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Surface effects in hydrogenated amorphous silicon studied by photothermal-deflection experiments

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The optical-absorption spectra of glow-discharge undoped *a*-Si:H films deposited on silica and Corning 7059 glass substrates have been determined between 0.6 and 2 eV, using both the photothermal-deflection-spectroscopy (PDS) and constant-photocurrent (CPM) methods. All the samples, with thicknesses ranging from 0.5 to 10 μm, had identical values of the optical gap and of the dark-conductivity activation energy (with the minor exception of the thinnest film for the latter). The results of conventional PDS experiments at low modulation frequency on films with different thicknesses confirm previously reported conclusions regarding the existence of substantial surface or interface absorption in device-quality undoped *a*-Si:H films. In contrast, the CPM-derived absorption spectra show very little, if any, surface or interface effect. They coincide within experimental uncertainties with the PDS-derived spectra obtained for the thickest films, down to about 1.1 eV. At lower energies, the CPM-derived absorption coefficient values decrease rapidly with decreasing energy, while the PDS-derived ones remain roughly constant for both types of substrates. In order to discriminate between bulk, surface, and interface absorption in this low-energy range, we used PDS experiments at high modulation frequency, in which we compared the values of the phase lag of the PDS signal with respect to the exciting beam, measured on thick (7–10-μm) films for front and rear illumination, the probe-beam–sample geometry remaining identical in both cases. We derive conclusive evidence that, for our films deposited either on silica or on glass substrates, the absorption measured by PDS at energies lower than 1 eV comes essentially from the free-surface region.

I. INTRODUCTION

Various experiments performed on hydrogenated amorphous silicon (*a*-Si:H) films prepared by glow-discharge decomposition of silane have shown surface-interface effects. It was first suggested[1–3] that the large scatter in the data observed in transport measurements could, at least partially, be explained by uncontrolled band bending at the film surfaces, due to a variable density of surface charges. The existence of surface layers with transport properties different from the "bulk" was confirmed by the analysis of the film thickness dependence of the dark conductivity and of the photoconductivity, both in undoped and doped samples.[4–7] However, the models proposed for the interpretation of these experiments did not allow one to determine unambiguously whether these surface layers were located at the film-free surface, or at the film-substrate interface, or at both surfaces. Moreover, it was difficult to decide whether such layers were the result of band bending induced by surface charges, or were attributable to structural inhomogeneities in the films near their surfaces.

More direct evidence for the presence of defective surface or interface layers was provided by electron-spin-resonance (ESR) experiments which showed that the spin density corresponding to the signal with $g = 2.0055$, ascribed to neutral dangling bonds, increased with decreasing film thickness.[8,9] The density of surface defects was found to be of the order of a few 10^{12} cm^{-2} for undoped samples, and seemed to be correlated with an enhancement of the hydrogen concentration near the film free surface. In more recent ESR experiments scanning a wide thickness range, the thickness of the defective layer was estimated to be of the order of 20 nm.[10,11]

Similar conclusions were deduced from studies of the sub-band-gap optical absorption by photothermal-deflection-spectroscopy (PDS) experiments. The apparent "optical" density of deep defects determined from the integrated low-energy absorption[12] was also found to increase with decreasing film thickness,[13,14] the estimated surface defect density being of the order of a few 10^{12} cm^{-2} (depending on the doping level),[13] in agreement with the previously mentioned ESR results. A careful analysis of the PDS data obtained for undoped samples covering a large thickness range later showed that the experimental results were best accounted for by a model assuming an exponential distribution of the defects from the surface, with a typical depth of the order of 20 nm,[14,15] again in agreement with the ESR conclusions. These experiments did not, however, permit a differentiation between surface and interface layers, as will be discussed below; the depth value entering the model must be considered as an "average" of surface and interface layer thicknesses, if both types of layers are present in the samples. The results of the sub-band-gap absorption studies conducted by the constant-photocurrent method[16] (CPM) are less clear. It has been shown that the CPM data are much less sensitive to surface states than the PDS data, which has been explained by the fact that the photoexcited carriers generated near the surface should have a reduced contribution to the photocurrent.[17] However, evidence for some surface effects in CPM measurements, especially for thin films, has also been reported;[11] these effects were an order of magnitude smaller than those found in ESR experiments on the same samples.

