Carrier population control and surface passivation in solar cells

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ABSTRACT

Controlling the concentration of charge carriers near the surface is essential for solar cells. It permits to form regions with selective conductivity for either electrons or holes and it also helps to reduce the rate at which they recombine. Chemical passivation of the surfaces is equally important, and it can be combined with population control to implement carrier-selective, passivating contacts for solar cells. This paper discusses different approaches to suppress surface recombination and to manipulate the concentration of carriers by means of doping, work function and charge. It also describes some of the many surface-passivating contacts that are being developed for silicon solar cells, restricted to experiments performed by the authors.

1. Introduction

Maintaining a high concentration of electrons and holes in a photon-absorbing semiconductor is a premise for the conceptual design of a solar cell. This is because the electrochemical energy of electrons and holes is directly linked to their concentration, and so is the eventual voltage produced by the device. Although they may be referred to as a gas, simplifying the statistical relationships that govern their population density, electrons and holes do not leak out of the surfaces of the semiconductor; rather, they recombine with each other at surface defects, with the same net effect of being lost and of causing a reduction of the electrochemical energy of the system. Hence, it is important to envelop the semiconductor absorber with a "skin" that passivates those surface defects [1]. Intuitively, passivation can be envisaged as the covalent bonding between atoms present in the "skin" material and the surface atoms of the semiconductor. An example is the bonding between oxygen and silicon that results from thermally growing a SiO_2 layer. The oxidation process still leaves a fraction of silicon bonds unsatisfied and it is usually complemented by supplying hydrogen, whose small size facilitates its diffusion towards those dangling silicon bonds.

While the concept of chemical passivation is intuitively clear and widely accepted, the term "passivation" is sometimes used to refer to other mechanisms that also result in a reduction of the recombination rate between electrons and holes. Generally, such mechanisms involve a large imbalance between the populations of electrons and holes near the surface, which indeed leads to a lower recombination rate, as

described below. To preserve the intuitive meaning of passivation as chemical bonding, we will refer to other, non-chemical mechanisms as "carrier population control".

Another premise for a semiconductor absorber to become a solar cell is that it should be able to deliver electrons to an external circuit. For that to occur, each carrier type must flow separately towards each of the two metallic terminals attached to the solar cell. This implies that each of those metallic terminals must be in contact with a region in the semiconductor where the conductivity for one carrier type is much greater than for the other carrier type [2]. Those two regions could be appropriately called selective electron and hole conductors, but given that they need to be at the surface and in contact with the metal terminals, they are frequently referred to as selective contacts.

The ability to manipulate the conductivity is, therefore, essential to construct a solar cell. Of the two components that determine the conductivity, mobility and charge carrier concentration, only the latter can be varied to a sufficient extent in practice. In silicon technology that is usually achieved by doping, but other methods can be used, for instance by depositing materials with a work function significantly higher or lower than that of the silicon absorber, as discussed in this paper.

The conceptual premises are clear, but their experimental implementation can be challenging. Metallic terminals are essential, but when a metal is directly deposited on silicon it causes a very high density of recombination centres, which draws to the surface both carrier types, thus undermining the objective of achieving single-carrier transport. Hence, it is important to find ways of implementing a highly

asymmetric conductivity to each of the two metallic terminals while minimising recombination. In conventional silicon solar cells surface passivation and selective conductivity are implemented "in parallel", which leaves the surface regions contacted by the metallic terminals de-passivated. An awareness of the limitations that recombination at the metal contacts cause has prompted the development of comprehensive contact systems where selective conductivity and surface passivation are implemented "in series". Indeed, the most effective contact systems developed so far combine several layers of different materials, each of them performing one of the required functions of selective conduction, surface passivation and contact formation to the external metal.

This paper summarises the main results of our work during the last five years on non-traditional surface passivating materials and carrier-selective passivating contacts. Please note that a substantial part of that work has been in collaboration with other researchers, as mentioned in the Acknowledgement. Given that this paper is intended for a special issue on surface passivation and passivating contacts, no attempt has been made to include the outstanding work done by other researchers on those topics, in order to avoid excessive repetition. It is expected that companion articles of the same issue will give the interested reader a more comprehensive overview of the topic.

