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Influence of silver nanoparticles on the photovoltaic parameters of silicon solar cells

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Abstract. Influence of Ag nanoparticles on optical and photovoltaic properties of, silicon substrates, silicon solar cells and glass have been investigated. Silver nanoparticles have been fabricated by evaporation of thin Ag layers followed by the thermal annealing. The surface plasmon resonance peak was observed in the absorbance spectrum at 470 nm of glass with deposited silver nanoparticles. It is demonstrated that deposition of silver nanoparticles on silicon substrates was accompanied with a significant decrease in reflectance at the wavelength 360-1100 nm and increase of the absorption at wavelengths close to the band gap for Si substrates. We studied influence of Ag nanoparticles on photovoltaic characteristics of silicon solar cells without and with common use antireflection coating (ARC). It is shown that silver nanoparticles deposited onto the front surface of the solar cells without ARC led to increase in the photocurrent density by 39% comparing to cells without Ag nanoparticles. Contrary to this, solar cells with Ag nanoparticles deposited on front surface with ARC discovered decrease in photocurrent density. The improved performance of investigated cells was attributed to Ag-plasmonic excitations that reduce the reflectance from the silicon surface and ultimately leads to the enhanced light absorption in the cell. This study showed possibility of application of Ag nanoparticles for the improvement of the conversion efficiency of wafer-based silicon solar cells instead of usual ARC.

Keywords: silver nanoparticles; plasmonic resonance; reflectance; silicon solar cells; efficiency

1. Introduction

Silicon solar cells are most widely used devices on photovoltaic energetic due to raw material abundance in nature, stability of the parameters and well established processing technologies. However manufacturing cost presents an issue for its wider applications. Simultaneous increase of efficiency and considerable reduction the cost of manufacturing are required for making photovoltaic sources of electricity competitive with other technologies. The main problem for solar cell is relatively low efficient of absorption of solar light.

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In last years have been suggested the new method of trap the light by nanoparticles deposited on the top of cell or embedded in the cell structure (Catchpole and Polman 2008, Atwater and Polman 2010, Pillai 2007). Incident light excites the localized surface plasmons in nanoparticles. Plasmon resonance can cause either efficiently scatter incident light increasing the optical path length in cell and/or can cause the near-field plasmonic absorption. The contribution of each mechanism depends on size, shape, spacing of the metallic particles and the dielectric properties of the surround medium. Metallic nanoparticles that responsible for surface plasmons have been shown to be able to provide advanced light trapping to significantly enhance the light absorption in solar cells due to the scattering and near-field effects. Overwhelming majority of works on plasmonic solar cells was devoted to using silver nanoparticles on thin-film amorphous silicon solar cells. Winans *et al*. (2015) have investigated effect of silver nanoparticles on the front, the back and both of thin a-Si:H solar cells and showed most increase in efficiency when silver nanoparticles were on both the front and back, that have been attributed the increased scattering. These researches demonstrated also the increased cell efficiency for larger silver particle sizes. Derkacs *et al*. (2006) achieved 8% overall increase in efficiency for thin-film amorphous silicon solar cells with gold nanoparticles. The conversion efficiency of amorphous silicon solar cells with Ag-embedded nanoparticles increased from 6.2% to 7.0% related with the scattering effect (Jung *et al*. 2013). Chen *et al*. (2012) using incorporated 200-nm silver nanoparticles in amorphous silicon cells to enhanced light absorption in a broadband wavelength range achieved efficiency of 8.1%. Increase of photocurrent of amorphous silicon solar cells embedded with a diameter of 180 nm Ag nanoparticles using the selective aerosol deposition technique was observed by Santbergen *et al*. (2012). Embedding of the larger silver nanoparticles on the front, inside or at the rear of the a-Si:H solar cells leads to the external quantum efficiency increased for wavelength longer 600 nm (Lang *et al*. 2010).

