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Characterization

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Photoluminescence Characterization of Hydrogenated Nanocrystalline/Amorphous Silicon

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ABSTRACT

The photoluminescence in a nc-Si/a-Si:H mixture has been investigated at varying excitation intensities, and temperatures We have also observed changes in the luminescence spectra, which are induced by sequential annealing at temperatures below the a-Si:H crystallization temperature (~ 600°C). Two predominant luminescence peaks are observed at ~ 0.95 eV and ~ 1.30 eV, which are attributed to band tail-to-band tail transitions near the nc-Si grain boundaries and in the a-Si:H bulk, respectively. The 0.95 eV band saturates approaching 500 mW/cm^2 excitation intensity. Annealing the nc-Si/a-Si:H mixture brings out a new low energy peak, centered at ~ 0.70 eV, and which we believe to be due to oxygen defects.

INTRODUCTION

In order to optimize hydrogenated nanocrystalline/amorphous silicon (nc-Si/a-Si:H) for photovoltaic applications we must better understand its electrical and optical properties, especially those at the nc-Si/a-Si:H interfacial regions. We present data from an exploratory round of photoluminescence experiments, which shed light on the nature of the electronic structure of nc-Si/a-Si:H. Investigating the luminescence behavior of a nc-Si/a-Si:H mixture under various excitation intensity and temperature conditions reveals several differences between the electronic structure of the nc-Si phase from that of a-Si:H.

Radiative transitions signified by emission at ~ 1.3 eV occur when excited carriers recombine radiatively across band-tail states in a-Si:H [1]. In poly-Si and mixed phase silicon the large number of defects in grain boundary regions, namely variation in bond lengths and angles, causes local fluctuations in the electric potential. These effects form localized states in the band gap and give rise to band-tails [2]. Emission at 0.9 eV in poly-Si [2, 3] occurs by carrier recombination across these band-tail states, and a band observed at ~ 0.9 – 1.0 eV in μc-Si/a-Si:H systems is believed to involve similar band-tail states [4].

The decay of PL with increasing temperature occurs due to the increased probability of non-radiative recombination when carriers have sufficient (thermal) energy to hop to nearby states [1]. Dangling bonds, interfaces, and defects provide pathways for excited carriers to lower their energy without radiative recombination.

Both the luminescence decay with increasing temperature and the excitation intensity dependence of PL depend on local electronic structure. Band-tail luminescence in a-Si:H typically increases with temperature at very low temperatures, plateaus at ~ 50 K, and decreases rapidly above 80 K [1, 5]. Detection of nc-Si luminescence at room temperature and its unique luminescence decay with increasing temperature suggests fundamental differences in the local electronic structure near nc-Si grain boundaries compared with a-Si:H. Excitation intensity dependence of the PL emitted by our nc-Si/a-Si:H mixture also shows a striking difference between nc-Si grain boundaries and a-Si:H. Observing that the band attributed to nc-Si saturates with increasing excitation intensity while the a-Si:H signal intensity continues to rise over the

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entire range investigated allows us to speculate about the relative density of luminescent states in these regions.

Changes in the luminescence profile induced by sequential annealing provide insight regarding thermally activated processes in this system. Several authors argue that a low energy PL band centered at ~ 0.7 eV arises from oxygen defect states in silicon systems [3, 4, 6]. In every case, thermal exposure seems to play a role in determining whether this band emerges. Based on past work and our observations we argue that thermal energy provided by annealing promotes oxygen agglomeration, and that 0.7 eV PL involves donor states related to oxygen precipitates.

EXPERIMENTAL DETAILS

United Solar Ovanic made the samples used in these experiments, which contain intrinsic nc-Si/a-Si:H mixtures characteristic of high quality PV devices. The nc-Si/a-Si:H layers, ~ 1 μm thick, were grown by PECVD on stainless steel substrates and capped with a transparent conducting oxide. The nc-Si/a-Si:H mixture is believed to be ~ 50% crystalline, and contain crystallites averaging 20 nm in grain diameter.