It seems therefore well established that surface-interface defects giving rise to an enhancement of both the spin density and the sub-band-gap optical absorption exist in a variety of *a*-Si:H samples, with an estimated density of the order of a few 10^{12} cm^{-2}. However, the problem of their location, either at the free surface, or at the film-substrate interface, is still a matter of debate. The decrease of the surface defect density by HF etching observed both in ESR (Ref. 10) and PDS (Ref. 18) experiments suggested that most of them are located at the film-free surface. The same conclusion was reached from the comparison of the CPM data obtained with illumination from the front and rear sides of the samples.[10] On the contrary, it was deduced from the analysis of the respective interference fringe contrast of the PDS spectra corresponding to front and rear side illumination that no absorbing centers were present at the film free surface, and that about 30% of the total absorptance was concentrated at the film-substrate interface.[19] It must, on the other hand, be emphasized that techniques which allow one to measure the free-surface density of states *in situ* just after sample deposition, namely Kelvin probe[20] and total yield photoelectron spectroscopy,[21] led for undoped samples to values of the order of one to a few 10^{11} cm^{-2}, that is an order of magnitude lower than the values estimated by more indirect techniques on samples submitted to ambient atmosphere. But adsorption of activated oxygen on the clean surfaces was found to increase the defect state density up to about 3×10^{12} cm^{-2}.[22]

In the present paper, we show that, by an appropriate choice of PDS experiments, it is possible, not only to give conclusive evidence regarding the existence of surface and/or interface effects as advanced by the earlier studies, but also to determine unambiguously where the corresponding defects are located. In the first part, we analyze the optical-absorption spectra deduced from PDS experiments performed in the usual way at low modulation frequency, i.e., under the conditions of thermally thin samples, as a function of film thickness for undoped and doped samples and for different substrates, and we compare these spectra to those obtained from CPM measurements on the same samples. In the second part, we describe how we used PDS experiments performed at high modulation frequency, in which the thermal diffusion length is comparable to the film thickness and the phase of the PDS signal can give information about the location of the heat sources in the samples, to establish that the defective layer is located at the free surface of our samples.

II. EXPERIMENT

A. Sample preparation

The *a*-Si:H samples were prepared at Harvard University[23] by glow-discharge decomposition of silane under the following optimized deposition conditions: rf power density, 30 mW cm^{-2}; total pressure, 200 mTorr; silane flow rate, 20 SCCM (where SCCM denotes cubic centimeter per minute at STP); substrate temperature, 230 °C. The film thickness, as determined from the analysis of the interference fringes of the transmission spectra, ranged from 0.5 to 10 μm. All the undoped samples had the same optical gap, $E_{04}=1.90+0.02$ eV, and the same dark-conductivity activation energy, $E_\sigma=0.83\pm0.02$ eV. However, for the thinnest films ($d\simeq0.5$ μm), the E_σ values tended to be larger, of the order of 0.9 eV. The P-doped samples, prepared by adding phosphine to silane at a concentration of 9 ppm in the gas phase, had the same optical gap as the undoped ones, and an activation energy $E_\sigma=0.35$ eV. For the same film thickness, all the results were very reproducible, irrespective of the nature of the substrates, either Corning 7059 glass or silica. For comparison, we also studied a thick undoped sample deposited at the same substrate temperature, but at a higher rf power density, 300 mW cm^{-2}, and with silane diluted in deuterium: $[\mathrm{SiH_4}]/[\mathrm{D_2}]=0.1$; this sample had a larger optical gap, was more disordered, and contained more defects, as we shall see below.

B. PDS experiments

The first series of PDS experiments was performed at a low modulation frequency, $f=13$ Hz, of the intensity of the exciting beam. The thermal diffusion length in *a*-Si:H, $\mu=(D/\pi f)^{1/2}$, where $D=K/\rho c$ is the thermal diffusivity, with K the thermal conductivity, C the specific heat, and ρ the density, is then much larger than the film thickness d: $\mu\simeq150$ μm, which means that the sample can be considered as thermally thin. By operating at low frequency, not only do we increase the sensitivity of the measurements and optimize the signal-to-noise ratio, but also we simplify considerably the analysis of the data leading to the determination of the optical-absorption coefficient. In the general case, the photothermal deflection Θ at a distance x from the sample surface is given in a one-dimensional model (under the assumption that the probe beam dimension is small compared to the spatial extent of the temperature distribution in the deflection medium) by[24]

$$\Theta=\frac{L}{n_0}\frac{\delta n}{\delta T}\sigma_f T_0\exp(-\sigma_f x)\exp(-i2\pi f t)\ , \qquad (1)$$

where L is the interaction length between the probe beam and the exciting beam, n_0 the room-temperature value of the refractive index of the deflection medium, and $\delta n/\delta T$ its variation with temperature, $\sigma_f = (1+i)/\mu_f$, and $T_0 = |T_0| \exp(i\varphi_0)$ the complex amplitude of the periodic temperature of the surface in contact with the deflection medium. Θ depends in a complex way on the thermal and optical properties of the sample through the surface temperature T_0. In the case of thermally thin samples, it can be shown that the modulus of the PDS signal is simply proportional to the film absorptance $A = 1 - (\mathcal{R} + \mathcal{T})$, with $\mathcal{R}$ and $\mathcal{T}$ being, respectively, the film reflectance and transmittance at the photon energy $\hbar\omega$:[25]

