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Transient photocurrents as a spatially resolved probe of carrier transport and defect distributions in silicon thin films

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ABSTRACT

Transient photocurrent spectroscopy (TPC) yields the energetic distribution of localised states in disordered semiconductors from an analysis of the decay of photocurrent with time following a short laser pulse. By comparing results at different laser excitation wavelengths, and hence absorption depths, information on spatial non-uniformities may also be inferred. Here we investigate the use of TPC as a spatial probe with reference to two thin-film silicon systems; amorphous silicon subjected to various light-induced degradation regimes, and microcrystalline silicon grown on a range of 'seed' layers. Computer simulation is used to support experimental findings, and to identify sensitivity and resolution limitations.

1. Introduction

Transient photocurrent spectroscopy (TPC) is a sensitive probe of the energetic distribution of band-tail and defect states in disordered semiconductors, which control key material parameters including carrier mobility and lifetime. The technique is based on inversion of the decay in photocurrent $I(t)$ following a nanosecond flash of laser light incident on a gap-cell under voltage bias, to yield the density of localised states (DOS) in terms of a multiple-trapping transport model [1,2].

We have previously shown that a degree of *spatial* sensitivity may also be obtained using TPC [3–5]. This variant, which we refer to here as S-TPC, utilises the differing absorption depths of the light flash with wavelength to generate carriers either uniformly, or preferentially at one or other surface. For example, in an amorphous (a-Si:H) or microcrystalline (μc-Si:H) silicon film 1 μm thick, carrier generation by red light is fairly uniform, but green light generates a much higher carrier concentration close to the incident surface. It was thus proposed that the resulting $I(t)$ will be linked to the DOS in this region. Similar claims have been made when using other photoconductivity techniques including steady state [6], constant-photocurrent method [7] and modulated photocurrent spectroscopy [8].

To investigate S-TPC experimentally, a film with a known, controllable, spatial distribution of defects is required. Working towards this goal, we have compared TPC decays obtained from an amorphous silicon film in a thermally annealed state, and after prolonged exposure to white light, and white light band-pass filtered with a peak transmittance at 520 nm (green). As light-soaking increases the density of dangling bonds in proportion to the carrier generation rate [9], it is anticipated that a variable (but at best semi-quantitative) spatial defect profile may be realised in this way.

Microcrystalline silicon films are substantially more stable to light-induced degradation, but given their inhomogeneous structure evolution during growth [10] electronic transport properties are also likely to be spatially non-uniform. Here we apply S-TPC to a series of microcrystalline films with thin 'seed' layers deposited on the glass substrate prior to the main film growth. Such layers influence the structure evolution, leading to a compact film with more uniform crystalline content and improved solar cell performance [11]. Investigation of electronic transport and defect distributions in such state-of-the-art material is thus both timely and of high relevance. The crystalline volume fraction was measured using Raman spectroscopy, using both red and blue exciting lines to enable variations in crystallinity between bulk and surface to be estimated [12].

Although photo-carriers will initially interact with localised states in the immediate vicinity, concentration gradients will inevitably lead to diffusion into the bulk of the film and, given the asymmetry of electron and hole transport, the subsequent

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spatial evolution with time is likely to be complex. The degree of success of the S-TPC method will depend upon these detailed interactions. To identify the key features we have carried out computer simulations in two-layer composite films with amorphous silicon-like DOS profiles, in which the defect density of a thin 'surface' layer is varied. By integration of the current components in each layer parallel to the film we obtain the measured $I(t)$ which is then processed to yield a DOS for comparison with the model input.

2. Experimental

Amorphous silicon films were prepared in a commercial 13.56 MHz PECVD reactor (InterSolar Ltd.) with a silane:hydrogen process gas concentration (SC) of 95%, chamber pressure 0.7 mbar and substrate temperature 200 °C. The film thickness was 1.7 μm. Chromium contacts 5 mm in length separated by 1 mm defined the gap cell. White light-soaking of amorphous films (referred to as WLS) was carried out using an ELH lamp providing 1000 W/m^2 at the sample. For green light-soaking (GLS) the same arrangement was used, but with a Spiers-Robertson BG18 band-pass filter placed in front of the sample. Each light-soaking session was 15 h in duration. Thermal annealing (TA) was carried out as required, in air at 180 °C for 2 h.

Microcrystalline silicon samples were prepared at IEK-5, Forschungszentrum Jülich by PECVD at 94.7 MHz with a power of 10 watts, gas pressure of 0.4 mbar and substrate temperature of 180 °C [13]. A layer approximately 50 nm thick was firstly deposited on to a Corning 7059 glass substrate, roughened to improve film adhesion. The crystallinity of this 'seed' layer was adjusted by setting the silane concentration SC_{Seed} between 2% and 5.3% in a series of five depositions. Each sample was completed by deposition at a gas ratio of 5.3% to give a total film thickness of 1 μm. The degree of crystallinity was estimated using Raman spectroscopy [12] in terms of the ratio of the integrated intensity of the crystalline bands to the total intensity (amorphous plus crystalline), referred to as I_{CRS}. The blue (488 nm) exciting line has an absorption depth of around 200 nm and gives an indication of the crystallinity towards the free surface of the film, whereas the red (647 nm) exciting line has an absorption depth of some 3 μm and hence will return a value averaged over the entire film thickness. 5 mm × 5 mm silver contact pads 0.5 mm apart were deposited on the top of the film to form a gap-cell.

