PRIMA

Small or medium-scale focused research project

SEVENTH FRAMEWORK PROGRAMME

THEME FP7-ICT-2009-4

INFORMATION SOCIETY TECHNOLOGIES

Deliverable 4.2 – Benchmark optimized plasmon-PV structures against current and emerging c-Si solar cell technology and against emerging thin film technology

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Version	Date	Author	Summary of main changes
1	19 oct 2012	Koen de K	
2	Dec 2012	Ounsi El Daif	Adding some experimental data

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1 Plasmon-enhanced bulk crystalline silicon solar cells

1.1 Introduction

This deliverable reports on the partial results obtained on plasmon enhanced bulk c-Si solar cells fabricated using Chalmers' hole colloidal lithography (HCL) technique. Since at the time of reporting the 1st benchmarking, Chalmers was not equipped to handle large 156 mm square wafers, integration of plasmon particles fabricated by HCL was delayed and postponed till the second benchmarking round. Results from the 1st benchmarking were incorporated as the experimental set-up was adapted to include scattering by Al nanoparticles at the backside of the solar cells as well as plasmon resonance by Ag nanoparticles. The consortium believes that the inherent ability of aluminium to self-seal upon oxidation would render Al based nanoparticles more resilient against high temperature steps than Ag nanoparticles that risk oxidizing all the way through.

1.2 Preliminary study – impact of high temperature steps studied by reflectance

Before fabricating plasmon-PERL cells, it was decided to test the impact of the high temperature steps in Photovoltech's plasmon-PERL process (i.e. SiN_x coating and co-firing) on the plasmonic/scattering behaviour of the nanoparticles. Model samples were prepared by coating the backside of pieces of wafers that were meant to become plasmon-PERL cells, with Al and Ag nanoparticles by Chalmers' HCL technique (cf. Figure 1). The particles were deposited on a Al_2O_3 spacer layer. Next, the nanoparticles were capped with a SiN_x layer and the samples were subjected to the same temperature profile used for co-firing the metallization of the plasmon-PERL solar cells. Reflectance was measured before and after the high temperature steps of SiN_x coating and co-firing.