The effect of metal nanoparticles on optical properties and performance of c-Si (wafer-based) solar cells as compared with thin amorphous silicon solar cells have been rare considered. The enhancement of photocurrent of thin-film and wafer-based silicon solar cells with silver nanoparticles was observed by Pillai *et al*. (2007). Thouti *et al*. (2013) have reported considerable reflectance reduction from c-silicon substrate after thermal evaporation of thin silver film (about 4 nm) and thermal annealing at 300^{o}C. The reflectance decrease in the UV-Vis-NIR regions of the spectrum (350-1300 nm) is very sensitive to the size and shape of particles and it is attributed to the surface plasmons of silver particles. Silver nanoparticles deposited on silicon solar cells by evaporation of thin Ag film (10 nm) followed by thermal annealing result in improve and deteriorate reflectance and spectral response of the cell depending on wavelength (Temple *et al*. 2009). Enhancement in photocurrent and efficiency by about 32% of c-Si solar cells with nanoparticles of indium on the front surface and silver particles on the rare surface have been attributed to the plasmonic scattering by In and Ag nanoparticles (Ho *et al*. 2014). Yun et el. (2013) have reported enhancement of the quantum efficiency by about 10-15% for ZnO/n-Si solar cells with silver nanoparticles embedded in ZnO film. Increase of the external quantum efficiency have been observed for silicon solar cells with silver nanoparticles deposited on silicon surface by chemical dissolving the $AgNO_3$ solution (Maity *et al*. 2013). It is seen from above, the influence of silver nanoparticles on optical properties and photovoltaic parameters of c-Si solar cells is weakly studied.

We studied influence of Ag nanoparticles on photovoltaic characteristics of solar cells with and without antireflection coating. The improved performance of investigated cells was attributed to Ag-plasmonic excitations that reduce the reflectance from the silicon surface.

2. Experimental procedure

Monocrystalline p-type boron-doped silicon wafers with orientation of (100), resistivity about of 3 **Ω** cm and thickness of about 200 μm were used for fabrication of solar cells by screen printed process (Green 2007, Agnihotri and Gupta 1981, Dzhafarov *et al*. 2012). The wafers were cleaned in NaOH:H_2O (1:4 in volume) at 80°C for 10 min, in HCl at room temperature for 10min and then etched in HF: H_2O (1:1 in volume) for 1 min. Then samples were dried in deionized (DI) water. Containing phosphorus spin-on dopant (SOD) (KFK-50-10T type) was used as phosphor source. Cleaned surface of wafer was coated with SOD by spin-on technique at room temperature with 2000 rpm for 10 seconds. Then the coated samples were baked at 600℃ for 2 min for destructization of the coating.

The n^+-p junction was formed by phosphorus diffusion from SOD into p-type silicon substrate at 950°C in vacuum 1.33×10^{-1} Pa for 25 min in a tube furnace. The phosphor-silicate glass layer was removed from the silicon surface with hydrofluoric acid solution (HF: H_2O, 1:9). n^+-emitter layer with 0.5-1.0 μm thickness and 15-20 **Ω**/□ sheet resistance was formed as a result of phosphorus diffusion. The thickness and sheet resistance was found by four-point method.

The electrical contacts were made by screen printed process with a Du Ponte photovoltaic silver paste for front and silver with 3% aluminum paste for the back contact. Samples with silver contacts were baked at 200℃ for 10 min and then metallization at 800 ℃ for 10 min in the conventional annealing furnace was done. Two types of solar cells were prepared in this work: without and with traditional SiO_x antireflection coating (ARC) (A-type and B-type cells respectively). The thickness of the last one with SiO_x antireflection coating prepared was 80 nm (Kim 2007). Active area of the cells was about 1.1 cm^2.

