Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Non-Crystalline Solids 352 (2006) 1217–1220
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Electronic states in a-Si:H/c-Si heterostructures

L. Korte *, A. Laades, M. Schmidt

Hahn-Meitner-Institut Berlin, Silicon Photovoltaics, Kekuléstr. 5, D-12489 Berlin, Germany

Available online 20 March 2006

Abstract

We have investigated PECVD-deposited ultrathin intrinsic a-Si:H layers on c-Si substrates using UV-excited photoemission spectroscopy ($h\nu = 4$–8 eV) and surface photovoltage measurements. For samples deposited at 230 °C, the Urbach energy is minimal, the Fermi level closest to midgap and the interface recombination velocity has a minimum. The a-Si:H/c-Si interface density of states is comparable to that of thermally oxidized silicon interfaces. However, the measured a-Si:H dangling bond densities are generally higher than in thick films and not correlated with the Urbach energy. This is ascribed to additional disorder induced by the proximity of the a-Si:H/c-Si interface and H-rich growth in the film/substrate interface region.

PACS: 73.20.At; 79.60.Jv; 79.60.Ht; 73.40.Lq; 71.55.Jv; 72.20.Jv

Keywords: Amorphous semiconductors; Silicon; Solar cells; Heterojunctions; Photovoltaics; Band structure; Defects

1. Introduction

The use of heterostructures for the realization of p–n junctions requires a careful analysis of electronic states in the involved solids and at their heterointerface. The main parameters determining charge transfer and recombination activity are the band offsets and the Fermi level position at the a-Si:H/c-Si interface as well as the density and energetic distribution of defects at the interface and in the thin amorphous layer. While structural properties and the growth mechanism of thin a-Si:H films have been investigated recently, e.g. [1], and a wealth of data on the distribution of gap states is available for thick (>100 nm) a-Si:H films, little is known about the electrical properties of thin films and their interfaces. For such thin films, the present work shows results concerning the distribution of occupied a-Si:H gap and a-Si:H/c-Si interface states, the interface recombination properties and the correlation of these parameters with preparation conditions.

2. Experimental

On 2″ wafers of ⟨1 1 1⟩ oriented, p-type crystalline silicon with a resistivity of $\rho \approx 0.5$–$1\ \Omega\,\mathrm{cm}$ ($N_D \approx 1$–$3 \times 10^{16}\ \mathrm{cm}^{-3}$), a deposition temperature series of intrinsic, 12–17 nm thin a-Si:H films were deposited by RF excited PECVD (13.6 MHz, $P_{RF} = 13\ \mathrm{mW/cm^2}$) using silane, SiH_4, as precursor at a gas flow of 10 sccm. Prior to a-Si:H deposition, all wafers were cleaned following the standard RCA-procedure, followed by etching in diluted hydrofluoric acid (1% HF in H_2O, 1 min). Immediately afterwards, the samples were transferred into the PECVD system. The time between the last cleaning step and reaching a pressure $p < 2$–5×10^{-7} mbar never exceeded 10 min to avoid reoxidation [2].

After transferring the samples into a UHV vacuum chamber without breaking the vacuum, photoelectron spectroscopy measurements of the internal yield Y_{int} of the emitted photoelectrons were carried out in constant final state (CFSYS) mode [3] by varying the photon energy, $h\nu = 3$–7 eV. From $Y_{int}(E_{kin}, h\nu) \propto N_{occ}(E_{kin} - h\nu)$ [4,5], we obtain the absolute values of the density of occupied states $N_{occ}(E)$ by normalization either at $h\nu = 6.2$ eV to $10^{22}\ \mathrm{cm}^{-3}\ \mathrm{eV}^{-1}$ as proposed in [6] or at the valence band

* Corresponding author. Tel.: +49 30 8062 1305; fax: +49 30 8062 1333.
E-mail address: korte@hmi.de (L. Korte).

0022-3093/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2005.10.046

edge, E_V, to 2×10^{21} cm^{-3} eV^{-1} [7]. E_V is determined from a plot of $\sqrt{Y_{int}}(E)$ as the onset of the parabolic distribution of valence band states. The normalization factors thus obtained agree within a factor of 2–3. Due to the limited photon penetration and electron escape depth, the measured distribution is a weighted average of the DOS of the sample up to a depth of 7–10 nm. For further details see [4] and references therein.

Surface photovoltage (SPV) is an electrical characterization technique for the determination of band bending and the density of surface/interface states [8,9]. The sample under test is sandwiched in a structure consisting of a transparent conductive front contact (TCO), an insulating slab of mica, the sample and a metallic back contact. Thus, an artificial metal–insulator–semiconductor (MIS) structure is created. Upon intense illumination of the sample by a short laser pulse ($h\nu = 1.35$ eV, pulse duration 160 ns, intensity 10^{19} photons/(cm^2 s)) through the TCO, excess charge carriers are generated in the sample, leading to a flattening of the bands and a split-up of the quasi-Fermi levels of electrons and holes. The surface photovoltage of the sample is then measured capacitively via the insulating slab as photovoltage pulse U_{SPV}. Because the sample is illuminated at a photon energy smaller than the band gap of a-Si:H (~1.7 eV), the latter acts as an additional window layer, the excitation of charge carriers takes place in the crystalline substrate and their main recombination path is via the defect states at the a-Si:H/c-Si interface. From measurements of the dependence of U_{SPV} on the external field, the distribution D_{if} of a-Si:H/c-Si interface gap states can be calculated [8] under the assumption that they do not change their charge state during the light pulse.

