Recombination mechanisms in hydrogenated silicon nanocrystalline thin films

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Abstract: The photoconductivity dependences on temperature and illumination intensity were investigated for thin films of hydrogenated nanocrystalline silicon (nc-Si:H) grown by very-high-frequency, plasma-enhanced chemical vapor deposition. The nanocrystalline phase was achieved by heavy hydrogen dilution of silane (SiH_4). We find that the activation energy of the photoconductivity is sensitive to the incident illumination intensity for illumination intensities below 6 mW/cm^2. The photocurrent follows a power-law dependence on illumination intensity ($I_{ph} \propto F^\gamma$), with γ ranging from 0.36 to 0.83. The illumination dependence of the photocurrent suggests 2 different recombination mechanisms depending on temperature. In the lower temperature regime (300–340 K), recombination appears to be dominated by a linear (monomolecular) process, while at higher temperatures (350–400 K), it is likely dominated by a sublinear (bimolecular) process.

Key words: Photoconductivity, photovoltaics, nanocrystalline silicon, recombination

1. Introduction

In spite of their many advantages in photovoltaic applications, hydrogenated amorphous silicon (a-Si:H) and its alloys suffer from a large density of Si dangling bonds that act as recombination centers and degrade electrical properties. Hydrogen added during or after film growth passivates these films by terminating the dangling bonds and improves properties, but prolonged exposure to light appears to regenerate them and degrade properties. Consequently, the photocurrent of a-Si:H falls below the minimum required for efficient conversion after light exposure. A minimum conductivity for efficient conversion should be in the range of 10^{-8} to $10^{-4}\Omega$ cm^{-1} [1].

Recently, hydrogenated nanocrystalline silicon (nc-Si:H) in the form of quantum wires or quantum dots embedded in a matrix of a-Si:H, SiO_x, or SiN_x has generated remarkable attention for use in photovoltaic and other applications. The processing technology of these materials remains fairly simple, but the advantages are many. The crystalline nature of the quantum structures exhibits many of the crystalline silicon properties of higher mobility and stability. The quantum confinement enables the tuning of the band gap and the fabrication of all-silicon cells in tandem. Furthermore, it breaks down the momentum conservation rule that restricts efficient excitation of carriers, and it may permit the generation of more than 1 exciton by 1 high-energy photon in a process called multiexciton generation [2].

Processing of nanostructured materials involves several techniques, including furnace annealing and rapid thermal annealing of amorphous films deposited by various chemical vapor deposition, evaporation, and sputtering techniques as well as heavy hydrogen dilution during plasma-enhanced chemical vapor deposition

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deposition of a-Si:H. The resulting structure consists generally of nanocrystalline silicon particles embedded in a-Si, SiO_x, or SiN_x matrix. The hydrogenated nanocrystalline silicon films consist of approximately 50%–80% nanocrystalline silicon particles with a grain size of 3–5 nm in an amorphous silicon matrix with interface region of 2–3 atomic spacing [3].

The optoelectronic properties of nanostructured silicon are controlled by the microstructure and the distribution of traps in the band gap. Various models have been proposed to explain the transport behaviors. While the photocurrent generally increases with increasing temperature over a wide temperature range, a photocurrent decrease with increasing temperature is reported for some temperature regions. These results were explained in terms of a thermal quenching effect, in which valence band traps are converted to recombination centers under light illumination at some temperatures [4–7]. Metal contacts and the formation of metal silicide regions at the contact interfaces play an important role in determining these properties.

In the present work, we explore the main optoelectronic properties of nc-Si:H thin films by means of dark and illuminated current analysis, using silver paste drops as the contact point, and explore the photocurrent behavior in the temperature range above room temperature.

