Embedded silver nanoparticle fabrication for surface plasmon-enhanced silicon photovoltaics

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ABSTRACT

To reduce cost and maintain viability of silicon-based solar cells for commercial applications, the absorption of thin silicon films, on the order of a few microns, must be enhanced. We are developing a method to increase absorption across the solar spectrum by exploiting the enhanced electric near field caused by surface modes of excited metallic particles. Previous research in the field has focused on deposition of these particles on a passivated Si surface, a technique that scatters light in directions lateral to the cell, but does not promote direct carrier generation, as the near field enhancement is too far from the Si itself. Consequently, we have developed a method using ion implantation and thermal evaporation to fabricate Ag nanoparticles below the Si surface, near the p-n junction, where the enhanced near field can greatly enhance the absorptive response of the silicon solar cell.

Keywords: Nanoparticles, surface plasmons, solar cells, silicon, silver

1. INTRODUCTION

A major factor limiting the economic feasibility of silicon wafer-based solar cells is the cost of the silicon feedstock itself. For cells on the order of a few hundred micrometers thick, raw silicon material can account for approximately a quarter of total device cost. Yet thinner monocristalline and large-grained multicristalline substrates and films, on the order of tens of microns, exhibit diminished performance resulting from the very
weak absorption coefficient of Si, particularly in the energy region immediately above the bandgap energy. As shown in Fig. 1, a 300 μm wafer of silicon will absorb 90% of the solar spectrum in the 300-1100 nm range, while a 2 μm Si film absorbs less than 35% far below that required to match the efficiencies of wafer based solar cells, which are nearing their theoretical limit.

As such, very effective light-trapping or absorption-enhancing schemes are required. One such scheme that has gained considerable attention in recent years is the use of trapped electromagnetic waves, or surface plasmons. It is well known that in addition to surface plasmon propagation along plane dielectric interfaces, plasmonic modes can also be supported through polarization of metallic nanoparticles. Past research has focused on the deposition of silver nanoparticles on the silicon surface, and has shown that light absorbance can be increased for very thin devices within specific energy ranges, especially near the bandgap where Si is normally very weakly absorbing.\textsuperscript{1,2} At particular incident wavelengths, these trapped modes can preferentially scatter light into a dielectric substrate, increasing the proportion of light that is absorbed by the semiconductor.\textsuperscript{3} It has been shown theoretically that a dipole, to which a nanoparticle of diameter much less than the photon wavelength can be approximated, when situated between two media of differing dielectric indices, scatters incident light preferentially into the substrate of higher index.\textsuperscript{4,5} Thus one may expect that nanoparticles atop a silicon wafer will act as an anti-reflection coating or backside reflector, as has been shown experimentally.\textsuperscript{1,2,6} In addition, it has also been shown that the light that is scattered is also scattered highly in directions that are within the critical angle for total reflection, effectively trapping the light within the solar cell.\textsuperscript{1,4,5}

A further effect that has been investigated is the possibility of directly impacting the transition rate of electrons between the valence and conduction band. Thus, while increased and preferential light scattering may affect the probability that a photon enters the region in which it may be absorbed, the absorption mechanism itself, i.e. the quantum mechanical transition rate, may also be affected by the presence of nanoparticles. This is a direct effect of the perturbation caused by the electric field surrounding the nanoparticle. A sufficiently small nanoparticle, when excited by incident radiation, acts to a very good approximation as an oscillating dipole. The outerlying electric field is then composed of both the radiative far field (1/r) and the nonradiative near-field (1/r\(^2\) and 1/r\(^3\) terms). Very close to the particle surface, the near field 1/r\(^3\) term dominates; this term is the same as that of a static electric point dipole whose amplitude is given by the amplitude of the electric field of the incident photon:\textsuperscript{7}

\[
E = (3n(n \cdot p) - p) e^{iwt} r^{-3} \text{.} \tag{1}
\]

Here, \( p \) is the dipole moment and \( n \) is the unit vector connecting the dipole to the point of measurement. \( p \) is proportional to the polarizability, \( \alpha \), which for a metal or dielectric sphere of volume \( V \) in a uniform electric field, is given by\textsuperscript{7,8}

\[
\alpha = 3V \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \text{.} \tag{2}
\]