A Coherent Inova 300 cw argon laser, and a Nicolet MagnaIR 860 spectrometer interfaced with Thermo Fisher Omnic software, produced the PL spectra. Filters transmitting in the spectral range of the sample emission reduced background noise and blocked reflected excitation radiation from the detector. Interference fringes, which arise from constructive and destructive effects in the nc-Si/a-Si:H layer, have been removed from all of the presented spectra as is customarily done in FTPL spectroscopy. An APD HC-2 helium compressor cryostat system was used to obtain the desired operating temperatures.

The temperature dependent experiments used 514.5 nm excitation, at 800 mW/cm^2, and the intensity dependent experiments used 488 nm excitation. Two intensity dependent experiments were performed at 18 K. In one case the power density was kept below 600 mW/cm^2, and in the other the power density was allowed to reach 1.2 W/cm^2. We normalized the two data sets by the luminescence detected at 240 mW/cm^2 to create a combined plot showing the PL dependence over the full intensity range investigated.

Isochronal annealing consisted of 20 minute exposures at the specified temperatures, with 20 minutes of ramp-up time, and several hours of cooling. A small passageway in the furnace wall permitted air flow at atmospheric pressure during annealing. The samples were successively annealed at 180°C, 260°C, 330°C, 400°C, 450°C, 500°C, and 550°C, and the luminescence was measured at 18 K after each anneal. SIMS characterization of several samples reveals the oxygen content in the nc-Si/a-Si:H layer before annealing and after a 350 °C exposure.

RESULTS

We attribute two strong PL bands in the unannealed nc-Si/a-Si:H mixture, centered at ~ 0.95 eV and 1.3 eV, to band tail-to-band tail transitions at nc-Si crystal surfaces and to band-tail to band-tail transitions in the bulk a-Si:H, respectively [1, 4].

The luminescence attributed to nc-Si surfaces (gain boundaries) varies with excitation intensity as $I_{nc\text{-}Si} \sim I_{ex}^{0.4}$ between 15 and 400 mW/cm^2, and saturates at power densities approaching 500 mW/cm^2. The a-Si:H luminescence increases with excitation intensity as $I_{a\text{-}Si}$

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~ $I_{ex}^{0.8}$ between 15 mW/cm^2 and 1.2 W/cm^2 with no evidence of saturation. Figure 1 shows the normalized PL signal from a-Si:H and nc-Si phases as a function of the excitation intensity.

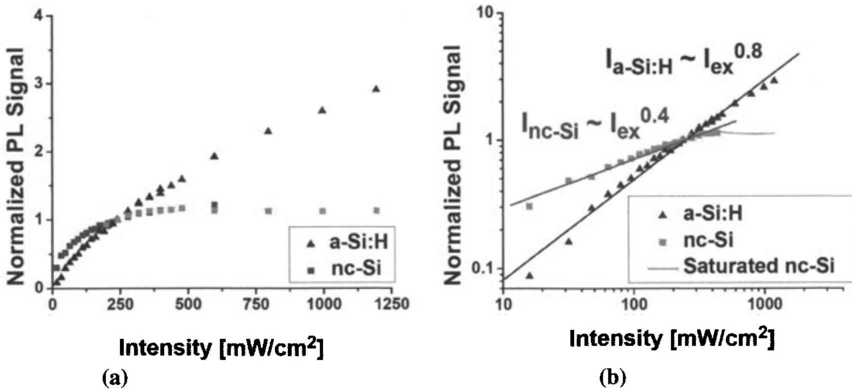
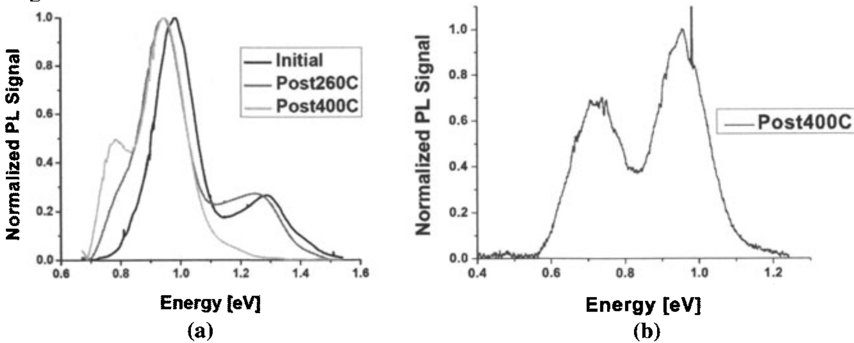