2. Experimental details

Device-quality nc-Si:H samples of approximately 2 μm thick grown at United Solar Ovonic LLC were provided by the Renewable Energy Materials Research Science and Engineering Center at the Colorado School of Mines, Golden, Colorado, USA. The samples were grown using very-high-frequency chemical vapor deposition on stainless steel substrates at a substrate temperature of about 200 °C. The nanocrystalline phase was achieved by heavy hydrogen dilution of silane (SiH_4) during growth. Raman spectroscopy measurements conducted on twin samples revealed that the volume fraction of the crystalline phase was about 60%–80% of the total volume. Due to their importance in photovoltaic applications, the electrical contacts to the films were investigated. Contacts were made of thin silver paste at the top surface. This paste consisted of Ag nanoparticles with a sheet resistance of <0.015 Ω/cm^2 at 25-μm coating thickness. The silver paste was thin enough to allow partial light penetration into the sample. Measurements of the dark and the photocurrent were taken at constant temperature by placing the sample on a hot plate to control temperature while illumination was made by a halogen lamp. The used halogen lamp had maximum emission at 620 nm and a spectral width of $\sim$100 nm only. This corresponds to incident photons with energies in the range of 1.88–2.22 eV, which is higher than the optical band gap of nc-Si:H of 1.7 eV. All incident photons were therefore expected to be absorbed by the 2-μm-thick film. Light intensity was varied by a calibrated change in the elevation of the light source above the sample. The short circuit photocurrent (I_{sc}) was recorded at various temperatures in the range of 300–400 K. The electrical data were recorded using a Keithley 485 picoammeter.

3. Results and discussion

Figure 1 shows transmission electron microscopy (TEM) images for a cross-sectional area of the film. The automated analysis of the images revealed a film thickness of approximately 1.5 μm. Grains of 6 $\times$ 20 nm crystals are visible within the a-Si:H film.
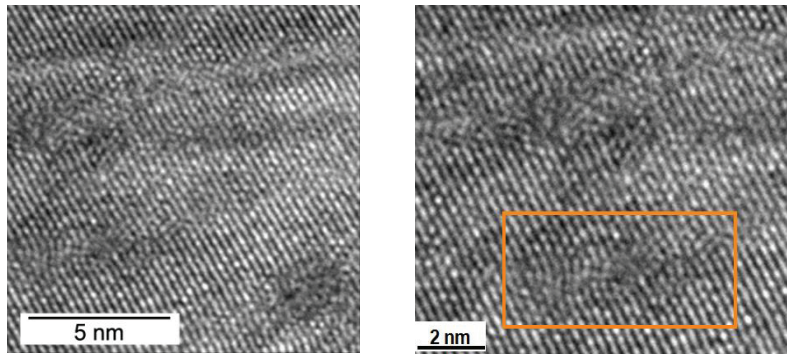
The top view high-resolution TEM images of Figure 2 clearly show the nanocrystalline Si phase impeded in the amorphous silicon matrix. A rough estimate of the volume ratio of these phases is consistent with the Raman spectroscopy measurement.

The dark (I_d) and illuminated (I_L) currents established across the film thickness between the top of the film and the stainless steel substrate were recorded. The current voltage characteristics of the Ag/nc-Si:H/Fe

structure are shown in Figure 3a, which reflects a clear rectifying behavior. The inset of Figure 3a shows the ohmic region of the forward-biased region. This region is important for studying the photokinetics of the rectifying diode. The photocurrent defined as $I_{ph} = I_L - I_d$ was calculated [8] from the measured data of I_d and I_L. The voltage across the contact terminals was kept constant at 1.0 V, which lies in the ohmic region.
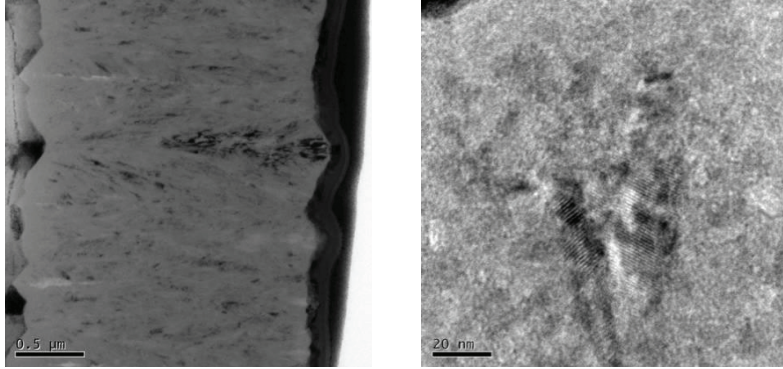

Figure 1. High-resolution TEM image of a cross-sectional view of the Si:H at different magnifications as indicated.


Figure 2. Top view high-resolution TEM images showing the nanocrystals impeded in the a-Si:H matrix.

Figure 3b shows the variation of photocurrent with temperature at various light intensities in the range of 1.8–46.6 mW/cm^2. For a given light intensity, the photocurrent appears to decrease with increasing temperature and follows the relation $I_{ph} \propto e^{Ea/kT}$, where E_a is the photoconductivity activation energy [4,5]. This result is commonly observed in amorphous silicon films at temperatures above 100 K and has been explained in terms of a thermal-quenching effect in which valence band tail traps are converted to dangling bond recombination centers induced by temperature or light [6,7].