$$|\Theta(\hbar\omega)| = \Theta_0 A(\hbar\omega) .$$

Θ_0 depends only on the thermal and geometrical properties of the system, and not on the film optical properties. A can therefore be obtained by a mere calibration procedure, as explained below, and the optical-absorption coefficient α is then easily determined. The phase of the PDS signal is in this case a constant with respect to the film optical properties, and does not bring any additional information.

We used a conventional PDS setup in the parallel configuration, with a 250-W tungsten-halogen lamp followed by a H25 Jobin Yvon monochromator as the exciting source, and a 1-mW He-Ne laser as the probe beam; the PDS signal was measured by a four-quadrant Si position detector. The sample was immersed in CCl_4 in order to enhance the PDS signal. The measurements were performed in the spectral range from 2 to 0.6 eV. The modulus of the PDS signal was first normalized to the exciting beam intensity measured with a pyroelectric detector. Special care was then paid to the calibration of these normalized spectra $|\Theta(\hbar\omega)|$. Instead of using the so-called calibration at saturation,[12] we preferred to fit each PDS spectrum to the corresponding absorptance spectrum $A(\hbar\omega)$ computed from the values of the optical constants n and k (real and imaginary parts of the complex refractive index) deduced from the analysis of the transmission spectrum of the same sample. Depending on the film thickness, we used for the computation of $A(\hbar\omega)$ either exact thin film formulas,[26] or approximate expressions valid for $k \ll n$:[27]

$$A_C = (1-r_0^2)\frac{1 - r_1^2 e^{-2\alpha d} - (1-r_1^2)e^{-\alpha d}}{1 + r_0^2 r_1^2 e^{-2\alpha d} + 2 r_0 r_1 e^{-\alpha d}\cos 2n\beta} ,$$

with $\alpha = 4\pi k/\lambda$ and $\beta = 2\pi d/\lambda$, for coherent multiple reflections in the film, and

$$A_I = (1-r_0^2)\frac{1 - r_1^2 e^{-2\alpha d} - (1-r_1^2)e^{-\alpha d}}{1 - r_0^2 r_1^2 e^{-2\alpha d}}$$

for incoherent multiple reflections (no interference fringes). r_0 and r_1 are, respectively, the approximate (real) values of the Fresnel coefficients at the CCl_4-film and film-substrate interfaces (n_0 and n_s being the refractive index of CCl_4 and of the substrate) for $k \ll n$:

$$r_0 = \frac{n_0 - n}{n_0 + n} , \quad r_1 = \frac{n - n_s}{n + n_s} .$$

We usually obtained a very good agreement between the $|\Theta(\hbar\omega)|$ and $A(\hbar\omega)$ spectra over a large spectral range in the high absorption region, i.e., for α values between 5×10^2–10^3 cm^{-1} and (1–5)$\times10^4$ cm^{-1}, where the absorption is due to transitions between extended states in both bands, or between extended states in one band and shallow states in the tail of the other band, and is therefore representative of the "bulk" optical properties of the films. The optical-absorption coefficient spectrum $\alpha(\hbar\omega)$ was then determined from the calibrated $|\Theta(\hbar\omega)|$ spectrum, using similar thin-film expressions. This procedure allows us in principle to get rid of the interference fringes of the PDS spectra, provided $n(\hbar\omega)$ and d are known with sufficient accuracy. For thick films, we used an averaging procedure based on the fact that A_I, which in the low absorption range ($\alpha d \ll 1$) is proportional to αd:[27]

$$A_I = \alpha d \frac{(1-r_0^2)(1-r_1^2)}{(1-r_0^2 r_1^2)}$$

is equal to the geometrical average of the values of the maxima and minima of the A_C interference fringes:

$$A_I = (A_M A_m)^{1/2} .$$

The $\alpha(\hbar\omega)$ spectrum over the whole spectral range was eventually obtained by combining the optical and PDS results.

The second series of PDS experiments was performed at high modulation frequency: $f = 5$ kHz, in order to decrease the thermal diffusion length in a-Si:H to a value ($\mu \simeq 8$–9 μm) comparable to the film thickness: $\mu \simeq d$. Under such conditions, both the modulus $|T_0|$ and the phase φ_0 of the surface temperature which enters the expression (1) of the photothermal deflection Θ depend on the spatial distribution of the heat sources inside the film. The phase of the PDS signal now depends on the optical properties of the film through φ_0, the phase of the surface temperature, and becomes a significant parameter. Its measurement will be used to locate the surface absorption, as explained below.

