Plasma Deposition of p-i-n Devices in a Single-Chamber Large Area PECVD Reactor : Reduction of the Boron Cross-Contamination

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Abstract

In this article, a new treatment to reduce boron contamination of the interface between the p- and i- layer is presented. An ammonia flush, performed at 5 mbar for 1 min, after deposition of the p-layer considerably reduces the boron contamination at the p-i interface of amorphous silicon p-i-n solar cells prepared in a single-chamber reactor. This treatment avoids the need to move the substrate out of the reactor during the full deposition process of a solar cell, thereby reducing costs. The measurement of boron contamination depth profile in the i-layer was done by Secondary Ion Mass Spectroscopy (SIMS) and the effectiveness of the treatment was supported by quantum efficiency and I-V measurements of solar cells.

Key words: boron contamination, solar cell, single-chamber process
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1 Introduction

Plasma-enhanced chemical vapour deposition (PECVD) of photovoltaic p-i-n solar cells in a single-chamber plasma reactor offers advantages of time and cost compared to multi-chamber processes which use separate reactors for production of the p-, i- and n-layers. The p-layer is a boron-doped silicon thin film

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deposited by plasma in a gas mixture containing silane and a boron source gas. In a single-chamber PECVD reactor, the silane plasma subsequently used to deposit the undoped silicon intrinsic film (i-layer) leads to the recycling of impurities [1]. This can cause boron contamination from the reactor walls, pumping ducts or the layer itself. Boron contaminates the i-layer at the p-i interface and thereby weakens the strength of the critical electric field in the i-layer close to the p-i interface. This provokes a less efficient carrier separation just in this zone and leads to a reduced collection efficiency in the solar cell, this results in a deterioration of the final solar cell performance (see Fig. 1) [4]. Therefore, for mass production of solar cells in a single-chamber reactor, it would be advantageous if some treatment applied between the deposition of the p- and i-layers could reduce the boron contamination at the interface and thus maintain cell performance. The fall of boron concentration at the p-i interface should be as sharp as possible so that the transition between the p-layer and i-layer is abrupt. Various treatments with encouraging results have already been studied [2,3]. Recently, a new treatment using a water vapour flush has been introduced, allowing the deposition of cells with high performance (due to reduced boron cross-contamination); such a water flush surprisingly does not aggravate the light induced degradation [4]. Based on this preceding study, we examine in the present paper the effect of an ammonia flush on the boron contamination. One advantage of ammonia is that it is already established in standard industrial installations. We will compare the performances of cells prepared with no treatment, with the water vapour flush treatment, and with the new ammonia flush treatment.

2   Experimental

The experimental apparatus is a modified version of the industrial KAI-S Plasma Box$^{\text{TM}}$ reactor commercialized by Unaxis Displays. It is a parallel plate capacitively-coupled reactor, 47 cm wide $\times$ 57 cm long, with a 2.4 cm gap between the RF electrode and ground electrode. A loadlock chamber was used to introduce substrates into the reactor without breaking vacuum. Sequences of p-i layers were deposited on silicon wafers laid on a glass substrate 47 cm $\times$ 37 cm $\times$ 1 mm to test the ammonia flush treatment between the p- and i-layers. Trimethylboron (TMB), $B(CH_3)_3$, instead of diborane, B_2H_6, was used as the boron source gas because of its superior thermal stability in the hot reactor thereby causing less contamination [5]. The gas flush parameters used for the p-layer were : flow rates 70/60/1/50 sccm of $SiH_4/CH_4/TMB/H_2$ at 0.4 mbar ; for the i-layer : flow rates 160/40 sccm of SiH_4/H_2 at 0.5 mbar. The excitation frequency was 40.68 MHz at 60 W RF power for an i-layer deposition rate of approximately 3 Å/s at a substrate temperature of 200°C. The effectiveness of the treatment was evaluated by means of Secondary Ion

Mass Spectroscopy (SIMS), allowing the study of boron concentration depth profiles across the p-i interface.