Thus, inserting equation 2 into 1 suggests that very high electric fields can be sustained in the near vicinity of metal nanoparticles when the surface plasmon resonance condition,

\[
\epsilon_p = -2\epsilon_m \text{,} \tag{3}
\]

is satisfied. Here, both increased scattering (radiative far fields) and enhanced proximal electric fields (nonradiative near fields) occur. It is the latter phenomenon that we are primarily concerned with. Both semiclassical and quantum treatments of direct carrier generation by enhanced electric near fields have been performed, and suggest that increases in transition probabilities of several orders of magnitude may occur close to metallic nanoparticles due to such high near fields.\textsuperscript{9,10} The enhancement however decreases to about 10% within distances of a few times the particle diameter. Deposition on the surface of the solar cell, therefore, cannot exploit this effect, being isolated from the silicon by the necessary passivating layer. It has been suggested that instead, such particles must be embedded into the silicon itself.\textsuperscript{10}
For photovoltaic purposes, one must choose a metal for which the condition (3) is satisfied in the visible or NIR range. This is true for three noble metals, Ag, Au, and Cu. In Fig. 2, the real part of the dielectric function of Ag, $\epsilon_{Ag}$ is superimposed with $-2\epsilon_{Si}$; where these graphs intersect, at 770 nm, the polarizability of an Ag nanosphere embedded in a Si dielectric becomes very large as indicated in equation 3. It is therefore expected that solar radiation may induce high near fields around Ag nanoparticles in Si, aiding direct carrier generation. This would increase the spectral response of thin silicon substrates that would otherwise be transparent for much of the solar spectrum.

![Figure 2. Real part of the dielectric function of silver and -2 times the real part of the dielectric function of silicon as a function of photon wavelength. The surface plasmon resonance occurs at the intersection of these two graphs, around 780 nm, well within the AM1.5 solar spectrum.](image)

To begin investigating this effect, we have successfully fabricated silver nanoparticles within a crystalline silicon substrate, and have characterized their dispersity and size using Rutherford backscattering spectrometry (RBS) and transmission electron microscopy bright field imaging (TEM). A combination of ion implantation, thermal deposition, and conventional furnace annealing were used to create Ag nanoparticles in Boron-doped silicon samples of resistivity 20-30 Ω-cm. By adjusting the implantation energy, particles may be fabricated at various depths, in our case ranging from 250 nm to 1150 nm below the surface. Thus one may in principle compare the effects of particles placed either in the acceptor, donor, or space charge region of the p-n junction solar cell simply by adjusting one parameter in the fabrication process.

The implantation was carried out in an Extrion 400 KV mass-analyzed implanter, and the current was kept below 200 nA/cm$^2$ to avoid significant sample heating during the implantation. During furnace annealing, an Ar ambient was used to avoid atmospheric contamination. RBS characterization was performed using a Dynamitron 4MeV accelerator, with a 2 MeV He+ incident ion, and TEM imaging was carried out on a 200KV JEOL 200CX microscope.

2. RESULTS AND ANALYSIS

2.1 RBS Characterization

The RBS spectra of samples annealed at various combinations of time and temperature are shown in Fig. 3. The total amount of Ag within the nanoparticles can reach a fluence of $5\times10^5$/cm$^2$, depending on the annealing conditions. The amount of trapped Ag is a sensitive function of both the annealing time and temperature, and the best results were consistently found within a temperature range of 850-900° C for 30 to 60 minutes. At temperatures higher than this, the nanoparticle clusters disassociate and Ag diffuses away as an atomic species.

Figure 4 shows samples annealed at the aforementioned conditions, but with varying implantation parameters. It is found that similar doses of Ag can be found within the nanoparticles for increasing depths, and that the nanoparticles can be formed at ranges of 250 nm to 1150 nm below the silicon surface. As such, the nanoparticle
Figure 3. RBS spectra of various samples with processing leading to Ag nanoparticle formation at 270 nm below the surface. For excessively high temperatures or annealing times, the amount of Ag found in the expected nanoparticle region is small, indicated by a lowering of the Ag peak at channel 800.

band can be tailored to lie in the preferred region, either the base, emitter, or space charge region. Since the nanoparticles are to act as a minority carrier generation mechanism, localization near or within the space charge region would be advantageous, as the internal collection efficiency in this case would be nearly unity, the carriers all being created within a diffusion length of the junction. Still, the effects of trap levels of the

Figure 4. RBS spectra indicating that the depth of the Ag nanoparticles can be tailored precisely by changing the implantation energy. The figures correspond to depths of 1150 nm, 500 nm, and 270 nm, respectively.

