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To cite this article: J Dulanto *et al* 2021 *J. Phys.: Conf. Ser.* **1841** 012003

Silicon interface passivation studied by modulated surface photovoltage spectroscopy

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Abstract. We demonstrate that the modulated surface photovoltage spectroscopy (modulated SPS) technique can be applied to investigate interface states in the bandgap, i.e. interface passivation, of crystalline silicon coated with a downshift layer such as hydrogenated aluminum nitride with embedded terbium ions by suppressing straylight with a cut-off filter. Different hydrogen contents influence the surface photovoltage spectra at photon energies below the bandgap of crystalline silicon. Modulated SPS reveals that at higher hydrogen content there is a lower signal and, thus, a lower density of surface defect states. Our experiments show that modulated SPS can become a powerful tool for characterizing defect states at interfaces which cannot be easily studied by other methods.

1. Introduction

Hydrogenated aluminum nitride doped with terbium ($AlN:H:Tb^{3+}$) has been recently studied for potential applications as a passivating, down-shifting material for silicon solar cells [1]–[4]. The luminescence properties of the Tb embedded in AlN:H and the optical properties of the layer [5],[6] have been studied thoroughly. However, little is yet known about the passivating properties of this thin-film on silicon. Here, we employ the modulated surface photovoltage spectroscopy (SPS) to investigate passivating properties when using this type of luminescent coatings.

SPS is a contactless technique for the characterization of semiconductor surfaces. It relies on illumination-induced changes in the surface potential measured as a surface photovoltage (SPV) [7]–[10]. Previous works used SPS to analyze other materials and interfaces such as ZrO_2/GaAs, SiO_2/GaAs, GaP/GaAs, $MAPbI_3$ Perovskite, CdSe quantum dot films and ZnO/GaP heterojunction [11]–[14] at the sub bandgap region. As remark, modulated SPS is extremely sensitive and has, compared to the measurements with a Kelvin probe, the advantage that it is sensitive only to those processes in a sample for which charge separation and relaxation can follow the modulation frequency, i.e. slow changes of the surface potential are suppressed.

Here, we use modulated SPS to assess the impact of the hydrogen dilution conditions on the passivation of the crystalline silicon (c-Si) surface. We apply this technique to study p-type c-Si passivated by a 80 nm thin layer of AlN:H:Tb^{3+} grown under different hydrogen flow conditions during the deposition process.

Chemical passivation of silicon surfaces by hydrogenated thin-film layers is well known [15]-[17]. Hydrogen atoms react with silicon dangling bonds, thus, reducing the density of related defects at the surface. For example, hydrogenated aluminum nitride (AlN:H) thin layers are suitable for the passivation of crystalline silicon [18], [19].

Studies revealed indirectly the improvement of the surface passivation by measuring the lifetime of the minority charge carriers in the bulk by quasi steady state photoconductance (QSSPC) measurements [20], [21] and the density of interface defect states (D_{it}) using the capacitance-voltage (C-V) method [22], [23]. Furthermore, it is also possible to estimate D_{it} from large signal transient SPV measurements by applying external potentials [24], [25]. However, numerous samples, as the sample investigated in this work, cannot be studied by QSSPC and C-V, for example, due to short lifetimes caused by high bulk or interface recombination rates, or due to leakage currents [26], [27], respectively. In contrast, modulated SPS measurements allow a very sensitive study of defect states below the bandgap of a semiconductor [28].

In the small signal case and for homogeneous absorption in the sensitive volume of a given sample, SPV signals are proportional to the generation rate, i.e. to the absorption coefficient of the semiconductor. It has been shown, that at sub bandgap photon energies the SPV signal can be more sensitive than optical absorption measurements [7], [9]. Therefore, a very interesting approach is the application of the modulated SPS method to investigate the impact of the hydrogen flow on the passivation properties of AlN:H:Tb^{3+} on c-Si.

2. Experimental

AlN:H:Tb^{3+} samples were produced by AC magnetron sputtering (LA440S VON ARDENNE) on polished c-Si wafer. The wafers were float-zone, p-type (100) with a resistivity of 1-3 Ωcm. The samples' deposition was done by reactive sputtering with 20 sccm of nitrogen flow and with the aluminum target at 200 W of power. The target to sample distance was about 8 cm. The layers were deposited at different hydrogen flows of 1 sccm, 3 sccm and 5 sccm to obtain different hydrogen concentrations in the thin films. After the sputtering process the samples were treated by rapid thermal processing (RTP) at 850 ºC for 300 seconds to activate the luminescent properties of the embedded Tb ions [1-3]. Such a thermal process can also activate fixed negative charges in the AlN layer for field-effect passivation [16],[17],[29].

