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Long-range disorder and the Staebler-Wronski effect in *N*-type amorphous silicon

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Experimental measurements of the Q function (a comparison of the dark conductivity and thermopower activation energies) as a function of light exposure are reported for a variety of n-type-doped hydrogenated amorphous silicon films. The samples studied represent a wide range of deposition conditions, including variations of the deposition temperature, the rf power during deposition, and the doping ratio of phosphorus to silicon. The Q function of these films is measured before and after light-induced defect creation. No significant change in the Q function was observed after light-induced defect creation for any of these samples, consistent with no light-induced change in the long-range disorder at the conduction-band mobility edge. Measurements of the non-Gaussian statistics which characterize the conductance fluctuations ($1/f$ noise) are also found to remain unchanged following light exposure.

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I. INTRODUCTION

A major obstacle which inhibits a-Si:H from fulfilling its technological potential is the increase in defect density following light exposure, termed the Staebler-Wronski effect (SWE), which is accompanied by a decrease in the semiconductor's dark and photoconductance and is reversible upon annealing above 150 °C. Since its first observation in 1977,[1] there has been extensive research aimed at elucidating the microscopic origin of light-induced defect creation. The generally accepted model for the SWE involves photoexcited electron-hole pairs which break strained Si-Si bonds[2] and form new dangling bond defects upon recombination.[3] Nearby hydrogen may then form a Si-H bond with one of the newly created dangling bond states, leaving one dangling bond on the neighboring silicon atom and one at the original position of the bonded hydrogen atom. Subsequent hydrogen diffusion can further separate the dangling bond pair. It remains to be determined if the SWE (and the corresponding decrease in conductivity) results from only changes in the local Si-Si bonding structure or whether changes in the long-range disorder of the mobility edge are also involved.

The long-range disorder at the mobility edge of a-Si:H results both from the nonuniform distribution of bonded hydrogen as well as potential fluctuations caused by randomly located charged defects. The hydrogen microstructure, along with any impurity atoms, will result in spatial variations of the band gap throughout the amorphous material, as will the Coulombic potential fluctuations caused by charged dopant atoms and oppositely charged dangling bonds. These fluctuations of the mobility edge occur on length scales of $\sim$10–100 nm, based upon estimates of the hydrogen microvoid density and the average number of charged dopants and dangling bonds in moderately doped a-Si:H. Since the inelastic scattering length in a-Si:H is on the order of $\sim$0.5–1.0 nm at room temperature,[4] conventional transport measurements cannot be directly used to measure disorder on longer length scales. Here we examine two experimental techniques which have been interpreted as being sensitive to the long-range disorder of amorphous silicon: measurements of the Q function and non-Gaussian statistics which characterize the current fluctuations ($1/f$ noise).

The long-range disorder, arising from either compositional morphology or potential fluctuations, is believed to be responsible for the difference in the value of the activation energy (defined as the conduction band energy E_C minus the Fermi energy E_F) obtained from measurements of the dark conductivity (E_σ) when compared to the same quantity measured by the thermoelectric power (E_S) or thermopower.[5] In a-Si:H, E_σ has been observed to be as much as 100–300 meV larger than E_S. A convenient means with which to compare these two measurements is the Q function proposed by Overhof and Beyer,[6]

$$Q=\frac{e}{k_B}|S|+\ln[\sigma\ (\Omega\ \mathrm{cm})]=Q_0-\frac{E_Q}{k_bT}, \tag{1}$$

where E_Q is defined as $(E_\sigma - E_S)$. In a-Si:H the magnitude of E_Q has been interpreted as a measure of the magnitude of the long-range disorder[5,6] and E_Q is expected to increase as the electronic quality of a sample degrades (as reflected in a lower dark conductivity and higher dangling bond defect density). Previous work has shown that E_Q increases when the deposition conditions under which the a-Si:H films are grown are varied, leading to higher hydrogen content and lower electronic quality.[7] An increase in E_Q in n-type-doped a-Si:H following light exposure would indicate a shift of the conduction band to higher energies, providing asymmetrical shifts in E_σ and E_S. Given the technological importance of the SWE and the single prior report of the influence of light soaking on the Q function on one n-type-doped a-Si:H film,[8] investigation of the broad range of samples described here is justified in order to resolve the question of whether the long-range disorder is sensitive to light-induced defect creation.

