Plasmonics for photovoltaic applications

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ABSTRACT

Plasmonics is a promising new approach to enhance the light trapping properties of thin-film solar cells. Metal nanoparticles support surface plasmon modes, which are used to couple light into the underlying optical modes of the semiconductor. Tuning the surface plasmon resonance can be used in order to enhance absorption in the wavelength region required. Excitation of surface plasmons is characterised by strong scattering and enhancement of the electric field around the vicinity of the metal nanoparticle. Photocurrent enhancements have been reported from both inorganic and organic solar cells due to either one of these mechanisms. This paper reviews recent progress in this area and also discusses the potential of surface plasmons in the third generation solar cells.

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1. Introduction

Plasmonics is an emerging field that makes use of the nanoscale properties of metals. Though plasmonics is a wide area of study, its application for solar cells has seen a recent surge of interest as is evident from the increasing number of publications over the last couple of years. Metals support surface plasmons that are the collective oscillation of excited free electrons and characterised by a resonant frequency. They can be either localised as for metal nanoparticles or propagating as in the case of planar metal surfaces. By manipulating the geometry of the metallic structures, the surface plasmon resonance or plasmon propagating properties can be tuned depending on the applications. The resonances of noble metals are mostly in the visible or infrared region of the electromagnetic spectrum, which is the range of interest for photovoltaic applications. The surface plasmon resonance is affected by the size, shape and the dielectric properties of the surrounding medium. Silver and gold have dominated experimental research in this area although other metals also support surface plasmons. Three different mechanisms that could be utilised for photovoltaic applications are (a) the scattering from the metal particles that also act as dipoles (far-field effect), (b) the near field enhancement and (c) direct generation of charge carriers in the semiconductor substrate. Most reported photocurrent enhancement results for inorganic devices are explained by the first mechanism of scattering and for organic devices by near field enhancement. This paper highlights results with particle plasmons or localised plasmons and does not discuss propagating plasmons.

2. Background

Thin-film solar cells are presently considered the route to low cost photovoltaics. This is achieved by reducing the phototactive layer, which is mostly silicon. However low cost is achieved by compromising the efficiency of these cells. This is because as the active layer is thinned down the charge transport properties deteriorate thereby affecting cell performance. For the same reason light trapping becomes an important factor. Conventional methods of light trapping use textures that have features that are comparable or much larger than the thickness of the actual thin-film solar cells. This would not be feasible for thin-film cells. Textured surface can also result in considerable surface recombination losses due to increased surface area, thereby degrading the cell performance. Hence one of the most crucial factors determining the efficiency of thin-film cells is the light trapping effect or the amount of light scattered into the substrate.

When excited, surface plasmon excitation can result in scattering and giant enhancement of the electric field. Metal particles in the order of wavelength of light act as miniature dipoles scattering the incident radiation, which is coupled to the modes of the underlying semiconductor. Metals show this behaviour because of the presence of free charge carriers. Highly doped semiconductors and metal oxides can also show plasmon effects but because of the lower number of free charge carriers, their resonance is mostly in the infrared. For small particles in the...
quasi-static limit, the scattering and absorption cross-sections are given by [1]

$$C_{abs} = \frac{2\pi}{\lambda} \mathrm{Im} \{\chi\} \quad \text{and} \quad C_{sca} = \frac{1}{6\pi} \left( \frac{2\pi}{\lambda} \right)^4 |\chi|^2$$  \hspace{1cm} (1)

Here \( \chi \) is the polarizability of the particle for a small spherical particle in vacuum, given by

$$\chi = 3V \left[ \frac{\varepsilon / \varepsilon_m - 1}{\varepsilon / \varepsilon_m + 2} \right]$$  \hspace{1cm} (2)

where \( V \) is the volume of the particle, \( \varepsilon \) the permittivity of the metal and \( \varepsilon_m \) the permittivity of the surrounding medium. The scattering efficiency \( Q_{sca} \) is given by \( Q_{sca} = C_{sca}/(C_{sca} + C_{abs}) \). For frequencies near their resonance, these nanoparticles can have a scattering or absorption cross-section much larger than their geometric cross-section [2]. For example the scattering cross-section of a 100 nm silver nanoparticle can be ten times more than the geometric cross-section at the plasmon frequency. The scattering from metal nanoparticles is a well known phenomenon and has been discussed extensively in many books [2,3].