Ag nanoparticles upon the recombination rates, and subsequently the short circuit current and open operating voltage, would complicate matters. It is well known that atomic species, particularly of transition metals can have deleterious consequences for carrier lifetimes, and that these effects can be very asymmetric with respect
to the semiconductor fermi level. Therefore, a more comprehensive investigation of the impact on lifetime is
currently being carried as a next step to the fabrication itself. However, these tests are still being carried out
and are not reported in this letter.

2.2 TEM Imaging

Since RBS characterization is predicated on elastic atomic collisions, it cannot be used to find the bulk nature
of the Ag itself, i.e. whether it is uniformly distributed as atoms or agglomerated in particles. Accordingly, we
have performed bright field TEM imaging at magnifications ranging from 40KX to 160KX. The TEM data is
shown in Fig. 5. The samples shown in both images received similar implantation and deposition processing,
but with differing thermal treatments. The RBS spectra of the sample shown on the left of Fig. 5 shows a small

Figure 5. Samples annealed with negligible amounts of Ag indicated by RBS measurements (left) and with a high dose of
trapped Ag (right). Both samples underwent identical processing prior to furnace annealing.

(< 5e14/cm^2) dose of incorporated Ag, while that on the right shows a dose of about an order of magnitude
higher (5e15/cm^2). The Z-contrast in the second image is indicative of filling by Ag, while in the first image,
contrast is due to the strain induced by outer edges of the cavities which, being transparent, are unfilled with
higher mass elements. The nanoparticles in the second image exhibit diameters of 20-100 nm. In addition, the
strain lines from a larger, unfilled cavity is seen in the middle of the image, slightly to the left of the band.
Nevertheless, it is seen that the vast majority of the Ag is indeed clustered in nanoparticles whose sizes are
ideal for high polarizabilities: a fraction of the wavelength of solar light, but not so small (< 10 nm) that ohmic
heating dominates.\textsuperscript{10}

2.3 Recombination Effects

It may be pointed out that the introduction of transition metals such as Ag, Au, or Cu may cause such degradation
in minority carrier lifetimes so as to render the expected surface plasmon-related photocurrent enhancements
meaningless. Typical bulk diffusion lengths of lightly p-doped CZ-Si exhibit diffusion lengths of 500 to 2000
m. Intentionally contaminated Cu can degrade lifetimes by 10 times in p-Si and up to 100 times in n-Si.\textsuperscript{12} For
severe contamination, in which Cu can exist in concentrations of more than 10^{18}/cm^3, the lifetime reduces to
100 \mu m.\textsuperscript{13} For thin solar cells of thicknesses less than 10 \mu m, this is not expected to cause much degradation,
because several times the device thickness. For Ag, the lifetime of a FZ b-doped Si wafer was found to drop from
20 \mu s to .1 \mu s with a heavy treatment of Ag contamination.\textsuperscript{14} With further anneals at lower temperatures, the
atomic Ag forms less electrically active precipitates and the lifetime recovers slightly to around 1 \mu s, or 30 \mu m.
This relative drop – 3 orders of magnitude – suggests a very high capture cross section for Ag contaminants in
Nevertheless, for even the worst case, a 30 μm diffusion length would be adequate for a device layer of less than 10 μm, as it is still 3 times the device thickness.

Due to its low absorption losses and high scattering cross sections, Ag nanoparticles are best suited for surface plasmon excitations in Si-based solar cells. When in precipitate form, they are less electrically active and contribute less to recombination activity than in atomic states. Unlike Cu, Ag does not form silicides and is not mobile in Si at room temperature, which for Cu can lead to outdiffusion after relatively short times. Such considerations must be investigated more fully, particularly with direct measurements of minority carrier lifetimes in Si samples with embedded Ag nanoparticles. This work is currently being undertaken.

3. CONCLUSIONS

In summary, we have developed a method for fabricating subsurface Ag nanoparticles in crystalline silicon substrates using a combination of ion implantation, thermal deposition and furnace annealing. Gettered doses of up to 5e15/cm² can be achieved using this method, and characterization by RBS and TEM indicate that the gettered Ag is in the form of bulk phase nanoparticles of diameters of a few to several tens of nm. The depth of the band of Ag nanoparticles can be tuned over a wide range of several hundred nanometers by adjusting the ion implantation energy. In addition, while previous work suggests that Ag-induced minority carrier lifetime degradation may occur, for very thin Si films, the literature indicates that it should have little effect. Contactless methods of determining the minority carrier lifetime in Si samples with embedded Ag nanoparticles are being carried out.

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REFERENCES


