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ESR study of the hydrogenated nanocrystalline silicon thin films

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Abstract

We studied the stability and light-induced paramagnetic centers in hydrogenated nanocrystalline silicon thin films (nc-Si:H) by electron-spin-resonance (ESR) and photothermal-deflection-spectroscopy (PDS). There is no measurable change in defect density upon illumination with white light with a light intensity of 300 mW cm^{-2} for 300 h. At low temperatures, upon illumination with sub-bandgap light, a light-induced ESR signal appears. This signal is similar to that in hydrogenated micro-crystalline silicon (μc-Si:H).

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1. Introduction

The hydrogenated nanocrystalline silicon thin films (nc-Si:H) have attracted intensive interest due to their potential applications in photovoltaic devices. These materials have much higher absorption coefficient at longer wavelengths, and there have been reports that they do not show light-induce degradation [1–3]. In addition, these materials are also of interest for the fundamental physics of disordered solids. Earlier devices were based on the so-called hydrogenated micro-crystalline silicon thin films (μc-Si:H), which have very high crystallinity. However, recent results show that the devices with best performance are made of materials within the transition region between the crystalline and amorphous phases [4,5]. Materials made within this region typically have a large volume fraction of the amorphous phase near 0.5, and they are highly inhomogeneous [5]. Neither the microscopic properties of the defects nor the mechanism of the optical absorption in these nanocrystalline materials is well understood. We have investigated the stability of nc-Si:H films and microscopic properties of the defects by electron-spin-resonance (ESR) and photothermal-deflection-spectroscopy (PDS).

2. Experimental method

The nc-Si:H samples were made at United Solar Ovonic, LLC. The samples were deposited on quartz ESR substrates. The sample thicknesses were about 1 μm. The hydrogen dilution ratio was varied during the growth to reduce the formation of large cone-shape aggregated grains [6]. An atomic-force-microscopy (AFM) image shows that the distribution of grain sizes is rather small, and the average size is about 20 nm [7]. Raman measurements on similar samples show that the crystallinity in the samples is about 50% [5].

PDS measurements were carried out at room temperature on a home-built PDS system. An ENX lamp from GE was used for the light-soaking experiment. The color temperature of the lamp is 3500 K. An infrared filter consisting of about 10 cm of water was inserted between the sample and the light source to filter out most of the IR light. The light intensity at the sample was about 300 mW cm^{-2}. The time of light-soaking was 300 h. The spin densities before and after light-soaking were measured

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at 77 K on a Bruker Elexsys 500 spectrometer at the National Renewable Energy Laboratory (NREL).

Transient, low temperature light-induced ESR spectra were measured with a Bruker EMX spectrometer. Three light sources were used. A high power LED with $\lambda = 810$ nm ($E = 1.53$ eV) was used for illumination above the intrinsic crystalline silicon (c-Si) indirect band gap. The light intensity at the sample is about 300 mW cm^{-2}. A pulsed YAG laser with 5 ns pulse-width was used for studying the decay of the light-induced ESR (LESR) signal. The energy from each pulse was 350 mJ, and the repetition rate was 1.25 Hz. A CW YAG laser was used to study the steady state LESR signal. For both lasers, the average light intensities at the sample were about 300 mW cm^{-2}.

The decays of the LESR signals were measured using the time-scan mode of the ESR spectrometer, details can be fund elsewhere [8]. Both the time constant and the conversion times of the ESR spectrometer were 300 μs, the shortest times available on this spectrometer. Due to limitations imposed by the laser repetition rate, only the decays at short times were measured.

3. Results

Fig. 1 shows the results of the light-soaking experiment. Trace (a) is from the sample before light-soaking, and trace (b) is from the sample after 300 h of light-soaking at a light-intensity of 300 mW cm^{-2}. The sharp line is from E' – centers located at the interface between the film and the substrate. The dashed line is a fit to the signal. Within the experimental error, the ESR signals before and after light-soaking are essentially the same. The peak-to-peak width of the signal is about 12 G, consistent with a previous report on μc-Si:H [9]. The zero-crossing field corresponds to a g-value of about 2.0036. Previous work on powdered μc-Si:H samples showed that the dark ESR lineshape exhibits a powder-averaged pattern [9]. The smaller signal-to-noise ratio from our films on substrates prohibits a detailed analysis of the lineshape in these samples. The defect densities were estimated to be about 5×10^{15} cm^{-3}, both before and after light-soaking.