The activation energy E_a represents the difference between the quasi-Fermi level and the conduction band for n-type or the valence band for p-type layers. The activation energy is calculated from the slopes of the straight line best fits of log I_{ph} versus inverse temperature as shown in Figure 3b, and is plotted as a function of illumination intensity in Figure 4. As observed from this figure, the activation energy decreases with increasing light intensity and reaches a minimum at about 6 mW/cm^2. This behavior is attributed to the electron-hole recombination following photon absorption. This process includes transitions from a trap level (such as a donor level) to the conduction band when the photon is absorbed. An electron moves from a donor level in the band gap to a level in the conduction band followed by a transition to a trap level that lies in the band gap, and a phonon is released. The released phonon contributes to the phonon-assisted hopping process, in which the conductivity is modulated by Fermi level shift.
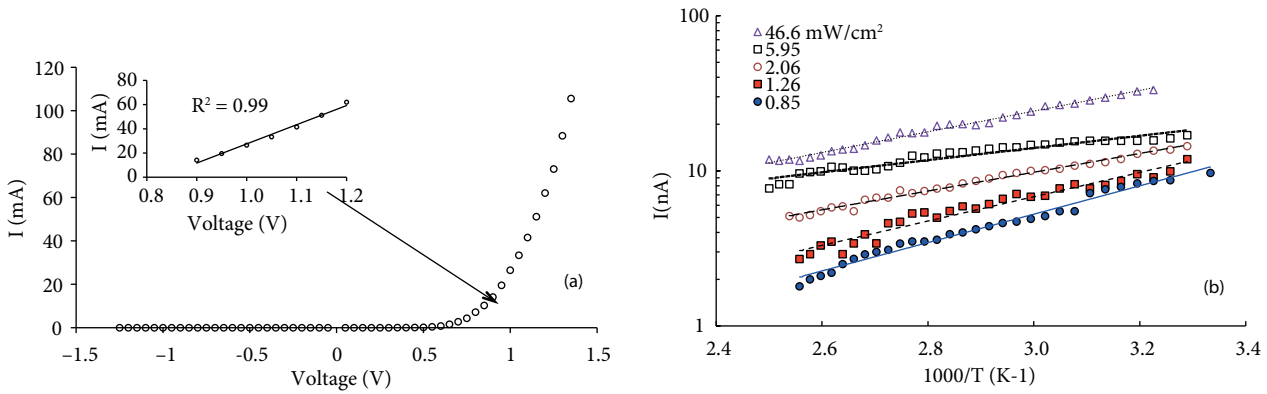
Figure 3. a) The current-voltage characteristics for the Ag/nc-Si:H/Fe sandwich structure; b) temperature dependence of photocurrent for nc-Si:H thin films at various illumination intensities as indicated.
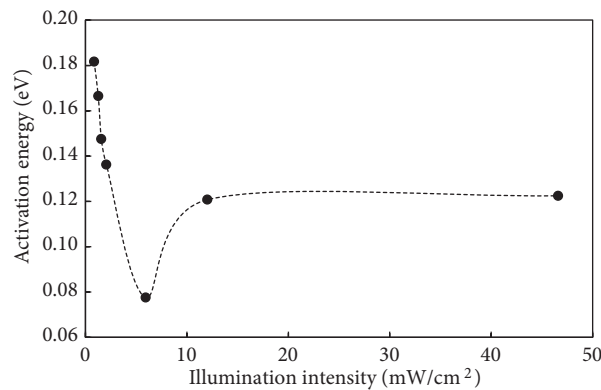

Figure 4. The activation energy (E_a) vs. illumination intensity (F).

The Fermi level position is controlled by conduction and valence band densities of states and the concentrations of free carriers. Under illumination, the Fermi level splits into 2 quasi-levels: the first falls between donor states and the conduction band while the other falls between valence band and acceptor states. Increased illumination intensity widens the shift and splitting probability of the Fermi level. On the other hand, as noted in Figure 4, the photoconductivity activation energy increases but starts to saturate above ~ 6 mW/cm^2. This behavior is related to the change in recombination mechanism from bulk recombination to surface recombination. The latter can be confirmed from the study of the effect of illumination intensity on the photocurrent at a particular temperature.

