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Infrared Charge-Modulation Spectroscopy of Defects in Phosphorus Doped Amorphous Silicon

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ABSTRACT

We present infrared charge-modulation absorption spectra on phosphorus-doped amorphous silicon (a-Si:H:P) with doping levels between 0.17% - 5%. At higher doping levels (1% - 5%) we find a sharp spectral line near 0.75 eV with a width of 0.1 eV. We attribute this line to the internal optical transitions of a complex incorporating four fold coordinated phosphorus and a dangling bond. This line is barely detectable in samples with lower doping levels (below 1%). In these samples a much broader line dominates the spectrum that we attribute to uncomplexed dopants. The relative strength of the two spectral features is in rough agreement with a model proposed by Street that has not been previously tested experimentally.

INTRODUCTION

The interfaces between thin-film layers in amorphous silicon (a-Si:H) solar cells are of course very important to the optoelectronic properties, and a particularly vigorous effort has gone into improving the junction between the *p*-type and intrinsic layers [1]. Despite their importance, we have only a fragmentary understanding of the science of these interfaces. Important structural information is available from *in situ* optical and photoemission studies of films as they are grown [2,3]. *Ex situ* measurements on working cells include *internal photoemission* studies (to establish band offsets) [4] and *capacitance spectroscopy* (to probe defect levels) [5].

For the last few years we have been developing an infrared modulation spectroscopy technique that probes the optical spectra of dopants and defects at the critical interfaces between the layers of amorphous silicon *pin* solar cells [6,7,8,9]. In brief, the reverse bias voltage across a cell is sinusoidally modulated, and the corresponding modulation of an optical transmission is detected. We illustrate such a spectrum as figure 1, where the modulation spectrum $\Delta T/T$ of the optical transmission through a *pin* solar cell is shown. The principal feature in this spectrum is the large peak near 1.85 eV; this feature, which depends upon the magnitude of the DC potential V_{DC} across the cell, is due to the well-known *electroabsorption* effect in the intrinsic, a-Si:H layer of the cell [10]. The much weaker infrared signal is nearly independent of V_{DC}, and is attributed to the change in optical transmission as the *charge state* of dopants and defects near the interfaces is modified by the sinusoidal modulation of the electric potential across the cell. The electroabsorption effect is quadratic in electric field, which leads to a signal quadratic in the modulated field and V_{DC}. The interface effect varies with the charge modulation at the interfaces, and is independent of V_{DC} when the capacitance is also independent of V_{DC}.

In the present paper, we studied a series samples with varying phosphorus-doping level in the *n*-layer. We found, for high doping levels (1% - 5%), a sharper spectral line near 0.75 eV with a width of 0.1 eV. This line is nearly absent in lower doping (below 1%) samples. We have

