

Chemical synthesis of silver nanoparticles for solar cell applications

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A novel approach to fabricate silver nanoparticles for light trapping applications in silicon based solar cells has been demonstrated. Silver nanoparticles of various sizes have been synthesized by chemical reduction reactions. The particle size in the colloidal solutions was varied by using two different reducing compounds in addition to al-

tering the compositions of the mixtures. In the present work, deposition of the silver nanoparticles onto a conventional bulk silicon solar cell shows an increase in the quantum efficiency at longer wavelengths, indicating the utilization of incident radiation that is normally lost in poor absorbing silicon.

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1 Introduction The cost of solar electricity is making the use of solar cells for electricity production an increasingly attractive solution. However, in order to get access to larger energy markets, the costs of solar electricity must be further reduced. One approach is to reduce material consumption through the use of deposited thin films or ever thinner silicon wafers. However, when the solar cells become optically thin, light trapping structures must be incorporated into the solar cell design in order to reduce losses due to transmission. This is particularly the case for crystalline silicon, where the indirect nature of the band gap causes a large amount of the incident near band gap radiation to be lost.

Conventional wafer-based cells take advantage of micrometer-sized pyramid-shapes in the surface to trap light, but the processes and dimensions involved are incompatible with very thin substrates. Instead, the use of metallic nanoparticles to enable light trapping has been described in scientific literature in the recent years. The excitation of surface plasmons on silver (Ag) nanoparticles applied on the surface of a solar cell, as shown in figure 1, has been shown to have the potential to increase absorption in both wafer-based and thin-film silicon solar cells [1,2]. Among the different preparation methods, chemical synthesis of metallic nanoparticles can be a simple and economical solution which can be applied in large scales as required for

industrial applications. In the present work we investigate how silver nanoparticles from two different chemical synthesis routes can be used to increase the light trapping of wafer-based solar cells, as evidenced by increases in the quantum efficiency (QE) of lower energy photons.

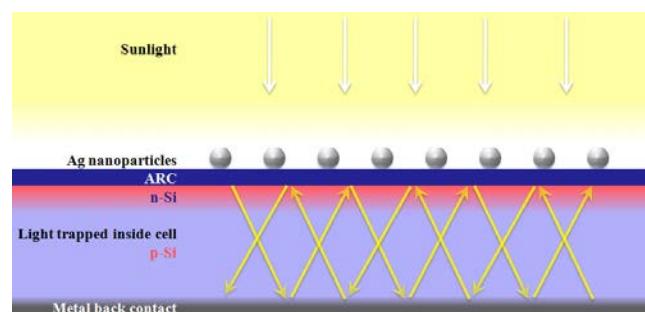


Figure 1 A schematic of a solar cell with silver nanoparticles deposited on top of the antireflection layer (ARC). Light scattered by the particles travels a longer distance inside the silicon and will thus have a larger probability of being absorbed.

2 Experimental

2.1 Sample preparation The silver nanocrystals studied in this work were made by wet chemical reduction syntheses. Two different methods were adopted to prepare

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1 particles of different sizes. Silver nitrate (AgNO_3 , 99.9%
 2 purity, Qualigens Fine Chemicals), sodium borohydride
 3 (NaBH_4 , 95% purity, Merck) and trisodium citrate dihy-
 4 drate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99.5% purity, NICE chemicals)
 5 were used as starting materials without further purification.
 6 All equipment was thoroughly cleaned by soaking in etha-
 7 nol and washed with distilled water.

8 Initially, a 0.6mM silver nitrate precursor solution was
 9 prepared using deionized H_2O , together with a 1.2mM
 10 aqueous sodium borohydride solution. All solutions were
 11 kept ice cold to prevent agglomeration of the formed parti-
 12 cles and vigorous stirring was maintained during the whole
 13 synthesis. The particles were obtained by adding the aque-
 14 ous silver nitrate drop by drop to the highly reducing solu-
 15 tion of sodium borohydride. The mole concentration of the
 16 sodium borohydride solution was twice that of the silver
 17 nitrate solution to ensure colloid stability, as suggested by
 18 Solomon et.al. [3]. By varying the amount of AgNO_3 (aq)
 19 relative to NaBH_4 (aq) in the final mixture, variations in
 20 particle-sizes and size distributions were expected.

21 A second synthesis was carried out by replacing the
 22 sodium borohydride with trisodium citrate dihydrate as the
 23 reducing compound. In a typical experiment, a 1mM aqueous
 24 silver nitrate solution was heated to boiling and a
 25 38mM trisodium citrate solution was then added in drops
 26 to the boiling solution using a burette. The solution was
 27 kept boiling and under vigorous stirring during the whole
 28 addition, which lasted for several minutes depending on
 29 the quantity of the solution and for an additional 11
 30 minutes after the addition was completed. Thereafter, the
 31 solution was cooled to room temperature.