3. Results

The energetic distribution of the densities of occupied gap states $N_{occ}(E)$ is shown in Fig. 1. The usual features, i.e. an exponential decay of the density of states (DOS) at $E - E_V = 0$ to ~0.4 eV and a Gaussian-shaped defect distribution up to the Fermi level E_F are observed. Fig. 2 shows parameters derived from Fig. 1: The Urbach energy E_{0v}, the Fermi level E_F and the integrated defect density of deep defects N_D vs. substrate temperature T_s. The observed trend, i.e. a minimum of $E_{0v} = 61$ meV and energetic separation of valence band edge and Fermi level, $E_F - E_V = 0.96$ eV (i.e. slightly above a-Si:H midgap), for $T_s = 230$ °C, is in good agreement with findings on thick films, e.g. [10]. In contrast to these data, the integrated defect density N_D shows, within the accuracy of the measurement, no appreciable variation ($N_D = 0.9$–2.9×10^{18} cm^3) and is slightly higher than the value of 8×10^{17} cm^3 measured by Winer and Ley on thick films using total yield photoemission [11]. The shift of E_F correlates with a shift of the defect band (Fig. 1).

The variations in a-Si:H quality with deposition temperature can be observed as well in the SPV transients presented in Fig. 3. The decay of the transient is an image

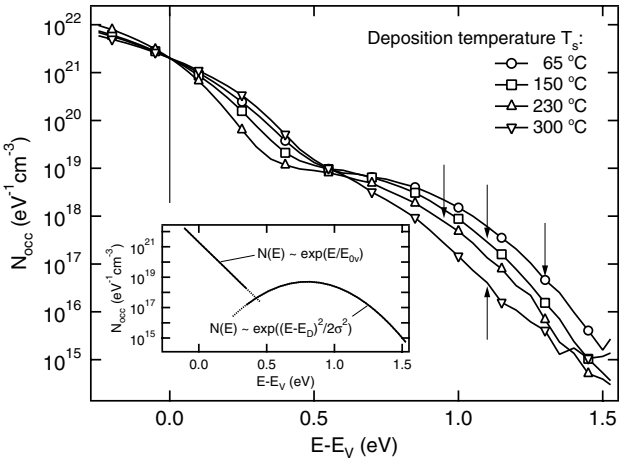

Fig. 1. Density of occupied gap states $N_{occ}(E)$, measured by constant final state yield spectroscopy, of a series of a-Si:H(i)/c-Si(p) samples with variation of the a-Si:H deposition temperature T_s. The valence band edge E_V is chosen as origin of the abscissa. Arrows mark the Fermi level positions. The spectra are normalized to 2×10^{21} states/(eV cm^3) at the valence band edge. See [4] for details. Inset: Decomposition of the DOS into Urbach tail and dangling bond distribution (schematic).

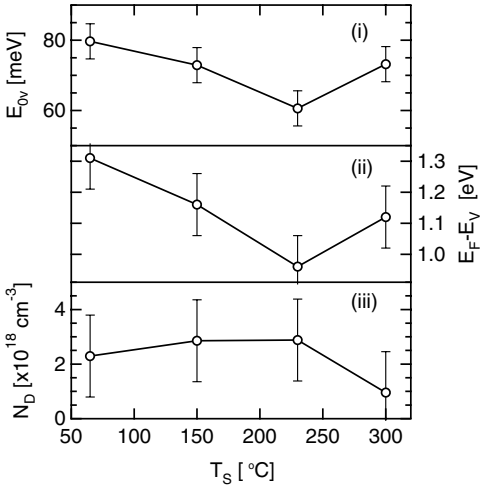

Fig. 2. Data derived from the series shown in Fig. 1: Dependence on T_s of (i) Urbach energy E_{0v}, (ii) Fermi level position $E_F - E_V$ and (iii) integrated defect density N_D.

of the recombination of photogenerated excess carriers that occurs predominantly at the a-Si:H/c-Si interface. The first ~50 μs of the decay are exponential, described by a time constant τ_{ini} that has a pronounced maximum at $T_s \approx 200$–230 °C due to the excellent suppression of interface recombination at this temperature. The minimum of the initial photovoltage, $|U_{SPV}^{max}| = 311$ mV, lies at the same deposition temperature and increases by 50 and 151 mV upon variation of T_s to 100 °C and 300 °C, respectively. As shown in [12], photoluminescence and the efficiency of solar cells processed with n-doped ultrathin a-Si:H emitters prepared under identical conditions have a maximum at the same temperature. The question arises as to whether the low recombination velocity is caused by a passivation of recombination active defects, or by pinning of the surface Fermi