報告番号	甲　第　14771　号

主　論　文　の　要　旨

論文題目　**Nanostructure Formation on Crystalline Si Surface Using Ag-Assisted Solution Process and their Applications in Solar Cells**
（Agを用いた溶液プロセスによる結晶シリコン表面へのナノ構造形成と太陽電池への応用）

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論　文　内　容　の　要　旨

In recent years, nano-sized silicon (Si) light confinement structures have attracted much attention for their application in crystalline silicon (c-Si) solar cells due to their excellent light absorption as well as small surface area and small etching margin. The mainstream means of fabricating Si nanotextures usually require the use of vacuum conditions, expensive equipment and complex operation, which are not conducive to cost reduction and large-scale industrial production. This dissertation aims to develop an original Ag-assisted wet etching method to fabricate nano-sized Si textures and to investigate the effect of Si nanotextures with different sizes and morphologies on the efficiency of c-Si solar cells.

Firstly, we propose an original method to fabricate nanometer-sized pyramids (nanopyramids) featuring an average size of ~500 nm or even smaller by using a simple one-step Ag-assisted solution process. The texture size can be controlled by the concentration of $AgNO_3$ in the alkaline etching solution where the generated Ag nanoparticles act as an etching mask as well as promoting the detachment of H2 bubbles from the reacting Si surface. This process enables the formation of uniformly distributed Si nanopyramids with a lower reflectance below 10% and a smaller etching margin less than 1.7 μm compared with the conventional micro-pyramids. Si heterojunction solar cells employing Si nanopyramids outperform those with the conventional micro-pyramids owing to the reduced optical reflectance while preserving excellent surface passivation and carrier transport properties. These results demonstrate the advantages of our method and the high potential of Si nanopyramids for various applications such as thin crystalline Si solar cells and perovskite/Si tandem solar cells.

Next，Si nanopyramids are applied as the double-sided textures in the Si bottom cell to be compatible with the solution-processed perovskite top cell in perovskite/Si tandem solar cells. Herein, an Ag-assisted alkaline etching method is applied to fabricate nanoscale Si pyramid textures and the influence of varying pyramid size (400-900 nm) on the interface morphology and the performance of perovskite/Si tandem cells is investigated. It is demonstrated that electrical shunting starts to increase, and the open-circuit voltage (V_{OC}) decreases as the texture size increases above 600 nm due to the non-uniform top-cell formation on a rough Si surface. However, when the texture size is reduced to 400-500 nm, all spin-coated perovskite top-cell component layers exhibit an even form over the nanopyramid Si, resulting in a high V_{OC} and an enhanced Si bottom cell current (~1.0 mA cm^{-2}) due to the suppressed reflectance at the top/bottom cell interface without using optical couplers. The both-sided nanopyramid

Si texture offers opportunities to increase tandem cell efficiency while reducing its production cost compared with the commonly used single-sided textured Si.

Finally, the Si nanotip structures were fabricated by improving on the metal-assisted chemical etching (MACE) method. The main parameters during the fabricating process of Si nanowires are figured out, and Si nanowires with different lengths and diameters are successfully fabricated. The effect of microporous Si formation on the morphology of nanowires is discovered, and Si nanotips are fabricated on this basis. Si nanotips with different morphology are fabricated by combing high H_2O_2 concentration etching and polishing treatment. The etching mechanism was explained on the basis of detailed pilot studies, and the control of the size and distribution of the Si nanotips was realized. Further, a thin PEDOT: PSS layer was coated on to Si nanowire structures by spin coating. It is demonstrated that Si nanotip textures are more favorable for conformal film formation of organic materials compared to conventional Si nanowires.

This study aimed to fabricate light confinement structures in nano scale on the surface of c- Si by Ag-assisted all-solution process, and the etching mechanism is discussed in depth so as to realize the controlment the size, distribution, and surface morphology of the Si nanotextures. In this paper, an original Ag-assisted anisotropic alkaline etching method was developed, and Si nano-pyramid textures with an average size varying between 390nm and 950nm was successfully fabricated; A method based on MACE etching and fabricated was developed and Si nanotips texture with adjustable height, diameter and distribution was successfully fabricated. The two nanostructures have been applied to monocrystalline Si solar cells with different structures, and have shown good anti-reflection effects and interface properties for passivation and conformal layer formation. Compared with traditional micron-scale Si light-trapping structures, the efficiency of solar cells has been efficiently improved by utilizing Si nanotextures.