32 Experiments performed on depositing the colloidal sil-
 33 ver onto a silicon substrate involved using 300 μm thick
 34 monocrystalline polished wafers.

35 In addition, conventional multicrystalline silicon solar
 36 cells were used to investigate the possible light trapping ef-
 37 fects of the nanoparticles. The cell substrates were boron
 38 doped Cz-Si and multicrystalline Si. The Cz-Si wafers
 39 were 300 μm thick and the mc-Si wafers had a thickness of
 40 180 μm . The wafers were subjected to standard solar cell
 41 processing at IFE including texturing, a 70-80 nm thick
 42 $\text{SiN}_x\text{:H}$ antireflection coating deposition and cut into 5x5
 43 cm pieces before screen-printing and firing.

44 **2.2 Characterization** The optical properties of the
 45 synthesized silver nanoparticles were studied by UV-Vis
 46 spectroscopy using a Cary100 UV-Vis spectrophotometer
 47 from Varian. To investigate the structural properties of the
 48 particles, High Resolution Transmission Electron Micro-
 49 oscopy (HRTEM) analysis was performed using a 200keV
 50 JEOL 2010F microscope equipped with a Gatan imaging
 51 filter and detector. AFM imaging of the distribution of the
 52 nanoparticles on silicon substrates was done with a Digital
 53 Instruments Dimension 3100 Scanning Probe Microscope
 54 operated in tapping mode. The QE of the solar cells was
 55 determined with a spectral response unit measuring QE as
 56 a function of the incident light wavelength in a region be-
 57 tween 400 – 1150 nm. The spot size was focused to fit in

between the front contacts on the solar cells, and illuminat-
 ed an area of approximately 2 x 2 mm.

3 Results and discussion

3.1 Optical and theoretical analysis During the ad-
 1 dition of the silver nitrate to the aqueous sodium borohy-
 2 dride solution, a light yellow colour slowly appeared in the
 3 mixture, indicating the formation of silver nanoparticles.
 4 Figure 2(a) shows the colloidal silver as synthesized by the
 5 borohydride method. The intensity and colour variations
 6 between the samples arise from the compositional differ-
 7 ences. The variation may be attributed to the number of
 8 particles and the size distribution in the sol. These differ-
 9 ences are more evident when looking at the UV-Vis spec-
 10 tra (as indicated in the legend) of the samples as repre-
 11 sented in figure 2(b). For the borohydride samples, all the
 12 compositions show an intense and narrow absorption at
 13 around 390 nm which is characteristic for the surface
 14 plasmon band for small nanoparticles of silver [3].

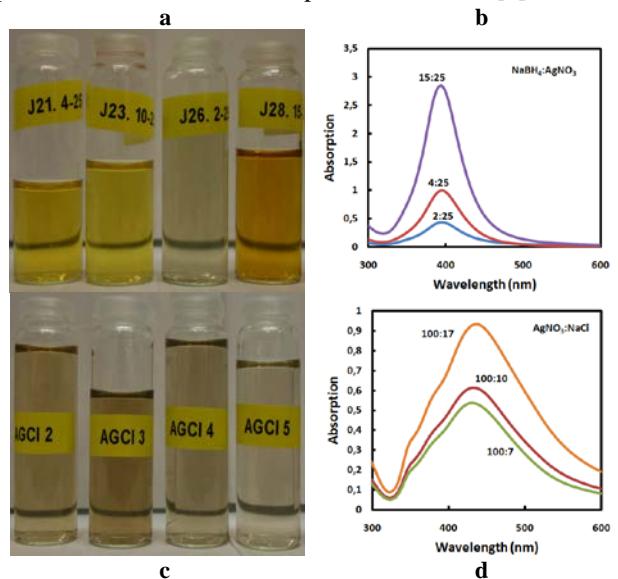


Figure 2 Silver sols prepared by the sodium borohydride (a) and sodium citrate (c) reduction methods. The corresponding UV-Vis spectra for the former (b) and latter (d) are shown for comparison. The composition variations in the different samples are clearly evident both in the pictures and in the spectra.

A similar colour transition appeared during the citrate synthesis, however just for a short time before the mixture darkened and acquired a more greenish/brownish appearance. A picture of the synthesized citrate-sols and the corresponding UV-Vis spectra are shown in figure 2(c) and (d), respectively. The varying silver nitrate to reducing compound ratios result in similar intensity differences as for the borohydride synthesis, but here the plasmon peak is located at around 430 nm in all cases (the beginning peaks at the shorter wavelengths are most likely to originate from the initial compounds and are thus not considered [4]).