Fig. 2 shows the result from PDS measurements on the samples at room temperature. For comparison, the absorption coefficient of bulk c-Si at 300 K is also plotted. Near the band gap energy of the c-Si, ($E_g = 1.12$ eV at 300 K), the absorption coefficient in nc-Si:H is about one order of magnitude higher than that in the bulk c-Si. In addition, the absorption coefficient remains quite high down to at least 1 eV, and there is no sharp drop-off in the absorption curve over the range measured. The reason for this behavior is not understood. Fig. 3(a)–(c) show the LESR signals in nc-Si:H at $T = 7$ K, with the samples illuminated by an 810 nm LED, a pulsed YAG laser, and a CW YAG laser, respectively. Fig. 3(d) shows the LESR signal of a-Si:H illuminated with a CW YAG at 7 K. The dark ESR signals have been subtracted from the total signals in each case. All three signals in nc-Si:H can be fitted with two Lorentzian functions, with full-width-at-half-maximum (FWHM) of 13 ± 0.5 G and 6 ± 0.5 G for the broad and narrow lines, respectively. In all three cases, the g-value of the fit to the broad line is 1.998 and the g-value for the fit to the narrow line is 1.996. The ratios between the broad and narrow lines are 2:1, 1.3:1, and 1:1 for excitation with 810 nm LED, pulsed YAG laser, and CW YAG laser, respectively. The LESR signal in a-Si:H can be fitted approximately by a Gaussian function with a peak-to-peak width of about 10 G. The g-value in the fit is about 2.005. This signal is similar to the LESR signal from electrons trapped in the conduction band tail. Within the noise, we did not observe the LESR signal due to the holes trapped in the valence band tail. This will be further discussed in Section 4.

The broad line and the narrow line in nc-Si:H are possibly due to the holes and electrons trapped at the grain

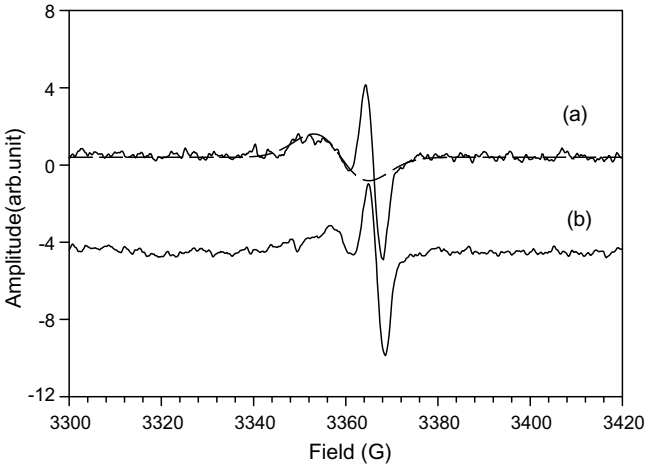

Fig. 1. ESR measurements of the defect densities before and after light-soaking (a) before light-soaking, and (b) after light-soaking for 300 h. The dashed line in (a) is a fit to the signal. The g-value of the fit is $g \approx 2.0036$. The peak-to-peak width of the fit is about 12 G.

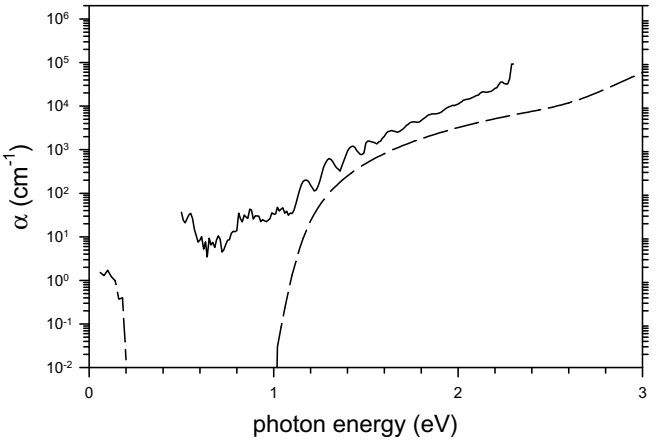

Fig. 2. PDS measurement on the nc-Si:H sample at room temperature. The solid line represents the data; the dashed line represents the absorption coefficient in bulk c-Si at room temperature.