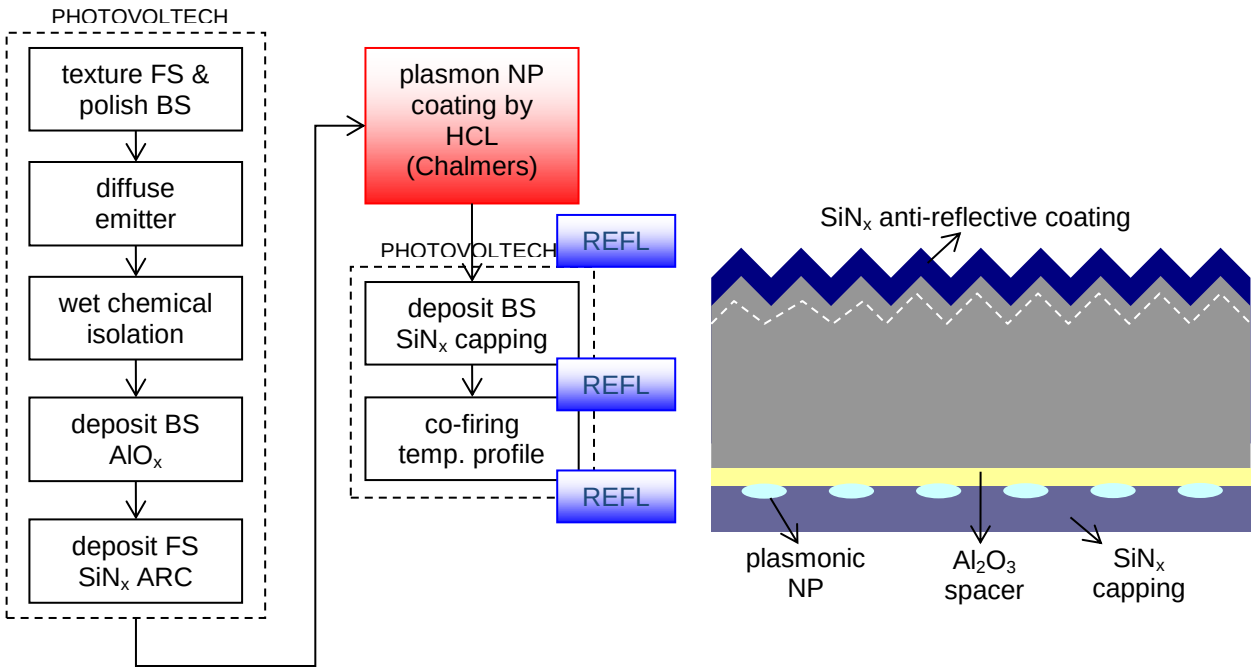

Fig. 1.a Fig. 1.b

Figure 1: Process flow (1.a) to prepare model samples to assess the impact of high temperature steps in Photovoltech's plasmon-PERL process flow (cf. deliverable D4.1); cross-section of model samples on the right (1.b)

After nanoparticle coating, the reflectance curves exhibit plasmon resonance, less than usual, most likely due to the absence of the capping layer (see Figure 2.a, the violet curve Ag total.). However, after the high temperature steps, even the mere SiN_x coating, the plasmon resonance of the Ag nanoparticles disappeared; also the Al nanoparticles do not seem to scatter any longer (see Figure 2.b).

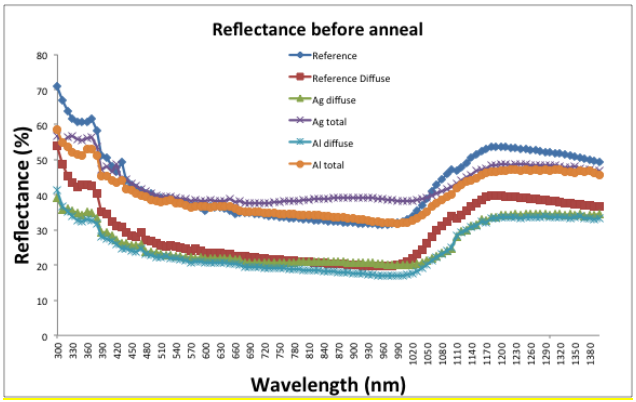

Fig. 2.a

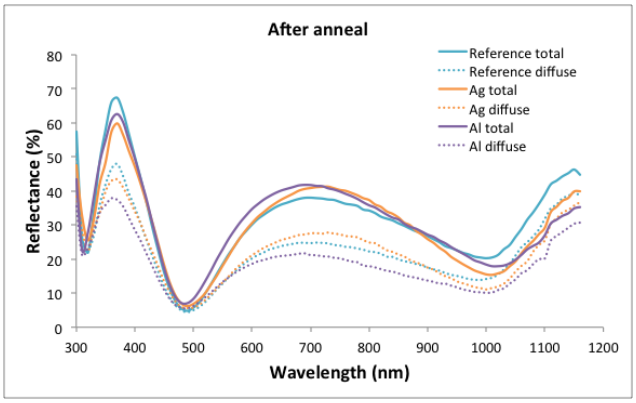

Fig. 2.b

Figure 2: Reflectance curves of nanoparticles coated model samples; immediately after nanoparticle coating, before any high temperature step (2.a) and after the high temperature steps (SiN_x coating and co-firing temperature profile) (2.b). Reflectance was measured from the front side.

A similar loss of plasmonic behaviour was already demonstrated before by Chalmers in case of Ag nanoparticles, but those samples were coated with different dielectrics and subjected to different temperature profiles (see Fig. 3). This loss had to be confirmed for Photovoltech's dielectrics, and for samples subjected to shorter but warmer temperature profiles as in the case of Photovoltech's metal contact co-firing.