Silver nanoparticles have been fabricated on top surfaces of silicon solar cells (of both A and B types), silicon substrates wafers and cleaned glass substrates by thermal evaporation of 10-15 nm Ag films followed by thermal annealing. Silver evaporation has been performed in vacuum of 1.3×10^{-3} Pa at room temperature. The thickness of the Ag film was measured during evaporation by using a Deposition controller (Inficon, Leybold). The solar cells, silicon wafers and glass substrates with silver films and the test samples without silver films were then annealed at nitrogen atmosphere in furnace at 500°C. It will be noted that best adhesion of silver nanoparticles to silicon surface was observed as result of thermal treatment at 500°C for 10-30 min. To investigate the surface morphology, the optical properties of silicon wafers and photovoltaic characteristics of the solar cells, we examined the size and density of the Ag nanoparticles by the atom-force microscopy (AFM, Solver NEXT, NT-MDT), the integrated reflectance and transmittance of the silicon wafers or glass substrates and the current-voltage (I-V) characteristics of the cells in each stage of processing. The silver nanoparticles have a surface coverage about 35-40%. The integrated reflectance and transmittance of the samples was measured at room temperature by UV-VI spectrometer ("Specord-210") in the wavelength range 300-1100 nm. The absorption spectra of samples were found from the reflectance and transmittance data of the samples. The absorption coefficient (α) is deduced from transmission spectra by solving α in the equation

$$T= (1-R)^2 \exp(-\alpha d) \tag{1}$$

Here R is reflectivity and d is the effective sample thickness. The absorption coefficient is determined from correlation

$$\alpha = \frac{1}{d} \ln\frac{(1-R)^2}{2} \tag{2}$$

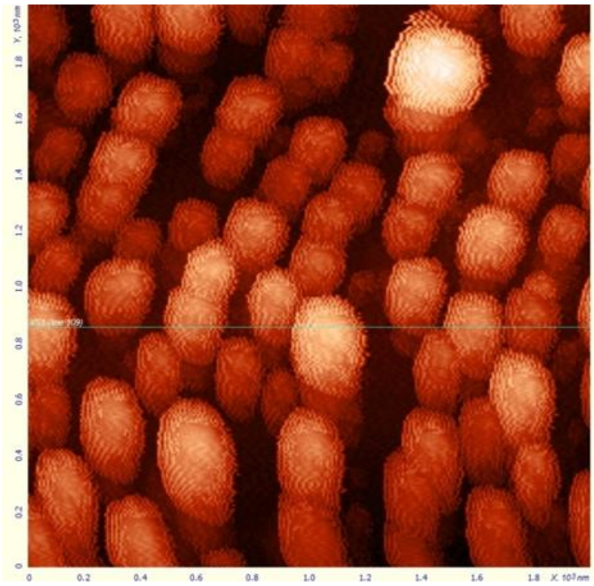

Fig. 1 AFM image of the Ag nanoparticles on silicon surface

An analysis of the absorption spectra of silicon with indirect band semiconductor and equal composition is determined by correlation

$$\alpha = A(h\upsilon - E_g - E_p)^2 \tag{3}$$

Here E_g is the energy band of silicon, E_p is energy of phonons and A is a constant
For the case of silicon with silver nanoparticles formula (3) is wealthy correspond.

The photovoltaic parameters of the cells with and without Ag nanoparticles and with ARC and Ag-nanoparticles coverage were determined from current-voltage measurements under illumination (AM 1.5) using Solar Analyzer ("Prova200") (Dzhafarov *et al*. 2012).

3. Results and discussion

Fig. 1 presents AFM image from Ag nanoparticles on silicon substrate formed by thermal annealing of silver film (thickness of 12 nm). This sample exhibits Ag particles with diameter about 120-160 nm and density of 2×10^8 cm^{-2}. The transformation mechanism of the silver film on substrate (silicon, glass etc.) to silver nanoparticles as result of the thermal treatment can be presented as follows. At first, the silver thin film breaks on small pieces during the thermal annealing due to difference in the thermal expansion coefficients of film and substrate. Then silver atoms located along the edges of pieces begin diffuse preferentially along the surface substrate and precipitate on defects, hollows and ledges of the surface relief. Finally, silver atoms coalescence in nanoparticles as formation of silver nuclei is thermodynamically favorably on defect positions where theirs the free energy smaller than that on flat surface.