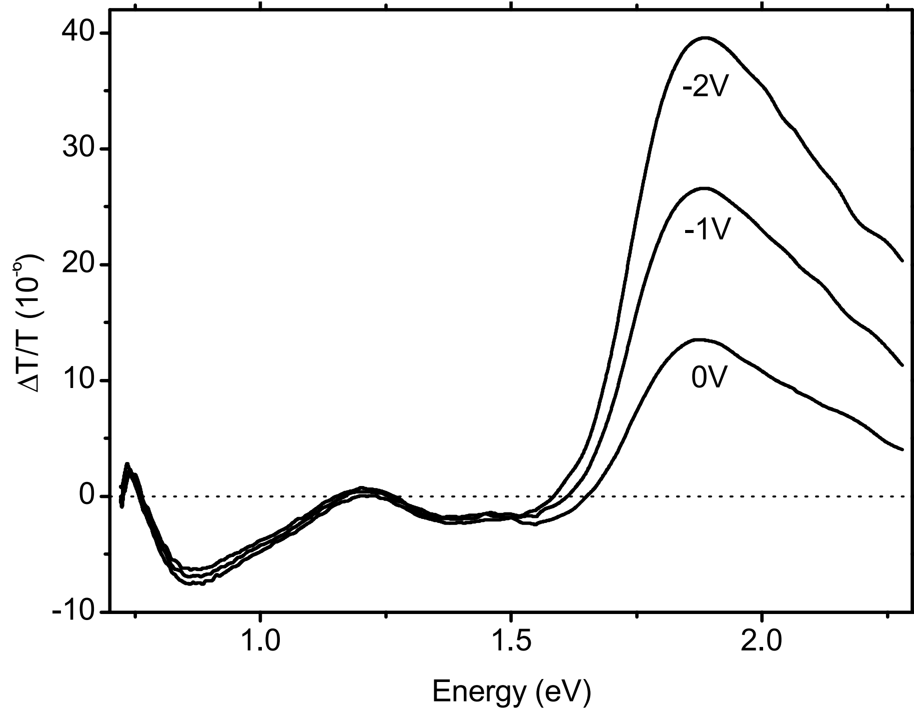

Figure 1. Transmittance modulation spectrum *ΔT/T* for an amorphous silicon-based *pin* solar cell prepared at BP Solar. Spectra were taken under three different DC reverse bias voltages (V_{DC}) as indicated. The larger, voltage-dependent peak near 1.85 eV corresponds to the well established *interband electroabsorption*, and depends linearly on V_{DC}. The weaker infrared response is due to charging and discharging of dopant and defect levels near the *n/i* and *p/i* interfaces, and shows little dependence on V_{DC}. Sample with 3% phosphorus doping level. Measured with 400Hz, 1.0 V_{pp} modulation.

previously attributed this line to the internal optical transitions of a "P_4D" complex incorporating both a fourfold-coordinated phosphorus atom (P_4) and a dangling bond (D) [7,11]. We have analyzed the present measurements to estimate the relative concentrations of "standard" dopant atoms P_4 (ie. those not in complexes) and dopant complexes P_4D. We are unaware of previous experimental estimates of this ratio, and we believe that they show the utility of infrared charge-modulation spectroscopy for interface studies. Our measurements are broadly consistent with the predictions of the model for doping developed by Street, although the measurements differ from this model in detail.

EXPERIMENTS

In this experiment, we measured the transmittance modulation spectra for a series of samples of phosphorus-doped amorphous silicon (a-Si:H:P) layer with gas-phase doping levels between 0.17% - 5%. These samples were made as a sequence at BP Solar; the substrate for each deposition was glass coated with textured SnO_2. The *p*-type layer deposited onto the SnO_2 was a-SiC:H:B, followed by a-Si:H and by *n*-type a-Si:H:P. Sputtered TCO was applied to the top and

used as the electrical contact. The intrinsic layers were around 200 nm thick as inferred from capacitance measurements. A buffer layer was deposited between *p*-type and intrinsic layers.

RESULTS AND DISCUSSION

Figure 2 shows the infrared charge-modulated transmittance spectra ΔT/T for samples with the indicated doping levels. Each spectrum has been normalized by its peak amplitude. We first noticed that for samples with doping levels below 1% there is a negative, broad peak in the modulation spectrum near 0.85 eV. We attribute this spectrum to occupancy modulation of isolated dopant atoms in the *n* and *p* layers; similar spectral features have been reported in photomodulated transmittance spectra of phosphorus-doped a-Si:H. We exclude the photodetachment of electron from D^- as possible source for this negative absorption spectrum. This is because the Fermi energy is at most 0.2 eV below conduction band, but D^- is located 0.9 eV deep below conduction band. Depletion of such a deep level should be negligible. This argument is also supported by the frequency-independent spectrum with modulation frequency range from 200 Hz to 20kHz, although we won't show this here.

