Electrical characterization of nitride silicon layers SiN:x enriched in silicon at different stoichiometry - photovoltaic application

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Abstract. The main objective of researches in the field of photovoltaic is to increase the efficiency. This work aims a new concept which is the integration of nanoparticles in the anti-reflection layer Si3N4 (silicon nitride), in order to improve the performance of solar cells. This concept is based on the up conversion, where the nanoparticles are characterized by the ability to function as a converter of infrared rays having high energies in the receptivity in the visible. The concept of conversion leads to a better exploitation of the solar spectrum, by widening the useful range of the spectrum. Firstly, we realized SiNx layers at different compositions and proved that variation by calculating the silicon excess and the gap energy. But the focus is on the analysis of photocurrent measurements for the vertical and lateral configuration to show the role of nanoparticles. And we finalize with measurement of currents at the test bench I-V to find the ideal stoichiometry for nanoparticles.

1. Introduction
The solar energy is one of the inexhaustible sources of energy for the Earth [1-8]. The electric energy is necessary for a person to conduct various experiments and studies [1, 2, 7, 9-25]. It should be noted that the production of electric energy from solar is a safer process for the environment than others [1, 3, 6, 8, 26-30]. The using of the solar panels allows to provide the autonomous operation of many research systems in space, in opening sea and other places [20-24, 31, 32]. In this case, the conversion of solar energy into electrical energy is very important, especially in the case of information transfer from an autonomous object [1, 2, 5, 8, 14, 32]. Therefore, the researchers are focusing particularly of the coefficient increase of the conversion of solar energy to electric by using photovoltaics.

The silicon is currently the most used material in photovoltaic systems. The semiconductor technology has been developed rapidly with the growth of microelectronics in recent decades. 90 % silicon is the main material of microelectronics [33]. Photovoltaic’s third generation is the combination between the first generation (silicon cells), which were developed mainly from silicon, these cells have only one PN junction, and the second generation (thin films), which is based on a thin layer deposited on a substrate.

In recent years, the reduction in the size of Silicon to nanostructure has open new functionalities that have made it possible to envisage several applications based on silicon nanocrystals (nc-Si).
Composite thin films of a dielectric matrix containing silicon nanoparticles can find various applications in optoelectronics: third-generation photocells, Bragg mirrors, semiconductor lasers, etc. [34]. At this point, wide changes in physical properties occur, mainly in energy characteristics; electronic levels, modes of atomic vibrations and their interactions with photons. This promises a lot of results and progress. One of the goals set is to use these nanosturctures as converters of high-energy photons into red photons that are better absorbed by the main cell. The main attention will be paid to the analysis of the properties of absorption and charge transfer of nanostructured layers in order to verify their photoelectric efficiency and assess the feasibility of manufacturing multi-junction elements based on these nanomaterials.

2. Methods of experimental characterizations

To measure the chemical composition of silicon nitride (anti reflection layer), analyzes were carried out by Mass spectrometry of secondary ions (SIMS). The SIMS technique allows obtaining the concentrations of each of the components in the atomic percentage of samples, which also allows to find out the total composition of these samples depending on the depth. The evolution of stoichiometry, which depend of the gas precursor ratio R = NH3 / SiH4, will be determined after the bombardment of the samples by an ion beam (primary ions) with energies from 0.1 KeV to 50 KeV.

2.1. Measurement of diffuse reflection

The main purpose of measuring reflectivity is to determine by scanning the solar spectrum the response of the sample by evaluating the absorption properties of Silicon nanoparticles depending on the stoichiometry of the SiNx layer. In this case, the wavelength range is well defined by the visible and near infrared range [35-38]. Obviously, this step is carried out immediately after applying a layer of silicon nitride with different stoichiometry.