The reflectance spectra for silicon surface without and with Ag nanoparticles are given in Fig. 2. Both samples have been annealed at the same conditions. Comparison of reflectance for silicon surface with Ag nanoparticles with "clear" silicon surface shows reduction average surface

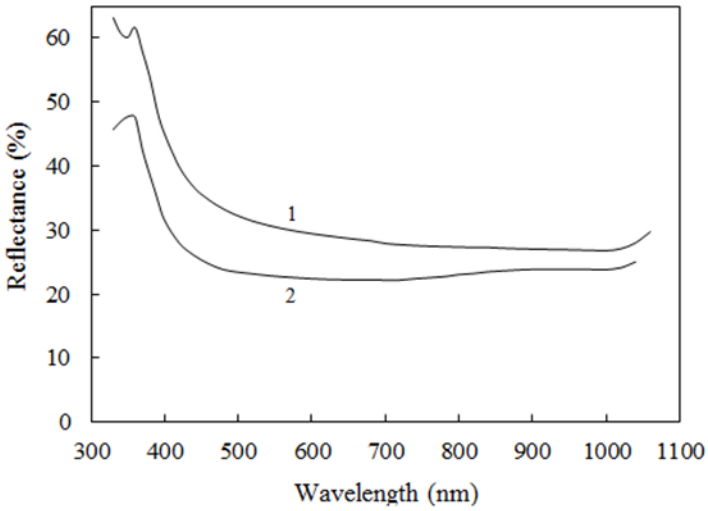

Fig. 2 The reflectance spectra of silicon surface without (1) and with Ag nanoparticles (2)

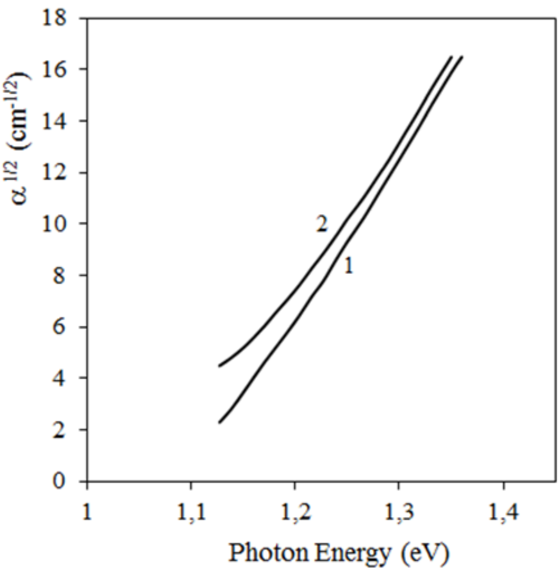

Fig. 3 The absorption spectra of silicon surface without (1) and with Ag nanoparticles (2)

reflectance by about 17.3% in the region from 600 to 1100 nm.

The absorption spectra for the silicon without and with silver nanoparticles samples are presented in Fig. 3. It is seen that the absorption spectrum for silicon without Ag nanoparticles is described by well-known absorption coefficient-photon energy ($\alpha^{½}$-hv) relation with indirect forbidden band gap E_g=1.08 eV for silicon at room temperature. We assume that absorption spectrum for Si with silver nanoparticles is described by the same ratio. In that case the shape of the curve weakly correspond to absorption of light from the system of nanoparticles. Nevertheless the absorption spectrum for Si with silver nanoparticles some deviates from this relation and values for absorption coefficient are larger (on average by 34%) than those for silicon all over investigated spectral region from 1.12 to 1.35 eV. Account must be taken of resonance frequency of silver nanoparticles (400-600 nm in dependency on particle size) is located in intrinsic absorption region of Si and therefore it is difficult to observe silver-stimulated plasmon effect in transmittance spectrum of Si with silver particles. Therefore we investigated the absorbance spectrum of silver nanoparticles on glass substrate obtained as result of the silver-coated glass annealed at 500°C for 10 min (Fig. 4). The absorbance curve of silver nanoparticles with the average radii about 80 nm on glass substrate determined from AFM measurements exhibits peak at 470 nm that can be caused by localized plasmons on the Ag-particle surface (Catchpole and Polman (2008). Moreover, deposition of Ag nanoparticles on silicon surface leads to absorption enhancement and reduction of the surface reflectance. Total absorption spectrum depends on the number of nanoparticles for square unit.