In chapter 1, the basic background of this study is briefly introduced, including: decarbonized society and solar energy, crystalline Si solar cells with thin substrates, anti-reflection design in Si solar cells, conventional Si texture fabrication method and Si nanostructures and application in crystalline Si solar cells. On this basis, the purpose of this study is to develop a low-cost and high-efficiency method for fabricating Si nanotextures, and to explore the practical application of Si nanotextures in monocrystalline Si solar cells. As described above, Si based solar cell is the current mainstream now, and reducing the manufacturing cost of solar cells is the market demand of great concern now, and this can be realized by the exploration of new device architectures and the implementation of new materials. Among them, the reduction of manufacturing cost has made the application of thin c-Si solar cells and c-Si heterojunction hybrid solar cells a development trend of new generation solar cells, and the application of Si nanostructures in these cell structures is of vital importance.

The reduction of the thickness of Si substrates and the combination of c-Si with new materials such as organic semiconductors, carbon nanotubes, and pervoskite place new demands on optimization of Si light confinement structures. Si textures fabricated by conventional wet etching methods are usually in micrometer size and unevenly distributed, making them difficult to be applied to next-generation c-Si solar cell structures. The fabrication of Si nanotextures, in turn, requires complex equipment. To overcome these problems, a new method is urgently needed to be developed to fabricate Si light confinement textures in nano scale simply and efficiently, as well as realizing the control of the morphology and distribution of Si textures. Thus in this study, we would like to optimize the Ag-assisted all-solution process to fabricated different Si nanotextures with both low etching margin and low fabrication cost, by employing Ag mask by electroless plating. We need Si nanostructures not only to have a size smaller than 1 μm and a uniformly dense distribution, but also to have a narrow size distribution, in order to achieve efficient light absorption, reduced surface defects, and facilitate the fusion of Si textures with other semiconductor materials.

In chapter 2, the main preparation instruments used in the fabrication of c-Si Si heterojunction cells, perovskite/Si tandem cells and organic/Si hybrid solar cells in this study, as well as the measurement methods used to evaluate the morphology of Si nanotextures and cell performance are introduced, including: Radio frequency (RF) magnetron sputtering, Plasma-Enhanced Chemical Vapor Deposition (PECVD), vacuum evaporation, spin-coating methods for solar cell fabrication and Scanning Electron Microscope (SEM), Energy-Dispersive X-ray spectroscopy (EDX), Spectrophotometer Transmission electron microscopy (TEM), Current-voltage (J-V) measurement, External Quantum Efficiency (EQE) for evaluation.

In chapter 3, a simple one-step chemical etching methodology using Ag-containing alkaline solution for controlling the size of Si pyramids is proposed. The effect of different conditions during the etching process on the formation of Si pyramids was investigated in detail. Nanopyramid textures with an average size of ~500 nm has been successfully formed on the Si surface with a narrow size distribution. This process enables the formation of uniformly distributed Si nanopyramids with a lower reflectance below 10% and a smaller etching margin less than 1.7 μm compared with the conventional micropyramids. SHJ solar cells with Si nanopyramids fabricated by this method showed higher cell performance than those with the conventional micro-pyramids, exhibiting an enhanced J_{SC} and conversion efficiency. that JSC increases gradually as the ratio of $AgNO_3$ increases, which shows an obvious enhancement from 37.9 to 38.4 mA/cm^2 owing to the improved light absorption. The nanopyramids obtained by our method feature regularly shaped tetrahedral structures with a narrow size distribution, which results in an enhanced light in-coupling and light trapping capabilities compared with Si micro-pyramids fabricated by the conventional alkaline etching. The etching margin of Si nanopyramids is also reduced by half. The mechanism of the etching process can be explained by the equilibrium reaction of $AgNO_3$ and KOH in the solution. Under proper conditions, Ag NPs are continuously generated on the Si surface during the etching process, acting as efficient etching masks as well as promoting the detachment of fine H_2 bubbles from the Si surface. As a result, dense nucleation sites and uniform chemical reaction over the Si surface are realized, and nanoscale Si pyramid textures with a narrow size distribution can be formed with a minimal etching margin. These features of Si nanopyramids are promising for applications such as thin Si solar cells, advanced screen-printed metallization and perovskite/Si tandem solar cells.

