

Gap-states distribution in amorphous-silicon films as obtained by photothermal deflection spectroscopy

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The paper reports results on intrinsic, device-quality amorphous silicon obtained with use of photothermal deflection spectroscopy. The gap-states distribution is obtained by means of a simple and reliable derivative procedure on the absorption-coefficient spectra. A comparison with other models is made. Finally, it is shown that the peak energy of the defects can be different for surface and bulk states, and so a shift of the occupied defect peak is observed if a considerable number of surface states are introduced. This explains the higher values for the dangling-bond correlation energy obtained by means of optical methods and agrees with other experimental evaluations of the distribution of surface states such as those carried out by means of total-yield spectroscopy.

INTRODUCTION

Photothermal deflection spectroscopy (PDS) (Ref. 1) is a versatile experimental tool for the determination of the absorption coefficient spectra of amorphous silicon films. These spectra are closely related to electronic transitions involving deep defects and shallow band-tail state densities so that quantitative information on the density of states (DOS) can be, in principle, deduced from optical-absorption data.²

In the case of amorphous semiconductors, the sub-band-gap region (with photon energies smaller than the optical band gap) has been extensively studied in the recent past.³ A widely accepted model for intrinsic, hydrogenated *a*-Si:H assigns an exponential energy dependence for both valence and conduction tails, while two peaks, considered as Gaussian, are located towards midgap.² These peaks, whose correlation energy is of the order of 0.2–0.4 eV,⁴ are generally ascribed to D^0 - D^+ and D^0 - D^- transitions.

It is also remarkable that similar results can be obtained by means of other techniques, like photoconductive spectroscopy.⁵ In that case, however, only electronic transitions involving filled defects are detectable in intrinsic, device-quality *a*-Si:H.

The dependence of PDS results on the film thickness has been recently addressed,² and this suggests that the surface defects play a non-negligible role in affecting the optical sub-gap properties of films with thicknesses of the order of 1 μm . Furthermore, the possibility of deep inhomogeneities in intrinsic *a*-Si:H films has been suggested.²

These spatial inhomogeneities have been studied extensively and it has been found that an exponentially decreasing distribution from surface to bulk can account for the thickness dependence of PDS spectra,² and, in some cases, for the mismatch between photothermal and photoconductive spectroscopies.⁶ At the present stage, little

is known about the spectral distribution of these surface defects: Schumm and Bauer⁷ have applied modulated primary photocurrent spectroscopy to study the influence of interfaces in the gap-state distribution of *a*-Si:H films. It has been found that interfaces with both doped amorphous silicon films and metal films show a density-of-states (DOS, $\text{cm}^{-3} \text{eV}^{-1}$) distribution which differs in a considerable way from that of intrinsic, bulk *a*-Si:H. The aim of the present study is to deconvolute the PDS spectra as obtained on intrinsic, device-quality *a*-Si:H films with different surface-to-bulk absorptance ratios in order to provide information about the surface and bulk DOS.

THEORY

We start from a model for the DOS (Ref. 8) of intrinsic *a*-Si:H which assigns a value of $E_\mu = 1.9$ eV for the mobility gap. A filled peak that can be ascribed to D^0 - D^+ transitions lies 0.9 eV above the valence-band edge. Assuming a correlation energy of 0.3 ± 0.1 eV a second (empty states, D^0 - D^-) peak is located 0.7 ± 0.1 eV below the conduction-band edge. The Fermi energy is assumed to be at 0.8 eV below the conduction-band edge.⁸

The absorption coefficient $\alpha(h\nu)$ can be considered as the convolution integral of initial N_i and final N_f states that are involved in the electronic transitions. Thus, if the optical-transition matrix element is assumed to be energy independent,² it can be written

$$\alpha(h\nu) = A \int_{-\infty}^{+\infty} N_i(E) N_f(E+h\nu) f(E) \times [1 - f(E+h\nu)] dE, \quad (1)$$

where A is a constant matrix element and $f(E)$ is the Fermi distribution that can be approximated by a step function.