Figure 1: Photoluminescence excitation intensity dependence of the 1.3 eV and 0.95 eV bands **(a)** on linear axes **(b)** on log scale axes

Annealing this nc-Si/a-Si:H mixture at temperatures below the a-Si:H crystallization temperature (~ 600°C) produces a red-shift in the a-Si:H and nc-Si luminescence peaks. This behavior is shown in Figure 2. The a-Si:H luminescence peak shifts to 1.25 eV after 20 minutes at 260°C, and moves further to 1.15 eV after a subsequent 20 minutes at 330°C. After 400°C annealing, the luminescence from the a-Si:H regions is no longer observed, and annealing at 550°C causes all of the luminescence peaks to vanish.

After annealing at 260°C for 20 minutes, a soft shoulder becomes apparent on the low energy side of the nc-Si peak. This peak, which we label here a "defect" peak, becomes more pronounced after annealing at 400°C. Using an MCT detector, which does not distort the line-shape, this peak is centered at ~ 0.7 eV (Figure 2.b). We note that the defect peak holds its position from 18 to 130 K, while the 0.95 eV PL shifts noticeably over the same temperature range.



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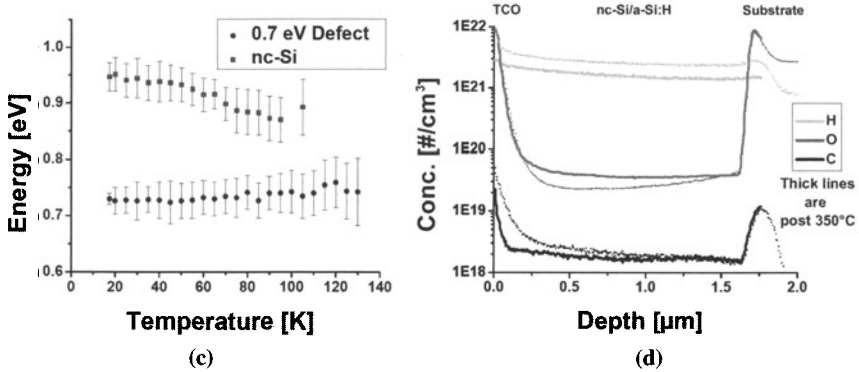
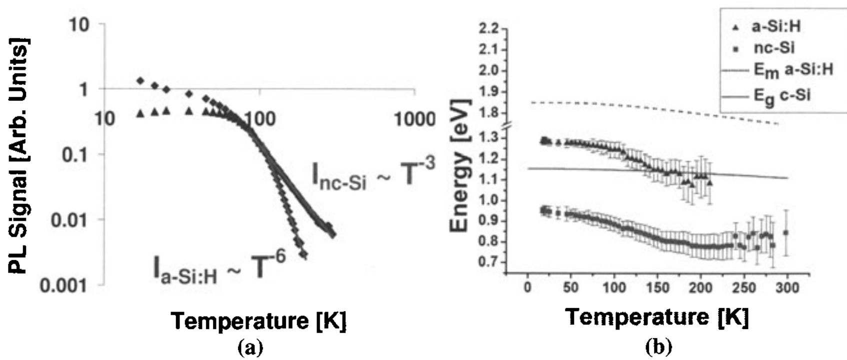