In chapter 4, the effect of size variation of Si nanopyramid textures of the bottom cell on the overall perovskite/Si tandem cell performance is explored. Double-sided Si nanopyramid textures with an average size of 400-900 nm and an improved size distribution were fabricated using an original Ag-assisted alkaline etching method and applied in the bottom cell of perovskite/Si tandem cells. As the size of the Si pyramid increases, the light absorption of the bottom cell gradually increases, while excessive pyramid size (>600 nm) causes severe shunting and thickness inhomogeneity in the perovskite absorber layer, resulting in the degradation in the performance of tandem cells, particularly in the V_{OC}. We find that the optimum Si texture size is around 400-500 nm, by which the perovskite top cell can be processed entirely by the conventional spin-coating method without creating an electrical shunting path in the top cell. Compared to the front-planar rear-textured reference Si bottom cell, the double-sided textured Si bottom cell with an average size of 530 nm provides a J_{SC} improvement by ~1.0 mA cm-2 and a higher PCE as a result of the increased spectral response in the Si bottom cell due to the suppressed interfacial reflection between the top and bottom cells. The results obtained in this study show the great potential for cost-effective tandem cell manufacturing using the solution-based top cell process without needing the costly multilayer optical coating at the top/bottom interface.

In chapter 5, the main parameters in Ag plating step and etching step of MACE method during fabricating process of Si nanowires were figured out. The concentration of Ag+ in the solution mainly determines the density of Ag particles formed on the Si surface, and the Ag plating time controls the Ag article size. For etching, the diameter of the Si nanowire is inversely proportional to the size of the Ag particles on the Si surface, and the length is proportional to the etching time. Si nanowires with different length of 0.5μm, 1μm, 5μm, 10μm and different diameters from 90nm to 200nm were successfully fabricated. Optical performance test showed that Si nanowire with a diameter of 100nm and a length of 0.5μm showed the best light absorptance property. Si nanotips with adjustable length/distribution and conical shape were successfully fabricated. The formation of microporous Si structure accompanied with the Si nanowire under the etching conditions of high H_2O_2 concentration was observed and the mechanism was discussed based on the principle of electrochemistry. Si nanotips improved the conformal film-forming properties of PEDOT:PSS and exhibit better light absorption than conventional Si nanowires, which is expected to be applied to hybrid heterojunction solar cells and further improve the performance with low fabrication cost.

In appendix chapter, Au-Ag core shell nanoparticles were successfully formed by depositing Ag shells on the surface of Au nanoparticles, and three-dimensional nanoparticles' structure of Au-Ag core- shell core-satellite structure are fabricated by self-assemblement of single-stranded DNA, and were decorated on the surface of flat Si/ TiO2 and three-dimensional structures such as Si pyramids and nanowires. The results of reflectivity and Raman measurement showed that the Au-Ag nanoparticles modified on the Si surface have the effect of improving the light absorption of the bottom device and can improve the Raman signal response of the bottom device due to the enhanced SERS effect and light scattering. Furthermore, by decorating the bottom of n-i-p perovskite cell with Au nanoparticles, the efficiency of the perovskite cell was increased by 0.54%. The self-assembly method of DNA-modified Au / Ag nanoparticles on Si surfaces is accurate, versatile, and reproducible. This approach creatively combines the fields of biology and materials, which can fix metal nanoparticles with controllable arrangements on surfaces of flat Si as well as Si nanostructures, and is expected to be applied to Si/ perovskite photovoltaic devices to further improve the efficiency.

In summary, the Si nanostructures fabricated in this research are expected to be applied to high-efficiency monocrystalline Si-based solar cells to achieve low-cost and high-efficiency industrial production. In addition, this study is helpful for a more systematic and in-depth understanding of the effects of different variables on the morphology of nanostructures in the Ag-assisted solution etching method, on the basis of which more ideal Si nanostructures are expected to be developed.