Another electronic measurement which has been interpreted as reflecting the influence of long-range disorder in a-Si:H is the non-Gaussian statistics characterizing the conductance fluctuations.[9–12] Previous noise measurements on a-Si:H films have found that the coplanar current fluctuations have a spectral density which is well described by a $1/f$ frequency dependence for frequencies f in the range $1<f$

<1000 Hz. Moreover, analysis of the non-Gaussian statistics of the $1/f$ noise suggests the presence of cooperative interactions between the fluctuators. Increasing the structural disorder of the a-Si:H film by varying the deposition conditions[7,13] decreases the correlations of the noise power, consistent with the suggestion that the non-Gaussian $1/f$ noise is sensitive to long-range disorder.

II. EXPERIMENTAL TECHNIQUES

In this study a number of n-type samples of a-Si:H (doped with phosphorus) were measured before and after illumination (or "light soaking"). The films studied here were synthesized under a range of deposition conditions in order to vary the hydrogen microstructure contained within the films, an increase of which has been experimentally correlated with an increase in the film's long-range disorder.[7] Films for which the deposition temperature, rf power, and ratio of the dopant to silicon have been systematically varied are examined here. The samples were all deposited at the University of Minnesota in a capacitively coupled rf (13.56 MHz) system using plasma-enhanced chemical vapor deposition (PECVD) of silane (SiH_4) and phosphine (PH_3) for n-type doping. The samples were deposited onto Corning 7059 glass substrates and chromium electrodes, approximately 500 Å thick, are deposited onto the silicon films in order to make Ohmic electrical contact to the semiconductor.

Both the dark conductivity and thermopower are measured in an electrically shielded vacuum chamber (pressure <100 mTorr). The sample is mounted across two heated copper blocks, with the 4-mm gap between the blocks aligned with the inside edges of the chromium electrodes. The temperature of each of the two blocks (heated by bullet heaters) can be controlled independently by means of an Omega CN3000 dual-channel temperature controller, allowing a temperature gradient to be applied across the a-Si:H film. The temperature is measured with type-T thermocouples which are attached to the edge of the chromium electrodes using silver paint. Two electrical leads, attached to the opposite end of the sample as the thermocouples (also using silver paint), are used for measurements of both the conductivity and of the voltage difference (for thermopower measurements). Measurements of the voltage difference are made with the aid of a Keithley 617 programmable electrometer, which is switched to resistance mode for the conductivity measurements. A scratch made across the sample using a diamond scribe electrically insulates the sections of the film used for temperature and voltage (or conductivity) measurements. Further details of this measurement system can be found elsewhere.[14]

Prior to any measurements, a sample is annealed at 180 °C for at least 1 h in order to remove any surface absorbates (such as water vapor) (Ref. 15) or the effects of previous light exposures.[1] The sample is then cooled to 50 °C at a controlled rate of one degree per minute. The state of the sample before light exposure is referred to as state A, while the condition following light exposure is defined as state B. Illumination is performed with ~100 mW/cm^2 of heat-filtered white light from a tungsten-halogen lamp. Measurements of both the conductivity and thermopower are made over the temperature range of 50–180 °C, and the resulting plots of $\ln\sigma$ or S against inverse temperature are used to determine the activation energies E_σ and E_S, respectively. To measure a sample in state B, the film is first annealed into state A and then illuminated at 50 °C prior to any measurements. The a-Si:H then equilibrates in the dark for approximately 1.5–2 h in order to allow the conductivity to stabilize. When conductivity or voltage measurements are made, at least 100 readings are taken at any given temperature and then averaged in order to eliminate the effects of minor temperature fluctuations.

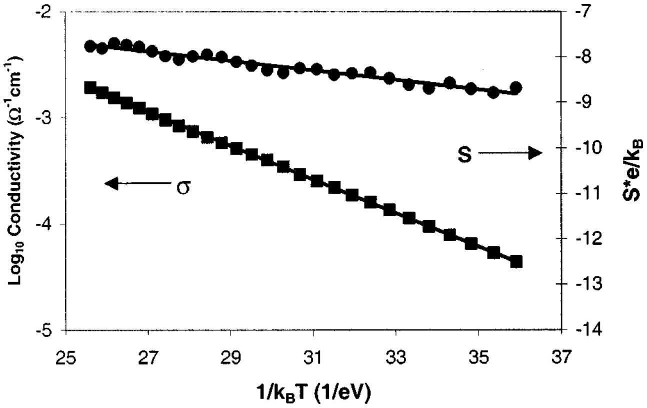

FIG. 1. Arhennius plot of the conductivity (squares) and linear plot of the thermopower (circles) against inverse temperature for an n-type a-Si:H film in state A deposited at 80 °C.

