

Effective interface state effects in hydrogenated amorphous-crystalline silicon heterostructures using ultraviolet laser photocarrier radiometry

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Ultraviolet photocarrier radiometry (UV-PCR) was used for the characterization of thin-film (nanolayer) intrinsic hydrogenated amorphous silicon (i-a-Si:H) on c-Si. The small absorption depth (approximately 10 nm at 355 nm laser excitation) leads to strong influence of the nanolayer parameters on the propagation and recombination of the photocarrier density wave (CDW) within the layer and the substrate. A theoretical PCR model including the presence of effective interface carrier traps was developed and used to evaluate the transport parameters of the substrate c-Si as well as those of the i-a-Si:H nanolayer. Unlike conventional optoelectronic characterization methods such as photoconductance, photovoltage, and photoluminescence, UV-PCR can be applied to more complete quantitative characterization of a-Si:H/c-Si heterojunction solar cells, including transport properties and defect structures. The quantitative results elucidate the strong effect of a front-surface passivating nanolayer on the transport properties of the entire structure as the result of effective a-Si:H/c-Si interface trap neutralization through occupation. A further dramatic improvement of those properties with the addition of a back-surface passivating nanolayer is observed and interpreted as the result of the interaction of the increased excess bulk CDW with, and more complete occupation and neutralization of, effective front interface traps. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4854595]

I. INTRODUCTION

Non-destructive characterization of multilayer semiconductor materials is important for device fabrication and optimization. It is especially important for submicron surface layers which are in wide use for optoelectronic devices. In particular, structures that include nanometer-thick amorphous-crystalline silicon heterostructures are widely used in the production of high efficiency photovoltaic devices.^{1,2} The amorphouscrystalline-silicon *p-n* heterojunction is a paradigm shift compared to more traditional thermally diffused junctions. The nano-thin hydrogenated amorphous silicon layer provides excellent passivation, allowing conversion efficiency increase of more than 23%,² while its low temperature (~250 °C) synthesis presents a cost advantage.³ Studies of this type of device are of considerable interest.

The transport parameters of the thin layer, of the c-Si substrate, and interface defects determine and limit the efficiency of solar cells. Various established methods such as photoconductance decay^{4,5} and surface photovoltage⁶ have been used for the evaluation of transport parameters and interface density of states. Among other methods, photothermal (PT) and photoluminescence (PL) techniques have been shown to be effective^{7–11} in measuring such parameters and are widely used. Photoconductance decay is a contacting method and is generally not amenable to nanolayer optoelectronic transport diagnostics because this type of configuration requires UV laser excitation. This, in turn, limits the photocurrent to extremely low values which make measurements unreliable, especially in the presence of surface-electrode contact. Nanosecond photoconductance has been used successfully⁵ to measure minority carrier lifetimes at the semiconductor-dielectric interface without having to form MOS test structures. However, this technique is not capable of measuring surface and interface defect state densities.

Surface photovoltage as applied to surface nanolayer diagnostics⁶ is an electrical method for the characterization of interface states, therefore, it also requires a thin transparent electrode in contact with the semiconductor surface and sub-bandgap excitation. 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. Therefore, the effects of defects within the surface nano-layer remain unknown and the interface defect (gap) states can be calculated under the assumption that they do not change their charge state during the light pulse. The presence of the transparent surface electrode prevents the use of suitable UV light sources to probe recombination processes within the nanolayer and/or confines itself at the electrode-semiconductor interface.

PT methods tend to be complicated in that signals depend on a large number of variables and parameters, including a superposition of thermal and electronic transport properties. Therefore, measurement accuracy and uniqueness of results is hard to ascertain while thermal effects tend to limit sensitivity to electronic recombination effects.

PL does not require contact electrodes and is, therefore, suitable for interrogating radiative recombination within surface layers. However, dc PL cannot monitor the optoelectronic carrier kinetics of near-subsurface regions due to its depth-integrated character through the signal dependence on the dc carrier diffusion length, thereby being sensitive to a complicated superposition of surface recombination velocity and subsurface recombination rates. PL spectroscopy of a-Si:H-c-Si heterostructures¹¹ requires spectral normalization (optical source calibration) and, to be quantitative, is subject to accurate absorptivity measurements and wavelength independence of interface reflection coefficients which amounts to neglecting the effects of the amorphous silicon layers. Laser-induced infrared photocarrier radiometry (PCR)^{12,13} is a dynamic near-infrared (NIR) modulated PL, spectrally gated to filter out the thermal infrared component of the radiative emission spectrum from de-exciting free photocarriers. As a result of its dynamic (frequencyscanning) character and the filtering out of thermal infrared photon emissions, PCR does not carry thermal information and is capable of rapid measurement of photocarrier electronic transport properties in electronic materials and devices through theoretical fits of frequency-scanned amplitude and phase data to appropriate carrier-wave diffusion models.¹² On the basis of a one-layer model, the main transport parameters such as bulk recombination lifetime, carrier ambipolar diffusion coefficient, and front- and back-surface recombination velocities have been evaluated for silicon wafers with various kinds of passivated or non-passivated surfaces.^{12,14,15} Detailed theoretical descriptions of carrier-density waves (CDWs) in composite optoelectronic materials have been developed;¹² however, surface-layer and interface traps have not been considered, although their influence on the PCR signal may be significant. It is especially important to take free photoexcited carrier traps into consideration in the case of thin surface layers deposited on bulk c-Si under optical excitation with short (UV) wavelength, when the optical absorption length is comparable to the thin-layer thickness. For this reason, UV excitation allows depth-resolved studies of nanolayer and interface contributions to the PCR signal which measures the effects of the deposited layer on the optoelectronic properties of the structure.