(c) (d)

Figure 2: Response of the nc-Si/a-Si:H mixture to annealing – PL **(a)** detected with an InGaAs detector, **(b)** detected with an MCT detector, **(c)** temperature dependence of the "defect" and nc-Si grain boundary bands. **(d)** SIMS depth profile before and after annealing

The temperature dependence of the peak attributed to nc-Si grain boundary regions shows several differences from that attributed to the a-Si:H bulk regions (Figure 3). The nc-Si signal decays rapidly from 17 to 80 K, then tails off slowly as the temperature increases further with detectable luminescence at room temperature. The a-Si:H signal increases slightly with temperature initially, plateaus between 25 and 50 K, and decreases rapidly above 80 K. The a-Si:H band falls below our detection limit above about 230 K. Above 80 K, the luminescence signal attributed to nc-Si decays more slowly than that from the a-Si:H, and appears to follow a power-law decay with increasing temperature as $I_{nc\text{-}Si} \sim T^{-3}$. The a-Si:H band decays as $I_{a\text{-}Si:H} \sim T^{-6}$ above 100 K. The luminescence peaks both red-shift as temperature increases from 17 to 300 K (Figure 3.b), and in each case the shift exceeds that of the crystalline Si band gap and the mobility gap in a-Si:H [7, 8].



(a) (b)

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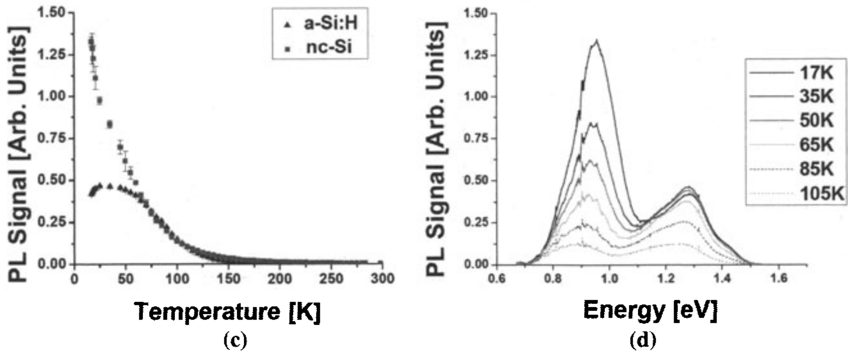

(c) (d)

Figure 3: **(a)** PL intensity temperature dependence power laws, **(b)** red-shifts, **(c)** signal decay, and **(d)** line shapes from the nc-Si/a-Si:H mixture at various temperatures

DISCUSSION

To interpret the saturation of the 0.95 eV band which occurs for excitation intensities approaching 500 mW/cm^2, one must consider the limiting quantities which determine photoluminescence intensity. Here we present the following relationship [1]:

$$I_{PL} = \frac{N_{occ}}{\tau} \quad (1)$$

In equation 1, N_{occ} is the number of occupied states which give rise to radiative recombination, and τ is the recombination lifetime.

The number of nc-Si surface band-tail states which we believe give rise to the observed 0.95 eV luminescence is finite, limiting N_{occ}. When these band tail states fill, additional carriers are unable to thermalize into them and are more likely to find pathways for nonradiative recombination [1]. When the rate of carrier generation approaches the radiative recombination rate, the corresponding luminescence saturates. Amorphous silicon band tail-to-band tail luminescence saturates by this mechanism at excitation intensities higher than those we investigated [1]. A rough calculation, assuming the relative density of nc-Si surface band tail states scales directly with the volume fraction of the grain boundary regions in the material, suggests that nc-Si surface band tail states make up only ~ 1% of the total density of states. This limited number of states is consistent with the fact that the nc-Si surface band-tail to band-tail luminescence saturates at lower excitation intensity than the luminescence band in a-Si:H.