A further approximation in (1) is to simplify the onset of the density of states at the conduction-band edge to a

step function⁸ $\Theta(E)$. This permits extracting the density of initial states by means of a simple derivative procedure on $\alpha(h\nu)$.

This approximation is valid in two particular cases when no transitions involving empty defects are detected: these are the cases of spectral photoconductivity (e.g., the constant photocurrent method, (CPM) (Refs. 5 and 8) and of spectral evaluations on *n*-type films.⁹ In these cases, in fact, the final states involved in the detected transitions are all extended states.

In the case of intrinsic *a*-Si:H films both transitions involving filled and empty defects are detected. According to the model previously assumed, these transitions occur at different energies: at ~ 1 eV for the transitions between filled defects and conduction bands and ~ 1.2 eV for those between valence bands and empty defects. Transitions involving tail states also contribute to the absorption process: if the valence-tail inverse slope is assumed to be 50 meV (Ref. 2) and the conduction tail one is of the order of 30 meV,¹⁰ it can be easily estimated that a non-negligible tail-to-tail contribution is present at 1.2 eV. On the other hand, it can be calculated that a valence-tail-empty-defect transition can occur at 1 eV. In this case, however, this contribution is negligible with respect to that arising from filled defects-conduction-band transitions, because of the much higher number of states involved in this process.

Thus, the conclusion that can be drawn is that the quantity $d[\alpha(h\nu)]/d(h\nu)$ represents the density of states of intrinsic *a*-Si:H only in two well-defined spectral regions: for $h\nu \approx 1$ eV (filled defects to conduction band) and for $h\nu \geq 1.9$ eV (valence band to conduction band). In the intermediate region, a further deconvolution has to be applied in order to separate the valence-band-to-empty-defect and the tail-to-tail contributions. As a consequence of this further deconvolution, results obtained on the distribution of the empty defects are affected by a higher degree of uncertainty.

EXPERIMENT

The application of the aforementioned derivative procedure on the absorption coefficient of intrinsic *a*-Si:H films requires PDS spectra with a very low signal-to-noise ratio. Furthermore, the unwanted modulation due to light interference within the film can complicate the analysis. Finally, much attention must be paid in minimizing the substrate contribution to absorption¹¹ that is non-negligible especially for device-quality films grown on glass substrates. The simplest way to solve these problems is to grow thick films on quartz substrates, the limitation being the possibility of sample peeling off.

Samples of device-quality, intrinsic *a*-Si:H were grown by rf plasma decomposition of silane. The deposition conditions and the predeposition and postdeposition treatments were approximately the same for all the samples. Slight deposition temperature variations (260–320 °C) between different runs were adopted in an attempt to change the bulk defect density of the samples within the range permitted for device-quality material. The idea behind this procedure is to change the defect

density of the samples without greatly affecting other optical properties, say the optical gap or the Urbach tail slope. In this way it is also possible to change the relative weight of bulk states with respect to surface states in the samples. In one case, a high density of “surface” defects has been artificially introduced within the sample by interrupting the deposition run several times and exposing the sample to air contamination. For all cases the sample thickness ranged from 2 to 4 μm , except for one sample whose thickness was 16 μm . In a separate case, a sample having a thickness of 1.6 μm has been considered in order to extract information about the surface defect density by means of an independent method which considers the anomalous value for the interference fringes contrast as linked to the surface absorption.¹²

The measurements were carried on in a conventional PDS apparatus, with CCl_4 as the deflecting medium. In order to further improve the signal-to-noise ratio a lock-in time constant of 1 s was chosen, and the data for a single energy value were averaged to obtain an uncertainty below 20%. It has to be noticed, however, that a double-beam PDS apparatus (as used by us) provides more reliable results.