In this paper, a modified 1-D theoretical two-layer CDW and PCR model is developed taking into account the effects of the unoccupied trap density at the nanolayer bulk and the nanolayer-substrate interface. Given that the PCR frequency range used in this work, $f \le 100 \text{ kHz}$, was adequate to measure the thickness-integrated transport properties by virtue of the very thin ac carrier diffusion length¹² within the thin intrinsic hydrogenated amorphous silicon (i-a-Si:H) surface layer, but too low to spatially resolve carrier-wave transport processes within the nanolayer, for simplicity the model uses an i-a-Si:H-c-Si interface trap formalism to describe both depth-integrated a-Si layer and interface trap effects ("effective interface trap model"). The mathematical model is then used to extract the spatially overlapped transport parameters of the thin i-a-Si:H layer and the c-Si substrate, including the unoccupied interface trap density.

II. INSTRUMENTATION AND MATERIALS

A schematic diagram of the experimental PCR system is shown in Fig. 1. A 355-nm laser (Lightwave Electronics, model XCITE) was used in our experiments as a photocarrier excitation source. The beam was harmonically modulated



FIG. 1. Schematic diagram of experimental PCR system. The entire instrumentation rests on an antivibrational optical table.

using an acousto-optic modulator in the frequency range of 0.01–100 kHz. The laser beam power was ~ 27 mW and beam diameter was ~ 0.85 mm. A long-pass filter LP1000 in front of the InGaAs detector prevented laser beam leakage onto the detector. As a result, the modulated photoluminescence spectral bandwidth was in the range 1.0–1.7 μ m. The long-pass spectral cutoff of the inGaAs detector in combination with the 1000-nm long-pass filter completed the PCR spectral window (bandwidth) for eliminating thermal infrared photons from the signal. Diffuse radiative recombination-induced PCR signals were collected and collimated with two off-axis paraboloidal mirrors and were focused on the detector. They were subsequently demodulated with a lock-in amplifier (EG&G Princeton Applied Research, model 5210) and displayed as PCR amplitude and phase vs. modulation frequency.¹⁶

The samples consisted of 290- μ m thick CZ silicon wafers, on which i-a-Si:H nanolayers were deposited by DC saddle field plasma enhanced chemical vapor deposition (DCSF-PECVD) from silane gas precursor, chamber pressure of 160 mTorr, anode current 34.5 mA, substrate temperature 170 °C, gas flow rate 30 sccm, and base vacuum $< 1 \times 10^{-5}$ mTorr. The thicknesses of i-a-Si:H were 10, 30, and 90 nm for wafers #437, #438, and #439, respectively. Another wafer (#451) was divided into four sections (quadrants) using masks. 30-nm i-a-Si:H were deposited on three quadrants (both sides, front side, and back side, respectively), while there was no deposition on the fourth quadrant. In what follows, the labels "front" and "back" are used for the illuminated side and the opposite side of the wafer, respectively. The deposition of i-a-Si:H on the silicon substrate leads to significant reduction in the density of surface states and defects resulting from the discontinuity in the covalent network.

III. THEORY

A detailed theoretical treatment of the one-dimensional CDW wave in composite electronic solids with an upper thin-film layer grown or deposited on a substrate was developed by Othonos *et al.*¹⁰ The ambipolar diffusion coefficient, excess carrier lifetime, absorption coefficient for each layer, front-surface, interface, and back-surface recombination velocities are parameters involved in the theoretical description. In what follows, the presence of

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photoexcited CDW traps is considered in a modification of that theoretical model. The one dimensional cross-sectional geometry of a two-layer composite optoelectronic solid is shown in Fig. 2. The boundary-value problem is described as follows:

$$\frac{d^2}{dx^2} N_1(x,\omega) - \sigma_1^2 N_1(x,\omega) = -\frac{I_0(1-R)\beta_1}{2D_1} e^{-\beta_1 x},$$

$$0 \le x < L_1,$$
(1)

$$\frac{d^2}{dx^2} N_2(x,\omega) - \sigma_2^2 N_2(x,\omega) = -\frac{I_0(1-R)\beta_2}{2D_2} e^{-\beta_1 L_1 - \beta_2(x-L_1)},$$

$$L_1 < x \le L_2,$$
(2)

$$D_1 \frac{d}{dx} N_1(x, \omega) \bigg|_{x=0} = S_1 N_1(0, \omega),$$
(3)

$$N_1(L_1,\omega) - N_T(L_1) = N_2(L_1,\omega),$$
 (4)

$$-D_1 \frac{d}{dx} N_1(x,\omega) \bigg|_{x=L_1} + D_2 \frac{d}{dx} N_2(x,\omega) \bigg|_{x=L_1} = S_i f n_T, \quad (5)$$

$$-D_2 \frac{d}{dx} N_2(x, \omega) \bigg|_{x=L_2} = S_2 N_2(L_2, \omega),$$
(6)

where

$$\sigma_1 = \sqrt{\frac{1 + i\omega\tau_1}{D_1\tau_1}}, \quad \sigma_2 = \sqrt{\frac{1 + i\omega\tau_2}{D_2\tau_2}}, \tag{7}$$

$$N_T(L_1) = fn_T = n_{Tf}, \quad f = \frac{n_{Tf}}{n_T}, \quad n_T = n_{Tf} + n_{To}.$$
 (8)

Here N_1 , D_1 , τ_1 , and β_1 are, respectively, excess CDW concentration, ambipolar diffusion coefficient, excess carrier lifetime, and absorption coefficient in layer 1. N_2 , D_2 , τ_2 , and β_2 are the respective quantities in layer 2. S_1 , S_i , and S_2 are front-surface, interface, and back-surface recombination velocities. ω is the angular frequency of laser power modulation. I_0 is surface photon flux, R is surface reflectivity, n_T is the trap density at the interface $x = L_1$, n_{Tf} is the number density of free (unoccupied) traps, f is the effective number density of occupied trap states.