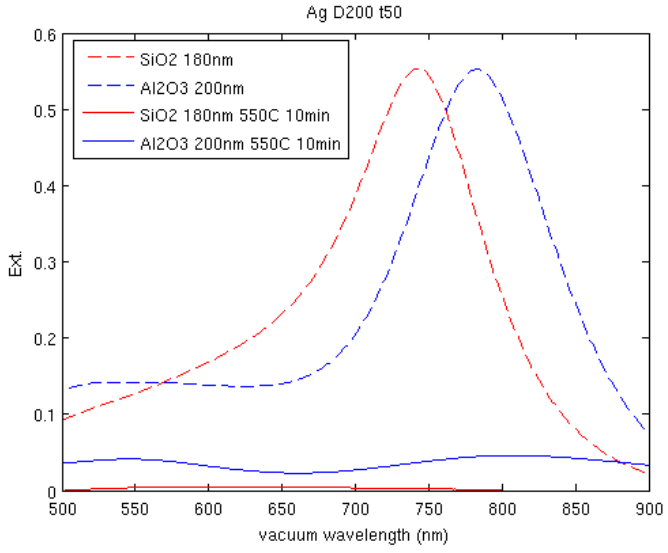

Figure 3: Extinction curves of samples with silicon/SiO_x/Ag-NP/SiO_2 or Al_2O_3 capping layer structure, before and after a long anneal at elevated temperature. Complete loss of plasmon resonance was observed after high temperature step; oxidation was thought to be the root cause.

In order to exclude disappearing nanoparticles, e.g. by diffusion into the bulk, as a cause for loss of plasmon resonance in the infra-red reflectance, scanning electron microscopy was performed on the samples after they were subjected to Photovoltech's high temperature steps.

By SEM it was confirmed that the nanoparticles were still present at the backside of the wafers, but that they had changed shape. The SEM pictures in Figure 4 illustrate that the Ag and Al nanoparticles remain on the surface but that they changed shape from cylindrical pillars to spheres. Contrary to ANU particles that are formed by coalescence at elevated temperatures, the nanopillars fabricated by Chalmers' HCL technique reside in a geometrical shape with non-minimal energy. Subjecting these nanopillars to elevated temperatures, grants them the opportunity to reshape into spheres in an effort to minimize their surface energy.

