Study of plasmonic effect in silicon solar cells with silver nanoparticles

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This article presents a study of the plasmonic effect of small-size silver nanoparticles in silicon (Si)-based solar cells. The particles were deposited on the surface of Si by the thermal evaporation method. The size of the particles and their distribution was studied using scanning electron microscopy. It is shown that the largest particle size was ≈ 32 nm. The samples were capped by SiO_x or SiN_x , and reflectance spectra measured. It was found that the reflectance decreases with increasing silver nanoparticle diameter. Annealing at 375°C did not cause qualitative change of the reflectance spectra. The particles were deposited on Si solar cells, and current–voltage dependence was measured.

1. Introduction

Most modern silicon (Si) solar cells are wafer-based, with thickness in the range 180–300 μm . The cost of the cells makes up $\approx 40\%$ of the final module price. For further reduction of the cost, it is necessary to reduce the thickness of Si to as little as ≈ 2 μm . However, Si is well known as an indirect band gap semiconductor, and its absorption coefficient of photons with energies near to the band edge is $< 10^{-4}/\text{cm}$. As a result, a thin Si film of thickness ≈ 2 μm absorbs a smaller amount of energy from sunlight than the 180–300- μm wafer.¹ Consequently, the efficiency of the thin-film Si cells would be less than that of wafer-based Si cells. To enhance the light-absorbing properties of the active part of the cells, it is necessary to incorporate other material(s) with improved light-absorbing properties, or some other methods should be applied. One such method is increasing the optical path of the sunlight inside Si. In Si wafers, it can be achieved by texturing the surface, which has led to good results.² However, this method cannot be applied to Si cells, because the height of the pyramids in the texturized surface is ≈ 3 –8 μm , which exceeds the thickness of the wafer. A method has been suggested in refs. 3–5, which is based on light trapping by

plasmonic effect. Plasmons are the type of waves that are excited on nanostructures of some metals by incident sunlight and move through the electrons at the surface of a metal. The plasmons formed at the surface of the particles deflect the photons under different angles so that they bounce back and forth within the cell, thus increasing the optical path length of the light and allowing longer wavelengths to be absorbed.^{6,7} Silver and gold are the most suitable metals for these purposes.^{8,9} Extensive research has previously been performed and interesting results have been reported. Reference 10 reports an enhancement of photovoltage in a graphene semiconductor structure due to the plasmonic effect. The efficiency of photodetectors has been increased by ≈ 20 times. By analysis of different mechanisms, it has been shown that the enhancement due to plasmonic effect was not because of the increase of the path length of photons, but because of the efficient field concentration in the area of a p – n junction.¹¹ The size and shape of the nanoparticles are found to play important roles in plasmonic effect to tune it from near ultraviolet (UV) and far out in the infrared (IR) spectrum.⁶ The nanoparticles can be fabricated by many ways such as, for example, lithographic techniques, thermal deposition,

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Figure 1. Schematic representation of Si solar cells with silver nanoparticles capped with SiO₂ or SiN_x

Figure 2. Reflectance spectra of Si with and without silver nanoparticles capped by SiO_x and SiN_x layers before and after firing

vapor phase reactions, aerosol thermolyses, plasma atomization, vapor deposition and wet chemical route. The chemical precipitation from solution, plus thermal deposition, is probably the easiest and cheapest method.¹² The aim of this work is to use thermal evaporated silver nanoparticles to investigate the influence of plasmonic effect on Si solar cells. Particular attention is given to the deposition of silver nanoparticles on different substrates and to different Si solar cell structures and their stability with respect to thermal processing.

2. Methods

Silver nanoparticles were deposited by thermal evaporation method. Particle size and shape were investigated using a Hitachi S-4800 scanning electron microscope. Process parameters such as deposited silver thickness and time and temperature of the annealing step were investigated. Optical properties of the samples were characterized using an Ocean Optics HL-2000-FSHA optical microscope with a

Figure 3. Current-voltage dependence of the Si solar cells with silver nanoparticles deposited from front side underneath the SiN_x layer

Annealing time : min	V: V	J _{sc} : mA/cm ²	Fill factor	Efficiency: %
Silver nanoparticles covered by SiN _x				
0:37	0:60	23:54	0:58	8:21
1:13	0:60	25:39	0:49	7:46
2:02	0:61	28:82	0:50	8:84
3:15	0:62	32:38	0:52	10:27
Silver nanoparticles covered by SiO _x				
2:00	0:60	19:87	0:50	6:12
3:15	0:62	19:41	0:28	3:32
5:00	0:62	0:45	0:25	0:07