Modulated SPS measurements were performed using a MIS capacitor setup with a prism monochromator and a halogen lamp [30], as depicted in figure 1. At the MIS configuration the modulated SPS method is very sensitive to small SPV signals (up to the <100 nV) [7]. To reduce stray light effects, we included a cut-off filter between the exit slit of the monochromator and the mechanical chopper (modulation frequency 8 Hz). The SPV signals were detected with a double-phase lock-in amplifier (EG&G 5210).

Any monochromator has "white" stray light which is usually suppressed by about 3 orders of magnitude at a given wavelength. First, stray light can cause SPV signals in spectral regions without any absorption, i.e. stray light can cause artefacts. Second, SPV signals caused by stray light very drastically reduce the sensitivity for signals related to very weak photogeneration as for defect states in the band gap. The purpose of the cut-off filters is to eliminate the stray light [30], [31], i.e. non-monochromatized light originating from the monochromator.

Figure 2 shows SPV spectra near the bandgap for the bare c-Si substrate without and with using cut-off filters at 1000 and 1100 nm (1.24 and 1.13 eV, respectively). The shapes of the spectra were unchanged below the cut-off energies whereas the signal heights were reduced by additional optical losses and reduced straylight. Since the absorption coefficient of c-Si strongly increases between 1.13 and 1.24 eV, the filter with the cut-off at 1100 nm has been used in the following.

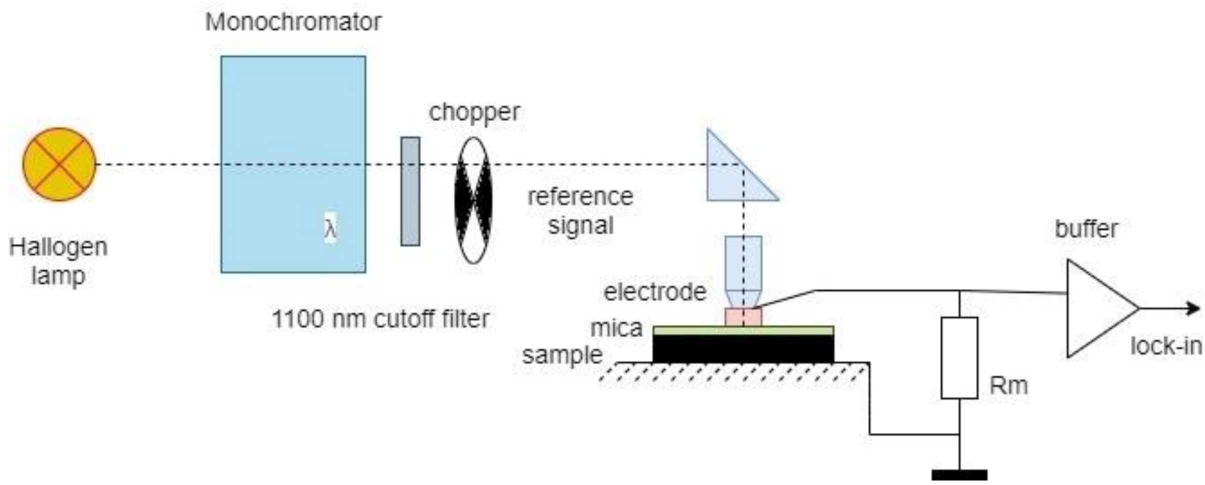

Figure 1. Schematic setup for a MIS capacitor SPS measurements, from left to right: halogen lamp, prism monochromator, cut-off filter, chopper, optical guide, MIS capacitor array for sample, measurement resistance (Rm) and high impedance buffer, adapted from [30].

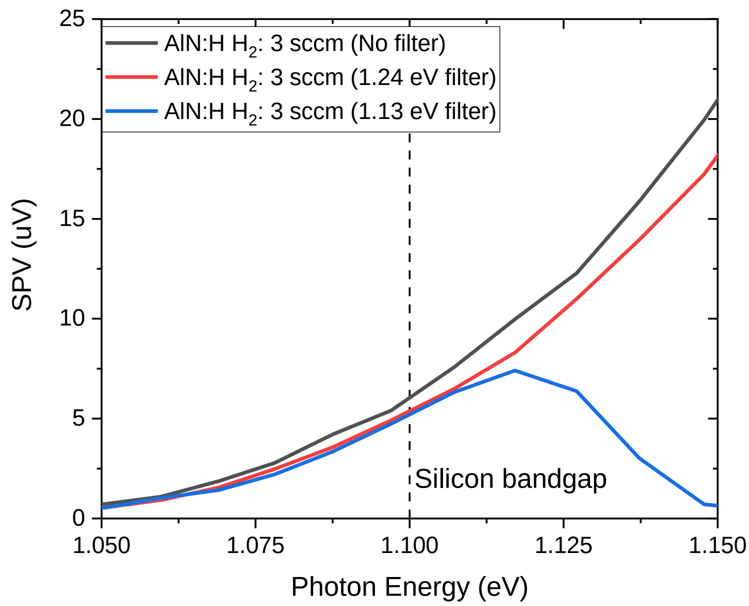

Figure 2. Modulated SPV spectra near the band gap of c-Si measured for the bare substrate without and with cut-off filters (no filter, 1000 nm, 1100 nm – black, red and blue lines, respectively).