It should be noted that if f = 0, then $N_T(L_1) = 0$, i.e., no traps are unoccupied and thus no carriers from layer 1 can be

trapped. The result is carrier density continuity across the interface and N_2 is maximum: $N_1(L_1, \omega) = N_2(L_1, \omega)$. If f = 1, then $N_T(L_1) = n_T$ and N_2 is minimum: $N_2(L_1) = N_1(L_1) - n_T$. Although here n_T represents trap density at the interface, it can also play the role of the integrated distribution of trap density across the surface nanolayer as the carrier density wavelength $\lambda_{CDW}(\omega) = 2\pi/|\sigma_1(\omega)|$ is longer than the nanolayer thickness even at the highest modulation frequency to axially resolve differences between depth-integrated distribution and interface traps. Therefore, n_T generally represents the integrated effect of trap distribution through the hydrogenated amorphous layer 1, conveniently expressed as effective interface trap density. It should be mentioned that the presence of defects (gap states) in the upper (amorphous) silicon layer mainly accounts for the values of the measured recombination lifetime and ambipolar diffusion coefficient, depth-integrated (averaged) over the layer thickness. The role of the interface trap density in this context in the model is to eliminate a fraction of the photocarrier density wave diffusing toward the interface under its concentration gradient.

The solutions for the carrier density-wave equations (1) and (2) coupled through the boundary conditions are

$$N_1(x,\omega) = A_1 \cosh(\sigma_1 x) + B_1 \sinh(\sigma_1 x) + \frac{I_0(1-R)\beta_1 e^{-\beta_1 x}}{2D_1(\sigma_1^2 - \beta_1^2)},$$
(9)

$$V_{2}(x,\omega) = A_{2} \cosh(\sigma_{2}x) + B_{2} \sinh(\sigma_{2}x) + \frac{I_{0}(1-R)\beta_{2}e^{-\beta_{1}L_{1}}e^{-\beta_{2}(x-L_{1})}}{2D_{2}(\sigma_{2}^{2}-\beta_{2}^{2})}.$$
 (10)

Expressions for the integration constants A_1 , B_1 , A_2 , B_2 can be found from the boundary conditions (3)–(6) in terms of parametric constants C_1 ,..., C_5 ,

$$C_{1} = \frac{D_{1}\sigma_{1}\sinh(L_{1}\sigma_{1}) + S_{1}\cosh(L_{1}\sigma_{1})}{D_{1}\sigma_{1}\cosh(L_{1}\sigma_{1}) + S_{1}\sinh(L_{1}\sigma_{1})},$$
 (11)

$$C_2 = D_2 \sigma_2 \cosh(L_1 \sigma_2) - C_1 D_1 \sigma_1 \sinh(L_1 \sigma_2), \qquad (12)$$

$$C_{3} = D_{2}\sigma_{2}\sinh(L_{1}\sigma_{2}) - C_{1}D_{1}\sigma_{1}\cosh(L_{1}\sigma_{2}), \qquad (13)$$

$$C_4 = D_2 \sigma_2 \cosh(L_2 \sigma_2) + S_2 \sinh(L_2 \sigma_2), \qquad (14)$$

$$C_5 = D_2 \sigma_2 \sinh(L_2 \sigma_2) + S_2 \cosh(L_2 \sigma_2). \tag{15}$$

The integration constants A_1, B_1, A_2, B_2 are given by

$$A_{2} = \frac{I_{0}(1-R)}{2(C_{3}C_{4}-C_{2}C_{5})} \begin{bmatrix} \frac{C_{2}\beta_{2}(S_{2}-D_{2}\beta_{2})}{D_{2}(\sigma_{2}^{2}-\beta_{2}^{2})}e^{-\beta_{1}L_{1}}e^{-\beta_{2}(L_{2}-L_{1})} + \frac{C_{4}\beta_{2}(C_{1}D_{1}\sigma_{1}+D_{2}\beta_{2})}{D_{2}(\sigma_{2}^{2}-\beta_{2}^{2})}e^{-\beta_{1}L_{1}} \\ -\frac{C_{4}\beta_{1}(C_{1}\sigma_{1}+\beta_{1})}{(\sigma_{1}^{2}-\beta_{1}^{2})}e^{-\beta_{1}L_{1}} + \frac{C_{4}\beta_{1}(D_{1}\beta_{1}+S_{1})[\cosh(L_{1}\sigma_{1})-C_{1}\sinh(L_{1}\sigma_{1})]}{D_{1}(\sigma_{1}^{2}-\beta_{1}^{2})} \end{bmatrix} \\ + \frac{C_{4}(C_{1}D_{1}\sigma_{1}+S_{i})fn_{T}}{C_{3}C_{4}-C_{2}C_{5}}, \tag{16}$$

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$$B_{2} = \frac{I_{0}(1-R)}{2(C_{2}C_{5}-C_{3}C_{4})} \begin{bmatrix} \frac{C_{3}\beta_{2}(S_{2}-D_{2}\beta_{2})}{D_{2}(\sigma_{2}^{2}-\beta_{2}^{2})}e^{-\beta_{1}L_{1}}e^{-\beta_{2}(L_{2}-L_{1})} + \frac{C_{5}\beta_{2}(C_{1}D_{1}\sigma_{1}+D_{2}\beta_{2})}{D_{2}(\sigma_{2}^{2}-\beta_{2}^{2})}e^{-\beta_{1}L_{1}}\\ -\frac{C_{5}\beta_{1}(C_{1}\sigma_{1}+\beta_{1})}{(\sigma_{1}^{2}-\beta_{1}^{2})}e^{-\beta_{1}L_{1}} + \frac{C_{5}\beta_{1}(D_{1}\beta_{1}+S_{1})[\cosh(L_{1}\sigma_{1})-C_{1}\sinh(L_{1}\sigma_{1})]}{D_{1}(\sigma_{1}^{2}-\beta_{1}^{2})} \end{bmatrix} + \frac{C_{5}(C_{1}D_{1}\sigma_{1}+S_{i})fn_{T}}{C_{2}C_{5}-C_{3}C_{4}},$$