In Figure 5, we plot the photocurrent versus illumination intensity at various temperatures. The photocurrent increases with increasing illumination intensity at all temperatures from 293 K to 393 K and follows the power-law dependence $I_{ph} \propto F^{\gamma}$, where γ is the photoconductivity exponent, calculated from the slopes of the resulting straight lines in the $\ln(I_{ph})$ vs. $\ln(F)$ graph shown in Figure 5.

As shown in Figure 6, the exponent (γ) starts at 0.83 at 290 K, falls to 0.50 at 340 K, and reaches 0.35 at about 380 K. The variation in gamma with temperature between 0.36 and 0.83 may be explained in terms of an exponential distribution of traps [4,8–10] into the band gap. Rose [11] modeled the exponent γ to follow $\gamma = T^* / (T^* + T)$, where T is the measurement temperature and T* is a characteristic temperature that represents the distribution of states in the gap. For $T^* = T$, $\gamma \rightarrow 0.5$, which is indicative of a process in which a sublinear (bimolecular) recombination dominates. In this mechanism, the trap density is clustered close to the

band-edge. As temperature decreases so that T* >> T, γ reaches unity, indicating a linear (monomolecular) recombination mechanism in which the trap states extend deeper into the gap. As illumination increases, the trapping state is converted to a recombination center quenching the photocurrent [5].
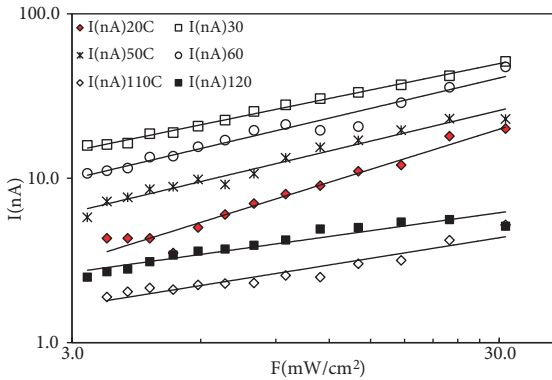

Figure 5. Photocurrent (I_{ph}) versus illumination intensity (F) on a log scale for nc-Si:H thin film at various temperatures.
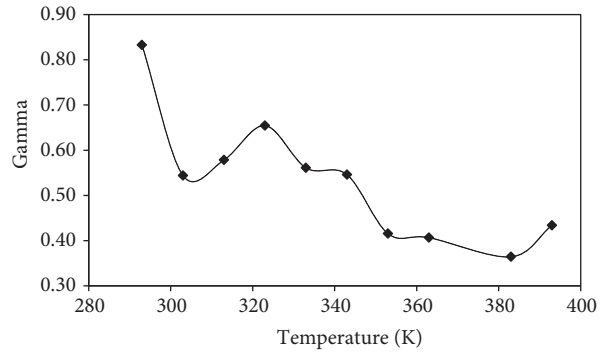
Figure 6. The exponential parameter (γ) versus temperature.

According to the above analysis, the decrease in the values of γ below 0.5 is probably attributed to the complicated exchange between the distributions of energy states in the band gap. Alternatively, it could also be attributed to the possible temperature dependence of T*, which requires further mathematical modeling beyond the scope of our study.

The above-reported recombination mechanism analysis at high and low temperatures indicates the ability of the Ag/nc-Si/Fe structures to produce short circuit currents under normal photovoltaic exposure of one sun [12]. In Figure 7, we show the open circuit voltage (V_{oc}) and short circuit current (I_{sc}) output of this structure.
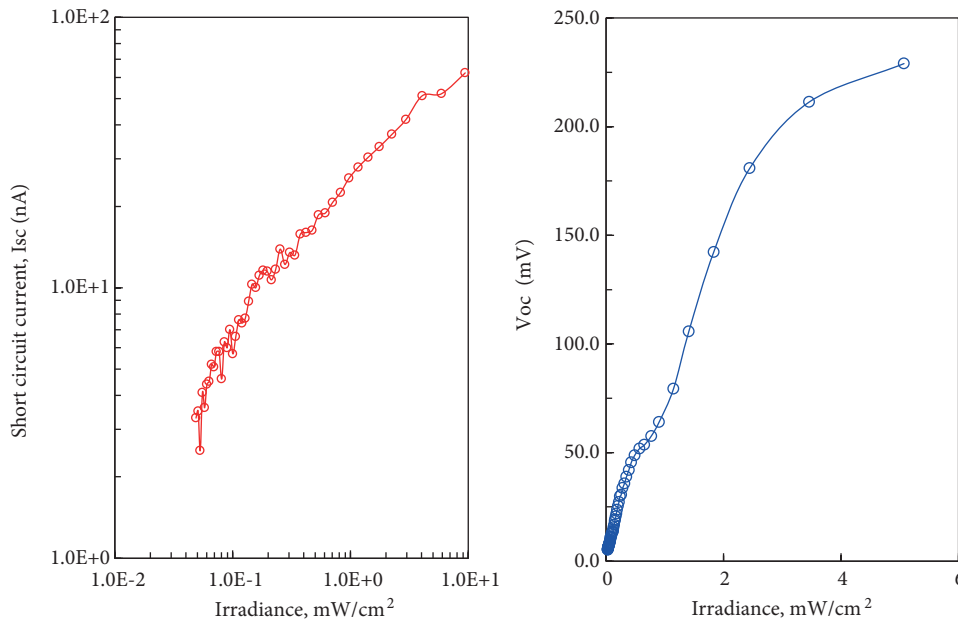
Figure 7. The open-circuit voltage (a) and the short-circuit current intensity (b) as a function of light intensity for nc-Si:H films.