The relative importance of absorption and scattering is size dependant. Therefore for photovoltaic applications the size of the particles needs to be optimised to ensure maximum scattering. Absorption dominates for small particles \(< 50 \text{ nm} \) and used for applications like solar glazing and therapeutic applications [4,5]. Scattering for particles around 100 nm is more relevant to solar cell applications. However the particle sizes cannot be too large as this leads to multipole oscillations which tend to decrease the scattering efficiency of the nanoparticles. Fig. 1 shows the effect of size on the scattering cross-section and also the effect of having the particles in a high refractive index medium like silicon using Mie scattering theory [6]. The polarizability of the particle is dependant on the size as well as the refractive index of the medium as is evident from Eq. (2). This in turn results in a higher scattering cross-section because of its dependence on \( \chi \) as shown in Eq. (1). Fig. 1(a) shows the normalised scattering cross-section (normalised to the geometric cross-section) of different sized spherical particles in air and the subsequent red shift for the same particles in Si is clearly evident in Fig. 1(b). This is because the resonance peaks shift to longer wavelengths with increase in size as well as under the influence of a substrate with high refractive index. The shift is desirable for Si devices as increased scattering at longer wavelengths would enable good light trapping close to the bandgap of Si, where Si normally absorbs weakly. But as particle size increases scattering decreases and also multipole oscillations are initiated as is clearly seen in Fig. 1(b) which cannot couple efficiently to the substrate modes and the energy is lost. Larger particles along with larger surface coverage lead to increased parasitic absorption and reflection reducing the desired optical absorption in the semiconductor layer [7]. The increase in scattering cross-section for 20 nm sized particles in Si when compared to air is clearly evident. However particles in this range tend to absorb more strongly (not shown in the figure), hence the overall scattering is compromised.

### 3. State of the art

In this section we discuss some recent state-of-the-art results that have been attributed to one or more of the mechanisms mentioned in Section 1.

#### 3.1. Scattering from the nanoparticles

In this case the energy from the surface plasmons is emitted as light and scattered in the direction of the semiconductor. This increases the path length of light within the semiconductor, leading to increased absorption. It was the pioneering work by Stuart and Hall on silicon photodiodes that attracted the interest of solar researchers. They demonstrated an 8-fold increase in photocurrent from 160 nm thick silicon-on-insulator (SOI) photodiodes at 800 nm from approximately 100 nm sized silver particles [8]. The particles were deposited by vacuum evaporation followed by low temperature annealing. Varying the size of the particles for the same sequence of work led to an enhancement of photocurrent by 27 times [9]. Since solar cells can use any technique that can provide efficient light trapping, subsequent research in the area of plasmonics for photovoltaic applications was built on Stuart et al.’s work. Following this Schaadt et al. [10] deposited gold nanoparticles on a silicon pn junction diode and observed an increase in photocurrent. In this case the metal nanoparticles of different sizes were deposited using spherical colloidal nanoparticles of gold and a maximum enhancement of 80% was noticed at around 500 nm with 80 nm particles. Derkacs et al. [11] used Au nanoparticles on thin-film amorphous silicon p–i–n solar cells to achieve an 8.3% overall increase in conversion efficiency.

Our group accomplished proof-of-concept results of not only enhanced absorption but also enhanced emission from thin-film solar cells and SOI light emitting diodes (LEDs) [12–14]. In this case, a thin film of silver was deposited under vacuum onto the devices and annealed to form metal islands. Photocurrents and electroluminescence measurements were made before and after the metal nanoparticle deposition and subsequent enhancements calculated from the solar cells and LEDs, respectively.
Photocurrent enhancements were measured from different thicknesses of 95 nm SOI cells, 1.25 μm SOI cells and 300 μm wafer-based planar cells. The maximum overall enhancements for the 1.25 μm SOI cell and 300 μm wafer-based cell when integrated across the AM1.5G spectrum were 33% and 19%, respectively with scope for further improvement. Larger particles have been shown to reduce the absorption in the visible wavelengths for this study. Applying the particles on the rear of thin-film structures can provide the benefit of light trapping at longer wavelengths without the problem of any parasitic absorption in the metal at the visible wavelengths. By the reciprocity of light propagation, a good absorber must be a good emitter as well. Hence electroluminescence measurements were conducted on 95 nm SOI LEDs and the maximum enhancement noted was 12% at 900 nm. This corresponds to an overall enhancement of 7 when integrated across the emission spectrum.