Solar cells were deposited in another KAI-S reactor. The deposition temperature of the a-Si:H layers and cells was 200°C keeping the pressure at 0.3 mbar and applying a RF power level of 60 W. The total feed gas flow was 150 sccm for the intrinsic layer deposition. To reduce powder formation the silane was diluted by hydrogen to a silane concentration of 70% during the i-layer deposition. Under these i-layer preparation conditions, deposition rates of 3.3 Å/s have been obtained. In this single-chamber reactor, 0.3 μm thick p-i-n a-Si:H solar cells were deposited on glass/TCO substrates (Type Asahi U, based on SnO_2:F). To obtain the full potential for high-efficiency a-Si:H solar cells, an optimized hydrogen-diluted buffer layer was inserted between the p- and the i-layer [4]. It should be noted that this buffer alone has usually already a beneficial effect on the boron cross contamination in the i-layer. Sputtered ITO and aluminium were used as a back contact. The boron contamination in the i-layer close to the p-layer was indirectly detected by performing voltage-dependent quantum efficiency measurements, as well as by monitoring the global cell performance, in particular the cell fill factor. The I-V characteristics were measured under AM 1.5 illumination using a Wacom WXS 140S-10 sun simulator. The cells were light-soaked for over 1200 hours under the light of a high-pressure sulfur lamp at 50°C. The spectrum of this microwave-powered sulfur lamp is close to the AM 1.5 spectrum and is adjusted to 100 mW/cm^2.

3 Results and discussion

3.1 SIMS analysis

Fig. 2 shows the SIMS boron profile at the p-i interface, when (a) treated with an ammonia flush, (b) treated with a water vapour flush, (c) not treated. We observe the sharpest transition in the case of the ammonia treatment and the least sharp transition (highest cross-contamination) for the case of no treatment. Water vapour treatment gives intermediate results.

Fig. 3 shows the SIMS oxygen profile of a p-i-p-i structure treated with an ammonia flush, and the profile of a p-i-p-i structure for which interfaces were treated with a water vapour flush. We see that one advantage of the ammonia treatment compared to the water vapour treatment is that it is not adding oxygen [4,7].

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Fig. 4 (a) and (b) shows the I-V curves for cells prepared with ammonia treatment for various flushing and pumping times, and for one cell prepared with the water vapour flush treatment, before and after light-induced degradation. Initially (Fig. 4 (a)), there is no significant influence of the ammonia flushing and pumping times. Ammonia-treated cells are comparable to the cell prepared with the water vapour flush, except for a loss in V_{oc} of 20 mV. Their efficiencies are markedly higher than the the performance of the cell prepared with 30 min pumping and no gas flush between p-layer and i-layer (Fig. 4 (c)). After light-induced degradation, (Fig. 4 (b)), similarly to water vapour treatment, the ammonia treatment does not worsen the cell degradation: all cells treated with the ammonia flush are better than the cell made with 30 min pumping and are comparable to the water vapour flush treatment cell.

In Fig. 5 (a) and (b) the quantum efficiencies of cells prepared with ammonia flush and water vapour flush are shown. Quantum efficiencies in the blue region of the spectra show only a small bias-voltage dependence compared to the one on Fig. 5 (c) for a cell prepared with only a 30 min pumping time (and no treatment) between p-layer and i-layer. As is well known, a weak voltage dependence of the quantum efficiency in the blue region indicates a good carrier collection in the i-layer close to the p-layer, and suggests, therefore, a low boron contamination at the p-i interface.

3.3   Discussion of the effect of ammonia on boron contamination

At present it is thought that the ammonia flush creates B-N complexes which selectively fix boron in the p-layer. The plasma chemistry of boron/ammonia has been previously investigated by infrared absorption spectroscopy [8]. Mixing ammonia and diborane gases as precursors leads to a rich variety of gas phase precursors. Solid compounds of diammoniate of diborane $[H_2B(NH_3)_2]^+[BH_4]^-$ and aminoborane ($H_2B=NH_2$) are produced [8]. We can suppose that similar reactions occur between boron and ammonia, for example, the formation of boron nitrides B:N:H, or amines $B(NH_2)_3$ instead of boric acid $B(OH)_3$ when using water [4,6].