At high modulation frequencies, the periodic surface temperature is lowered and the thermal diffusion length in the deflection medium μ_f decreases significantly. This implies first that the PDS signal is considerably reduced, second that it is necessary to bring the probe beam very close to the sample surface, especially in CCl_4. These experimental difficulties were partially overcome by using air as the deflection medium ($\mu_f = 37$ μm in air compared to $\mu_f = 2.2$ μm in CCl_4, at $f = 5$ kHz). Besides, in order to increase the signal-to-noise ratio, we used a high-sensitivity compact mirage cell[28] coupled with a 250-W xenon arc followed by wideband filters for selecting appropriate spectral ranges (the light-power density being of the order of 0.1 W cm^{-2}) as the exciting source.

C. CPM experiments

Photoconductivity measurements in the low absorption range can be used to determine the optical-absorption spectrum since, for $\alpha d \ll 1$, the film photoconductance per unit area σ can be written in first approximation:[29]

$$\sigma=(\phi\alpha d)e\eta\mu_D\tau_R ,$$

where ϕ is the incident photon flux per unit area, η is the carrier generation quantum efficiency, μ_D is the drift mobility of the dominant photocarrier, and τ_R is the response time of the photoconductivity. If the measurements are performed at constant photocurrent by adjusting the incident photon flux $\phi(\hbar\omega)$, the concentration of photogenerated carriers is presumably kept constant and one gets[16]

$$\alpha(\hbar\omega)\simeq|\phi(\hbar\omega)|^{-1} .$$

The CPM experiments were performed on samples codeposited with the PDS samples on Corning 7059 glass substrates, using evaporated Cr contacts in the coplanar surface-cell geometry. Photoexcitation was provided by a tungsten-halogen lamp followed by a Leiss double prism monochromator and calibrated neutral density filters. All the photocurrent data were taken in the dc mode (without light modulation) using two Keithley 602 electrometers. The sample temperature was kept constant within ±0.5 °C in each spectral measurement. The *I*-*V* curves were found to be slightly sublinear near the applied field of 100–200 V cm^{-1}, both in the dark and under illumination. However, this *I*-*V* sublinearity was found to be spectrally invariant, hence the photocurrent spectra or the CPM data were not affected by the electrical contacts. The CPM spectra were obtained both in the light-exposed state and after thermal annealing in high vacuum (about 4×10^{-6} Torr) at 180 °C–190 °C for 40 min. The near-midgap absorption in the light-exposed state was found to be typically higher by a factor of 2–3 than that obtained after annealing. In this paper, only data from the annealed state will be presented.

Like the PDS spectra, the CPM spectra must be calibrated in order to obtain correct α values. In order to ensure a meaningful comparison with the PDS results, we have used the same method of fitting to the optical data at high energies. The calibration procedure is, however, less straightforward in this case because the CPM-derived absorption coefficient shows an apparent decrease at photon energies a little greater than the onset energy for extended state to extended state transitions. This effect (also observed in measurements on crystalline semiconductors) is attributed to surface recombination of the carriers, the majority of which are then created very close to the surface due to the decrease of the light penetration depth. The fit to the optical data can therefore be obtained only in the exponential part of the edge, where the absorption is due to transitions between localized band tail states on one side and extended states on the other side. It happens that, in *a*-Si:H, the optical Urbach edge is determined by transitions from occupied localized states in the wider valence-band tail to empty conduction extended states,[30] while the photoconductivity in this absorption range is dominated by the same type of transitions which create more mobile photoexcited electrons.[29] The calibration which we used is therefore correct, and should give CPM results identical to the PDS ones in the Urbach edge region.

III. EVIDENCE FOR SURFACE-INTERFACE EFFECTS

We discuss here the results of the first series of PDS experiments performed as a function of film thickness. Figure 1 presents the optical-absorption coefficient spectra $\alpha(\hbar\omega)$ obtained for undoped *a*-Si:H films deposited on Corning 7059 glass substrates, with thicknesses varying from about 0.6 to 7.5 μm. These samples were measured in their as-deposited state, but no change in the data could be detected after one hour annealing at $T_A=190\,^\circ\mathrm{C}$. All the spectra coincide in the high-energy range, down to about 1.6 eV; the inverse slope of the exponential part of the edge [written as $\alpha=\alpha_0\exp(\hbar\omega/E_0)$] measured in the $10-10^2$ to 5×10^3 cm^{-1} α range for all samples is equal to $E_0=55\pm2$ meV. At low energies, on the contrary, the apparent absorption increases with decreasing film thickness, as already reported.[13–15,31] This is a clear indication of the presence of surface and/or interface absorption. Indeed, what we measure in PDS experiments is the film absorptance $A(\hbar\omega)$, which, in the low absorption range ($\alpha d \ll 1$), is simply proportional to αd. In the presence of a surface or interface layer with absorption coefficient α_s and typical thickness d_s, one can write in first approximation