In a recent work Moulin et al. [15] reported improved light absorption from silver nanoparticles integrated on the rear of thin-film microcrystalline solar cells. Matheu et al. [16] have reported an increase in power conversion efficiency of 2.8% and 8.8% from Si-based devices using 100 nm Au colloidal particles and 150 nm silica particles, respectively. The effect of surface plasmon scattering has been reported not only for the case of silicon but also for other semiconductors as well. Recent work by Derkacs et al., similar to the work by Matheu et al. has shown nanoparticle scattering to have improved the performance of InP/InGaP quantum-well solar cells [17]. Both silica and gold particles were used again and this time the efficiency improvements were 17% and 1%, respectively. Plasmonics has also been used to enhance light absorption in thin-film GaAs solar cells resulting in an 8% increase in the short-circuit current density of the cell [18]. 110 nm silver particles were deposited onto GaAs cells using an anodic aluminium oxide mask and the shape and density of the particles were uniformly controlled.

It is also interesting to note that these metal nanoparticles can act as an antireflection coating as well in the entire visible region [13]. Lowering of reflectivity and an increased photocurrent are due to the fact that these metal nanoparticles scatter more efficiently into the high refractive index semiconductor rather than to air because of the high density of optical modes. This has been further verified by modelling a point dipole on a substrate [19]. The distance of the particle from the substrate also plays an important role as the fraction scattered into the substrate decreases with increasing distance. This also correlates to decrease in surface plasmon coupling with the waveguide modes of the semiconductor.

3.2. Near field effect

The electric field near an emitting dipole has non-radiative components with its field many times stronger than the field radiated from the dipole, localised to a few tens of nanometers around the particle. If a semiconductor is close to the field, absorption is enhanced because of the high density of states of the photons. This effect can be further enhanced by decreasing the spacing and size/shape of the particles. Following this effect, increased numbers of e–h pairs were generated near the junction of organic thin-film tandem solar cells, increasing the absorption capability before they recombine [20]. The fact that they used 5 nm particles is a clear indication that these particles would not support scattering. Also the surface plasmon resonance exists far from the regime where photocurrent enhancement was observed.

One of the earliest reports of enhancement of PV conversion efficiency from organic solar cells was using Au, Ag and Cu metal clusters at indium tin oxide (ITO) copper phthalocyanine interface [21]. The intention of this work was to use the electrical field enhancement to increase the number of photogenerated charge carriers which was successfully achieved with a maximum enhancement of 2.7 from Cu clusters. Similar enhancements were reported for CdSe/Si heterostructures [22] and organic bulk heterojunction cells [23]. In another work, effects of surface plasmons were investigated on photochemical cells using dye sensitised TiO2 film electrodes and an increase in photoresponse was observed in the visible region with silver mass thickness of 3.3 nm [24]. Enhanced charge carrier generation rate was found on similar structures with gold disks [25].

In the near field, nanoparticles can directly excite e–h pairs when placed close to the semiconductor. This can play an important role in having the nanoparticles inside the active layer for solid state devices rather than on the front or rear of the cells [26] as is the case for organic cells. However many other factors like interface and surface effects on the near field still need to be understood and also call for improved cell design. At this stage applying the particles on the front or rear looks like a better option as the optical properties of the metal are totally isolated from the electrical properties of the solar cell, allowing easy and independent optimisation of the plasmon properties.

Very few literature is available for the third mechanism. However surface plasmon excitation followed by direct injection of electrons has been attributed to the increase in photocurrent at the interface of an ITO and ZnInP Schottky junction using silver metal clusters [27].