According to the Mie theory, the particle size can be directly related to the surface plasmon peak position. The

spectra obtained for the colloidal silver display only one such plasmon peak, implying electron oscillations along one principal axis [5]. This is an important consideration since the theory is applicable to spherical particles only.

Figure 3 presents the position of the absorption peak as a function of the diameter of Ag nanoparticles situated in water. The calculations were performed with the computer simulation program “MiePlot v.4.2.02” [6], based on the Mie theory as presented by Bohren and Huffman [5]. For the smallest particles, there is no significant shift of the absorption peak for changes in the particle diameter. However, the increased cross-section of the particles will cause a stronger resonance peak that is observable when plotting the extinction as a function of the wavelength for different particle sizes. For larger particles, the red-shift of the extinction peak becomes more evident as the diameter increases.

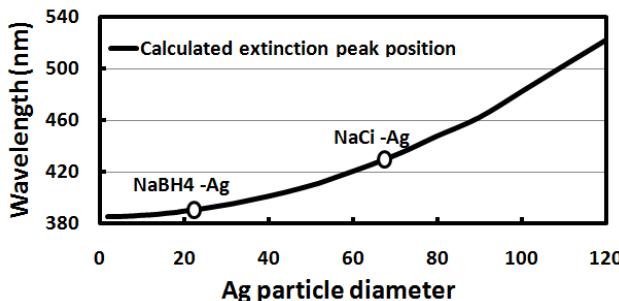


Figure 3 The calculated surface plasmon extinction peak position as a function of particle diameter. The calculation is based on the Mie theory and considers spherical silver nanoparticles embedded in water.

Comparing the theoretical calculations to the experimental data, the two synthesis methods clearly produce particles of different size regimes as indicated in figure 3. The borohydride reduced silver nitrate produces a peak at around 390 nm, which coincides with particle diameters of approximately 20 nm. The sodium citrate synthesized silver particles which peak at roughly 430 nm should, according to figure 3, have diameters close to 70 nm.

3.2 TEM investigations TEM was used to investigate the structure and morphology of the synthesized silver nanoparticles. The silver particles obtained with the sodium borohydride reduction method were predominantly spherical with diameters ranging from a few nanometers to well above 20 nm, depending on the composition of the sample. A typical TEM image used for the particle size determination is presented in figure 4. The samples made with the lowest AgNO_3 (aq) to NaBH_4 (aq) amount ratio (4:25 mL), had an average particle diameter of around 8-10 nm, while the highest ratio samples (25:25 mL) contained particles with approximately twice the diameter. Higher amounts of silver nitrate also seemed to produce sols containing a greater variation in the particle sizes, with some particles being several tens of nanometers in diameter.

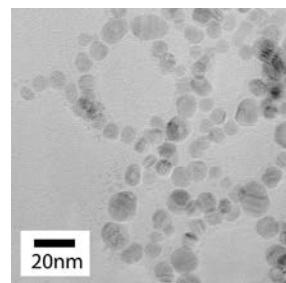


Figure 4 TEM image of Ag nanoparticles produced by the sodium borohydride reduction of silver nitrate with a AgNO_3 to NaBH_4 ratio of 6:25 mL.

TEM studies of the sodium citrate reduced samples showed larger silver nanoparticles, but with a wider size distribution and a higher amount of particles with pseudo-spherical shapes. Agglomeration also seemed more evident in these samples. The boiling time is believed to be of critical importance for obtaining disperse and non-agglomerated particles.

3.3 Solar cell quantum efficiency enhancement

To study the possible effects of applying the silver nanoparticles on to solar cells, spectral response measurements were performed on cells before and after the deposition of the colloidal silver. Preliminary deposition experiments were performed in advance to investigate the distribution of the nanoparticles. Tapping mode AFM was used as the imaging tool and planar substrates were employed for the testing since the surface structure of the solar cells results in poor depth resolution. Following a substrate purification process, planar monocrystalline Si wafers were exposed to a colloidal silver solution (from NaBH_4 method with 7:25 ratio) followed by a drying step, each performed in three turns, to study the distribution of the particles.

Due to the “coffee-stain-like” rings of material deposits left when drops of colloidal solutions dries on a surface [7], the nanoparticles were only well distributed in small areas like the one seen in the AFM picture in figure 5(a). For high quality depositions in larger areas, techniques involving spin-on or spray-on using more suitable solvents appear necessary.