In a double-beam PDS apparatus, the pump beam outcoming from the monochromator is split by a beam splitter (we use a chopper wheel with a specular surface) and the reference beam is directed to a detector (in our case a photoacoustic cell with carbon black). The responsivity of the system has been measured by comparing two photoacoustic cells, one of them placed in the sample position. This configuration reduces the experimental errors deriving from the standard procedure in which two separate measurements are done, one for the sample and one for the reference. These errors are dramatic in the case of nonstable discharge lamps (as in our case). More generally, in the double-beam apparatus the errors on the grating positioning or on the exit slit width, thus on the photon energy values, do not propagate to the α spectrum.

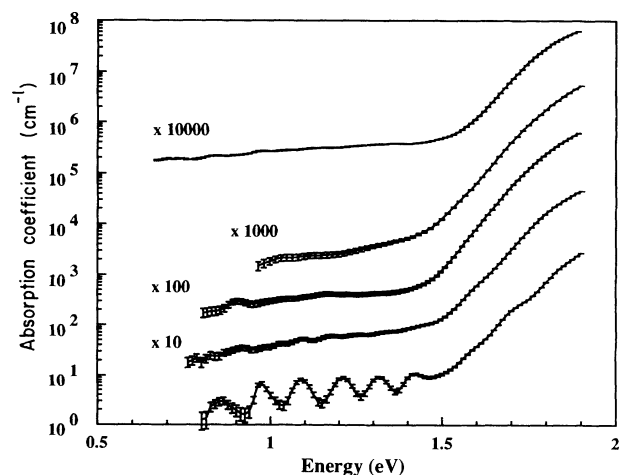


FIG. 1. Some typical PDS spectra as obtained on the samples under study. The curves are shifted by 1 decade for clarity purposes.

In Fig. 1 some spectra, as obtained on the samples under study, are reported. The lower curve pertains to the sample showing the anomalous value of the fringes contrast (3–3.5) while the upper curve is related to the sample in which a number of interfaces have been introduced as described above.

The (small) noise affecting the spectra has been further reduced by means of fast Fourier transform filtering. The same method has been used to eliminate the interference fringes modulation¹³ when necessary.

RESULTS AND DISCUSSION

Figure 2 shows some example of the first derivative spectra obtained on different samples. A broad structure around $E_{\text{expt}} \approx 1$ eV is detectable. This structure can be ascribed to D^0 - D^+ transitions. In fact, the energy position E_{peak} of the peak above the valence-band edge can be easily obtained by means of

$$E_{\text{peak}} = E_{\mu} - E_{\text{expt}} \quad (2)$$

This energy position seems to change from sample to sample. As a comparison, the same deconvolution procedure as carried out on a typical CPM spectrum is reported, leading to an energy shift of 0.1–0.2 eV. The derivative structure shows a Gaussian shape with half-width $\sigma \approx 0.1$ –0.15 eV: this result is in excellent agreement with other evaluations² and confirms the reliability of our deconvolution procedure.

As it can be recognized, another structure is embedded in the exponentially steep increase at $E \approx 1.4$ eV. This structure can be ascribed to D^0 - D^- transitions. In order to extract more quantitative information about this defect band, a further deconvolution procedure has been applied to the high-energy portions of the first derivative spectra, assuming that they are composed of a Gaussian curve and an exponential function. For this purpose, the program MINUIT, which fits the spectra in the five-