4. Plasmons for third generation solar cells

The third generation solar cells are often referred to as the ‘future’ of solar cells because they promise low cost high efficiency solar cells aiming to achieve efficiencies closer to the thermodynamic limit of 93% [28]. This requires circumvention of the Shockley–Queisser limit of single bandgap devices. One such approach is using multiple energy threshold devices like tandem cells, where a series of varying bandgap materials are stacked in series in the decreasing order of bandgap. This increases the spectral sensitivity of the device thereby increasing the conversion efficiency. The bandgap of the structures can be engineered using quantum dot (QD) structures and a ‘hot carrier’ cell approach taken to capture the electrons before they thermalise. Enhancing photocurrent in low dimensional structures like quantum dot or quantum-well structures can be quite challenging because of the low conductance of these structures, which is the effect of poor optical and electrical properties of these devices. The near field could possibly be exploited for increasing the efficiency from quantum dots which have a short carrier transport distance. Hence surface plasmons can provide wavelength dependant light trapping for tandem cell applications where shorter wavelengths are coupled in the top layer using smaller metal nanoparticles and the longer wavelengths absorbed in the subsequent layers using larger sized metal nanoparticles as shown in Fig. 2.

Photoluminescence (PL) or electroluminescence (EL) energy is associated with the size of QDs, but an increase in the intensity of PL or EL using surface plasmons would indicate increased emission. Here again based on the reciprocity principle an increase in emission would correlate to an increased absorption in the QD structures. Surface plasmons have demonstrated increased photoluminescence and electroluminescence from silicon nanostructures by electromagnetic coupling of the silicon quantum dot emission dipoles with dipolar plasmon modes of Ag nanoparticles [29,30]. Similar emission has also been reported.
from CdSe nanocrystals [31]. More recently increased photocurrent was reported from Si nanocrystal photodetectors mainly attributed to the coupling of the nanocrystals to the localised surface plasmons of silver islands [32]. Fig. 3(a) show the PL measured for Si nanocrystals in a 15 bilayer Si rich oxide/SiO₂ superlattice with and without the silver metal nanoparticles. The particle sizes are around 120–150 nm in diameter. The samples were illuminated using a 10 mW, 532 nm Nd:YAG laser and the emission was captured on a thermoelectrically cooled Si-CCD camera. The peak emission is at 823 nm which corresponds to a bandgap of 1.5 eV and is increased by almost 50% at this wavelength using silver nanoparticles. It is expected that the enhancement peak at 950 nm as shown in Fig. 3(b) could be easily tuned to the desired wavelength by varying the particle size, e.g., in this case going for smaller particles which will shift the resonance to the blue side. These results are promising proof-of-concept results and incorporating them into solar cell structures can potentially boost the performance of the cell making a third generation cell more realisable.

The enhanced electric field around the surface plasmons has the potential to aid non-linear processes like up-conversion, one of the important aspects being looked into for the third-generation solar cells [33,34]. In the up-conversion process two or more below bandgap photons are usually absorbed into a luminescent material behind a solar cell and emitting photon with higher energy which can then be absorbed. If the luminescent material is situated in the vicinity of the enhanced electric field, the process is likely to be enhanced many fold. Enhancement of up-conversion luminescence of erbium-doped Al₂O₃ has been reported by placing it near silver island films of varying sizes. A maximum enhancement of 220 times was seen at 520 nm [35]. The increase in power from the up-conversion process to date has been very modest but surface plasmons can potentially increase this value by many fold contributing to an increased overall cell efficiency. The advantage of this process is that the luminescent material is electrically isolated from the solar cell thereby providing more optical tunability along with the plasmons.

5. Modelling of plasmons

Much more work needs to be done to explain the effects of shape, dielectric of the surrounding medium around the particles, optimal spacing and distribution, on the photocurrent of solar cells. Simulations studies in the area of plasmonics particularly in the scattering by particles behaving like dipoles have helped in giving deep insight into the various processes described in this paper and acting as accurate optimisation tools. Cole and Halas [36] in their paper determine a model to suggest the ideal distribution of spherical metal nanoparticles, both nanoshells as well as nanospheres for optimum light harvesting of solar energy. According to their simulation 30% coverage of nanoparticles can scatter almost all the incident radiations and 105 nm silver colloidal particles can scatter 571.5 W/m² out of the available 578 W/m². Their particles were on glass substrate in air hence interaction with the substrate is not accounted for. In a similar study Akimov et al. have used an effective medium model to study the effect of nanoparticle size and surface coverage and suggest particle sizes in the range of 25–50 nm radii as the optimum size [37].