4   Conclusions

A new gas treatment for controlling the boron contamination at the p-i interface has been studied. This treatment consists of an ammonia flush between the deposition of the p-layer and the deposition of the i-layer, the substrate re-

maining in the reactor. The exposure of the reactor walls and substrate surface to the ammonia considerably reduces the boron contamination at the p-i interface because the transition between the p- layer and the i- layer is observed to be abrupt. The advantages of the ammonia treatment for the production process of amorphous silicon photovoltaic modules are: (1) a single-chamber can be used for the full solar cell deposition process; (2) the substrate can remain within the reactor during the whole deposition process; and (3) the treatment time is short. Moreover, as ammonia is often already installed in the gas line for other plasma processing, it would not in this case need special installation.

Performances of cells prepared with the ammonia treatment are comparable to those of the cell prepared with the water vapour treatment [4] and reach cell specifications as obtained with a standard multi-chamber process: after degradation during 1000 hours at 50°C, a V_{oc} value of 859 mV and a fill factor of 63.7 %. We note that there is no worsening of the cells' degradation due to the ammonia flush. We speculate that N-H groups react with boron compounds to form stable boron amine or nitride compounds, which may be fixed in the p-layer.

5   Acknowledgements

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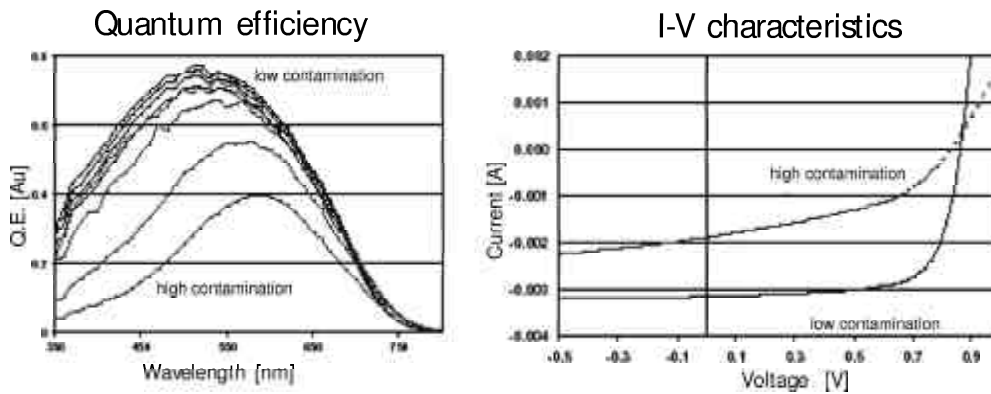[8] D. Franz, M. Hollenstein, Ch. Hollenstein, Thin Solid Films **379**, 37 (2000).