Current noise measurements were performed in a shielded vacuum chamber in which the sample temperature is controlled by means of a heated copper block. A constant voltage (provided by batteries) is applied, and the fluctuations in the dc current passing through the film are amplified by an Ithaco 564 current preamplifier and Fourier transformed using an HP 3561A spectrum analyzer. Details of the $1/f$ noise measurements have been described previously.[12]

III. RESULTS

All the samples examined here were measured in both states A and B, following a light exposure of ~24 h. Each of these films displayed a SWE, reflected in shifts in both E_σ and E_S following illumination, which was reversed upon annealing. A series of films synthesized at different deposition temperatures (ranging from 80 to 250 °C) with an rf power of 3 W and a doping ratio of $[PH_3]/[SiH_4]=4\times10^{-4}$ is described first. Figure 1 shows a plot of the temperature dependence of the conductivity and thermopower in the annealed state A for an n-type a-Si:H film deposited at 80 °C. It is apparent from Fig. 1 that the slope of the conductivity curve (that is, E_σ) is greater than that of the thermopower data (E_S). The temperature dependence of the Q function for this same sample is shown in Fig. 2 for both states A and B. While this film exhibits a small but clear increase in the conductivity and thermopower activation energies E_σ and E_S following light exposure, there is no corresponding change in

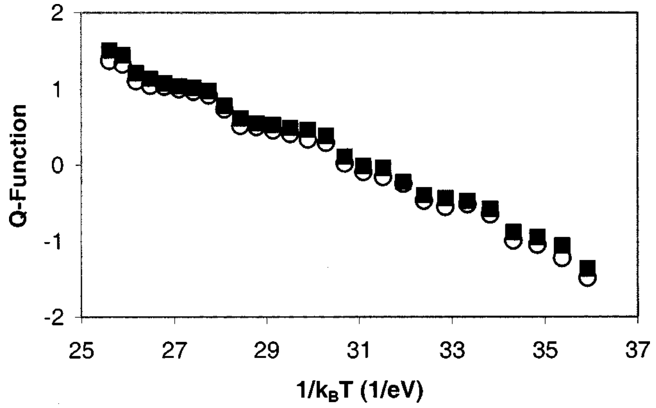

FIG. 2. Plot of the Q function against inverse temperature for the sample deposited at 80 °C (Fig. 1) in state A (solid squares) and state B (open circles).

the value of E_Q, consistent with a negligible change in the sample's long-range disorder.

The other films in the temperature deposition series (deposited at 100, 150, and 250 °C at an rf power of 3 W) display a similarly unchanged E_Q following illumination, as shown in Fig. 3. Figure 3 plots the change in the dark conductivity activation energy following light exposure (ΔE_σ) along with ΔE_Q (ΔE_S is omitted for clarity) against the film's value of E_Q in state A for all of the samples investigated in this study. Here ΔE is defined as the activation energy difference between its value in state B and in state A ($E^{\text{state B}} - E^{\text{state A}}$). All of these films exhibit a clear shift in E_σ (and E_S), which is reversible upon annealing, but no significant shift in E_Q. An increase in the magnitude of the activation energy values E_σ and E_S is observed as the temperature of deposition is decreased, while ΔE_Q remains negligible for all films in both states A and B.