2. Pathways to reduce surface recombination

2.1. Surface passivation by chemical bonding

Surface passivation refers, in its purest form, to the chemical attachment of atomic or molecular species to the unsatisfied "dangling" bonds of silicon atoms at the surface of the semiconductor. Usually, a certain amount of interface defects remains after an oxidation process or after depositing a dielectric material on a silicon wafer. The density of such defects, or traps D_{it} can be drastically reduced by means of a hydrogenation treatment. For example, Eades et al. measured $D_{it} \sim 10^9$ cm^{-2} for *alnealed* SiO$_2$ [3], a remarkably low number in comparison with the $\sim 7 \times 10^{14}$ cm^{-2} density of bonds present at the (100) silicon surface. The application of a hydrogenation treatment, preferably in atomic form, is a common denominator of all the approaches that have led to high quality surface passivation, including semiconductors, like a-Si: H, and dielectrics like SiO$_2$, SiN$_x$, Al$_2$O$_3$, Ga$_2$O$_3$, etc. For some of them it is difficult to measure accurately the density of interface traps, due to their non-negligible conductivity. This obviously applies to materials that are attractive for selective contact systems precisely because they are conductive. Fig. 1, updated from the original version in
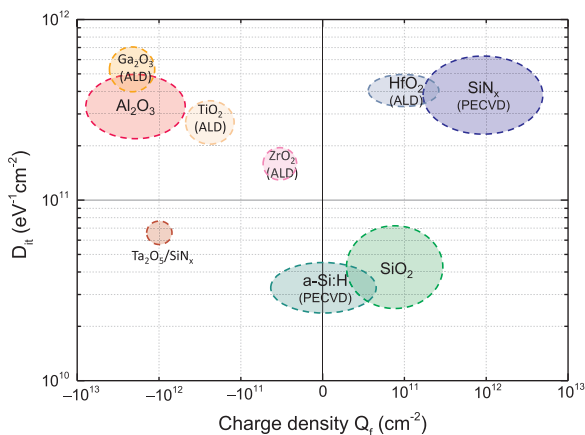
[4], gives a qualitative summary of the approximate levels of D_{it} and fixed charge reported for a variety of passivating films, reflecting the substantial spread of the values reported in the literature. Note that this D_{it} corresponds to the middle of the energy bandgap of silicon and, although useful to compare the quality of chemical passivation by different materials, it should only be regarded as a proxy for the complex statistics of Shockley-Read-Hall recombination.

2.2. Controlling the population of electrons and holes by means of doping

The product of the concentrations of electrons and holes drives the rate at which they recombine. It is intuitive to understand that this reaction rate is highest when the concentration of the two reactants is similar to each other. Therefore, it is possible to control electron-hole recombination by manipulating their respective concentrations, basically, by making one of the two much smaller than the other. To illustrate that, let us consider SRH recombination in silicon caused by a relatively high density of mid-gap defects. It is straightforward to calculate the net recombination rate for any combination of dopant densities in the semiconductor using the well-known SRH expression, plus the relationship between the pn product and the difference between the electron and hole Fermi energies E_{Fn} and E_{Fp},

$$(p_o + \Delta p)(n_o + \Delta n) = n_i^2 \exp\left(\frac{E_{Fn} - E_{Fp}}{kT}\right) \tag{1}$$

where p_0 and n_0 are the equilibrium hole and electron concentrations, $\Delta p = \Delta n$ their respective excess concentrations under illumination, n_i the intrinsic carrier density, k the Boltzmann constant and T the temperature. In a moderately doped p-type semiconductor $p_0 \approx N_A$ and $n_0 \approx n_i^2/N_A$, where N_A is the concentration of acceptors. Fixing the difference $(E_{Fn}-E_{Fp})/q$ to a particular level, for example 600 mV allows us to determine the excess carrier concentration and, eventually, the recombination rate when we change the dopant concentration in the semiconductor. Fig. 2 shows the recombination rate as a function of the ratio between the electron and hole concentrations for two different recombination centres, one that presents a capture cross-section for electrons 100 times greater than for holes (k = σ_n/σ_p = 100) and

Fig. 1. Qualitative summary of the approximate ranges for the density of interface defects and the charge measured experimentally for different materials deposited on the surface of crystalline silicon. The vertical axis indicates the level of chemical passivation, whereas the horizontal axis indicates the ability of charge (both polarities) to assist in controlling the carrier density at the interface.
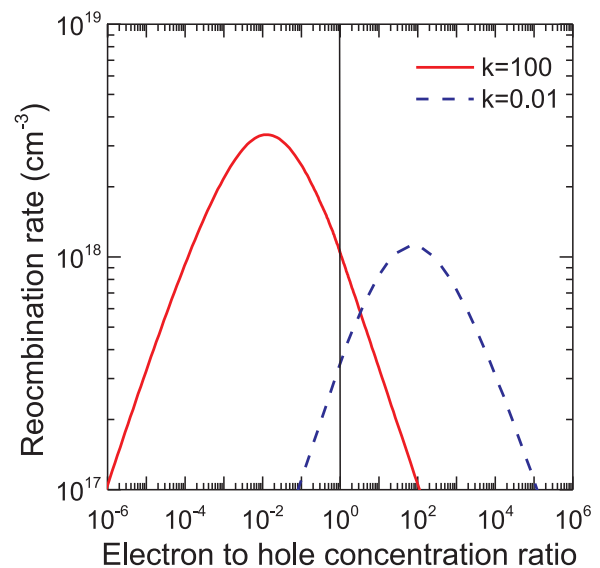

Fig. 2. Recombination rate in silicon as a function of the electron to hole concentration ratio for a fixed separation between the electron and hole quasi-Fermi energies of 0.6 V. The two cases shown correspond to recombination centres with a capture cross-section for electrons ($\sigma_n = 10^{-13}$ cm^{-2}) 100 times greater than for holes (k = 100) or 100 times smaller (k = 0.01, $\sigma_n = 10^{-15}$ cm^{-2}). A density of defects 3 times lower for the second defect ($N_{t2} = 3 \times 10^{10}$ cm^{-3}) has been assumed.