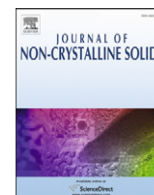
Journal of Non-Crystalline Solids 436 (2016) 44–50

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol



Impact of band tail distribution on carrier trapping in hydrogenated amorphous silicon for solar cell applications

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A R T I C L E I N F O

Article history:
Received 2 November 2015
Received in revised form 5 January 2016
Accepted 11 January 2016
Available online 12 February 2016

Keywords:
Carrier trapping
Optical pump-probe technique
Hydrogenated amorphous silicon (a-Si:H)
Solar cells
Photocurrent

A B S T R A C T

Carrier trapping in hydrogenated amorphous silicon (a-Si:H) has been investigated by means of an optical pump-probe technique. The trapped carriers (electrons) at the conduction band tail are detected as an increment of the photocurrent, and their density is quantitatively determined under the assumption of carrier generation and recombination kinetics. We find that carrier trapping strongly depends on the band tail distribution in addition to the pump light intensity. Specifically, the trapped electron density increases with the Urbach energy that characterizes the valence band tail broadening. Under the condition of a pump light intensity of 10 mW/cm^2 operated at 532 nm, the trapped electron density is determined to be $\approx 4 \times 10^{17}$ cm^{-3} for an intrinsic a-Si:H film with an Urbach energy of 45 mV. The effects of carrier trapping on the device performance are studied in single-junction a-Si:H p-i-n solar cells. The results suggest that carrier trapping causes a reduction in the fill factor of the solar cells.

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1. Introduction

Carrier trapping is a key factor that restricts carrier transport in amorphous semiconductor devices [1–5]. Once carriers are trapped in those devices, particularly in the active layer, the trapped carriers result in the Shockley–Read–Hall (SRH) recombination [6], and thereby the carrier lifetime is reduced. Besides, an accumulation of trapped carriers induces the quasi-Fermi level shift accompanying band bending [7,8], which may degrade the carrier collection. The carrier trapping thus impacts on the carrier recombination and collection so that studies on carrier trapping are beneficial for understanding the carrier transport and improving the device performance.

In amorphous semiconductors such as hydrogenated amorphous silicon (a-Si:H), carriers can be trapped at gap states (also called localized states) associated with various defects. The gap states are usually classified into two groups: the band tail states and the mid-gap states [9,10]. The band tail states, related to the network disorder, are extended from the conduction and valence band (CB and VB) edges. The CB tail states exhibit electron traps whereas the VB tail states exhibit hole traps [6]. Because of the existence of these traps, the carrier mobility, μ, is strongly limited. On the other hand, the mid-gap states, originating from dangling bonds (DBs), are formed near the middle of bandgap. They behave as recombination centers for carriers. So, the carrier lifetime, τ, is often governed by the density of these mid-gap states [6].

Among amorphous semiconductors, a-Si:H is widely used for various device applications. For example, in thin-film Si solar cells [11,12], an a-Si:H film is used as a photovoltaic layer that plays important roles in carrier transport as well as light absorption. In amorphous/crystalline Si (c-Si) hetero-junction solar cells [13,14], a thin layer of a-Si:H is employed to passivate the c-Si surface and also selectively transfer carriers, i.e., either electrons or holes to electrodes. The passivation and selective transfer are known to be required for this kind of high-efficiency solar cells [15].

So far, carrier trapping in an a-Si:H film has been well studied by time of flight technique [2–5]. The gap states, i.e., the origin of carrier trapping, have been characterized by several methods such as constant photocurrent method (CPM) [16–19], Fourier transform photocurrent spectroscopy (FTPS) [20,21], modulated photocurrent (MPC) spectroscopy [22], and deep level transient spectroscopy (DLTS) [23–25]. Particularly, the density of mid-gap states, related to DBs, have been quantified by electron spin resonance (ESR) [26,27]. Furthermore, the distribution of the mid-gap states is studied by dual-beam photoconductivity (DBP), in which the bias light is used to precisely control the quasi-Fermi level [28]. Nevertheless, the impact of the gap state distribution on carrier trapping and the device performance have not been investigated systematically.