The 0.9 eV band attributed to band tail-to-band tail transitions at nc-Si grain boundaries has previously been observed in polycrystalline Si to follow a power law dependence as $I_{0.9\,eV} \sim I_{ex}^{0.6}$ [2]. Our 0.9 eV band was less sensitive, varying with intensity only by $I_{0.9\,eV} \sim I_{ex}^{0.4}$. The luminescence attributed to a-Si:H shows the strongest dependence on excitation intensity.

Transitions involving band tail states have a unique temperature dependent signature. As the temperature increases, carriers trapped in localized states are able to thermalize either to higher energy localized states or to the mobility edge. This enhanced diffusion allows carriers to find non-radiative recombination pathways more easily. In addition, the depopulation of shallow states reduces the number of transitions which give

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rise to the higher energy part of the band tail-to-band tail luminescence band [2]. Since the 0.7 eV defect band does not shift with increasing temperature, this band is unlikely due to band-tail to band-tail transitions [4]. In fact, at least one of the carriers involved is probably deeply trapped.

The emergence of the defect band in all of the Si systems investigated appears to be thermally activated and associated with the c-Si phase. Tajima observed 0.7 eV PL in annealed CZ-grown c-Si and proposes that oxygen precipitates form during annealing and create oxygen donor states [6]. In the μc-Si/a-Si:H experiment [4] films deposited at substrate temperatures above 300°C show 0.7 eV PL, while films grown on cooler substrates do not. Furthermore, of the films grown at high substrate temperature, only those with significant μc-Si phase formation show 0.7 eV PL [4]. We observe the defect band in nc-Si/a-Si:H only after annealing, and higher temperature exposure causes this band to become more pronounced.

To monitor oxygen levels in our samples, we subjected several to SIMS analysis (Figure 2.d). The oxygen content in the middle of the nc-Si/a-Si:H layer, initially ~ 2×10^{19} /cm^3, almost doubles in response to a 350°C anneal. The SIMS depth profile shows that the oxygen concentration decreases moving deeper into the nc-Si/a-Si:H layer, which suggests that the transparent conducting oxide (TCO) provides additional oxygen to nc-Si/a-Si:H during annealing. However, it remains unclear whether additional oxygen from the TCO causes the formation the defect giving the observed 0.7 eV luminescence, or whether the nc-Si/a-Si:H mixture develops this defect state given thermal energy regardless of the presence of a TCO. Diffuse oxygen incorporated during deposition of the nc-Si/a-Si:H may be enough to form the oxygen agglomerate donor states described by Tajima [6]. Whatever the source of the oxygen in the nc-Si/a-Si:H mixture, the SIMS data supports the conclusion that the emergence of 0.7 eV luminescence in nc-Si/a-Si:H is thermally activated, and related to oxygen defects.

ACKNOWLEDGEMENTS

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Infrared photoconductivity in heavily nitrogen doped a-Si:H

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ABSTRACT

High frequency steady-state photoconductivity in nitrogen doped hydrogenated amorphous silicon (a-Si:H-N) films has been demonstrated at infrared (IR) frequencies of 650 to 2000 cm^{-1}. This allows IR photoconductivity to be excited using a simple thermal source. In order to produce high frequency photoconductivity effects, the plasma frequency must be increased to the desired device operation frequency or higher as described by the Drude model. IR ellipsometry was used to measure the steady-state permittivity of the a-Si:H-N films as a function of pump illumination intensity. The largest permittivity change was found to be $\Delta\varepsilon_r = 2$ resulting from a photo-carrier concentration on the order of 10^{22} cm^{-3}. IR photoconductivity is shown to be limited by the effective electron mobility.

INTRODUCTION

Thin film systems with IR conductivity or permittivity that may be actively tuned with the application of a DC electric field, have been of interest for some time to IR designers. As an alternative, photoconductive devices have been proposed for active IR systems. The carrier concentration can be actively changed by illuminating a-Si:H with source energy above the band gap and thus out of the IR band. This illumination results in the generation of electron-hole pairs, and a sufficient density of these carriers will result in a change in the material's permittivity in the IR frequency range. Thus, by varying out-of-band pump power, an active IR system may be achieved.