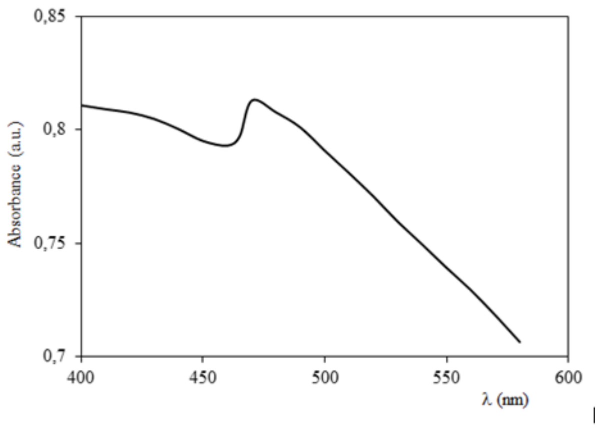

Fig. 4 The absorbance spectrum of the Ag nanoparticles on glass substrate

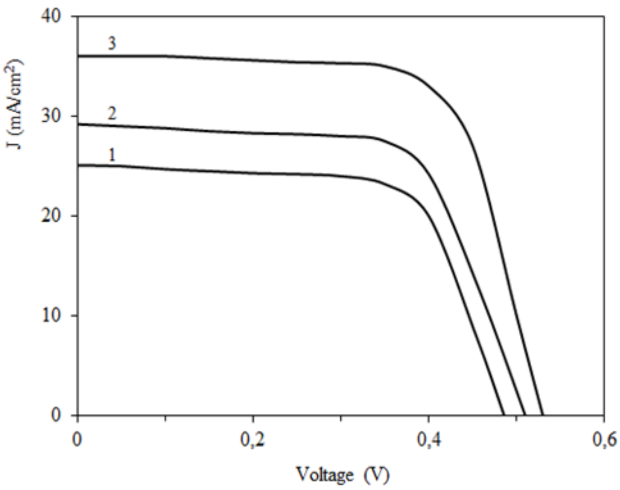

Fig. 5 Photocurrent density-voltage characteristics of silicon solar cells without ARC (A-type cells): the untreated cell (1) and thermal treated cells without (2) and with Ag nanoparticles (3)

Table 1 The photovoltaic characteristics of Si solar cells without ARC (A-type cells)

Parameters of cell	Primary cell	Thermal treated cell	Ag-thermal treated cell
J_{sc} (mA/cm^2)	25.1	29.2	36.0
V_{oc} (V)	0.486	0.510	0.530
η (%)	8.17	9.52	13.20
FF (%)	0.69	0.64	0.70

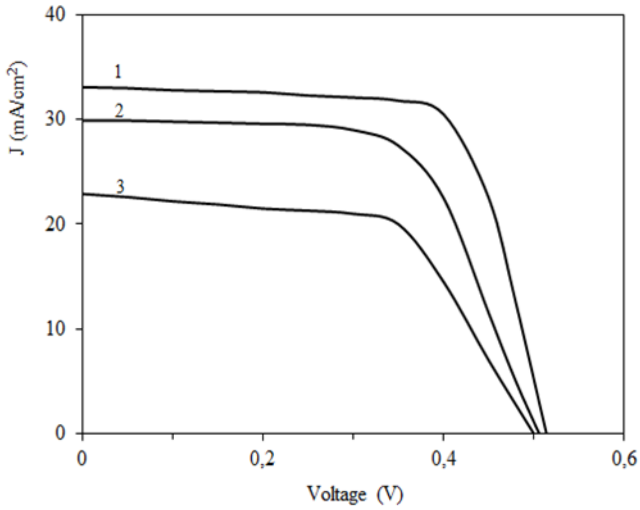

Fig. 6 Photocurrent density-voltage characteristics of silicon solar cells without ARC (B-type cells): the untreated cell (1) and thermal treated cells without (2) and with Ag nanoparticles (3)