3. Results and discussion

Figure 3 shows the modulated SPV spectra of three AlN:H:Tb^{3+} layers deposited onto c-Si substrates with different hydrogen flows during deposition (1 sccm, 3 sccm, 5 sccm). The dashed lines show the SPV spectra without a cut-off filter (1.13 eV). The in-phase SPV signals were positive. This means that the modulated charge separation was dominated by drift across an inversion layer in the p-type doped silicon, i.e. a relatively large amount of negative charge was fixed in the AlN:H layers near the interface.

For the measurements without the cut-off filter, the maxima of the SPV signals were reached at about 1.35 eV and amounted to about 1 mV, 300 µV and 300 nV for 1, 3 and 5 sccm, respectively. Therefore, the interface conditions were extremely different for each sample. At sub bandgap energies and without the cut-off filter, the SPV signals consisted of an only slightly changing background (about 2 – 4 μV for 1 sccm, 0.7 – 1.4 μV for 3 sccm and within the noise level for 5 sccm).

Using the cut-off filter, all SPV signals up to about 0.7 – 0.8 eV reduced to values in the order of the noise level, i.e. SPV signals related to photogeneration from electronic states around midgap could not be observed by SPV under the given conditions. For the sample grown with the hydrogen flow of 5 sccm, no SPV signals could be observed without the filter, i.e. the sensitivity was much too low for detecting defect states for this sample. The situation was different for the samples grown with the hydrogen flows of 1 and 3 sccm. For these samples, two well pronounced shoulders appeared between approximately 0.8 and 1.05 as well as 1.05 and 1.1 eV, respectively. Additionally, the SPV signals amounted to about 1 μV (1 sccm) and 350 nV (3 sccm) and about 60 (1 sccm) and 12 μV (3 sccm) at 1.0 and 1.1 eV, respectively. Therefore, the sensitivity for the detection of defect states increased with increasing SPV signals for fundamental absorption. This correlation means that one mechanism dominated the modulated charge separation.

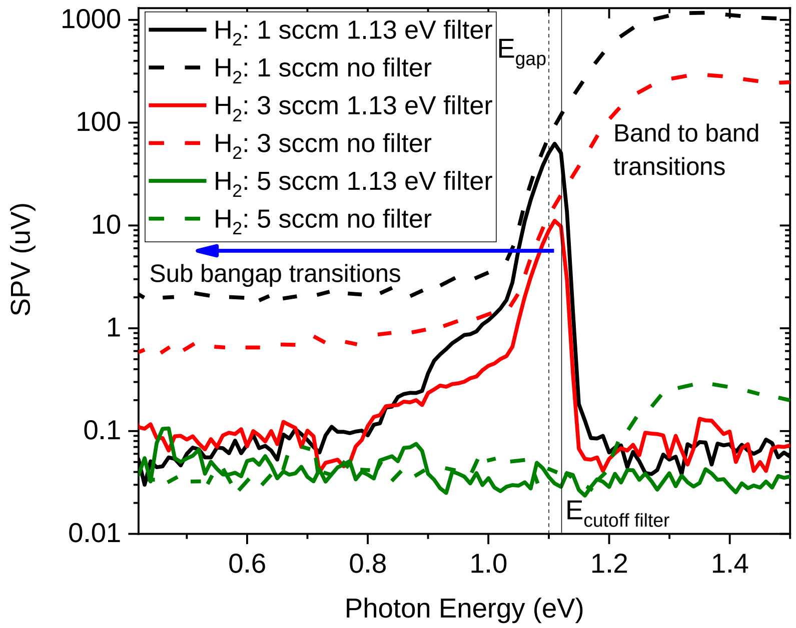

Figure 3. Modulated SPV spectra of samples with AlN:H:Tb^{3+} layers grown on c-Si with hydrogen flows of 1, 3 and 5 sccm (black, red and green lines, respectively) measured without (dashed lines) and with a cut-off filter at 1.13 eV (solid lines).

The SPV responses in figure 3 indicated that a higher hydrogen content in the sample leads to a reduced SPV signal. These changes in response could be attributed to the interface defect passivation by the hydrogen. At higher hydrogen contents more defects near or at the interface are passivated, thus, reducing their charge and band bending in the c-Si. This may be translated into a reduced SPV signal.