In the TPC experiment [14], nanosecond light pulses were generated by a Laser Science VSL337N$_2$ laser plus dye attachment. Wavelengths of 510 nm and 640 nm were selected by insertion of the appropriate dye cuvette. These are referred to hereafter as GL (green laser) and RL (red laser), respectively. The pulses were attenuated to give a total flux of 10^{11} photons cm^{-2} at the sample, corresponding to a photocarrier density of order 10^{15} cm^{-3}.

When light-soaking, and also when performing the TPC experiment, either side of the sample could be illuminated by rotating the sample holder. The sides of the sample illuminated in a given experiment are referred to hereafter as contact side (CS) (the film/air interface) and substrate side (SS) (the film/glass interface).

All TPC measurements were made at room temperature with an applied voltage bias of 100–300 volts. Following appropriate preamplification, current transients from 1 ns to 10 s were recorded on a Tektronix TDS3052 digital storage oscilloscope. Averaging of successive transients reduced noise to an acceptable level. Data were transferred to a PC and processed into a single logarithmically spaced file.

The DOS was extracted by firstly applying a discrete Fourier transform to the $I(t)$ data, to obtain the ac current $I(\omega)$ where ω is the angular frequency. Within a multiple-trapping formalism, $I(\omega)$ may then be mapped directly to the DOS via the simple approximate relationship [15]:

$$\mathrm{DOS}(\omega) \propto \frac{\sin(\phi(\omega))}{\left|I(\omega)\right|} \tag{1}$$

where $\phi(\omega)$ is the phase angle of the photocurrent relative to the excitation. More usefully, the DOS may be plotted against energy (relative to the conduction band mobility edge) by noting that

$$E = kT\ \ln(\nu/\omega) \tag{2}$$

where k is Boltzmann's constant, T the absolute temperature and ν the attempt-to-escape frequency. This approach enables an arbitrary DOS to be extracted from TPC data with a resolution of order kT.

Computer simulation of film parameters was carried out using the SC-Simul program developed at the University of Oldenburg [16]. This is a one-dimensional numerical simulation which solves the Poisson equation, the continuity equations for electrons and holes, and the current transport equations including drift, diffusion, and thermionic emission over barriers, if present, in the valence and conduction bands. Further details are given in Ref. [16].

The model structure consisted of three parallel layers in contact: (i) a 100 nm layer of a-Si:H representing the surface region, (ii) a 900 nm layer of a-Si:H representing the bulk film, (iii) a 1 mm insulator restricting current flow normal to the film. Spatially uniform sets of localised states (exponential band tails and amphoteric dangling bonds) were specified in layers (i) and (ii). In this study only defect densities were varied. Conduction and valence band tail slopes of 30 and 50 meV, respectively, and a Gaussian defect distribution of width 0.15 eV centred at 0.9 eV below the valence band edge with a correlation energy of 0.25 eV were used throughout, all other parameters being maintained at default values. The SC-Simul program is designed primarily to simulate currents normal to the plane of the film, in structures such as solar cells, and a post-simulation numerical integration of the carrier density in each slice of the film parallel to the substrate (typically 10 nm thick) was performed to calculate the co-planar current. The DOS was extracted from the simulated $I(t)$ curve in an identical manner to the experiment.

3. Results and discussion

3.1. S-TPC of amorphous silicon films

Fig. 1(a) and (b) shows the $I(t)$ decays and resulting DOS for the a-Si:H sample following light soaking with white light from the contact side of the film. The annealed state curves are shown for comparison.

In the case of materials with band tails and deep defects, such as silicon thin films, the $I(t)$ decay in the ns to s range generally consists of [1]: (i) a region of constant slope at the beginning of the observable range (10^{-9}–10^{-8} s) due to carrier thermalisation in the band-tail; (ii) a steeper fall in current due to carrier trapping into deep defects; (iii) a complex combination of trapping and emission involving deeper tail states and defects; (iv) a sharp fall at the onset of free carrier loss (recombination). It is seen in Fig. 1(a) that the main difference in the $I(t)$ curves is associated with the onset of region (ii) (carrier trapping into deep defects). This occurs at progressively shorter times with increasing deep defect density.

Thus in common with previous studies of disordered silicon films and devices using TPC, including polysilicon thin-film transistors [17] and amorphous silicon sensors [18], we find the photocurrent to be dispersive, and the DOS to be comprised of band-tails and defects. The band-tails appear to be unaffected by light-soaking, but the defect density is significantly modified. The