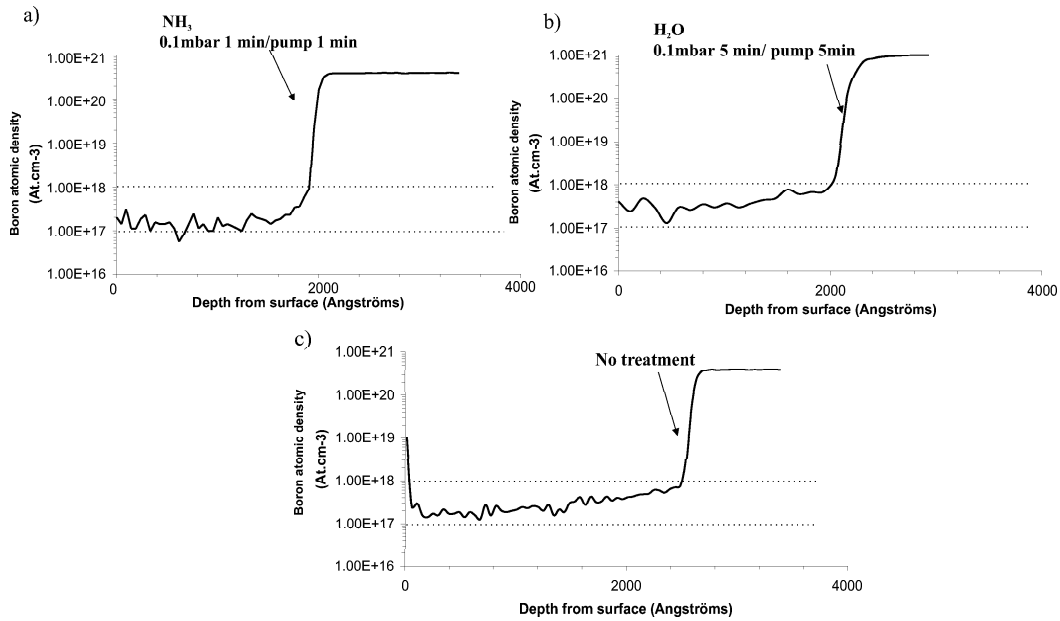Fig. 1. *Deterioration of cell performance with different degrees of boron contamination : spectral response and IV characteristics.*