$$(17)$$

$$A_{1} = \frac{I_{0}(1-R)}{2[D_{1}\sigma_{1}\cosh(L_{1}\sigma_{1}) + S_{1}\sinh(L_{1}\sigma_{1})]} \left[\frac{D_{1}\sigma_{1}\beta_{2}e^{-\beta_{1}L_{1}}}{D_{2}(\sigma_{2}^{2} - \beta_{2}^{2})} - \frac{D_{1}\sigma_{1}\beta_{1}e^{-\beta_{1}L_{1}} + \beta_{1}(S_{1} + D_{1}\beta_{1})\sinh(L_{1}\sigma_{1})}{D_{1}(\sigma_{1}^{2} - \beta_{1}^{2})} \right] + \frac{D_{1}\sigma_{1}[A_{2}\cosh(L_{1}\sigma_{1}) + B_{2}\sinh(L_{1}\sigma_{1}) + fn_{T}]}{D_{1}\sigma_{1}\cosh(L_{1}\sigma_{1}) + S_{1}\sinh(L_{1}\sigma_{1})},$$
(18)

$$B_1 = \frac{I_0(1-R)\beta_1}{2D_1(\sigma_1^2 - \beta_1^2)} \left(\frac{S_1}{D_1\sigma_1} + \frac{\beta_1}{\sigma_1}\right) + A_1 \frac{S_1}{D_1\sigma_1}.$$
(19)

Finally, the PCR signal is proportional to the CDW depth integral and can be expressed as

$$S_{PCR}(\omega) = C_{L1} \int_{0}^{L_1} N_1(x,\omega) dx + C_{L2} \int_{L_1}^{L_2} N_2(x,\omega) dx, \quad (20)$$

where C_{L1} and C_{L2} are constants which depend on instrumental factors and the radiative recombination efficiencies in layer 1 and layer 2, for the i-a-Si:H layer and the c-Si substrate, respectively. It should be mentioned that two radiative emission bands are observed in a-Si:H, one at about 0.9 eV due to defects and another at 1.3-1.4 eV due to band-tail-toband-tail recombination of electrons and holes.¹⁷ Room temperature PL efficiency is significantly reduced by about four orders of magnitude; however, it is measurable under the high signal-to-noise ratio of lock-in PCR detection. The main peak of the PL and electroluminescence (EL) spectra shifts from 1.3-1.4 eV to 1.1-1.2 eV when the temperature increases to 300 K,^{18,19} whereas the 0.9 eV peak remains practically unshifted within a wide temperature range.¹⁹ These results imply that the experimental PCR signal is a superposition of contributions from (a) the upper i-a-Si:H



FIG. 2. Schematic representation of the cross-sectional geometry of a twolayer optoelectronic solid.

layer as a relatively weak radiative channel complementary to non-radiative recombination into defects associated with the layer and its c-Si interface, and (b) c-Si bulk recombination of those carriers that diffuse successfully past the i-a-Si:H-c-Si interface traps. Due to the small absorption coefficients of c-Si and a-Si:H in the optical range 1–1.7 μ m, the effects of reabsorption have been neglected. Here, it is assumed for simplicity that $C_{L1} = C_{L2} \equiv C_L$. Nevertheless, setting $C_{L1} \neq C_{L2}$ does not significantly change the values of parameters extracted from best-fitting the model to the data. The influence on $S_{PCR}(\omega)$ of various major parameters of the foregoing theoretical model was explored in order to gain physical insight into signal dependence on transport processes. The frequency dependence of $S_{PCR}(\omega)$ on the unoccupied interface trap density is shown in Fig. 3. An increase in unoccupied trap density leads to amplitude decrease due to increased carrier trapping instead of radiative recombination, and to a decrease of the phase minimum and shift to lower frequencies, Fig. 3(b). The phase minimum is the result of the trade-off between a trend for larger phase lag with increased frequency due to the finite recombination lifetime of photocarriers mostly in the substrate, and a counter-trend for shorter phase lag due to increased trapping rates closer to the surface (at the interface). The trend of the phase minimum in Fig. 3(b), in turn, is explained by the decreased diffusive flux of free photocarriers into the substrate resulting in increased carrier-wave centroid¹³ domination by short lifetime carriers within the hydrogenated amorphous layer and carrier loss at the interface. These processes result in an overall smaller phase lag closer to the front (detection) surface. Quantitatively, the substrate integral contribution to $S_{PCR}(\omega)$, Eq. (20), decreases with increased free trap density compared with the hydrogenated amorphous layer integral.

The effect of upper layer thickness with $fn_T = 1 \times 10^{19} \text{ m}^{-3}$ and $fn_T = 0$ is presented in Figs. 4 and 5, respectively. A thickness increase leads to a decrease of the $S_{PCR}(\omega)$ amplitude and the appearance of a minimum in



the phase frequency dependence when the contribution of the upper layer becomes significant. The presence of unoccupied traps enhances this phase feature. The decrease in amplitude with thickness is due to the increased recombination of short lived carriers in the hydrogenated amorphous layer which greatly reduces their density before they can diffuse to the substrate, and thus reduces the PCR amplitude. At the same time, the presence of a phase minimum even under continuity conditions, i.e., with no unoccupied traps, Fig. 5, is due to carrier-wave confinement and interference (carrier standing wave) within the upper layer. As the upper layer thickness increases, the phase minimum (antinode) decreases and shifts to lower frequency as also observed in Fig. 3(b). In summary, Figs. 4 and 5 show that the presence of interface traps enhances PCR signal sensitivity to the thickness of the hydrogenated amorphous layer.

