Electronic states in extremely thin a-Si:H layers as part of a-Si/c-Si heterostructures

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Extremely thin layers play a crucial role as quantum layers or functional layers in heterostructures. In order to understand their electronic properties of ultra-thin layers, it is important to gather information on the gap state density distribution, Fermi level position, interface state density distribution, band offsets etc. We report on a variant of photoelectron spectroscopy which yields such data by using photoelectron excitation with near-ultraviolet light (NUV-PES). Additionally, surface voltage measurements (SPV) were utilized as an analytical tool for band bending and interface state analysis.
The NUV-excitation (hν=4-8eV) results in an electron escape depth up to 10nm and in an optical excitation probability enhanced by several orders of magnitude compared to excitation with soft X-rays. This allows the direct observation of the density distribution of occupied gap states N_{OCC} (E) and of the Fermi level position E_F [1]. Due to the limited photon penetration and electron escape depth, the measured distribution N_{OCC} (E) is a weighted average of the DOS of the sample up to a depth of 7 to 10 nm.
Using the constant final state yield spectroscopy (CFSYS) mode of NUV-PES [2] which provides the highest sensitivity and best signal-to-noise ratio, $N_{OCC}(E)$ was measured for a-Si:H/c-Si heterostructures with 2-100nm thin intrinsic, n- and p-doped a-Si:H layers of varying doping level. The layers were prepared by PECVD using the precursor gases silane (SiH_4), phosphine (PH_3) and diborane (B_2H_6).
Applied to an a-Si:H(i) deposition temperature series, CFSYS shows that the Urbach energy is minimal (61meV) and the Fermi level closest to midgap for a deposition temperature of T_S=230°C. This correlates with a minimum in interface recombination rate at the same temperature, as derived from the decay of surface photovoltage over time [3]. The corresponding interface state density amounts to about $D_{it}=1\times10^{12}$ cm^{-2} eV^{-1} at midgap, as estimated by field dependent SPV (FD-SPV).

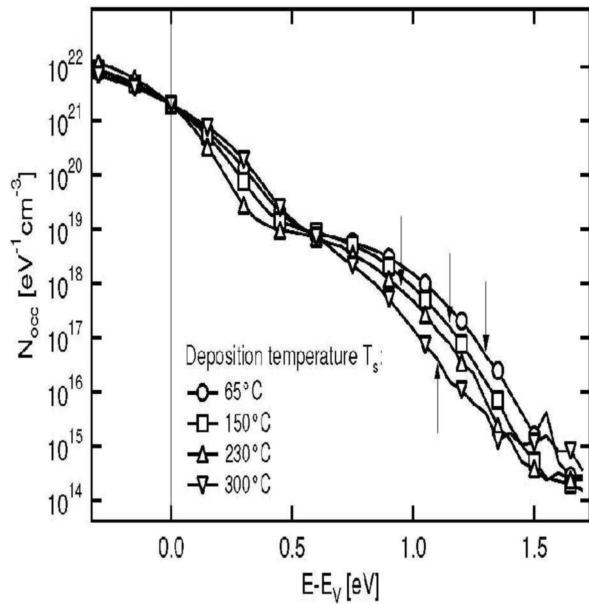

Fig. 1. Density of occupied gap states N_{OCC} (E) of a series of a-Si:H(i)/c-Si(p) samples with variation of the a-Si:H deposition temperature T_S, measured by constant final state yield spectroscopy. Note that the valence band edge E_V is chosen as origin of the abscissa. Arrows mark the Fermi level positions. The spectra are normalized to 2 10^{21} states/(eV · cm^{-3}) at the valence band edge.

The Urbach energy increases up to 80meV for layers deposited below and above T_S=230°C.
Field dependent SPV measurements clearly show that the interface state density follows the same trend as the Urbach energy. This hints on a direct coupling of the tail states with the fast interface states by charge transfer processes. Thus, by FD-SPV we determine an effective interface state density. The density of a-Si:H gap states, caused by dangling bonds in the amorphous network, has a value of about 1-3 x10^{18}cm^{-3}, which remains nearly independent of the deposition temperature. This value is in agreement with findings of other authors on extremely thin films [4] but about a factor of ten higher than in a-Si:H bulk, as measured by ESR and CPM [5].
For a-Si:H layer thicknesses below 4nm, we obtain a contribution of c-Si valence band states to the photoemission signal. Describing these spectra as the superposition of a-Si:H and c-Si densities of states yields excellent fit results and allows the exact determination of the band o□set between a-Si:H(i) and c-Si(p,<111>), to ΔE_V=0.38 eV± 0.06 eV. This was cross-checked for a-Si:H(p) on c-Si(n,<111>) which gave in both cases values of ΔE_V=0.36eV±0.1eV and ΔE_C=0.2eV±0.1eV, assuming an a-Si:H band gap of 1.7±0.1eV as determined for 100 nm thick layers by photoconductivity measurements. These quantities are very important for the application of such heterostructures in devices such as solar cells, because charge transfer and recombination activity depend on the band offset and the position of the Fermi level at the interface.
For the a-Si:H/c-Si system, we now have a nearly complete description of the major electronic quantities of the a-Si:H and its interface to the c-Si. The relevance of this data for the optimization of a-Si:H/c-Si heterojunction based devices is illustrated by our findings that the maximum of a-Si:H/c-Si solar cell efficiencies is reached when measured a-Si:H tail state density and concomitently the effective interface state densities are minimal.
Finally, we discuss the preconditions for applying the NUV-PES to the detection of surface states and/or gap states in layers which show quantum size effects. Some first experimental results will be presented.

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