Fig. 2. *SIMS boron profile at the p-i interface with: a) ammonia flush treatment, b) water vapour treatment, c) no treatment. The pressure and duration of the flush, and the duration of the post-flush pumping time, are shown on the figures.*
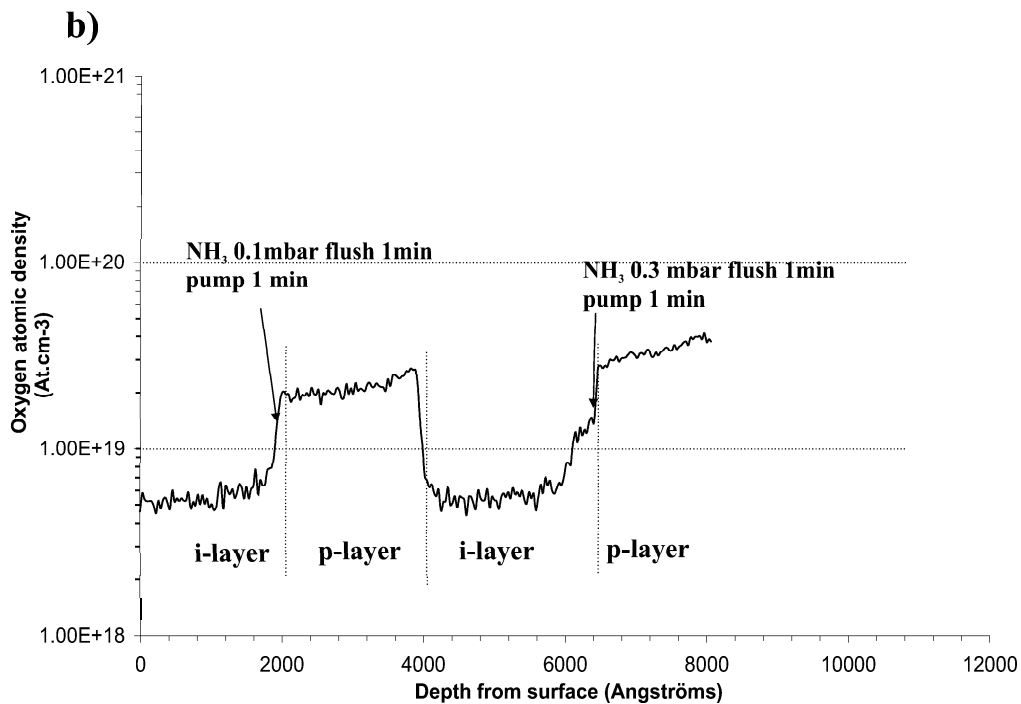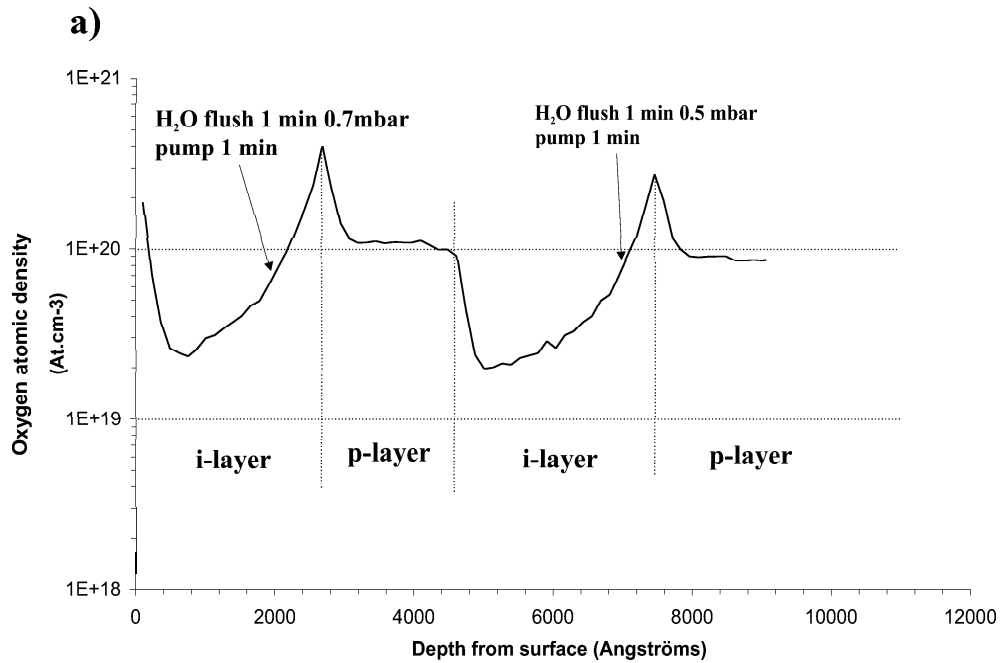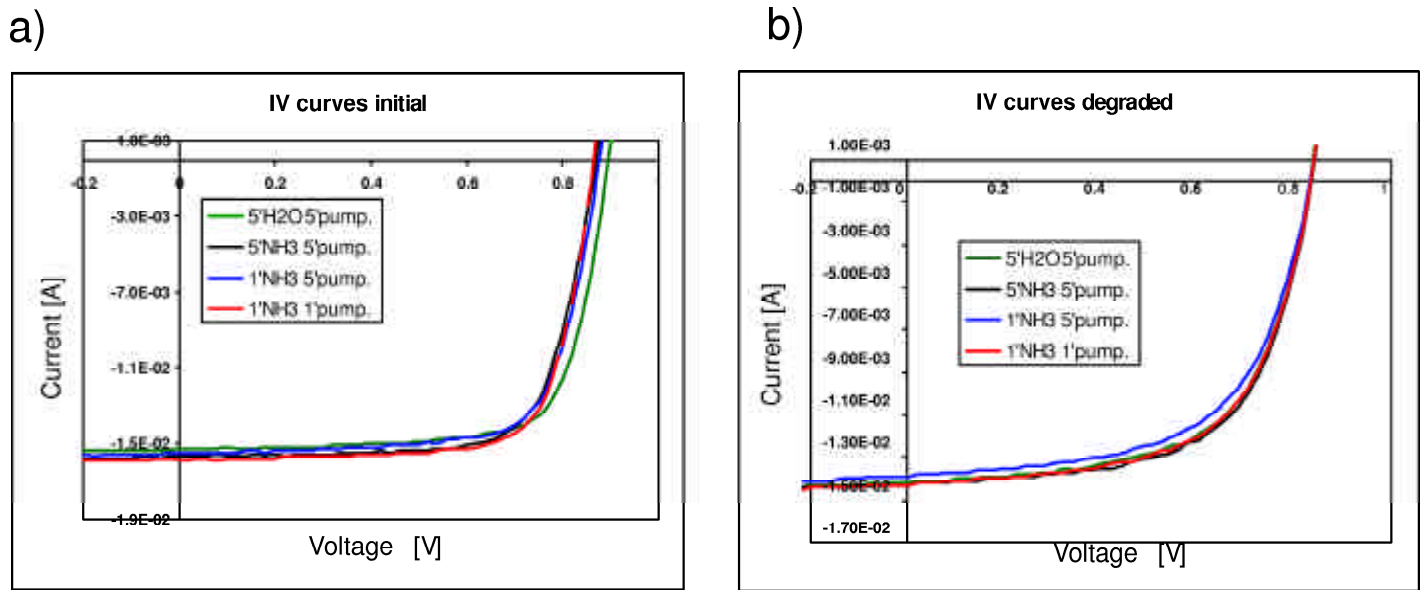
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a)

