. 4. The first step is Ar ion milling and the second step is reactive ion etching.

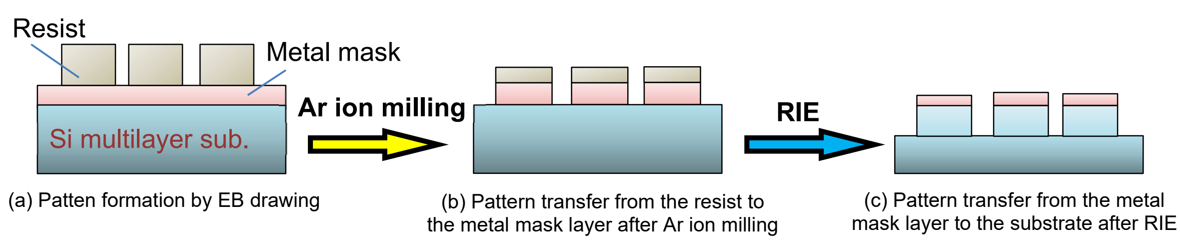
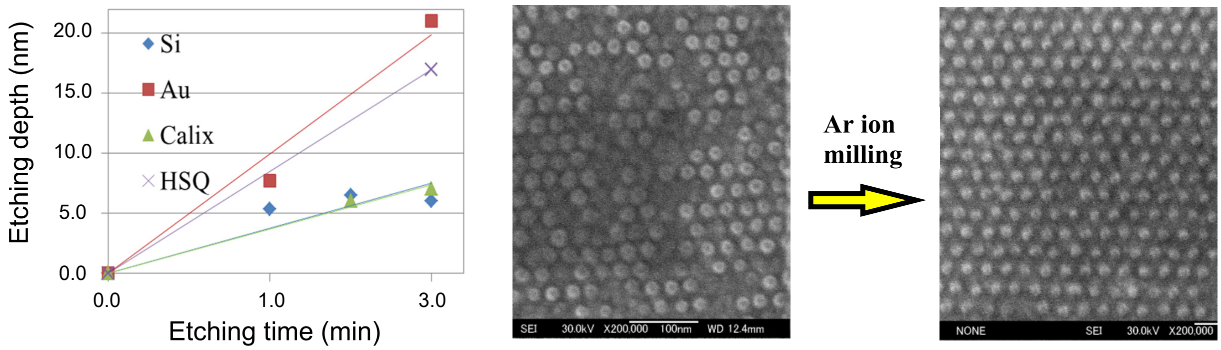


Fig. 4. Nanofabrication of quantum dots with a 2-step etching method.

Etching experiments were conducted to determine the etching selectivity. Au was selected as a metal mask here and two possible high-resolution negative-tone EB resists of HSQ and calixarene were selected. The relationship between the etching depth and the etching time is shown in Fig. 5(a). 200-V Bias and 30-mA current were set when Ar ion milling was conducted. Based on the etching rate ratio, it is clear that the calixarene resist must be a good choice. Using the same experimental condition, calixarene nano resist dots were successfully transferred to the Au metal mask layer. The fabricated calixarene and Au nano dots are shown in Figs. 5(b) and 5(c), respectively.



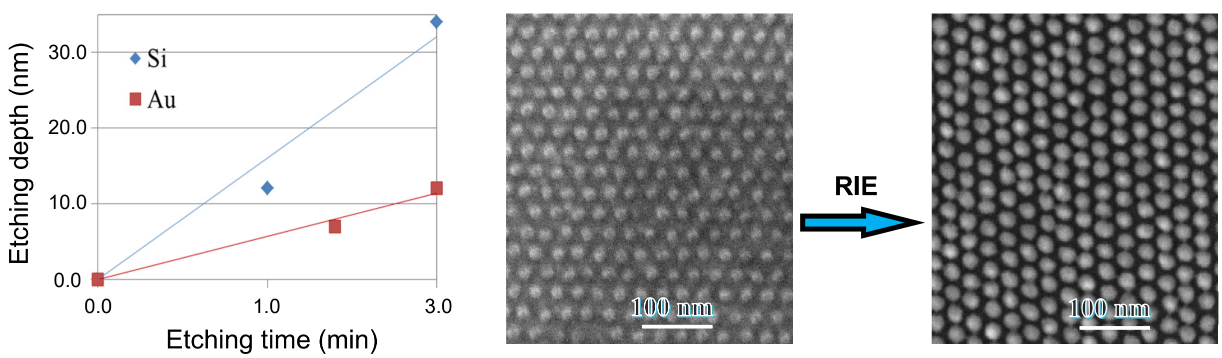
(a) The relationship between the etching depth and the etching time

(b) Calixarene resist pattern after EB drawing and development

(c) Au nano dots after Ar ion milling

Fig. 5. The first step etching.

The second step etching was shown in Fig. 6. Etching depth as a function of etching time is shown in Fig. 6(a). CF_4 gas was used in the experiment. The gas flow rate was 5 sccm. Pressure was 1 mtorr. Maximum etching time was 10 min. From the relationship between etching depth and etching time, the etching ratio of Si to Au is about 3. Under the same experimental conditions, the Si dots were fabricated. These dots were very uniform and highly ordered. This implies that the nanofabrication in this study is very suitable for the quantum dot solar cells with a high conversion efficiency, in which uniform and ordered quantum dots are necessary.



(a) The relationship between the etching depth and the etching time

(b) Au nano dots after Ar ion milling

(c) Si dots after RIE

Fig. 6. The second step etching.

5. Conclusions

In this study, a novel nanofabrication using EB drawing and two-step etching was proposed for high-efficiency quantum dot solar cells. From the characteristics of the simple multilayer n-i-p solar cells, 1-nm-thick tunnelling layer should be suitable for the quantum dot solar cells. Si nano dots with good uniformity and ordered arrangement were successfully obtained after Ar ion milling and RIE.

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