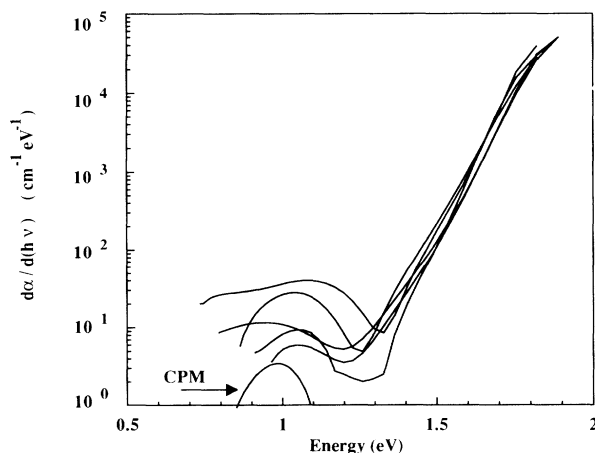


FIG. 2. First derivative spectra obtained for the samples whose absorption curves are reported in Fig. 1. The lower part of the first derivative spectrum as calculated on a CPM curve is shown for comparison.

dimensional space of the parameters, has been used. For both peaks, a numerical fit was carried out and the covariance matrix was extracted. The energy position of the filled (empty) defect peak has been evaluated with an uncertainty of the order of 8% (15%) while the error on the half-width is of the order of 3% (5%). The error affecting the evaluation of the peak intensity is 13% (50%). As a matter of fact, the errors on the unoccupied defects distribution are considerably higher than those typical of the filled defect distribution as a consequence of the further deconvolution procedure. Figure 3 summarizes some typical results showing the defect bands in the gap. The origin for energies has been fixed at the valence-band edge. The hatched regions represent the estimated uncertainty in the determination of the parameters of the defect distributions. As can be seen, the peaks are well correlated both in width and intensity, suggesting an equilibrium between filled and empty dangling bonds.

In the case of the upper curve in Fig. 3, the empty-defect distribution is quite narrow, if compared with the other evaluations. A possible explanation for this effect arises if the corresponding upper curve in Fig. 2 is considered. This curve, which has been obtained on a high-interface-defect sample, shows a broadening of the structure at 1 eV towards lower energies. If we ascribe this effect to a partial filling of empty defects, due to a Fermi-level shift, a narrower distribution of the “residual” emp-

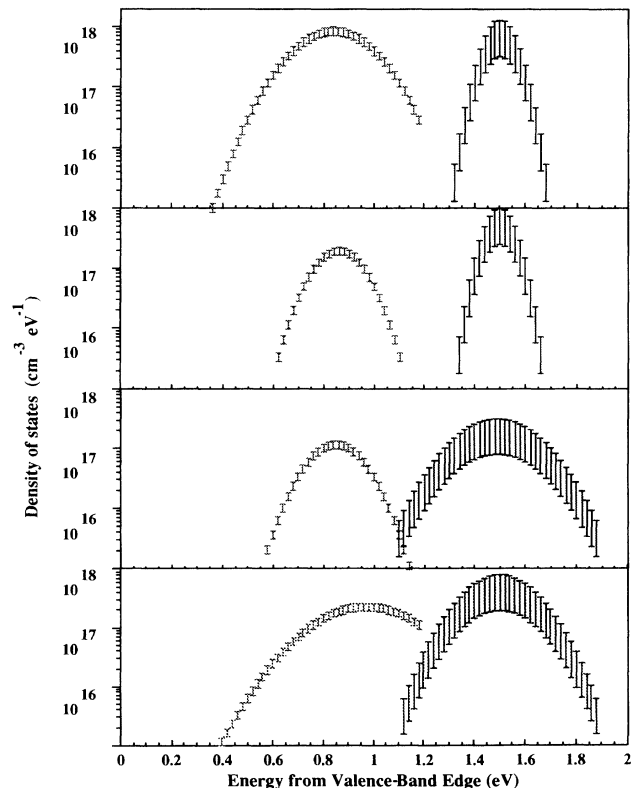


FIG. 3. Some defect distributions as inferred by deconvoluting the first derivative spectra. The hatched regions represent the uncertainty in determining the defect distribution.

ty defects is expected.