The effect of front-surface, interface, and back-surface recombination velocities at $fn_T = 1 \times 10^{19} \text{ m}^{-3}$ on the simulated $S_{PCR}(\omega)$ frequency dependence is presented in Figs. 6–8. The increase of front-surface recombination velocity affects mainly the amplitude, leading to its decrease, Fig. 6(a), as expected, since it results in diminished free CDW and radiative recombination events. Increase in the

FIG. 3. CDW-integral amplitude (a) and phase (b) dependencies on modulation frequency at various unoccupied trap densities, fn_T : 0, 5×10^{18} , 1×0^{19} , 2×10^{19} , and 2.26 $\times 10^{19}$ m⁻³ Simulation parameters: $I_0 = 8.5 \times 10^{22}$ m⁻² s⁻¹, R = 0.549, $L_1 = 3 \times 10^{-8}$ m, $L_2 = 2.9 \times 10^{-4}$ m, $\beta_1 = 5 \times 10^8$ m⁻¹, $\beta_2 = 1.05 \times 10^8$ m⁻¹, $\tau_1 = 1.5 \times 10^{-9}$ s, $\tau_2 = 3 \times 10^{-4}$ s, $D_1 = 2 \times 10^{-8}$ m²/s, $D_2 = 8 \times 10^{-4}$ m²/s, $S_1 = 4$ m/s, $S_i = 1.8$ m/s, $S_2 = 200$ m/s.

FIG. 4. CDW-integral amplitude (a) and phase (b) dependencies on modulation frequency with thickness of upper layer, L1, as a parameter: 1 nm, 10 nm, 20 nm, 30 nm, and 34 nm. Simulation parameters: $I_0 = 8.5 \times 10^{22}$ m⁻²s⁻¹, $L_2 = 2.9 \times 10^{-4}$ R = 0.549, m. $\beta_1 = 5 \times 10^8$ m^{-1} . $\beta_2 = 1.05 \times 10^8$ 9 s, $\tau_{2} = 3 \times 10^{-4}$ s, $\tau_1 = 1.5 \times 10^{-10}$ m $= 2 \times 10^{-8}$ m²/s, $D_2 = 8 \times 10^{-4}$ D_1 $S_1 = 4 \text{ m/s},$ $S_i = 1.8 \text{ m/s},$ m^2/s , $S_2 = 200 \text{ m/s}, fn_T = 1 \times 10^{19} \text{ m}^-$

interface recombination velocity leads to significant changes in both amplitude and phase dependencies, caused by changes in CDW contributions from both the upper layer and the substrate. The increase of interface recombination velocity leads to results similar to increases in unoccupied trap density: a decrease of PCR amplitude and a more pronounced minimum in the phase frequency dependence, with the minimum shifting to lower frequencies, Fig. 7. This effect, however, is not as drastic as that due to the change in interface trap occupancy, Fig. 3. This is so because S_i and/or n_T affects the rate of interface trapping but not the number of carriers trapped. The latter results in much more pronounced PCR amplitude decreases and phase changes. The existence of S_i or n_T alone, without a critical nanolayer thickness, cannot give rise to a phase minimum. This is clearly shown in comparing Figs. 3(b), 4(b), and 7(b). Finally, the increase of back surface recombination velocity leads to amplitude decrease at low frequencies and to a shift of the "knees" of amplitude and phase dependencies to high frequencies. These effects are similar to those observed with decreased bulk recombination lifetime and point to an equivalence between the depth-integrated effects of substrate lifetime decrease and back-surface recombination velocity increase.



FIG. 5. As in Fig. 4 but with $fn_T = 0$.

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It is observed that the high-frequency phase upturn is not affected by the value of S_b , again a manifestation of the fact that it is controlled by the thin hydrogenated amorphous layer parameters on the other (front) side of the optoelectronic solid.

IV. RESULTS AND DISCUSSION

The PCR frequency scans of the four quadrants of Si wafer #451 (i-a-Si:H deposited on both sides; on the upper, or front, side only; on the back side only; and without i-a-Si:H deposition) are shown in Fig. 9. Consistent with the



FIG. 6. CDW-integral amplitude (a) and phase (b) dependencies on frequency at various front surface recombination velocities, S₁: 0, 1, 2, 5, parameters: Simulation $10 \, {\rm m/s}$. $m^{-2}s^{-1}$, $I_0 = 8.5 \times 10^{22}$ R = 0.549. $\begin{array}{c} L_1 = 3 \times 10^{-8} & \text{m}, \ L_2 = 2.9 \times 10^{-4} & \text{m}, \\ \beta_1 = 5 \times 10^8 & \text{m}^{-1}, \ \beta_2 = 1.05 \times 10^8 \end{array}$ $\begin{array}{ll} \beta_1 = 5 \times 10^8 & \text{m}^{-1}, & \beta_2 = 1.05 \times 10^8 \\ \text{m}^{-1}, & \tau_1 = 1.5 \times 10^{-9} & \text{s}, & \tau_2 = 3 \times 10^{-4} \end{array}$ s, $D_1 = 2 \times 10^{-8} \text{ m}^2/\text{s}$, $D_2 = 8 \times 10^{-4}$ $S_i = 2 \, \text{m/s},$ $S_1 = 4 \text{ m/s},$ m^2/s , $S_2 = 200 \text{ m/s}, fn_T = 1 \times 10^{19} \text{ m}^{-3}.$

FIG. 7. CDW-integral amplitude and phase dependencies on frequency at various interface surface recombination velocities, S_i : 0, 1, 2, 5, 8 m/s. Simulation parameters: $I_0 = 8.5 \times 10^{22}$ m⁻²s⁻¹, R = 0.549, $L_I = 3 \times 10^{-8}$ m, $L_2 = 2.9 \times 10^{-4}$ m, $\beta_1 = 5 \times 10^8$ m⁻¹, $\beta_2 = 1.05 \times 10^8$ m⁻¹, $\tau_I = 1.5 \times 10^{-9}$ s, $\tau_2 = 3 \times 10^{-4}$ s, $D_I = 2 \times 10^{-8}$ m/s, $D_2 = 8 \times 10^{-4}$ m/s, $S_I = 4$ m/s, $S_2 = 200$ m/s, $fn_T = 1 \times 10^{19}$ m⁻³.

