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Rare-earth doped glasses and light managing in solar cells

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Abstract. Glasses doped with rare earth elements possess unique photoluminescence properties. They find application in several devices, such as lasers, optical amplifiers, and sensors. More recently, rare-earth doped glass thin films have been the subject of investigation for the development of frequency-converting layers able to increase the efficiency of silicon solar cells. Another approach to the improvement of the performance of a solar cell is based on the capture of a larger flux of light by the detector, which can be obtained by surface texture, plasmonics, or waveguide structures. Here, the recent advances in this area will be briefly reviewed.

1. Introduction

Rare earth (RE) elements, discovered at various times between the end of XVIII century and mid XX century, are now indispensable in many electronic, optical and magnetic applications. Rare earth magnets, for instance, are exceptionally powerful and have facilitated the development of advanced medical diagnostic technologies, such as MRI (Magnetic Resonance Imaging).

The photoluminescence properties of oxides and minerals containing rare earths started to be studied at the end of XIX century: Sir William Crookes, in his presidential address to the British Association for the Advancement of Science, in 1898, was proudly communicating that "among the groups of rare earths giving phosphorescent spectra in the visible region there are others giving well-defined groups of bands which can only be recorded photographically."[1]. One year later, in 1899, a patent application was filed for an electric-lighting apparatus, in which the "luminant or glower" was composed of a rare earth or a mixture of rare earths [2]. The full understanding of the electronic transitions in RE ions made a crucial step forward in 1962, with the publication of the works by Judd [3] and Ofelt [4]. Since then, there has been a growing number of optical applications of RE-doped glasses, due to the large number of absorption and emission bands available in the visible and IR regions using the various RE elements. A phenomenon which makes RE-doped materials very useful in various applications is the frequency conversion: in photon up-conversion, two or more incident photons of relatively low energy (usually in the infrared) are absorbed and converted into one emitted photon with higher energy, namely in the visible or ultraviolet region. In the down-conversion, vice versa, one blue or UV photon is converted into two near-IR photons.

The last decades have also seen many efforts focused on the development of novel or advanced devices in the field of renewable energies. A silicon solar cell, for instance, is based on the absorption process of light via excitation of electron-hole pairs and the extraction of these generated charge carriers; its efficiency is mainly limited by two factors: a) the loss of light due to the reflection at the front surface

of the cell and to the limited capacity of trapping the photons from various incident directions; b) the mismatch between the spectral sensitivity of the silicon and the solar spectrum.

Here we will briefly discuss how the efficiency of a Si solar cell may be significantly increased by properly designing its structure and including one or two RE-doped glass layers acting as frequency converters.

2. Light managing in solar cells

The classical layout for a solar cell is a p-n junction, namely a junction between an n-doped and a p-doped semiconductor (here we refer in particular to silicon). Both the semiconductor components are connected to contacts, where the migrating charge carriers are extracted. Due mainly to the cost issue, a consolidated industrial trend is to use thinner and thinner silicon slices, or even Si crystalline thin films; to keep the absorption volume large enough to generate many charge carriers, it is therefore necessary to adopt solutions which can anyway guarantee long paths of the light inside silicon. It can be achieved by using scattering structures, such as textured surfaces or nanoparticles, or by taking advantage of waveguide confinement.

A frequent solution in thin-film Si solar cells is represented by the use of randomly textured surfaces, which can be either in the front of the cell (superstrate configuration, or p-i-n) or in the back (substrate configuration, or n-i-p). It was demonstrated that the front texture enhances light absorption and external quantum efficiency from the visible region to the near-infrared region, while the rear texture increases these properties only at wavelengths longer than around 600 nm [5]. One can also combine front and back contact textures, but their optimization is a real challenge [6]. Optical simulations have shown that the highest efficiency is achieved if different front and back textures are used [7]. Figure 1 shows the cross-section of a microcrystalline Si solar cell in superstrate configuration, which can have (a) standard flat contact; (b) identical front and back contact textures; (c) different front and back contact textures.
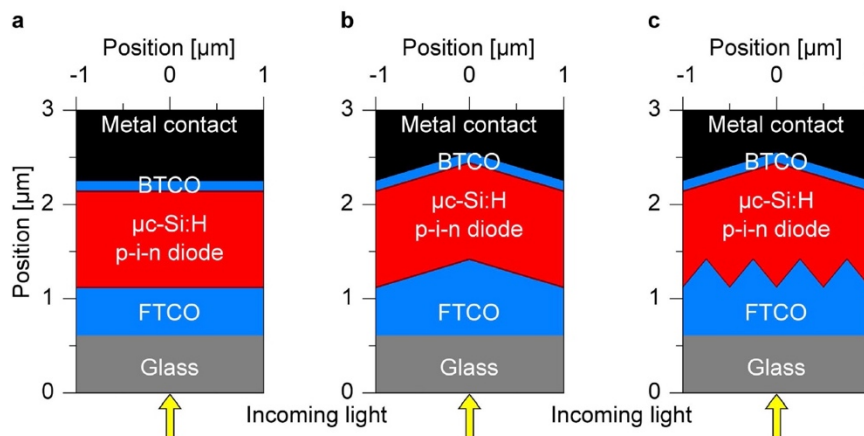

Figure 1. Schematic view of the cross-section of various configurations of a p-i-n Si solar cell: a) flat front and back contacts (FBC); b) identical FBC textures; c) different FBC textures. FTCO = front transparent conductive oxide; BTCO = back transparent conductive oxide. *Figure reproduced from [6] under Creative Commons license*.