As a matter of interest, no structure at ~ 1.4 eV can be seen in CPM derivative spectra, confirming that only transitions leading to free electrons are detected. Recently,⁸ a similar structure has been detected by CPM on illuminated samples: the interpretation for this effect has that an additional defect band arose close to the valence tail because of light degradation. This interpretation has, however, to be verified: in fact, as clearly stated by Kocka, Vanecek, and Triska,⁵ in light-soaked material the mobility-lifetime product for electrons is comparable with the same quantity for holes, thus all the electronic transitions involving filled and empty defects are detectable, as in the case of PDS. The detected structure could thus be due to empty defects, as in the present work.

The calculation of the defect density is a key step in the characterization of amorphous silicon films. Among the various methods suggested to achieve such quantitative information, the integration rule of Jackson and Amer¹⁴ has been widely used. In this approach, a spectrum of defect-related absorption coefficient α_{expt} is obtained by subtracting the exponential Urbach slope $\alpha_{\text{Urbach}} = \alpha_0 \exp(h\nu/E_0)$ (E_0 is the Urbach energy) from the experimental absorption coefficient α :

$$\alpha_{\text{expt}}(h\nu) = \alpha(h\nu) - \alpha_{\text{Urbach}}(h\nu) \quad (3)$$

from the lowest energy for which α is obtainable to the energy where the defect absorption is supposed to terminate. To compute N_s (cm^{-3}), α_{expt} is integrated with respect to photon energy:

$$N_s = \text{const} \times \int \alpha_{\text{expt}}(h\nu) d(h\nu), \quad (4)$$

where the constant was taken to be $7.9 \times 10^{15} \text{ cm}^{-2} \text{ eV}^{-1}$. This procedure has been recently questioned¹⁵ on the basis of the fact that the optical sum rule (4) is incorrectly applied to electronic transitions.

The deconvolution method suggested in the present paper, on the other hand, provides detailed and reliable information especially for the distribution of filled defects. Thus a quantitative evaluation for the concentration of such defects can be extracted by integrating with respect to energy the Gaussian peak present in the first derivative spectra and centered at ≈ 1 eV. The derivative spectra need to be normalized to a value of the density of states. As it has been explained in the preceding sections, the first derivative spectrum represents, with a good accuracy, the density of states in the energy ranges $h\nu \geq 1.9$ eV and $h\nu \approx 1$ eV. Thus, normalizing the spectra at 1.9 eV to the density of states allows one to obtain the concentration of filled defects. At $h\nu = 1.9$ eV the DOS can be assumed⁵ to be $2 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$.

Figure 4 reports the results obtained by means of this procedure and compares them with those extracted following Ref. 14. It can be seen that a close correlation occurs suggesting that the integration rule, even if it has to be considered as an empirical approach,¹⁵ is able to provide realistic results in the case of intrinsic, device-quality *a*-Si:H.

The examples of defect DOS reported in Fig. 3 suggest a high effective correlation energy for the peaks. As a

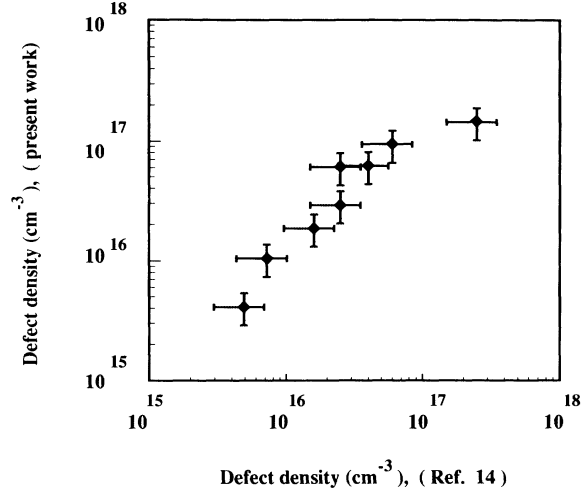


FIG. 4. Correlation between the defect density as inferred by our method and the same quantity as obtained according to the integration rule (Ref. 14).

matter of fact, the average value, as calculated on our set of samples, is $U_{\text{eff}} = 0.5 \pm 0.1$ eV.