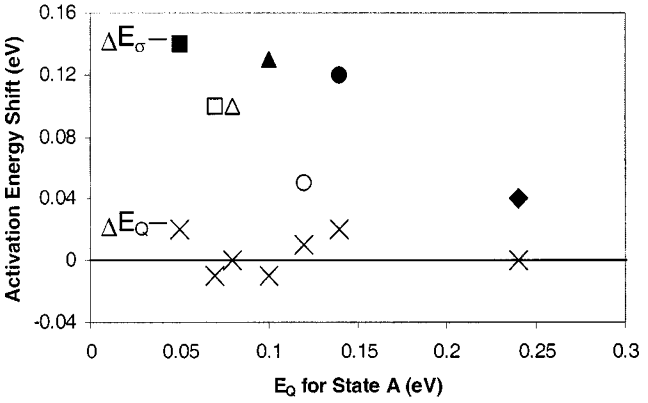

FIG. 3. Plot of the shift in activation energy for the conductivity and Q function with respect to the E_Q value in state A. The solid symbols are the values of ΔE_σ for the films in the temperature deposition series described in the text. The square, triangle, circle, and diamond represent the 250, 150, 100, and 80 °C films, respectively. The open triangle and open square are for the films deposited at 1 and 10 W, respectively, with a doping of 4×10^{-4}, while the open circle is for the film deposited at 3 W with a doping of 4×10^{-3} (all deposited at 250 °C). The value of ΔE_Q for a film is given by the X plotted directly beneath its value for ΔE_σ.

Figure 3 also shows the values of ΔE_σ and ΔE_Q for films deposited at 250 °C with rf powers of 1 and 10 W, with the same doping level as the temperature deposition series. No change in E_Q is observed for the 1 W film, while its value of E_σ changed from 0.12 to 0.22 eV after light exposure and E_S changed from 0.04 to 0.14 eV. Similarly, the 10 W film exhibits no significant change in E_Q from state A to state B. An a-Si:H film with a higher doping level of $[\mathrm{PH_3}]/[\mathrm{SiH_4}]=4\times10^{-3}$ was also examined (deposited at 250 °C with an rf power of 3 W); its values of ΔE_σ and ΔE_Q are included in Fig. 3. Measurements of this sample show that increasing the doping ratio by a factor of 10 does not lead to any significant shift in E_Q following light exposure. Figure 3 also indicates that as the electronic quality of the a-Si:H film decreases, reflected by an increasing E_Q value, the relative SWE (that is, the ΔE_σ) also decreases, consistent with higher defect densities in state A for poorer quality materials.

All of the films studied here were examined in a state B produced by ~24 h of light exposure. However, it is possible that this period of illumination may not be sufficient to produce a detectable shift in E_Q. Hauschildt, Fuhs, and Mell reported a change in E_Q in a 10^{-4} $[\mathrm{PH_3}]/[\mathrm{SiH_4}]$-doped a-Si:H film after 60 h of illumination.[8] We have therefore also measured the Q function for an a-Si:H film deposited at 250 °C at an rf power of 3 W with a doping ratio of $[\mathrm{PH_3}]/[\mathrm{SiH_4}]=4\times10^{-4}$ after light exposures of 1, 24, 100, and 340 h. This sample was chosen since it displayed one of the largest Staebler-Wronski effects after a 24-h light exposure. The corresponding ΔE_Q ($E_Q^{\text{state B}} - E_Q^{\text{state A}}$) values for this film for light exposures of 1, 24, 100, and 340 h are 0.02, 0.03, 0.02, and 0.03 eV, respectively. It is clear that even a light soak of over 300 h does not produce a noticeable shift in E_Q even though such an illumination results in a significant SWE as reflected by a decrease in the dark conductivity. Consequently, even if a longer light exposure were to produce a shift in E_Q, it is clear that any corresponding increase in the long-range disorder cannot be the dominant mechanism for the metastable degradation in the conductivity and thermopower observed in the SWE.

Studies of $1/f$ noise[12] and random telegraph switching noise[16] in a-Si:H have been interpreted as reflecting fluctuations in inhomogeneous current filaments whose resistance varies with both time and temperature. These current measurements may arise through the medium- and long-range disorder present due to compositional microstructure and potential fluctuations.[7] Fan and Kakalios suggested that these filaments interact through correlated hydrogen motion, mediated by the silicon strain fields.[17] These interactions are reflected in the non-Gaussian noise of the a-Si:H, with an increase in the filament interaction leading to an increase in the slope of the second spectra. An increase in the long-range disorder of a-Si:H would weaken these interactions, for then the silicon strain field would presumably change sign multiple times between filaments, reducing the correlations between microchannels even though the current filaments themselves might not be greatly affected. If the SWE was accompanied by an increase in long-range disorder, this would suggest that the $1/f$ noise would become more Gauss-