b)

Fig. 3. *SIMS oxygen profile of p-i-p-i sandwiches with: a) water vapour pressure treatment, b)ammonia flush treatment. The pressure and duration of the flush, and the duration of the post-flush pumping time, are shown on the figures.*

a)

IV curves initial

Legend:
- 5'H2O 5'pump.
- 5'NH3 5'pump.
- 1'NH3 5'pump.
- 1'NH3 1'pump.

Current [A]
Voltage [V]

b)

IV curves degraded

Legend:
- 5'H2O 5'pump.
- 5'NH3 5'pump.
- 1'NH3 5'pump.
- 1'NH3 1'pump.

Current [A]
Voltage [V]

ammonia treatment, cell performance :

Initial	After degradation
Voc 863 mV	Voc 859 mV
FF 74.1	FF 63.7

c)

	Initial
Voc [mV]	892
Isc [mA/cm²]	14.45
Fill Factor [%]	67.7
Efficiency [%]	8.7

30 min pumping

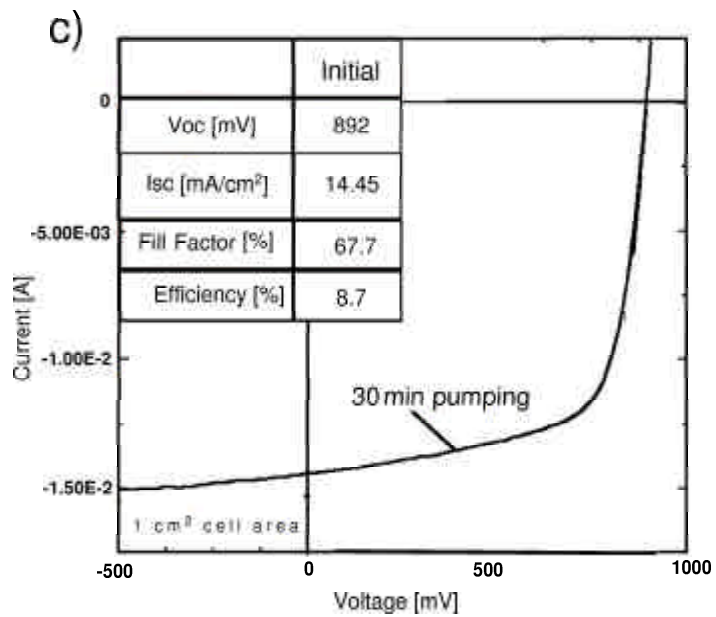1 cm² cell area

Current [A]
Voltage [mV]

Fig. 4. *Effect of ammonia flush on the I-V characteristics of a-Si:H cells, compared with the water vapour flush treatment : a) initial, and b) after light-induced degradation. Results for cells prepared with various flush durations, and various pumping durations, are shown. c) Initial I-V characteristics of an a-Si:H cell with 30 min pumping between p-layer and i-layer.*

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a)