FIG. 8. CDW-integral amplitude and phase dependencies on frequency at various interface surface recombination velocities, S_2 : 0, 1, 10, 100, 500 m/s. Simulation parameters: $I_0 = 8.5 \times 10^{22} \text{ m}^{-2} \text{s}^{-1}$, R = 0.549, $L_I = 3 \times 10^{-8} \text{ m}$, $L_2 = 2.9 \times 10^{-4} \text{ m}$, $\beta_1 = 5 \times 10^8 \text{ m}^{-1}$, $\beta_2 = 1.05 \times 10^8 \text{ m}^{-1}$, $\tau_1 = 1.5 \times 10^{-9} \text{ s}$, $\tau_2 = 3 \times 10^{-4} \text{ s}$, $D_1 = 2 \times 10^{-8} \text{ m}^2/\text{s}$, $D_2 = 8 \times 10^{-4} \text{ m}^2/\text{s}$, $S_1 = 4 \text{ m/s}$, $S_i = 2 \text{ m/s}$, $f_{II} = 1 \times 10^{19} \text{ m}^{-3}$.

theoretical model, the presence of the 30-nm hydrogenated amorphous silicon layer leads to the appearance of the pronounced minimum in phase frequency dependence, but no minimum appears without this layer. Because the absorption coefficient of Si at 355 nm is $1.05 \times 10^8 \text{ m}^{-1}$ (Ref. 20) corresponding to only ~10-nm optical absorption length, free photocarrier excitation originates mainly in the hydrogenated amorphous layer. The forward diffusion from this layer is the major source of carriers in the substrate along with direct excitation due to transmitted, but heavily (exponentially) attenuated, UV photon flux. It is observed that the PCR amplitude of the two-side-deposited (and passivated) Si

> FIG. 9. PCR frequency scans in four quadrants of c-Si wafer #451 with deposited 30 nm i-a-Si:H on both sides, only front side, only back side, and without deposition. (a) Amplitude and (b) phase. A schematic of the four quadrant combinations of i-a-Si:H and c-Si on the wafer is shown in the inset in (b).

I his article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to J IP: 128.100.48.8 On: Wed, 09 Jul 2014 00:25:23 quadrant is significantly larger than the front-side-only deposited quadrant. This is due to the passivation and reduction of recombination on the back surface of the former quadrant, which in turn leads to higher CDW density in the bulk of the substrate c-Si and a concomitant reduction in the density of unoccupied traps at the front interface. The trade-off between carrier bulk radiative recombination and interface trapping amounts to an effective lifetime which, in the case of the two-side-deposited quadrant, is a net lifetime increase manifesting itself as a significant shift of amplitude and phase "knees" to lower frequencies compared to the curves from the front-side-deposited quadrant. It is concluded that hydrogenated amorphous layer deposition acts as a passivation region reducing surface recombination and providing neutralization of traps/defect states through occupation at the interface or throughout the hydrogenated amorphous layer by means of the increased free carrier concentration in the c-Si substrate. It is this combined double beneficial effect of the hydrogenated amorphous layers on both surfaces that accounts for the strongly enhanced PCR signal in the double-deposited quadrant of Fig. 9.

Results of multiparameter best-fits to the data of the theoretical model are shown in Table I. Both amplitude and phase are needed together to fit uniquely the data with the large number of free floating parameters. The coefficient C_L was fixed at $3.06 \times 10^{-16} \text{ mV} \cdot \text{m}^2$ for all fits. This value was calculated from fitting PCR scans of the samples with i-a-Si:H deposited on the front surface, so that theoretical and experimental amplitudes would coincide at the first (lowest frequency) point. It should be mentioned that for simplicity reasons the model does not include back-surface interface traps. This omission is not crucial because a smaller density of diffusing photocarriers reaches the opposite side than those generated and recombining at, or near, the front surface. Therefore, in terms of the PCR signal, the back-surface-deposited hydrogenated amorphous layer can be considered as passivating the back surface, decreasing the local recombination velocity which also includes the neutralization of traps through photocarrier occupation. The evaluated transport parameters of the upper hydrogenated amorphous layer ("front side") in Table I, column 3, exhibit considerably smaller values than those of the c-Si substrate, as expected from the rich defect structure of the nanolayer. This is manifested by the front-side-deposited PCR amplitude and phase frequency curves which show a "knee" at much higher values and higher surface recombination velocity than those for the back-side-deposited wafer quadrant, Fig. 9. A comparison between the responses of the non-deposited ("no") and the front-side-deposited quadrants, while very close in amplitudes and low-frequency phases, clearly shows divergence in the high-frequency phases as the former continues to monotonically increase and saturate at $\sim -80^\circ$, while the latter exhibits the aforementioned minimum at ca. 30 kHz, Fig. 9(b), a characteristic of the presence of the surface nanolayer. The response of the two-surface-deposited quadrant ("both sides") clearly shows a very strong signal with a very long lifetime leading to a long carrier ac diffusion length, $1/|\sigma_2(\omega)|$, Eq. (7), at low frequencies compared with the laser beam diameter, therefore indicating the need for a 3-D model. A partial fitting of frequency dependences between 0.74 kHz and 100 kHz shown in Fig. 9 was performed in the case of the two-side deposited sample in order to retain the validity of the 1-D model approach. In that frequency range, the ac diffusion length shrinks and becomes small compared to the laser beam spotsize, so that the 1-D approach is valid.²¹ The data in Table I show that the unoccupied trap density at the interface significantly decreases as expected from the filling of traps at high excess carrier density in the case of both sides having been passivated compared to the rest of the structures. The diffusion coefficient in the substrate decreases in the case of both deposited sides due to carrier-carrier scattering at higher density.^{22,23} However, the carrier lifetime significantly increases due to the combined higher carrier injection level to the substrate from the hydrogenated amorphous layer and back-surface

TABLE I. Evaluated transport parameters of the front surface i-a-Si:H nanolayer and the substrate.