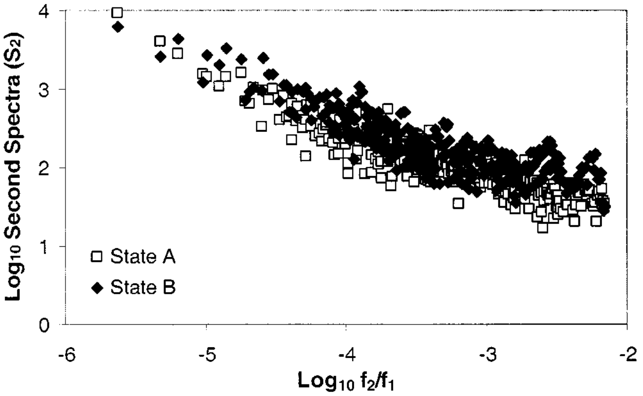

FIG. 4. Log-log plot of the spectral density of the noise power fluctuations (second spectra) against the scaled frequency (f_2/f_1) for the 150 °C film in state A (open squares) and state B (solid diamonds). The frequency axis for the long-time fluctuations of the noise power f_2 has been scaled by the appropriate octave center frequency f_1.

ian following light exposure, reflected in a decrease in the slope of the second spectra.

The noise power spectra of the current fluctuations in the a-Si:H film deposited at 150 °C were measured at 320 K for both states A and B. The applied voltage is adjusted so that the same current passes through the sample in each state. The amorphous silicon exhibits clear $1/f$ noise behavior in state A which remains unchanged in both magnitude and spectral slope [comparing 1000 rms averages of individual fast Fourier transforms (FFT's)] following 24 h light exposure. To examine the time dependence of the noise a series of 1024 power spectra, each the result of 10 rms averages, are taken over approximately a 90-min period and each spectra is summed into 6 separate octaves (ranging from 10 to 640 Hz). By Fourier transforming the resulting plot of noise power against time, a second spectra is obtained which characterizes the fluctuations in the noise power.[11,12] The scaled second spectra for the 150 °C film are shown in Fig. 4. The second spectra for this film also display an approximate $1/f$ frequency dependence, reflecting the non-Gaussian nature of the noise. The second spectra of a Gaussian noise source would be frequency independent. As indicated in Fig. 4, no consistent change is observed in the second spectra following a 24 h light exposure, indicating that there is no substantial change in the filament interactions, and in turn that the long-range disorder is unaffected, consistent with the Q function results.

IV. DISCUSSION

On one level the results described here are surprising, given the body of research that has observed a change in the long-range disorder accompanying the Staebler-Wronski effect.[8,18] For example, Fan and Kakalios found in their study of the $1/f$ noise in n-type a-Si:H an increase in the Gaussian behavior of the $1/f$ noise, reflected in a reduction in the correlation coefficients between octaves following light exposure.[17] These measurements were repeated several times, and their results were reproducible over multiple thermal cycles, despite the fluctuations observed in the magnitude of the noise power. These authors interpreted these measurements as demonstrating that the interactions between filaments are sensitive to the creation of defects by the Staebler-Wronski effect. Also, as previously mentioned, Hauschildt, Fuhs, and Mell reported finding a change in E_Q in an n-type film following light exposure.[8] In contrast, Quicker, West, and Kakalios reported finding no change in E_Q for four different samples: two n-type films (one very lightly doped), a compensated film (doped with both phosphorus and boron), and a sulfur doped film.[19] Also, neither the lightly doped film nor the compensated film displayed a change in the non-Gaussian statistics following light exposure. Quicker *et al.* did, however, observe an increase in the Gaussian behavior of the noise for the other n-type film (with a doping ratio of 4×10^{-4}) and found that the correlation coefficients of this film changed after 7 h light exposure.

While in certain films a change in the long-range disorder may possibly accompany the SWE, the work reported here suggests that this is not universally the case and that an increase in the long-range disorder is not the primary mechanism that drives the SWE. A change in long-range disorder following light exposure may in actuality be a side effect of the SWE rather than its cause. Furthermore, as our measurements focused primarily on the Q function, these results do not directly contradict reports of light-induced changes in other measurements (such as the infrared absorption).

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