$$A\simeq\alpha_b d+\alpha_s d_s$$

if α_b is the bulk absorption coefficient. Since in our analysis of the PDS data we have ignored any surface layer, what we obtain is an "apparent" absorption coefficient $\bar{\alpha}$ given by

$$\bar{\alpha}=\frac{A}{d}=\alpha_b+\frac{\alpha_s d_s}{d}=\alpha_b+\frac{\alpha_s^{\square}}{d} , \tag{2}$$

$\alpha_s^{\square}$ being the surface-interface absorption per unit area.

For sufficiently thick samples ($d \gg d_s$) where the surface term can be considered as negligible, $\bar{\alpha}$ must tend towards α_b, i.e., towards the "bulk" film properties. As the

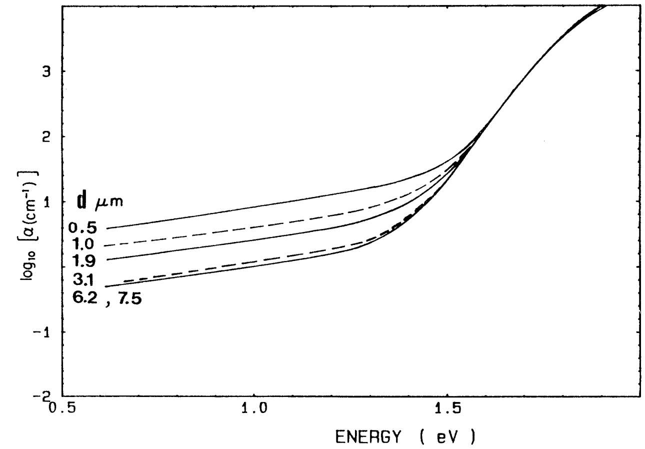

FIG. 1. Optical-absorption coefficient spectra deduced from a combination of optical and PDS measurements for a series of undoped *a*-Si:H films deposited on glass substrates under identical optimized conditions, with thicknesses varying from 0.49 to 7.5 μm.

film thickness decreases, however, the surface term becomes more and more important, which results in an increase of $\bar{\alpha}$.

It can be seen from Fig. 1 that there is already very little difference between the sub-band-gap absorption of films with thickness, respectively, equal to 3.1 and 7.5 μm, which means that in our case PDS measurements on films a few μm thick allow us to reach the material bulk properties. In similar studies conducted on *a*-Si:H films prepared by a very high frequency glow-discharge technique leading to high deposition rates, the surface-interface contribution was shown to be negligible only for films thicker than 40 μm.[15] These conflicting results can be explained by a different balance between bulk and surface absorption, and emphasize the sensitivity of surface phenomena to the sample preparation conditions.

In order to compare our results with those of previous studies, we tried to estimate the respective densities of bulk and surface-interface defects from the analysis of the optical-absorption data presented in Fig. 1. Although the validity of such a procedure can be questioned in many respects (see, for example, Ref. 32), we deduced an "optical" total defect density N_D from the integral of the excess sub-band-gap absorption $\Delta\alpha$ obtained after subtraction of the extrapolated exponential edge contribution: $\alpha=\alpha_0 \exp(\hbar\omega/E_0)$, through the relation proposed and discussed in Ref. 12, and used up to now in most PDS studies:

$$N_D = 7.9\times 10^{15} \int \Delta\alpha(\hbar\omega) d(\hbar\omega) \ .$$

According to expression (2), a plot of the N_D values determined in this way as a function of the reciprocal film thickness d^{-1} should allow us to estimate both the bulk defect density $N_D(b)$ and the surface-interface defect density per unit area $N_D(s)$. We found $N_D(b) \simeq (2-3)\times 10^{15}$ cm^{-3} and $N_D(s) \simeq (4-5)\times 10^{12}$ cm^{-2}. It is worth noting that we obtained the same ratio between bulk and surface-interface contributions by simply plotting the α values at $\hbar\omega = 1$ eV as a function of d^{-1}. The large uncertainties on our defect densities can be partly explained by the small number of samples investigated (especially thin ones), but could also be related to slight differences in surface-interface effects between these samples. Our results are, however, in good agreement with previously reported ones.[13,15] It can be noticed that, for a 10-μm thick film, the bulk and surface contributions to the defect density (defect absorption) are of the same order of magnitude.