Table 1. Performance of Si solar cells with silver nanoparticles covered by SiN_x or SiO₂ layers after thermal processing for different annealing time

light source of wavelength in the range 260–2000 nm. The surface of the wafers was polished. The thickness of the wafers considered in this article is about 300 μm. The wafers were cut by laser into smaller 1–2 cm² structures. Before thermal evaporation, the samples were washed in distilled water and dried in an atmosphere of N₂. Si solar cells were prepared with silver nanoparticles capped with SiO₂ or SiN_x (Figure 1). Current-voltage characteristics (*J*–*V*) of the Si solar cells were investigated. Annealing was performed on a hot plate with a ceramic surface in an N₂ atmosphere at 375°C within 0.3–4.0-min intervals.

3. Results

Silver nanoparticles of different sizes were deposited on Si substrates. The size and shape of the particles are not regular. Surrounding the particles with circles, the average diameter of the particles was estimated to be ≈ 30 nm. The analysis showed that the diameter of the particles increases linearly with increasing thickness of silver. The maximum size of the particles obtained in this work is ≈ 32 nm. Shape of the nanoparticles is also non-uniform and is close to an ellipse.

After the analysis of their size and shape, the nanoparticles were capped. Two different capping layers, SiO_x and SiN_x , were used. Reflectance spectra of the capped and non-capped samples were studied before and after thermal processing. The results are presented in Figure 2. Analysis shows that the reflection spectra strongly depend on particle size and on capping material. Without firing, the reflectance from both SiO_x - and SiN_x -capped samples decreases with increasing silver nanoparticle diameter. In the SiO_x -capped samples with a particle size of ≈ 20 nm, a peak located at ≈ 750 nm is seen. Annealing at 375°C did not lead to qualitative change in the reflectance spectra, and it remained smaller than for the samples not containing the silver nanoparticles. On the one hand, this could be due to the influence of the capping layer; on the other hand, it could be because of the smaller size of the silver nanoparticles. The silver nanoparticles of diameter between 4 and 10 nm were capped with SiN_x . Reflectance spectra for the samples are smaller than for those without silver and decrease with increasing particle diameter. On annealing at 375°C , reflectance spectra of the 10-nm-diameter samples decreased further. This is in contrast to the samples capped by SiO_x , which exhibited annealing-induced increase of reflectance. This result is probably related to oxidation of silver nanoparticles in the SiO_x -capped samples.

In addition to the above-documented findings, the largest silver nanoparticles were deposited on top of Si solar cell structures with aluminum back contact. Figure 3 shows the J - V curve of one of the samples with silver nanoparticles. The efficiency of the cells is ≈ 10 –30%. The open-circuit voltage (V_{oc}) is 0.61 V, the short-circuit current (J_{sc}) is 32.4 mA/cm^2 , the fill factor (FF) is 52% and the optimal power (P_{opt}) is 1026 mW/cm^2 . Analysis showed that the efficiency of the cells with silver nanoparticles was less than the efficiency of cells without the particles. Probably, it is related to the smaller size of the silver nanoparticles, because light absorption is enhanced. Really, the color of the cells has been changed from bluish to greenish.

The influence of thermal annealing on electrical parameters was studied at different annealing temperatures for cells with silver nanoparticles capped by SiN_x and SiO_2 . The results are shown in Table 1 for V_{oc} , J_{sc} , FF and P_{opt} . Analysis showed that the performance of the cells with silver nanoparticles increases with increasing annealing time if the cells are capped by SiN_x and decreases if capped by SiO_2 . The silver nanoparticles were also deposited on the back side of Si. Subsequently, the cells were

capped by Al contact by magnetron sputtering. The efficiency of the cell was much lower than those without the silver nanoparticles. The authors suggest that this is due to smaller size of the particles. The increase of the photocurrent due to the plasmonic effect has been reported previously in many studies. However, in these articles, the average diameter of the nanoparticles is much larger than those in the present work.

4. Conclusion

In this work, the authors studied silver nanoparticles deposited by thermal evaporation for Si solar cell applications. Study of the morphology by scanning electron microscopy shows that the shape and size of the particles are not uniform, and the average diameter has been estimated. The maximum average diameter achieved was found to be ≈ 32 nm. It is established that the diameter of the nanoparticles increases with increasing thickness of silver. Reflectivity spectra of Si with silver nanoparticles capped and not capped by SiN_x and SiO_2 has been studied. It has been shown that the reflectivity spectra decrease with increasing diameter of silver nanoparticles. Annealing at 375°C did not lead to qualitative changes in the reflectivity spectra. Particles were deposited on the surface of silicon solar cells, and current–voltage dependence was studied.

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