This result is in very good agreement with the evaluation as carried out by means of another “purely optical” method like photomodulation spectroscopy¹⁶ (PM). Other evaluations, based, e.g., on photoconductivity,⁵ provide a lower value for U_{eff} . Furthermore, Fig. 2 clearly shows that the experimental energy for transitions involving filled defects differs from sample to sample and depends on the spectroscopic technique. As an example, the CPM evaluation assigns to the peak energy within the gap the value $E_{\text{peak}} \approx 0.9$ eV. It is remarkable that such a value has been extracted also by other workers⁸ by means of the same method on several samples.

We will focus on the filled defect peak energy, because this quantity is extracted with a low uncertainty. We suggest that the particular sensitivity of purely optical techniques like PDS or PM to surface states is responsible for such a mismatch. The relative weight of surface states with respect to bulk states W can be calculated in a simple way:

$$W = \frac{1}{d} \frac{N_{\text{surf}}}{N_{\text{tot}}}, \quad (5)$$

where N_{surf} is the surface-state density (in cm^{-2}), N_{tot} is the total defect density as evaluated by means of our method described above, and d is the film thickness. We assume $N_{\text{surf}} \approx 3 \times 10^{12} \text{ cm}^{-2}$ in agreement with the data available in literature.² In the case of the sample showing the anomalous fringes contrast (Fig. 1, lower curve) the density of surface defects has been evaluated to be $N_{\text{surf}} \approx 7 \times 10^{12} \text{ cm}^{-2}$. The absorption properties of the sample in which interfaces have been artificially introduced have been assumed as dominated by surface ($W = 1$). In the case of CPM, due to the relative insensitivity of this technique to surface states, it has been assumed that $W = 0$. Figure 5 reports the results relative to the peak energy as a function of the parameter W . As it

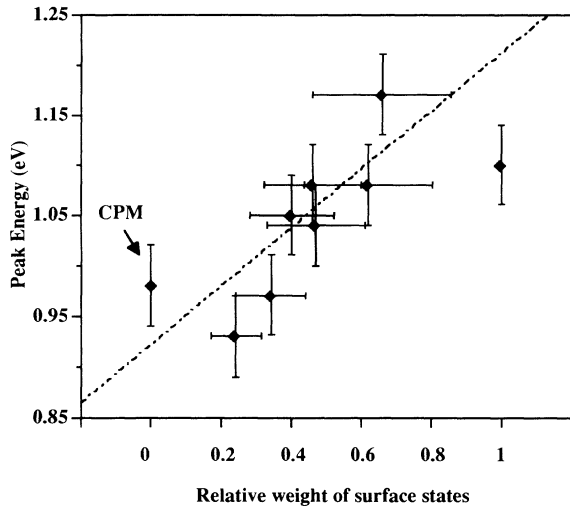


FIG. 5. Dependence of the experimental peak energy (Fig. 2) on the relative weight of surface states in the absorption process. The straight line is the linear fit of the data.

can be seen, besides the experimental uncertainties, the experimental peak energy increases together with the relative weight of surface states. Thus, the filled defect peak should increase in intensity and shift towards the valence band ($E_{\text{peak}} \approx 0.8$ eV) when moving from bulk to surface. A confirmation for this interpretation is suggested by the results inferred by total-yield spectroscopy,^{17,18} which demonstrate that a filled defects peak is located at $E_{\text{peak}} \approx 0.6$ eV. This technique probes the first 5–10 nm of the sample, thus it is intrinsically sensitive to surface states. PDS, on the other hand, averages the surface, interface, and the bulk absorption contributions. It seems very realistic to forecast for the results obtained by PDS a situation that averages between the opposite behaviors of total-yield spectroscopy and CPM. Some of the main differences between the physical systems investigated by PDS and total-yield spectroscopy are summarized below.