2.2 Measurement of photocurrent in vertical and lateral configuration

Photocurrent spectroscopy is a characterization technique that allows knowing details on the electronic states and the absorption spectrum of the material analyzed. The principle of this technique is based on the generation of carriers caused by the absorption of photons with energy equal or superior to material’s gap. Depending on the wavelength, the photo-generated carriers will be able to occupy the different energy levels of the semiconductor. In the case of nc-Si, this technique is particularly interesting since it makes it possible to explore and determine the absorption threshold (and indirectly the gap Eg) associated with the size distribution of the crystallites. Two types of measurements were carried out, measurement in vertical configuration to measure the entire cell current, and measurement in lateral configuration to measure photocurrents figures 1 and 2.

![Figure 1. Reflection spectrum of silicon nitride composite layers at 7 different silicon concentrations.](image-url)
3. Results and discussions

Interest will be focused only on the SiNx anti-reflective layer of the samples. It consists of two essential elements, silicon Si and nitride N. According to these results, it is possible to develop alloys of silicon nitride which contains an excess of silicon compared to the standard stoichiometry Si3N4. It is an essential prerequisite for obtaining the precipitation and crystallization of silicon Nanocrystals in a matrix of silicon nitride.

According to the obtained graphs, the more samples are rich in silicon, the more we notice a shift in the reflection spectrum to the near infrared, diagrams in figure 3, this suggests that the effective refractive index increases with the rate of Silicon within the SiNx layer [35], we also notice that the fringes are not regularly spaced.

To measure the photocurrent (PC) in our structures, we first used a vertical transport configuration in which the lighting is done through a contact grid and the photogenic carriers are collected between the contact grid and the substrate figure 4. We found that the photocurrent is dominated by the signal from the substrate.
Figure 4. Photocurrent spectra obtained for (R = 3) in the vertical and lateral configurations.

The contribution of the nitride layer does not appear in the vertical configuration since the photocurrent associated with the silicon nanoparticles risk being easily masked by the substrate. For this reason measurements under lateral configuration are necessary.

Figure 5. Spectrum of photocurrents taken in lateral configuration of samples with ratios R = 2, 3 and 4 compared to the spectrum of the reference which is R = 8.

In figure 5 the difference between the curves with different ratios is clearly highlighted. This difference is explained by an additional absorption associated with nc-Si due to the widening of the Si gap caused by quantum confinement. In terms of high excitation energies (> 1.6eV), the additional PC would come from the absorption of photons in small nanocrystals. [39, 40]

The analysis of these spectra allows us to notice the existence of an absorption threshold at 1.1 eV for the reference which moves towards high energies, as well as a peak of PC at 1.46 eV for the samples R = 2 and R = 3 which contain Np-Si having the largest sizes. The absorption threshold is assigned to the current generated in the silicon substrate. Indeed, the diffusion of the deposit of Aluminum on the anti-reflective layer following the annealing of the contacts leads to the transport of the photocarriers created in the substrate to the electrodes. For the samples R = 2 and R = 3, the Nc-Si have a smaller size and the maximum of PC is thus displaced towards the large energies.

These observations make it possible to attribute the photocurrent measured in these multilayer structures to the generation and transport of the photogenerated charges in the layers containing Np-Si.
4. Conclusion
Research on silicon nanocrystals for photovoltaic applications is barely in its infancy. Numerous research and development efforts will be necessary to ensure sufficient engineering of nanostructures so that they become a technological and industrial reality. The results obtained by this work are promising. The principle consists in obtaining silicon nanoparticles (Si-np) in a Si$_3$N$_4$ matrix. The variation of the ratio of gases $R = \text{NH}_3 / \text{SiH}_4$ to allows in turn to vary the concentration of silicon therefore the size of the nanoparticles due to the photo-current technique we determined the absorption levels in nc-Si using two different configurations (vertical and lateral). Thus, we have proved that a lateral transport configuration has better sensitivity than a vertical configuration and that it provides more information on the different absorption thresholds due to a very considerable reduction in the contribution of the substrate.

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