The structure is important for high-voltage, low-current applications because the maximum obtainable voltage at bright sun is $\sim$0.25 V. The plots in Figures 7a and 7b show the response ability of the device even at very low light intensity.

Recalling that the device cross-sectional area is $\sim 8 \times 10^{-3}$ cm^2, the highest obtainable current of 0.06 μA is equivalent to a current density of 7.6 μA/cm^2, which is suitable for solar cell production. The value of the current density is relatively low when compared to commercial solar cells, indicating that some modifications must be done to improve the device performance [12].

4. Conclusions

The main optoelectronic properties of nc-Si:H sandwiched between a silver contact and stainless steel substrate (Ag/nc-Si:H/Fe) have been investigated by means of illumination- and temperature-dependent photoconductivity, using silver paint as the top contact and stainless steel as the substrate and second contact. The recombination kinetics of the films are highly influenced by the exponential trap distribution in the energy gap of nc-Si:H. The anomalous temperature dependence of the photocurrent may be attributed to a thermal quenching effect associated with the amorphous silicon matrix. Further measurements are needed to determine the onset of thermal quenching in these films. The Ag/nc-Si:H/Fe structure was observed to exhibit photovoltaic characteristics even at extreme conditions of high temperature and low illumination intensity. It appears to be suitable for solar energy conversion in regions where static field generators are preferable.

References

[1] Zhang, R.; Chen X. Y.; Zhang, K.; Shen, W. Z. *J. Appl. Phys.* **2006**, *100*, 104310–104314.

[2] Nozik, A. J. *Chem. Phys. Lett.* **2008**, *457*, 3–11.

[3] Hu, G. Y.; O'Connell, R. F.; He, Y. L.; Yu, M. B. *J. Appl. Phys.* **1995**, *78*, 394–3948

[4] Qasrawi, A. F.; Gassanly, N. M. *J. Phys. Condens. Matter* **2009**, *21*, 115801–115804.

[5] Ram, S. K.; Kumar, S.; Vanderhaghen R.; Drevillon B.; Cabarrocas P. *Thin Solid Films* **2006**, *511–512*, 556–561.

[6] Tran, M. Q. *Philos. Mag. B* **1995**, *72*, 35–66.

[7] Fritzsche, H.; Tran, M. Q.; Yoon, B. G.; Chi, D. Z. *J. Non-Cryst. Solids* **1991**, *137–138*, 467–470.

[8] Bube, R. H. *Photoelectronic Properties of Semiconductors*; Cambridge University Press: Cambridge, 1992.

[9] Tiwari, G. N., Dubey, S. *Fundamentals of Photovoltaic Modules and Their Applications*; SD RSC Publishing: London, 2010.

[10] Wu, J.; Li, H.; Liu, Y.; Xie, C. *J. Appl. Phys.* **2011**, *110*, 123513–123518.

[11] Rose, A. *Concepts in Photoconductivity and Allied Problems*; Interscience Publishers: Singapore, 1963.

[12] Mueller, T. *Heterojunction Solar Cells (a-Si/c-Si): Investigations on PECV Deposited Hydrogenated Silicon Alloys for Use as High-Quality Surface Passivation and Emitter/BSF*; Logos Verlag: Berlin, 2009.