To discuss this hypothesis, in figure 4 a) we assign the SPV signals at different photon energies for the 1 sccm and 3 sccm samples (with filter) to possible electronic transitions as depicted in figure 4 b). For this interface (AlN:H:Tb^{3+} / c-Si) we propose three possible transitions: A) band to band transitions from valence (E_V) to conduction band (E_C) for $E_{hv} \geq E_{gap}$; B) from tail states or acceptor states (E_a) to conduction band for E_{hv} below but close to E_{gap}. An exponential function in figure 4 a) estimates an onset of the fundamental absorption (E_{on}) around 1.02 eV [32]; and C) sub bandgap transitions from interface defect states, represented by Gaussian functions in figure 4 a), to conduction band when E_{hv} is smaller than E_{gap}. In the latter case, we postulate that after the transition from an interface defect state to the conduction band (C), the promoted electron is repelled by the negative charge in the dielectric

($AlN:H:Tb^{3+}$), as depicted in figure 4 b). The resulting separation of charges induces a change in the band bending which gives rise to the SPV signal [8]. The amount of these transitions depends on the number of defects: a higher defect density results in a higher SPV signal. Hence, we can conclude that the sample deposited at 1 sccm of hydrogen flow has more defect states near or at the interface and, thus, a higher SPV signal. Whereas the 3 sccm sample has a lower defect state density and, thus, lower SPV signal. In the case of the 5 sccm sample, the defect state density is below the sensitivity of the modulated SPS technique. Therefore, in figure 3 only the signal from band-to-band transitions (A) can be observed without the filter.

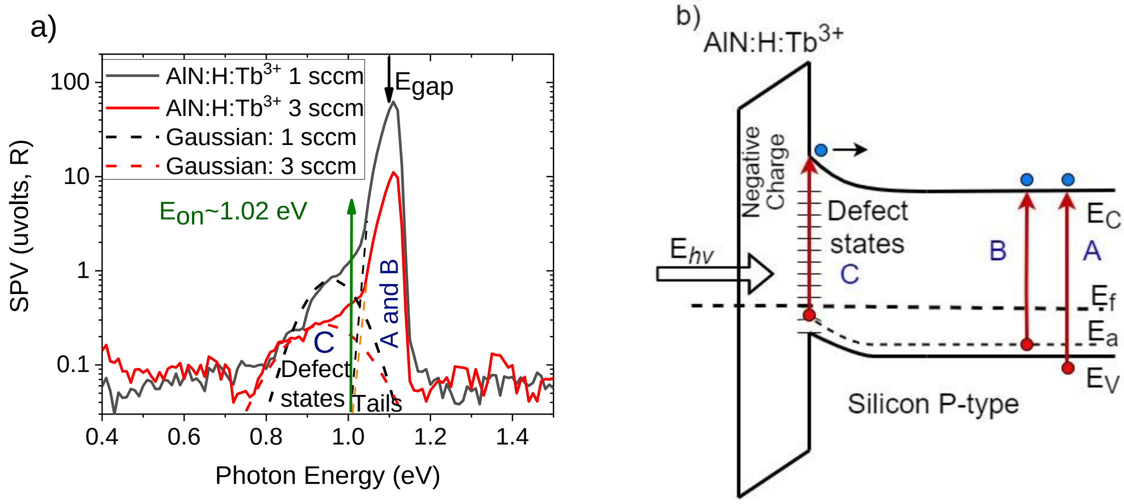

Figure 4. a) SPV spectra with marked transitions A, B and C b) Schematic band diagram with transitions observed by modulated SPS: A: band to band, B: acceptor/tail states to conduction band, C: Interface defect states to conduction band.

4. Conclusions

The present study shows that modulated SPS can be a suitable alternative or complementary technique to study the impact of hydrogen in novel downshift layers like $AlN:H:Tb^{3+}$ used also as a surface passivators for crystalline silicon. Particularly, when high interface defect densities and leakage currents prevent the analysis via more traditional techniques, such as QSSPC and CV, modulated SPS can provide information about defect states. By efficiently suppressing straylight with a cut-off filter, the modulated SPS technique was highly sensitive to defect states in the bandgap and to demonstrate the enhanced passivation due to the increment of the hydrogen content in the sample under inversion condition. For higher hydrogen flow during deposition a lower SPV signal was detected due to a lower interface defect state density and/or reduced density of negative charge in the $AlN:H:Tb^{3+}$ layer. Therefore, modulated SPS is a powerful technique giving access to the investigation of defect states at internal interfaces and opening in this way new opportunities for further optimization and control not only for passivation of interfaces in solar cells but also for the further development of materials for luminescence, photocatalysis and sensors.

Acknowledgements

Financial support has been provided by the Peruvian National Fund for Scientific and Technological Development (FONDECYT) through Contract N°124-2018-FONDECYT. Additional support was provided by the Pontificia Universidad Católica (PUCP) vicechancellorship for research (project no. CAP-2019-3-0041/702). The author J. Dulanto has been supported by the Huiracocha Scholarship of the PUCP.

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