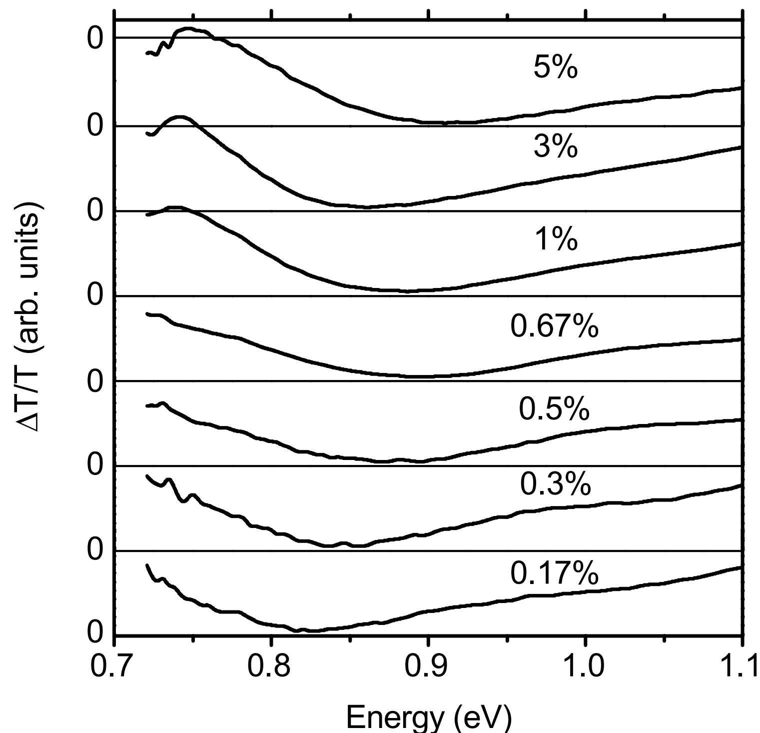

Figure 2. Normalized modulated infrared absorption spectrum. Samples were prepared at BP Solar with varying phosphorus doping levels (from 0.17% to 5% as indicated). At higher doping levels (1% and above), there is a line spectrum at 0.75 eV of about 0.1 eV wide. This line is essentially absent in samples with doping levels below 1%. This sharp line indicates the internal optical transitions of a complex incorporating four fold coordinated phosphorus and a dangling bond.

At high doping levels (1% and above), we find a sharper, positive peak at 0.75 eV with a width of 0.1 eV. This line is nearly absent in low doping samples. The existence of a sharp absorption line suggests transitions between the ground state and a localized excited state of some center in phosphorus-doped a-Si:H. In our previous work we suggested the possibility that P_4D complexes are responsible for this spectral feature [7]. Positron annihilation measurements [11] are also consistent with complexing at high doping levels. Figure 3 shows a simple possible level diagram for a P_4D complex, and corresponding absorption spectrum for an internal optical transition. As we can see from figure 3, when the Fermi energy is lowered, the depletion of P_4D states near band edge promotes the internal transition to these states from deeper complex states.

Street [12] has previously noted that formation of P_4D complexes is favored at high doping levels, while lower doping levels favor the formation of uncorrelated P_4 and D-centers in essentially equal concentrations. In the next a few paragraphs, we will discuss briefly, based on samples studied in this paper, about the doping models proposed by Street [12]. The standard doping model involves nearly equal densities dangling bonds (D centers) and of phosphorus atoms bonded to four silicon atoms (P_4 centers). The corresponding densities can be represented by [12]

$$N_{P_4} = N_D = \left(K_S N_{Si_4}\right)^{1/2} \left(N_{P_3}\right)^{1/2} , \quad (1)$$

where K_S is the rate constant and P_3 denotes a phosphorus atom with threefold coordination. The concentrations of pairs depends linearly on phosphorus concentration [12]:

$$N_{pair} = K_P N_{Si_4} N_{P_3} = \left(K_P N_{Si_4}\right)\left(N_{P_3}\right) , \quad (2)$$

where K_P is the rate constant for pair generation. Low P densities favor isolated P_4 and D centers; higher densities favor complexing.

To analyze our spectra, we assumed that the two spectral features (broad/negative, and narrow/positive) in Figure 2 originate with P_4 and P_4D configurations. We fit the infrared spectrum with two Gaussian peaks. Figure 4 shows a typical fitting result for the sample made with 3% P. The dashed line represents the positive peak; the dotted line represents the negative

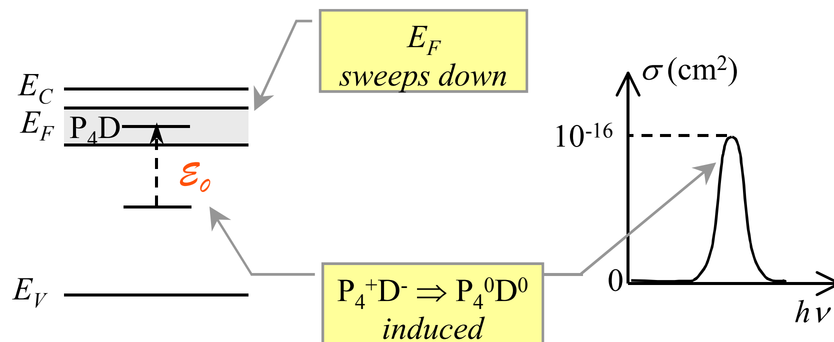

Figure 3. Optical effects resulting from a change in the Fermi energy in heavily phosphorus doped a-Si:H (probably at doping level of 1% and above). The drawing on the left indicates an internal electron excitation from a deep level to a shallower level of a complex, which incorporats four fold coordinated phosphorus and a dangling bond. The depletion of occupied states near the band edge of a-Si:H, as the Fermi energy is lowered, induces this internal transition, which account for a sharp, positive absorption spectrum.