Examination of the substrates revealed a general increase in the particle diameter in comparison with the TEM investigations of the colloidal state. The linescan performed across the thin line in figure 5(a) and presented in figure 5(b) shows particles around 25 nm in diameter, but much larger particles were also observed in other areas of the substrate. The reason for this has been suggested to be aggregation of silver nanoparticles on silicon substrates [8], but there is also a chance that the particles can be subjected to oxidation effects leading to growth.

Conventional bulk silicon solar cells with surface texturing and antireflection layers were used in the light trapping investigations. The sodium borohydride produced nano-Ag was tested on the multicrystalline solar cells, while the sodium citrate reduced particles were applied to both mono- and multicrystalline cells. The same procedure

as for the silicon wafer deposition was used to apply the particles on to the cells.

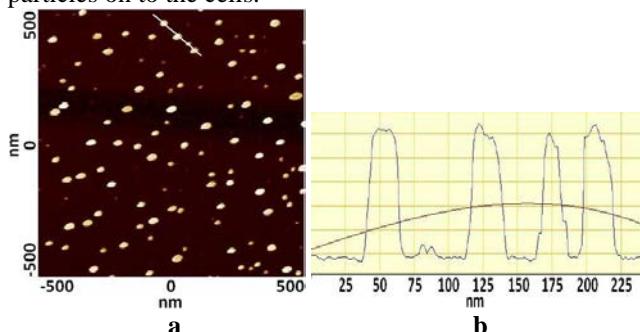


Figure 5 (a) AFM image of a planar Si wafer with colloidal silver nanoparticles deposited on the surface. (b) The results from the linescan performed across the surface following the line seen in (a), revealing diameters of approximately 25 nm.

Figure 6 shows the QE measurements performed on the different cells and with silver nanoparticles synthesized from the two methods. The borohydride-silver produces an enhancement peak at around 1000nm with a 9% increase in the quantum efficiency. The citrate-silver also exhibits some QE enhancement, but blue-shifted and with less intensity. The negative values observed for all samples at the shorter wavelengths can be attributed to the absorption in the metal nanoparticles, as this prevails over scattering in this region. Also, residues from the precursors in the chemical experiment may be responsible for some of the enhancement drop seen at these wavelengths.

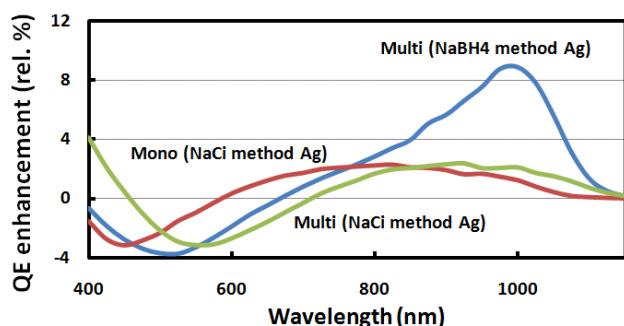


Figure 6 Quantum efficiency enhancements following the deposition of chemically synthesized silver nanoparticles on wafer based silicon solar cells.

The enhancement seen at the longer wavelengths is believed to originate from nanoparticle scattering leading to increased optical path length inside the silicon. This has earlier been demonstrated on planar wafer based solar cells, but with physical deposition methods [1]. The drop closer to the band gap of silicon is however something that is only observed with the chemically synthesized nano-Ag. The enhancement differences between the two synthesis methods are likely to come from the different morphologies of the particles. While the citrate method produced particles of high shape irregularity and size distribution, the borohydride method produced smaller particles, but more spheri-

cal and with smaller size variations. While the latter have shown to form well distributed agglomerates of silver on the surface of silicon, the behaviour of the particles from the citrate method after being deposited on a substrate needs more investigation.

When comparing the enhancements from the cells subjected to the nano-Ag from the citrate method, there seems to be a greater enhancement at the longer wavelengths for the multicrystalline sample than for the mono-Si. Reason for can be due to the different surface textures and the substrate thicknesses, since the $\approx 180 \mu\text{m}$ thick mc-cell clearly have more long-wavelength light potentially available for plasmonic light trapping than the $300 \mu\text{m}$ thick mono-cell.

4 Conclusions A simple and novel approach towards increasing light trapping in silicon solar cells by the use of chemically synthesized silver nanoparticles has been demonstrated. Silver nanoparticles of two different sizes were obtained, and the deposition of these onto silicon wafers and wafer-based solar cells was investigated by the use of UV-Vis spectroscopy, TEM, AFM and a spectral response unit as characterization tools. It was shown that the chemically produced particles could be distributed evenly in small areas on silicon surfaces. The same deposition on wafer based solar cells resulted in an enhancement of the quantum efficiency at the longer wavelengths, but further investigations are needed to see more of the potential that lies in this chemical approach to plasmonic light trapping.

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