Another effective approach to increase the light concentration and trapping exploits the properties of plasmonic structures, consisting of patterned metal films or nanoparticles. Plasmonic nanoparticles (PNP) can be embedded in a solar cell in different configurations, which are sketched in Figure 2. The PNP may be a) deposited on the surface of the cell; b) embedded into the semiconductor active layer; c) placed at the bottom interface between the semiconductor and the metal [8]. Depending on their localization, the PNP play a different role; in the a) and c) configurations, for instance, the light is scattered and trapped by the semiconductor thin film due to multiple and high-angle scattering, so increasing the effective optical path length inside the cell. When the PNP are embedded (Fig. 2.b), a

strong localization and enhancement of the electromagnetic near-field in the proximity of the particles occurs and increases the production of electron–hole pairs within the semiconductor. If a metal grating consisting of a periodic array of nanostructures is fabricated at the back surface (Fig. 2.c_2), the incoming light is coupled to surface plasmon polaritons (SPP), which propagate in the plane of the semiconductor layer.
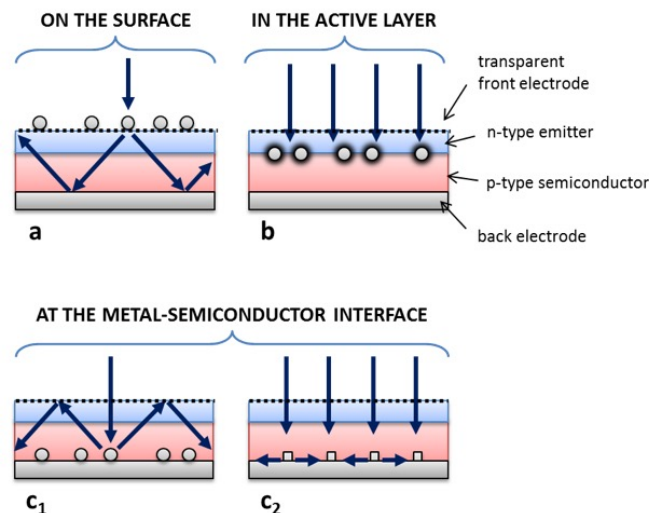
Figure 2. Light-trapping configurations with metal plasmonic nanoparticles (PNP) in a thin-film solar cell: a) PNP on the surface of the solar cell; b) PNP embedded in the semiconductor; c) PNP or periodic array of metal np at the metal/semiconductor interface. *Figure reproduced from [8].*

2.1. Frequency conversion

As already mentioned, another cause of the poor efficiency of a Si photovoltaic solar cells is related to the limited spectral absorption of the silicon, which does not exploit the whole broadband solar spectrum. Indeed, over 40% of the potential efficiency of a Si solar cell is lost due to the thermalization or to the non-absorption of photons with energies lower than the bandgap of Si. Rare-earth ions with their rich spectrum of optical transitions among the F and D levels may be well used for up- and down-conversion processes, where two lower energetic photons are absorbed and a higher energetic photon is emitted (up-conversion, UC), or where a higher energetic photon is absorbed and two lower energetic photons are emitted (down-conversion, DC). These processes are graphically sketched in Figure 3.
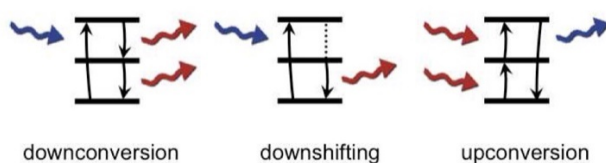
Figure 3. Schematic energy diagram of a rare earth ion, showing absorption and emission of higher (blue) and lower (red) energetic ions. *Figure reproduced from [9].*

Thus, frequency conversion may be exploited to reduce the mismatch between the spectrum of the solar light and the absorption band of Si: luminescent conversion layers maybe introduced in front or in the back of the solar cell. Usually, as depicted in Fig. 4, DC or down-shifting layers are located on top of solar cells, where they can convert incoming UV and blue photons into red and near-infrared ones; UC layers, instead, are preferably placed in the back, so to convert IR photons that are not absorbed by the solar cell (and are reflected back by a mirror layer) into the NIR or visible part of the spectrum, which may effectively be absorbed by silicon.
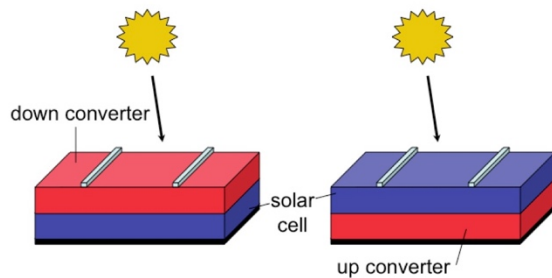
Figure 4. Sketch of a single-junction solar cell having a DC layer on top or a back reflector and an UC layer at the bottom. *Figure reproduced from [9]*.

Various rare earths may be used for frequency conversion. The pairs Pr^{3+}/Tb^{3+}, Er^{3+}/Eu^{3+}, Ce^{3+}/Tb^{3+}, Tb^{3+}/Yb^{3+} are frequently used for down-conversion; another possibility is to use a single lanthanide ion in association with a sensitizer, which absorbs in the UV and transfers the energy to the RE ion [9-12]. Silver and Si nanocrystals have proven to be effective sensitizers [9,12]. An improvement of performance of the solar cell may also be obtained by down-shifting of the incoming light [13,14]. Finally, Erbium is the best candidate for up-conversion in Si cells [9,15].

3. Conclusions

Several materials and structures have been tested with success in order to increase the efficiency of single-junction Si solar cells. Improvements have been obtained either by acting on the structure(s) to get a more efficient light trapping or by introducing frequency conversion layers able to guarantee a better matching between the solar spectrum and the absorption spectrum of silicon.

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