The surface of the samples studied by PDS is covered by a layer of native oxide. This layer is due to room-temperature oxidation in the air and has a thickness of a few nanometers.¹⁹ The conclusion is that an *upward* band bending²⁰ at *a*-Si:H surfaces covered with native oxide is present. Of course, this bending cannot be revealed by PDS. Moreover, because of the extremely low intrinsic surface-state density in *a*-Si:H, oxidation produces surface gap states that pin the Fermi level. All these phenomena tend to affect the optical properties of the film surface because the absorption coefficient depends on the amount of defects, on their energy position with respect to the band edges, and also on the occupation probability.

There is, however, another subtle difference: in total yield, due to the short light penetration depth, both extended and localized states are probed on the sample surface; in PDS, most of the localized states which are detected are on the surface, but the extended states are bulk states. The reason is that even at high energies (2

eV), the penetration depth is of the order of the sample thickness (10^{-4} cm). In the case of small variations of the optical gap on the surface, due to alloying with oxygen, the resulting effect could be a different value for E_{peak} .

The same considerations could be applied to the case of the empty-defect peak located at ~ 1.4 eV from the valence-band edge. It can be reasonably assumed that this peak shifts towards conduction-band edge when moving from bulk to surface. This is because the D^+ and D^- levels could be symmetrically displaced from midgap²¹ (“charge conjugation symmetry”). A confirmation to this reasoning derives from the analysis of PDS spectra as obtained on very thick samples. In fact, as it can be concluded by comparing Figs. 1 and 3, there is a close correlation between the *knee* energy in PDS spectra and the energy position of the empty-defect level. This is because the *knee* represents the transition between tail-dominated and empty-defect-dominated absorptions. The comparison between spectra as obtained on films having different thicknesses² shows that the *knee* shifts towards lower energies when the thickness increases, say, the relative weight of surface states decreases. In fact, in the case of the sample having a thickness of 16 μm the *knee* is detected at lower energies (1.4 eV). The deconvolution between a Gaussian and an exponential function shows that the Gaussian peak is centered at 1.3 ± 0.1 eV, thus the empty levels lie deeper in the gap. It is not possible, however, to search for a correlation like that described in Fig. 5 for the filled peak due to the large errors affecting the unoccupied defects distribution. It is interesting, however, that the partial result in the case of a very thick sample provides support to our interpretation.

These results can be explained by considering a defect pool²² mechanism for defect creation. We assume that three types of defects, namely *A*, *B*, and *C* defects, can be created in the film. Defects of type *B* are located near midgap, while *A* and *C* defects are shifted towards the valence band and conduction band, respectively. Furthermore, the formation energy of groups *A* and *C* is greater than group *B*. In the bulk the number of sites with *B* defects is much higher than the number of sites with *A* and *C* defects. At the surface, on the other hand, the oxygen-induced band bending resembles in a higher carrier concentration. This carrier concentration lowers the formation energy of either the *A*- and *C*-type defects, so defects which are *invisible* in the bulk can be dominant on the surface. A similar mechanism could also be considered for the substrate interface. Thus, the conclusion that can be drawn is that defect bands that can be detected by PDS in commonly thin films (1 μm) are of a different type than those detected by PDS in thick films (10 μm) or by other, surface-insensitive techniques.

CONCLUSIONS

The first results on the distribution of defect states on *a*-Si:H oxidized surfaces, as inferred by PDS, are provid-

ed. It is shown that, even if a great deal of complications is present, these results can be compared with those by total-yield spectroscopy. A method for the evaluation of the defect content in *a*-Si:H is suggested: this method agrees with other empirical models but allows a deeper physical insight. The high values for the defect effective correlation energy as obtained by purely optical methods are interpreted in terms of sensitivity of such techniques to surface states. These states should lie closer to the cor-

responding mobility edges according to a "defect pool" formulation.

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