The typical current-voltage characteristics of Si solar cells without traditional ARC (A-type cells) are presented in Fig. 5. The best improvement of photovoltaic characteristics is observed for Si solar cells covered with silver nanoparticles. Parameters of A-type solar cells are given in Table 1. Some enhancement the efficiency of thermal treated cells (without Ag film) compared to the primary cells can be attributed to partial redistribution of uncontrolled impurities from p-n junction region.

As stated above the collective oscillations of electrons in metal nanoparticles excited by incident light lead formation of polarization charges on the particle surface i.e., origin the localized surface plasmons. Plasmonic effect consists in trapping of the incident light by plasmons due to either due to absorption and (or) scattering depending upon the nanoparticle size. The absorption by plasmons dominates for metallic particles with size much smaller than the Plasmon wavelength of light. However, as the particle size increases, plasmonic scattering prevails for light wavelength around the plasmonic resonance (Pillai *et al*. 2007). The angular spread of light is accompanied by enhancement in path length in silicon substrate and thereby increased absorption and generation of electron-hole pairs. Finally, both processes must lead to enhanced absorption of light in substrate. Observed on Fig. 4 and Fig. 5 the reduced reflectance from silicon substrate and the enhanced absorption of light in substrate ultimately lead to the performance improvement of silicon solar cells with silver nanoparticles.

Table 2 The photovoltaic characteristics of Si solar cells with ARC (B-type cells)

Parameters of cell	Primary cell	Thermal treated cell	Ag-thermal treated cell
J_{sc} (mA/cm^2)	33.1	29.9	22.9
V_{oc} (V)	0.514	0.506	0.507
η (%)	12.20	9.63	7.06
FF (%)	0.72	0.63	0.60

The complementary effect was observed for the cells with Ag nanoparticles deposited on silicon cell surface with the traditional ARC (B-type cells) (Fig. 6). The photovoltaic characteristics of cells with Ag-nanoparticles is worse than those for both primary cells and thermal treated cells (without Ag film) (Table 2). This effect can be caused by Fano interference (Fano 1961, Giannini *et al*. 2011, Cortes-Juan *et al*. 2013). Oxidation of silver film deposited on ARC (SiO_x) during the thermal annealing can be other reason for lower photovoltaic parameters of Ag-nanoparticles coated solar cells. The experiments on the influence of the size, shape and density distribution of silver nanoparticles on the photovoltaic parameters of silicon solar cell are being carried.

4. Conclusions

It is demonstrated that deposition of the silver nanoparticles on surfaces on silicon substrates decreases the reflection about of 17.3% in the wavelength interval of 600-1100 nm and increases the absorption about of 34% in the wavelength ranger of 900-1100 nm. Silicon solar cells with the silver nanoparticles on front side (without the standard ARC and *without thermal treated cells*) showed enhancement in efficiency of 39% compared to the silicon cells without Ag nanoparticles. This enhancement is attributed to mainly light scattering effect of silver nanoparticles. Nanoparticles deposited on front surface of silicon solar cells increasing the performance of the cells due to surface plasmonic effect play role of antireflection coating. Simplicity and variety of physical and chemical technologies formation of nanoparticles is advantage as compared with the traditional ARC deposition methods. The deterioration of the photovoltaic parameters of silicon solar cells with silver nanoparticles deposited on ARC-containing surface was observed. Nature of this effect must be investigated later on.

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