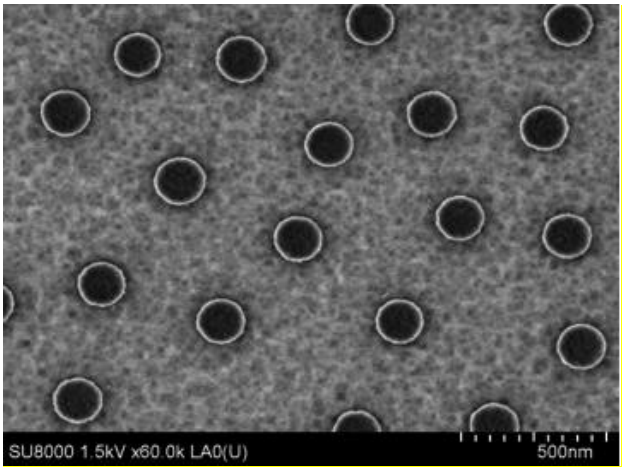

Fig. 4.a

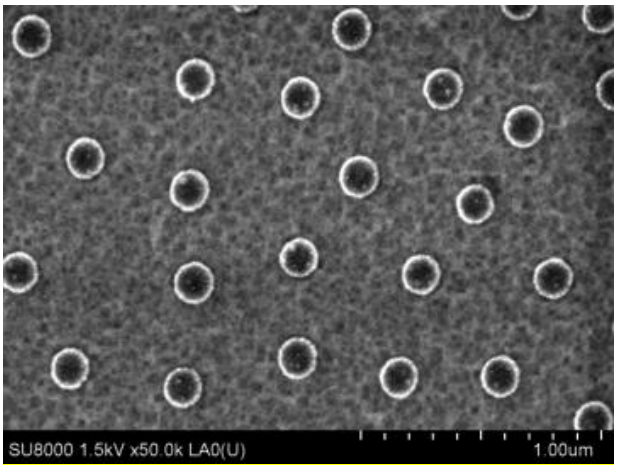

Fig 4.b

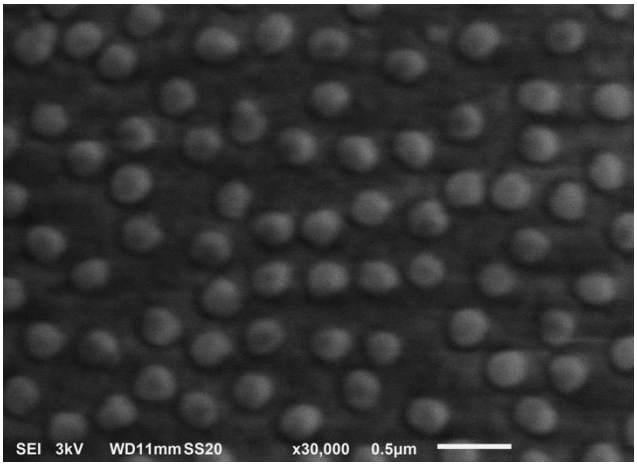

Fig. 4.c

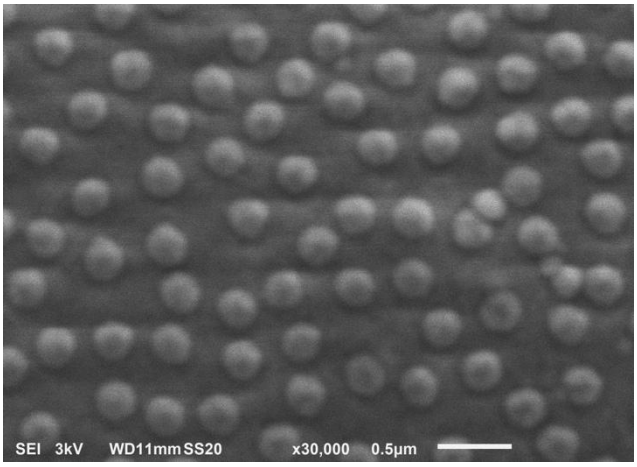

Fig. 4.d

Figure 4: Scanning Electron Microscopy pictures of Ag and Al nanoparticles before and after high temperature steps. 4.a: Ag, before, 4.b: Al before, 4.c: Ag after SiN_x deposition and co-firing, 4.d: Al after SiN_x deposition and co-firing. Note the pillar shape before and the spherical shape after.

As demonstrated by ANU's modelling (see the 2nd annual report) the spherical shape of the nanoparticles would reduce their plasmonic resonance. However, the complete absence of any resonance effect indicates that there is more to the root cause than a mere change in shape. Complete

oxidation would e.g. cause the Ag nanoparticles to lose their plasmonic behaviour entirely. XPS might have shed some light on the chemical binding state of the metal in the nanoparticles.

1.3 Benchmark

The electrical performance of solar cells enhanced with Chalmers' plasmon-PV structures could not be benchmarked. Due to the multitude of tests needed to develop a process flow that could handle the large size of 156 mm square wafers, no cells were left at Chalmers by the time the preliminary tests on the impact of high temperature stability were finalised. By that time, Photovoltech's shareholders had decided to shut down the factory and stop production, which cancelled any opportunity to prepare new wafers and cells for further development.

1.4 Conclusions

Direct incorporation of plasmon nanoparticles in the backside dielectric passivation stack of PERL cells seemed to be the most logical and cost-effective way to integrate plasmon-PV structures, but it turned out to be not straightforward. The plasmon-PV structures seem to be incompatible with Photovoltech's current industrial PERL process flow. Direct incorporation seems to be plagued by high temperature non-stability and oxidation of the particles, and compromised integrity of the dielectric stack (cf. D 4.1)