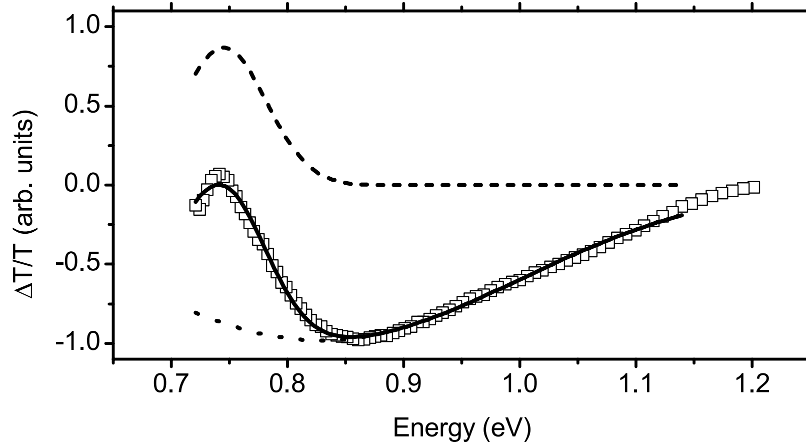

Figure 4. Spectrum analysis. Fit infrared spectrum with two Gaussian spectrum peaks. Symbols indicate the measurement; lines indicate the fitting results (dashed: positive Gaussian peak t 0.75 eV; dotted: negative Gaussian peak at 0.84 eV; solid: sum of these two peaks).

peak. As can be seen, the sum of these two spectrum peaks (the solid line in the figure) fits the actual spectrum quite satisfactorily. We plotted the ratio of the strengths of these two spectral lines for all of our samples as the open symbols in Figure 5. We believe that this value is proportional to the ratio of the densities of the two types of dopant configurations.

From Eq. 1 and 2, we calculate the ratio of concentrations as:

$$N_{pair} / N_{P_4} = \left(K_P / K_S \right) \left(N_{Si_4} \right)^{1/2} \left(N_{P_3} \right)^{1/2} . \qquad (3)$$

We fitted the resulting proportionality (to $P^{1/2}$) to the measurements in Figure 5. The fitting accounts fairly well for the dependence of the ratio of spectral line strengths upon the

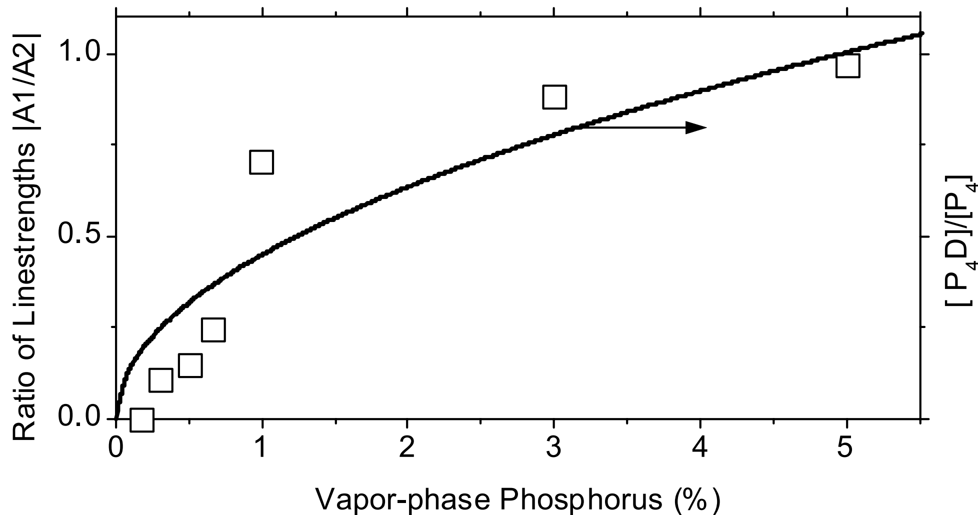

Figure 5. Relative peaks strength. Symbols indicate the ratio of the strength of the positive peak over that of the negative peak. Line indicates the fitting result of Eq.3 in text. The fitting coefficient was 4.5.

phosphorus concentration, and thus supports to some degree our identification of the two spectral features. There does appear to be sharper structure near a "critical" phosphorus level of 1% that is not reproduced by the fitting, and we hope that further measurements will clarify this possibility.

ACKNOWLEDGEMENTS

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