The optical-absorption spectra deduced from CPM measurements on undoped *a*-Si:H films with different thicknesses deposited simultaneously with those studied by PDS are presented in Fig. 2; the interference fringes were not averaged out deliberately. The PDS-derived spectrum of the thickest film (7.5 μm) is also reported for comparison. The samples were annealed at $T_A = 190\,^\circ$C during an hour before the photoconductivity measurements, in order to eliminate any Staebler-Wronski effect. It can be seen in Fig. 2 that all the CPM-derived spectra coincide within experimental uncertainties over the whole accessible spectral range. Moreover, they are in very good agreement with the PDS-derived spectrum typical of thick films, down to about 1 eV. This indicates that there is very little, if any, surface contribution to the photoconductivity in our *a*-Si:H samples. It should be noted that our CPM-derived absorption coefficient values do not fall below the PDS-derived ones in the 1.5–1.1-eV spectral range, as reported in a previous study.[17] Since our CPM spectra were carefully calibrated by fitting to the optical data in the high-energy part of the Urbach edge region, this suggests that in our case, the relative contribution of transitions generating mobile photoelectrons in the conduction band to the total optical absorption stays the same from the calibration region down to about 1 eV.

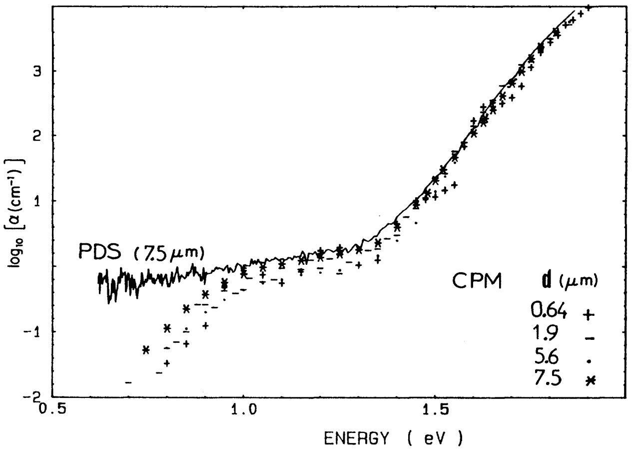

FIG. 2. Optical-absorption coefficient spectra deduced from a combination of optical and CPM measurements for a series of undoped *a*-Si:H films deposited on glass substrates under the same optimized conditions as the films used for the PDS mesurements (see Fig. 1), with thicknesses varying from 0.64 to 7.5 μm; the PDS-derived spectrum for the thickest film (7.5 μm) is also reported for comparison.

The deviation between the CPM- and PDS-derived spectra at low energies ($\hbar\omega < 1$ eV) has already been pointed out.[31,33] We have argued that the CPM-derived absorption coefficient starts to drop when the photon energy is no longer sufficient to allow transitions creating mobile photoelectrons in extended states of the conduction band.[31] The correlation observed in doped samples between the energy below which the two types of spectra separate and the position of the Fermi level supports this interpretation.[31] However, it is difficult to explain why the PDS-derived absorption coefficient remains nearly constant down to 0.6 eV in Fig. 1, even for thick samples, since the density of tail states which act as initial or final states in low-energy optical transitions decreases exponentially over a rather narrow energy range.[33] In order to rule out any influence of substrate absorption, which was suggested to play an important role at low energies,[34] we have repeated the PDS experiments on a series of undoped *a*-Si:H films with different thicknesses, deposited under the same conditions as before but on silica substrates. For the same film thickness, we obtained

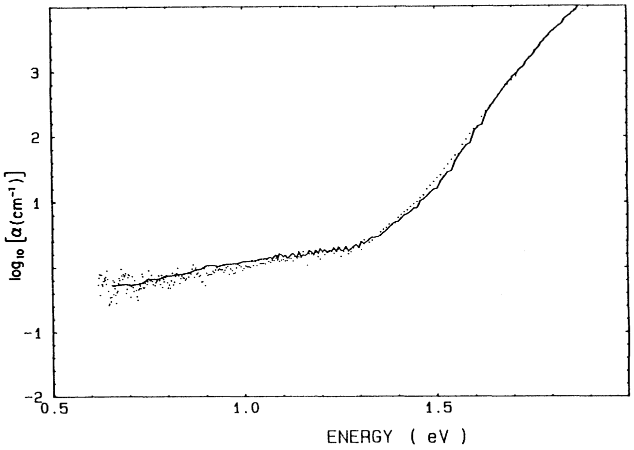

FIG. 3. Comparison between the optical-absorption coefficient spectra deduced from PDS experiments for two thick films ($d = 7.5$ and 8.9 μm) deposited under identical optimized conditions on glass (dots) and silica (continuous line) substrate, respectively.

exactly the same results over the whole spectral range for the two types of substrates; this is illustrated in Fig. 3 in the case of thick films ($d \simeq 7-9$ μm). One must therefore consider the possibility that surface absorption in the films dominates the PDS-derived data at low energies, even for thick ones.