Another recent theoretical study using FDTD calculations has found that cylindrical and hemispherical particles are likely to give a greater path length enhancement when compared to their spherical counterparts because of the enhanced near field coupling [38]. In this case the particles size, shape, dielectric environment and the particle material were varied to study the impact of each on the light trapping in solar cells. It was found that hemispherical and cylindrical particles scattered more light into the substrate than spherical particles because of increase in enhanced near field coupling. Also it was shown that silver particles gave a much higher path length enhancement than gold particles and that the scattering cross-section was increased when
the particles were placed close to the substrate. As the particles were moved away from the substrate, a greater fraction of the incident light was radiated into air than to the substrate [19]. For a more realistic simulation, interparticle interaction as well as interaction with the substrate has to be accounted for. Varying the local dielectric environment of the particle can help increase the absorption by tuning the resonance close to the bandgap of Si where Si absorbs weakly. This has been demonstrated experimentally as well by enhancing the external quantum efficiency by a factor of 2.3 at 1100 nm [39]. Another study encompasses both the near field effects and the coupling effect to attain a 43% enhancement in the short circuit from a 2D periodic array of Ag strips on 50 nm Si with 10 nm silica as spacer layer [40]. With so many variable parameters for optimisation, an optimum combination of the parameters needs to be considered for an overall improvement in the solar cell performance.

6. Plasmonics for photovoltaics: outlook

There is a clear need for technologies that lead to better light absorption in thin solar cells in order to allow higher efficiencies and hence lower overall costs of electricity production. Plasmonics has the potential to revolutionise the photovoltaic industry and deliver high efficiency, low cost solar cells. Light trapping and concentration of light using the tiny metal nanoparticles can open avenues for a range of solar cell designs in particular for the third generation photovoltaic technology involving quantum dots and quantum wells and also up-conversion process. Since the incorporation of the nanoparticles with the present approach is at the final stage of device processing for Si-based cells, no major disruption to the existing fabrication process would be involved. Hence current research is focussed at reducing the fabrication cost of the metal nanoparticles and also enabling its fabrication on large area devices. Present lithographic techniques like e-beam lithography and focussed ion beam lithography enable fabrication of nanoparticles with high precision but is expensive and not suitable for large area processing. Development of new techniques such as nano-imprinting or soft lithography [41,42] is gaining popularity as a robust practical production process for plasmonic solar cells. This technology in conjunction with existing deposition techniques (like thermal evaporation or sputtering) promises control of the size, shape and distribution of the nanoparticles with accuracy at the nanoscale, allowing more freedom for optimisation irrespective of the nature of the semiconductor used.

Optimisation of the various parameters mentioned earlier is not an easy task due to the many variables involved. Hence it envisages the need to a good understanding of the technology in particular the interaction of light with the metal nanoparticles and the surrounding environment. Powerful simulation tools which can give a more realistic interpretation of results (accounting for the dielectric medium surrounding the particles and also the effect for the neighboring particles) are needed to predict the photocurrent enhancements to enable fabrication of optimal nanoparticle arrays for light trapping applications.

7. Conclusion

We have reviewed the recent results which have emanated from the use of plasmons for different solar cell structures. Two cases of enhancement have been discussed. In the first case the energy from the surface plasmons is emitted as light and scattered in the direction of the semiconductor. This increases the path length and in the process excites e–h pairs which is then absorbed ( indirect absorption). From these results the potential of incorporating plasmonics into solar cell structures looks very promising. It allows the drastic reduction in the thickness of the active semiconductor layer and simultaneously boosts the performance from materials with poor charge carrier transport. There is no doubt that photovoltaic research will benefit immensely from plasmonics, enabling use of low quality low cost materials and delivering cells with high performance and low cost.

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