In this paper, we investigate carrier trapping in intrinsic a-Si:H films from the viewpoint of the band tail distribution. The trapped carrier (electron) density at the CB tail are determined quantitatively, using an optical pump-probe technique. This technique has been already applied to in-situ monitoring of film growth processes in a-Si:H [29]. Because of its high sensitivity and convenience, we extend this technique to ex-situ characterization of a-Si:H in this article. One advantage of this technique is that one can evaluate the density of electron traps in the samples with a thickness of up to several hundred nm [29],

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http://dx.doi.org/10.1016/j.jnoncrysol.2016.01.021
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which includes the typical thickness in the state-of-art a-Si:H solar cells [11,12]. This is in contrast with the case of time-of-flight technique, where the samples having a thickness of several micron meters are necessary [2–5]. Using this pump-probe technique and CPM, a correlation between the trapped electron density and the VB tail broadening is studied. The effects of carrier trapping on the device performances are examined in a-Si:H p-i-n solar cells.

The paper consists of the following parts. In the next section (Section 2), a theory for carrier generation and recombination is briefly described to derive the trapped carrier density. In experimental section (Section 3), we explain sample preparation, trap characterization techniques, and a-Si:H solar cell structure. In results and discussion (Section 4), the trapped carrier density, the tail state distribution and the device performance are reported. The occupation, the origin of traps, carrier transport and trapping are then discussed. Finally, the solar cell performances are examined in terms of carrier transport and trapping.

2. Theory

The trapped carriers are detected by an optical pump-probe technique, using the experimental setup shown in Fig. 1. The pump generates carriers and fills the traps, whereas the probe emits trapped carriers to the CB (see also Fig. 2(a)). The pump pins the quai-Fermi level that is not influenced by the probe (this will be confirmed in Section 4.1). The generated carriers are collected with contacts and measured as a photocurrent. The photocurrent is slightly increased while a sample is illuminated with the probe in addition to the pump [30]. This increase originates from de-trapping of carriers, and thus trapped carriers are measured as an increment of the photocurrent. We hereafter call it a trap current.

In a steady state, the photo and trap currents, I_p and I_t, are given by

$$I_p = eg_v\tau v_d, \quad (1)$$

$$I_t = eg_t\tau v_d, \quad (2)$$

where e, g_v, g_t, τ, and v_d are the elementary charge, the carrier generation rates under pump and probe illumination (Fig. 2(a)), the recombination lifetime and the drift velocity of carriers, respectively. Here, the recombination is characterized by τ, and is predominated by a trap mediated SRH type [6] for large mid-gap states and tunneling phenomena for large band tail states [9]. For carrier generation, g_v and g_t, are expressed as follows.

$$g_v = n_v\sigma_v\Gamma_{\text{pump}}, \quad (3)$$

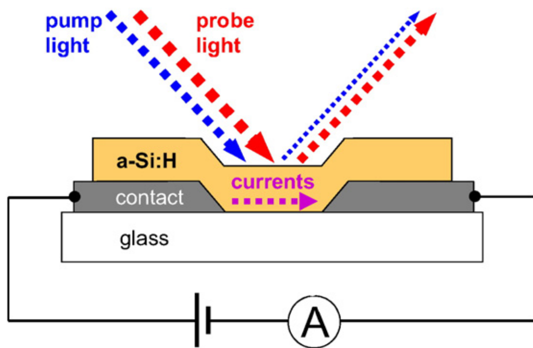

Fig. 1. Schematic view of experimental setup. An a-Si:H film is illuminated with the pump and probe light to induce the photo and trap currents. The pump and probe light intensities are modulated at different frequencies, and the oscillating photo and trap currents are detected with a lock-in technique. The sample structure is a-Si:H film (220 ± 10 nm) on a glass substrate with interdigitated contacts. The contacts are biased at 10 V with respect to each other.