For completeness, Fig. 4 shows the optical-absorption spectra deduced from PDS experiments for two P-doped films with different thicknesses; the interference fringes were deliberately not averaged out. The two spectra are identical within experimental uncertainties. This does not necessarily mean that there is no surface absorption in these samples, since the sub-band-gap absorption is noticeably increased with respect to undoped films due to defect creation by doping. The bulk absorption is therefore likely to conceal any surface absorption of the order of that evidenced in undoped samples.

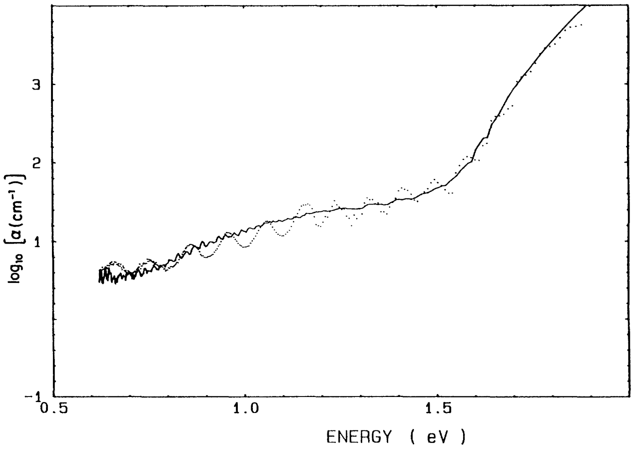

FIG. 4. Optical-absorption coefficient spectra deduced from PDS experiments for two P-doped a-Si:H films deposited on glass substrates under identical optimized conditions, with different thicknesses: $d = 1.56$ μm (dots) and 7.06 μm (continuous line).

IV. LOCATION OF THE SURFACE-INTERFACE OPTICAL ABSORPTION

In order to discriminate between surface and interface absorption in the sub-band-gap energy range, we used phase measurements in PDS experiments performed at high modulation frequency on thick films. As already pointed out in Sec. II B, the phase of the PDS signal depends on the spatial distribution of the heat sources in the film when the thermal diffusion length in the material μ is of the order of the film thickness d. One can intuitively predict that, for the usual probe-beam–sample configuration, the phase lag of the PDS signal with respect to the exciting beam will be larger if the heat sources are localized at the film-substrate interface than if they are localized at the film-free surface, due to thermal diffusion across the film. If, on the contrary, the heat sources are uniformly distributed over the film thickness, the phase lag will be equal to some average of these two extreme values.

The localization of the heat sources at the free surface and at the film-substrate interface can easily be achieved by shining strongly absorbed light ($\alpha d \gg 1$) from the front side and the rear side of the sample, respectively. As the optical-absorption coefficient decreases, the penetration depth of the incident light in the material increases and, if bulk absorption prevails, the spatial distribution of the heat sources will extend more and more into the film. Figure 5 shows the theoretical variations of the phase of the surface temperature for front (φ_F) and rear (φ_R) illumination as a function of αd, for different d/μ values.[35] For a given d/μ value, i.e., a given modulation frequency f, the computed φ_F and φ_R values are comprised between the two asymptotes corresponding to $\alpha d \rightarrow \infty$, which are separated by $\Delta\varphi_\infty$ given by the simple expression[36] (valid for $\alpha d \gg 1$ and $\mu d \gg 1$)

$$\tan(\Delta\varphi_\infty)=\tan\left[\frac{d}{\mu}\right]\frac{\left[1-\frac{(1-b)}{(1+b)}\exp\left[-\frac{2d}{\mu}\right]\right]}{\left[1+\frac{(1-b)}{1+b}\exp\left[-\frac{2d}{\mu}\right]\right]}\,, \qquad (3)$$

where $b = e_s/e$ is the ratio of the substrate (e_s) and film (e) effusivities [with $e = (K\rho C)^{1/2}$], which accounts for a possible thermal mismatch between the film and its substrate; in the computations reported on Fig. 5, b has been taken equal to 1 for simplicity. As αd decreases, φ_F increases and φ_R decreases in absolute values, as if the heat sources were moving away from the free surface and film-substrate interface, respectively, deeper into the film. For $\alpha d \rightarrow 0$, φ_F and φ_R eventually tend towards the same "average" value, which corresponds to a uniform distribution of the heat sources across the film.