Fitted parameter	#451 30 nm a-Si on both sides	#451 30 nm a-Si on front side	#437 10 nm a-Si on front side	#438 30 nm a-Si on front side	#439 90 nm a-Si on front side
Recombination lifetime	1.44×10^{-3}	$4.54 imes 10^{-4}$	$7.01 imes 10^{-4}$	6×10^{-4}	6.4×10^{-4}
in c-Si wafer τ_2 , s					
Diffusion coefficient	$1.73 imes 10^{-4}$	$8.11 imes 10^{-4}$	$8.48 imes 10^{-4}$	$8.01 imes 10^{-4}$	$8.61 imes 10^{-4}$
in c-Si wafer D ₂ , m ² /s					
Interface surface recombination	1.19	2.26	9.57	8.16	6.61
velocity S _i , m/s					
Front surface recombination	2.57	3.03	8.69	3.9	7.89
velocity of i-a-Si:H upper layer S1, m/s					
Back surface recombination	3.56×10^{-1}	$1.5 imes 10^2$	$3.5 imes 10^2$	1.62×10^{2}	3.26×10^2
velocity of c-Si wafer S2, m/s					
Diffusion coefficient in i-a-Si:H	$1.62 imes 10^{-9}$	$9.02 imes 10^{-8}$	$7.14 imes 10^{-8}$	$9.59 imes 10^{-8}$	$3.43 imes 10^{-7}$
upper layer D_1 , m ² /s					
Recombination lifetime in	$1.1 imes 10^{-9}$	$1.54 imes 10^{-9}$	$1.05 imes 10^{-9}$	$2.65 imes 10^{-9}$	1×10^{-8}
i-a-Si:H upper layer τ_1 , s					
Absorption coefficient of	$2.24 imes 10^8$	2.48×10^8	$9.45 imes 10^8$	3.97×10^8	$7.64 imes 10^8$
i-a-Si:H upper layer β_1 , m ⁻¹					
Density of free (unoccupied)	$7.58 imes10^{17}$	2.77×10^{20}	$3.76 imes 10^{20}$	$2.81 imes 10^{20}$	2.91×10^{20}
traps at interface fn_T , m ⁻³					

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passivation. As a result, traps at the hydrogenated amorphous layer-substrate interface are occupied and the free-carrier capture probability decreases yielding a high density of free carriers with the longest lifetime resulting in the highest amplitude and lowest-frequency phase lag of all four quadrants. The high-frequency phase lag exhibits the familiar minimum associated with the nanolayer presence.

PCR frequency scans of Si wafers #437, #438, and #439 deposited with 10, 30, and 90 nm thickness of i-a-Si:H on one (front) surface, respectively, are shown in Fig. 10. The experimental frequency dependencies follow the features shown in the simulations of Fig. 4. The phase extremum appears only for upper layer thicknesses above 10 nm, it shifts to lower frequency and decreases in depth with increasing layer thickness. The amplitude decreases with increasing layer thickness and becomes very small at 90-nm hydrogenated amorphous silicon thickness due (a) to the very small photoluminescence from the upper layer where transport parameters are significantly worse than in the substrate, and (b) to the small number of carriers that can diffuse through the interface into the substrate. The best-fit parameters to Eq. (20) for substrate and upper layer with the three i-a-Si:H thicknesses are shown in the last three columns of Table I. The i-a-Si:H laver thickness change on the front surface from 10 nm to 90 nm does not lead to any noticeable changes in substrate transport parameters, and the lifetime and diffusion coefficient of the i-a-Si:H layer remain significantly lower than those of the substrate for all tested thicknesses. From the foregoing UV PCR results, it is concluded that carrier transport in the i-a-Si:H-c-Si system is largely controlled by the upper layer and/or interface defects, the density of which only weakly depends on layer thickness. This result is consistent with the well-known fact that high quality crystalline silicon has good enough bulk properties so that lifetime in particular is very much dominated by surface effects, in particular dangling bond states.

FIG. 10. PCR frequency scans of silicon wafers #437, #438, #439 with deposited i-a-Si:H on one side with thickness 10 nm, 30 nm, and 90 nm with configuration of i-a-Si:H on the front.

PCR frequency scans from the side with the i-a-Si:H layer are shown in Fig. 10, and those performed from the side without i-a-Si:H layer are shown in Fig. 11. The samples were simply flipped over to probe the configuration with the hydrogenated amorphous nanolayer on the back surface. The results are similar to those observed in Fig. 9 for the case of no i-a-Si:H on the front surface and all phases exhibit saturation at high frequencies. The theoretical model was further used to describe the so called "dead layer"²⁴ when no i-a-Si:H is deposited on the front surface. This layer is clearly observed in semiconductors as a threshold voltage in the cathodoluminescence (CL) intensity dependence on accelerating voltage that can change the excitation depth over a wide range. Little or no CL is observed when the electron range is below the "dead layer" thickness. The nature of the "dead layer" is usually explained by the presence of a surface space charge region with high density of surface states, or by a high concentration of lattice defects in this layer. The details of the surface charge region effects on the PCR signal are described elsewhere.²⁵ Involving the concept of the dead layer is necessary in the description of near-surface UV-PCR characteristics without the a-Si layer. Normally, the concept of finite surface recombination velocity is sufficient for describing the state of a semiconductor surface using long excitation wavelengths with large optical absorption length. It is shown that the surface recombination velocity is very large for all non-deposited back surfaces, as can be seen for samples # 451, 437, 438, and 439 in Table I. Those measurements are feasible due to carrier diffusion and recombination at the rear surface. However, for front-surface UV excitation of non-deposited samples, the role of a dead layer becomes important due to the very small absorption depth under 355-nm laser excitation. Consistent with the CL results, the invocation of this very thin layer beyond the surface recombination velocity, with its own transport parameters,



FIG. 11. PCR frequency scans of the same silicon wafers as in Fig. 9 with the sample flipped over so that i-a-Si:H was on the back side. (a) Amplitude and (b) phase.