1' NH₃ + 1 'pump

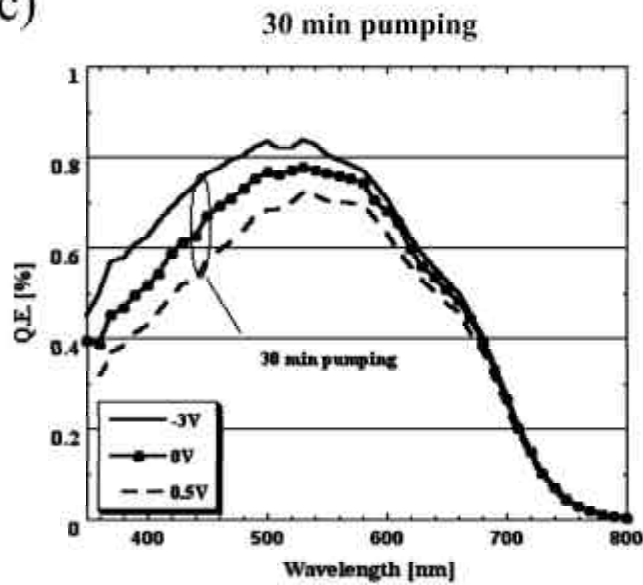b)

5' H₂O + 5' pump

c)
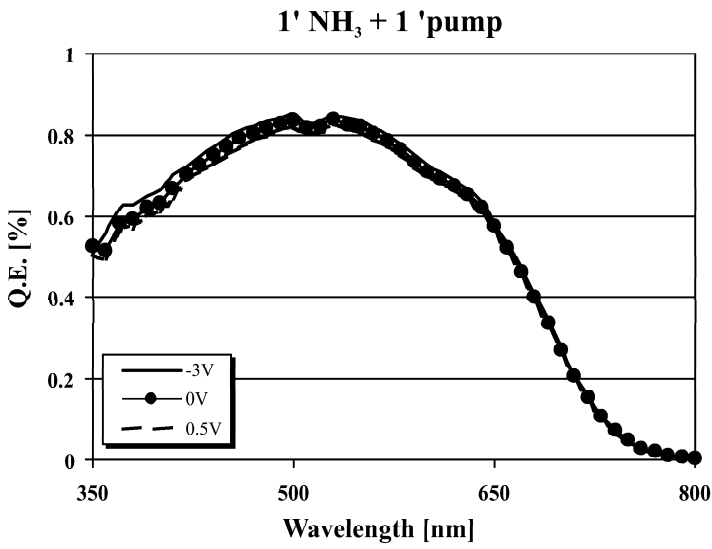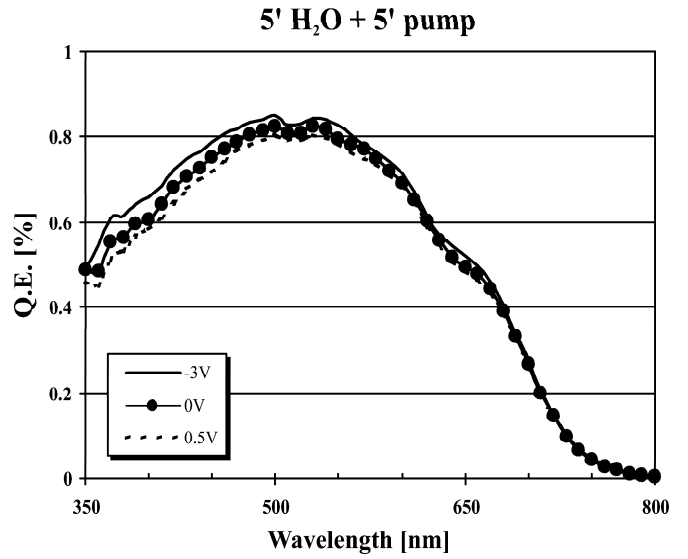
30 min pumping

Fig. 5. *Effect of a) ammonia flush, b) water vapour flush and c) 30 min pumping on the bias-voltage dependent quantum efficiencies.*