Further investigation is required but cost-effectiveness is a paramount factor that should not be overlooked while developing dedicated plasmon-PV compatible process steps. The impact of high temperature steps might be reduced by changing the order of process steps in the plasmon-PERL process flow, or by looking into contact formation at reduced temperatures (sintering). Oxidation of the nanoparticles might be avoided by adapting the process conditions during deposition of the dielectric capping layer. A denser and thicker capping layer might also alleviate oxidation during subsequent high temperature steps, and help to ensure its integrity in order to avoid the backside electrode punching through upon co-fring despite a rougher topography due to the particles. Aluminium nanoparticles are more likely to be compatible with backside contact formation as they are less likely to adversely interact with the LBSF. ANU's approach is currently not only the better candidate for industrial implementation, but since it relies on particles that have shaped into lower surface-energy states by coalescing at elevated temperatures, the ANU nanoparticles could prove to be more resilient against high temperature steps. Still, if a low temperature back-end process flow could be developed, Chalmers' approach might be the better choice since it yields particles with an inherently stronger plasmon effect.

2 Thin film silicon solar cells

Since the start of the PRIMA project the PV market landscape changed drastically, and the project's consortium itself is a witness of this very tough evolution. This includes also the share of various technologies on the market. In 2007 and 2008, the silicon feedstock was not yet solved (or about to be) and the silicon price was a major limitation.
This is not the case anymore at all, and the main driver in the cost reduction of silicon cell is the system cost, which concretely yields at the cell level that the cell efficiency is a key issue. A decrease of the share of thin film amorphous silicon (aaSi) based cells was therefore witnesses, see Fig.2.1 (from EPIA's publication "Solar Generation 6", see http://www.epia.org/news/publications/).

These elements, added to the elements developed in Part one of this deliverable, show that it is unfortunately now irrelevant to compare plasmon assisted cSi cells to plasmon (or not) assisted aSi cells. However, the share of aSi is still expected to increase again in the future, given the increasingly high number of niche markets developing (the most important being building integrated PV) and it is relevant to discuss the impact of plasmon assistance on aSi itself, comparing the aSi standards to what plasmons can do. This was performed in the frame of PRIMA, thanks to an industrial outcome of the project: collaboration on this point with the leading thin film PV company Kaneka. This specific point was dealt with in deliverable 3.9 submitted at month 33 and confirmed the interest from Kaneka, which, given the demonstration that the integration of plasmons is possible in aSi cells, is currently performing the assessment of these cells against its own benchmarks.

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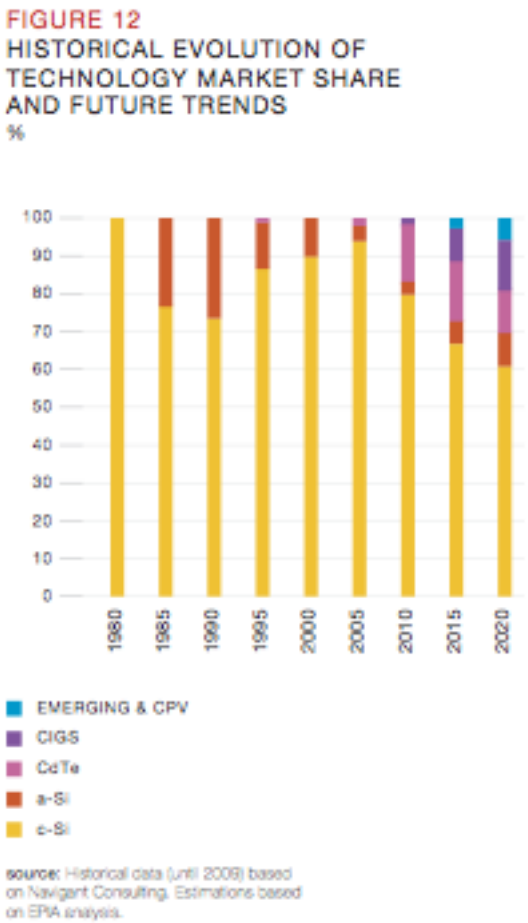

Figure 2.1 Evolution of the market share of various PV cell technologies. It is clear that aSi technologies have lost market shares in the last 10-12 years.