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FABLE II. Evaluated transpo	ort parameters of the	"dead layer" a	and the substrate	without i-a-Siz	:H nanolayer or	the front surface.
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Fitted parameter	#451 30 nm a-Si on back side	#451 no a-Si	#437 10 nm a-Si on back side	#438 30 nm a-Si on back side	#439 90 nm a-Si on back side
Recombination lifetime	3.51×10^{-4}	$3.9 imes 10^{-5}$	3.69×10^{-4}	$3.7 imes 10^{-4}$	$3.39 imes 10^{-4}$
in c-Si wafer τ_2 , s					
Diffusion coefficient in c-Si wafer D ₂ , m ² /s	$7.18 imes 10^{-4}$	6.45×10^{-4}	7.21×10^{-4}	$6.4 imes 10^{-4}$	6.7×10^{-4}
Interface surface recombination velocity S _i , m/s	3.42	2.42	8.22	1.84	1.8
Front surface recombination velocity of "dead layer" S ₁ , m/s	3.38	4.83	5.35	2.46	2.7
Back surface recombination velocity of c-Si wafer S ₂ , m/s	1.09	$1.98 imes 10^2$	2.88	6.11×10^{-1}	1.23
Diffusion coefficient in "dead layer" D_1 , m ² /s	8.21×10^{-5}	2.54×10^{-4}	$1.73 imes 10^{-4}$	4.86×10^{-5}	9.53×10^{-5}
Recombination lifetime in "dead layer" τ_1 , s	$1.31 imes 10^{-4}$	2.88×10^{-5}	$1.13 imes 10^{-4}$	$1.89 imes 10^{-4}$	8.95×10^{-5}
Absorption coefficient of "dead layer" β_1 , m ⁻¹	3.02×10^8	3.31×10^8	4.61×10^8	$2.54 imes 10^8$	$2.84 imes 10^8$
Density of free (unoccupied) traps at interface fn_T , m ⁻³	2.65×10^{21}	2.48×10^{21}	1.33×10^{21}	4.19×10^{21}	4×10^{21}

Table II, is necessary in the application of the UV-PCR theory to the non-deposited samples in order to achieve reasonable agreement with the experimental data, as the optical penetration length becomes commensurate with the surface charge region (~a few nm). In practice, without the introduction of the dead layer it is impossible to derive from the PCR frequency curves physically sensible transport parameters of the substrate with and without a hydrogenated amorphous silicon layer by fitting the data with the same constant C_L , Eq. (20). In the present case, the thickness of the dead layer was assumed to be 10 nm. This value was chosen because both amplitude and phase frequency scans for c-Si without a deposited hydrogenated amorphous layer, Fig. 9, and with 10-nm i-a-Si:H on the front surface, Fig. 10, are very close. It is also true that small variations in the real thickness of the dead layer from 10 nm can be compensated by an adjustment in the transport parameter values while the trends in the parameters are the same. Results of multiparameter fitting to the two-layer theoretical model developed in this work with the upper layer taken as the dead layer are shown in Table II. The derived values for the front surface recombination S_1 , interface recombination S_i , diffusion coefficient D_1 , lifetime τ_1 , and absorption coefficient β_1 describe the dead layer in this case. The hydrogenated amorphous silicon on the back side of the substrate was characterized only by a back-surface recombination velocity S_2 . The evaluated transport parameters show a degree of similarity with those of the substrate c-Si for the flipped-over samples with i-a-Si:H on the back side. The absence of hydrogenated amorphous silicon on the back surface leads to a decrease in carrier recombination lifetime in the substrate and significant increase of the back-surface recombination velocity. Recombination or carriers on the back surface leads to an overall carrier density decrease in the substrate which, in turn, increases the density of unoccupied traps at the interface, leading to interface recombination rate increase and bulk carrier lifetime decrease.

V. CONCLUSIONS

Optical excitation of passivating hydrogenated amorphous nanolayer semiconductor structures on c-Si with a UV laser beam and use of the PCR frequency response yields excellent depth resolution in optoelectronic transport studies of the thin upper nanolayer due to its high absorption coefficient at 355 nm. A standard 1-D two-layer PCR theoretical model was modified to introduce effective photocarrier traps at the interface or, equivalently, to account for trapping rates across the thickness of the nanolayer and at the interface. Using a variance minimizing multi-parameter fitting procedure, carrier recombination lifetimes, ambipolar diffusion coefficients, front- and back-surface and interface recombination velocities, as well as effective unoccupied trap densities at the interface and the absorption coefficient of the i-a-Si:H layer at the UV excitation wavelength were evaluated from the PCR amplitude and phase frequency dependences. The physical picture emerging from these quantitative results concluded that i-a-Si:H deposited on both sides of a c-Si wafer leads to very significant increase of carrier lifetime and density in the substrate, accompanied by a concomitant decrease of the effective unoccupied traps density at the interface. It was also shown that a defect or surface-stateinduced "dead laver" familiar from cathodoluminescence (a surface space charge region with high density of surface states) is present at surfaces not deposited with a passivating hydrogenated amorphous layer and the developed theoretical model was used to characterize the dead layer.

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