Metal nanoparticles for thin film solar cells - DTU Orbit (01/10/2019)

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Among the different renewable ways to produce energy, photovoltaic cells have a big potential and the research is now focusing on getting higher efficiency and at the same time saving the manufacturing costs improving the performance of thin film solar cells.

The spectral distribution in the infrared wavelength region longer than 800 nm accounts for ~40% of the entire solar energy observed on Earth, and only a few solar cells can efficiently convert solar energy with such a long wavelength. The goal of this work is the harvesting of these NIR photons in order to increase the solar cells efficiency in such spectral range; after an overview of the different technologies available today, the employment of localized surface plasmons (LSPs) through the incorporation of metallic nanoparticles within the photovoltaic device is chosen as a cheap and simple method.

The LSP resonance wavelength and intensity depends on the nanoparticle’s size, shape, and local dielectric environment, thus absorption enhancement in a defined wavelength range can be achieved varying these properties (tuning the LSP resonance). Even though scattering enhancement of photons above the gap of the semiconductor is useful to increase light trapping and can come along regardless, we aim, as first target, to absorb forbidden (for the semiconductor) photons by the NPs which can excite hot electrons inside the metal NP and emit them directly into the conduction band of the solar cell semiconductor, without going through the promotion of electrons from the valence band of the semiconductor. The photoemission would extend the spectral response of the photovoltaic device.

Thus, NPs are placed at the metal/semiconductor interface (in order to exploit the localization characteristic of the LSP enhancement) and are used as active nanoantennas absorbing photons with energy smaller than the semiconductor gap but larger than the Schottky barrier height between metal and semiconductor.

The optimization of the fabrication process of GaAs and a-Si:H Schottky solar cells is first conducted and subsequently, the incorporation of Au or Ag nanoparticles at the interface between the semiconductor and a transparent conductive oxide layer (TCO), used to complete the Schottky junction and as top electrode, has followed.

A model representing the device structure with GaAs, ITO and incorporated Au disks or Ag ellipsoids in between, is developed and used for FDFT simulations, in order to identify the set of parameters (NPs size and array periodicity) which could show LSP resonance in the NIR range.

Two techniques are here used to fabricate NPs: electron beam lithography (EBL), to deposit ordered arrays of gold and silver NPs, simple to be compared with modelling; and electroless plating, to grow silver nanocrystals with a cheap technology, producing random distribution of particles. These techniques are studied and optimized aiming to obtain NPs patterns of different size, periodicity and density on the substrates required for the incorporation within the solar cell structure (GaAs, SiO₂, Si₃N₄, AZO/Cr), in order to investigate the LSP resonance and tune it to exploit it below the energy band gap of the semiconductor.

EBL is a difficult technique when working by lift-off on critical size (20-50 nm) nanoparticles. The optimization of the process saw a change from ZEP resist to double layer of PMMA and always requires preliminary exposure dosee-tests and final particular attention for lift-off step. EBL resulted to be more suitable for silver NPs, since the deposition of gold (on top of an adhesion thin titanium layer) leads to a variation and non-regularity in the shape of the NPs: truncated cones with varying bottom and top radius. The difference in shape causes broadening of the resonance peak (as demonstrated by simulations).

Electroless plating is a technique, based on chemical reactions, which makes use, in the process chosen for this work, of AgNO₃ powder, diluted in water, and HF at very low concentrations. This kind of deposition is very cheap but precise optimization of recipes, strictly depending on the substrate surface, is needed and limited by the chemistry involved. Thus, the NPs grown with this method are characterized by broad distribution of size and shape of NPs bigger than what can be obtained by EBL.

The nanoparticles, after being deposited on different substrates and eventually coated with TCO, are first optically characterized: reflection and transmission are measured with an integrating sphere and consequent absorption spectra are calculated.

A variety of metal nanoparticles on GaAs and a-Si:H is studied. Only Ag nanoparticles have measurable photon absorption while no effect is seen with Ti/Au nanoparticles. SEM and AFM measurements show that size, shape and height are very variable with Ti/Au nanoparticles fabricated by EBL, within the pattern, and this combined with small density of patterns might be a reason for the unmeasurable absorbance enhancement.

The behavior of ordered Ag NPs fabricated by EBL depends on their size and thickness: 24-34 nm of diameter, array pitch of 100 nm and 15-30 nm of thickness give absorbance enhancement in the visible range between 500 and 600 nm of wavelength. Ag NPs of 20-34 nm size and 30 nm thick, incorporated into a-Si:H solar cell structure (thus covered by TCO) with varying array pitch (60/80/100 nm) show 3 localized surface plasmon resonances (LSPR): around 450 nm, 560 nm and 740 nm. LSPR at 560nm originates from scattering, while LSPRs at 450nm and 740nm, are due to NPs absorption. The tail of the peak at 740nm, falls below the gap of the semiconductor (a-Si:H) and the energy of the photons exciting the LSPs, can be translated in consequent emission of hot electrons.

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**EELS measurements** are conducted on Ag NPs deposited by electroless plating in order to investigate the nature of the absorption enhancement, which is not found on similar ordered patterns. Particular dimers (forming nano-bridges) and elongated particles are the responsible of the plasmonic excitations in the energy range of 0.9-1.5 eV, corresponding to part of the NIR range characterized by absorbance enhancement.
Finally, after optical characterization, the NPs are incorporated within the entire diode structure and electrically characterized. Spectral responses are measured and in two types of measured GaAs solar cells (with Au and Ag nanoparticles) there was no clear efficiency enhancement in the NIR spectral range. In the case of Au nanoparticles it could be explained in similar way to the absorption data: the effect being broad is too weak. The absence of the expected plasmonic enhancement below the gap in devices with Ag NPs suggests that the energy of absorbed photons does not lead to photoemission but is dissipated through heat. GaAs is known to have very fast surface recombination and possibly it was not reduced well enough with the introduced Si₃N₄ layer.

On the other hand, quantum efficiency of a-Si:H solar cells show enhancement corresponding to the 3 LSPRs found in absorption spectra, but absorption contribute by NPs is enhanced by LSP less effectively than scattering; furthermore, it is also less effective than absorption in semiconductor so really only worth it if the peak can be shifted below the bandgap. Finally, the variability of the enhancement corresponding to the resonances due to absorption is hard to understand, thus possible surface recombination, due to processing variations, might play an important role. Further developments are needed in the solar cell structure in order to reduce surface recombination and exploit the photoemission below the semiconductor energy gap; nevertheless, promising optical results showed here confirmed the possibility to use nanostructures, in particular randomly distributed, to extend solar cells spectral response to longer wavelengths, through possibly cheap and simple technologies: EBL can be substituted by colloidal solutions implementation and electroless plating is not expensive and results to be effective within a broad set of parameters (size, shape, density). Another application of the studied NPs can be in NIR photodetectors.

General information
Publication status: Published
Organisations: Department of Photonics Engineering, Metamaterials
Contributors: Gritti, C.
Number of pages: 162
Publication date: 2014

Publication information
Place of publication: Kgs. Lyngby
Publisher: Technical University of Denmark (DTU)
Original language: English