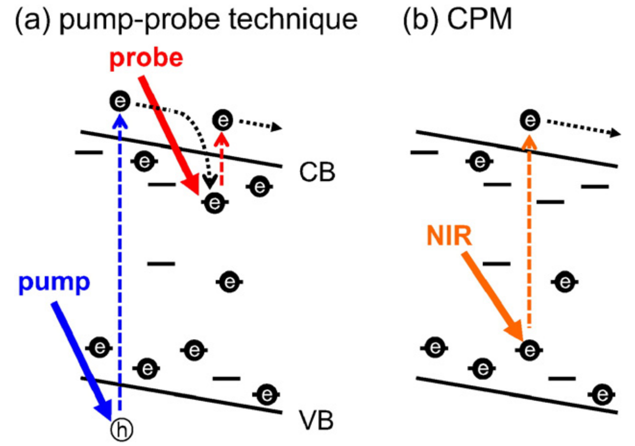

Fig. 2. Carrier dynamics in a pump-probe technique and constant photocurrent method (CPM). (a) In a pump-probe technique, the pump light generates free carriers and fill the traps, whereas the probe light emits trapped carriers (electrons) at the CB tail to the CB. (b) In CPM, quasi-monochromatic near infrared (NIR) light excites electrons at the VB tail to the CB.

$$g_t = n_t\sigma_t\Gamma_{\text{probe}}, \quad (4)$$

where, n_v, n_t, σ_v, σ_t, Γ_{pump}, and Γ_{probe} are the densities of the valence and trapped carriers (electrons), the photoabsorption cross sections of the valence and trapped carriers (electrons), and the photon fluxes of the pump and probe light, respectively. Dividing I_t by I_p, the trapped carrier density, n_t, is derived as follows.

$$n_t = \frac{\sigma_v\Gamma_{\text{pump}}}{\sigma_t\Gamma_{\text{probe}}}\frac{I_t}{I_p}n_v. \quad (5)$$

We remark here that n_t is not a function of τ since it is canceled out when dividing I_t by I_p. For convenience, we normalize n_t by n_v. The normalized trapped carrier density, n_t/n_v, is thus given by

$$n_t/n_v = \frac{\sigma_v}{\sigma_t}\frac{\Gamma_{\text{pump}}}{\Gamma_{\text{probe}}}\frac{I_t}{I_p}. \quad (6)$$

In this study, we assume $\sigma_v/\sigma_t = 1$ since the optical matrix elements of a-Si:H films are less-dependent on the photon energy in a range of $h\nu = 0.6$ to 3.0 eV [31]. A similar assumption is also described in Ref. [32] for examining the sub-gap absorption spectra. The pump and probe photon energies used in this study are included in this range, described later (Section 3.2).

3. Experimental

3.1. Preparation of a-Si:H films

In order to demonstrate the usefulness of the optical pump-probe technique for evaluating the density of trapped electrons in a-Si:H, we have applied this technique to a series of a-Si:H samples where the growth temperature was varied. Intrinsic a-Si:H films were prepared on glass substrates by means of plasma enhanced chemical-vapor-deposition (PECVD), at various growth temperatures of T_g = 373 K–593 K. Our PECVD was operated using a 60 MHz capacitively-coupled discharge of a hydrogen (H_2) and silane (SiH_4) gas mixture in parallel-plate configuration. The gas mixture was introduced from the powered (PWD) electrode showerhead; the H_2 and SiH_4 flow rates were 50 sccm and 10 sccm, respectively. The discharge was sustained between the PWD and electrically grounded (GND) electrodes by applying a voltage of 35 V peak to peak at a pressure of 0.3 Torr. The electrode gap was set at 22 mm. We placed a glass substrate on the GND

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