Photoconductive elements have been used for optically generated grid arrays and as switches for reconfigurable antennas at 40 GHz [1]. In these low frequency designs high resistivity Si wafers have been used as the photoconducting elements. Due to the nanoscale size of IR systems patterned a-Si:H thin films must be used for photoconducting elements, and a higher carrier concentration is required for a contrast in permittivity. The generated electron-hole pairs form a pseudo-metallic plasma with behavior described by the Drude model. Eq. 1 gives the permittivity of the photoconductive semiconductor as the difference between the dark permittivity $\varepsilon_L(\omega)$ and a photo-plasma term

$$\varepsilon_r(\omega) = \varepsilon_L(\omega) - \frac{\omega_p^{\ 2}}{\omega^2 - \frac{1}{\tau^2}} \times \left(1 + \frac{i}{\omega\tau}\right) \qquad (1)$$

where ω_p is the plasma frequency, ω is the IR radiation frequency, and τ is the electronic relaxation time [2]. The plasma frequency depends upon the photo-carrier density in equation 2

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$$\omega_p^{\ 2} = \frac{q^2}{\varepsilon_0} \times \frac{n_{ilum}}{m^*} \qquad (2)$$

where q is the charge on the electron, ε_0 is the permittivity of free space, and m^* is the effective mass of the photo-carrier, and n_{ilum} is the photo-carrier density as a function of power from the thermal pump source. n_{ilum} should be greater than 10^{20} cm^{-3} for significant IR photoconductivity to occur.

THEORY

The photo-carrier density, n_{ilum}, depends on the photon density, $G(P)$, and the recombination time, t, for electron hole hairs as shown in equation 3.

$$n_{ilum} = G(P) \times t \qquad (3)$$

The recombination time t is the average time required for electron-hole pairs to recombine thus eliminating the photo-carrier. For intrinsic a-Si:H t is on the order of a microsecond which means that for significant IR photoconductivity to occur $G(P)$ needs to be on the order of 10^{26} $s^{-1}cm^{-3}$. By comparison a focused spot from a 100 W thermal source generates a $G(P)$ on the order of 10^{23} $s^{-1}cm^{-3}$. Larger $G(P)$ values may be obtained using a pulsed source such as a strobe light, but this would result in non-steady-state photoconductivity. In order to make IR photoconductivity accessible with a simple thermal source, a slow t is required on the order of millisecond or longer.

Figure 1 shows density of state functions versus energy for intrinsic and n type a-Si:H.

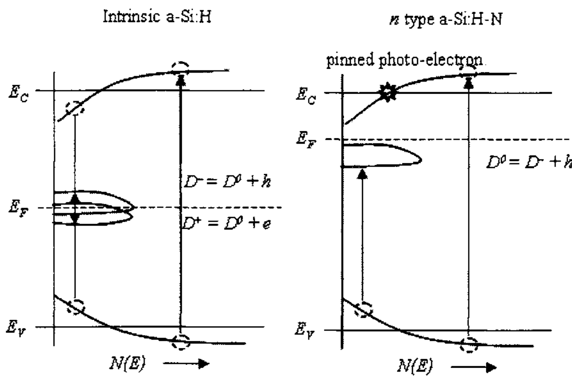

Figure 1. Density of states ($N(E)$) for a-Si:H.

In both cases E_C and E_V represent the energy of the mobility edge of the conduction and valence bands respectively while E_F is the Fermi energy. Near E_F in the forbidden gap of intrinsic a-Si:H are neutral dangling-bond states that may combine with electrons and holes to produce the charged dangling-bond defect reactions shown in the left half of Fig. 1. The production of charged dangling-bonds results in microsecond recombination

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