The principle of our method was therefore the follow-

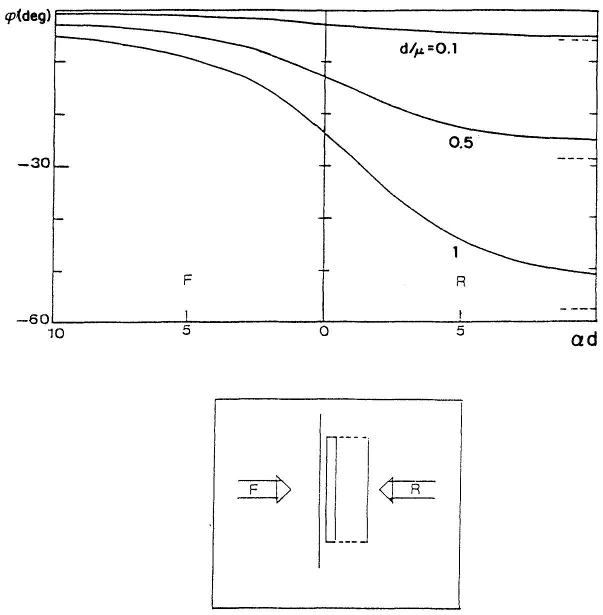

FIG. 5. Theoretical variations of the phase φ of the surface temperature of a film with thickness d and optical-absorption coefficient α, for front (F) and rear (R) illumination (as illustrated in the lower part of the figure), as a function of αd, for different values of the thickness to thermal diffusion length ratio d/μ; the substrate to film effusivity ratio b has been taken equal to 1 for simplicity.

ing. In a first experiment, we determined the "reference" phase values corresponding to surface and interface absorption by front and rear illumination of the sample with strongly absorbed light, the probe-beam–sample geometry remaining identical in both cases. Such a "differential" method has the advantage of eliminating the thermal diffusion in the deflection medium. Then we repeated the experiment with moderately absorbed light, in a region where the optical absorption is still essentially a bulk effect, in order to check the validity of the method. Eventually, we selected a low-energy range where surface-interface absorption was thought to dominate, and we compared the measured phase values for front and rear illumination with the "reference" values obtained in the first experiment. It can be seen from Fig. 5 that the difference between φ_F and φ_R for any αd value increases with increasing d/μ; this indicates that the measurements should be done on thick films at high modulation frequency. However, since the PDS signal decreases with increasing f, a compromise value must be found in order to have both a measurable phase difference $|\varphi_F - \varphi_R|$ and a good signal-to-noise ratio. We chose $f = 5$ kHz and film thicknesses ranging from 7 to 10 μm.

In order to interpret our data correctly, a thermal characterization of our films was first necessary. We used a method[36] which consists in analyzing the variation with the modulation frequency f of the difference $\Delta\varphi_\infty$ between the phase values corresponding to front and rear illumination with strongly absorbed light. According to expression (3), $\Delta\varphi_\infty$ depends only on the film and substrate thermal properties through μ and b, and on the modulation frequency f through μ. Figure 6 presents the theoretical variations of $\Delta\varphi_\infty$ with d/μ (or $f^{1/2}$) for different b values;[37] for large enough d/μ values, $\Delta\varphi_\infty$ is simply proportional to d/μ. The film diffusivity D and the parameter b can easily be deduced from measurements of $\Delta\varphi_\infty$ versus $f^{1/2}$ over a sufficiently broad modulation frequency range. These experiments were performed with an argon laser ($\hbar\omega \simeq 2.5$ eV) as the exciting source and the high-sensitivity compact mirage cell mentioned in Sec. II B. Figure 7 shows the experimental $\Delta\varphi_\infty$ values as a function of $f^{1/2}$ in the 0–20 kHz range for three typical thick samples deposited on Corning glass substrates: an undoped ($d = 7.5$ μm) and a doped ($d = 7.06$ μm) film deposited under standard conditions, and an undoped ($d = 9.9$ μm) film prepared with SiH_4 diluted in D_2 (see Sec. II A). The film diffusivity D is first deduced from the slope of the linear behavior observed at high frequency; the b parameter is then determined by fitting the data at low frequencies with expression (3).[37] The D and b values for the three samples are summarized in Table I. The two samples deposited under standard conditions, either undoped or doped, have very similar thermal properties, while the third sample has both a smaller diffusivity $D = K/\rho C$ and a smaller effusivity $e = (K\rho C)^{1/2}$ (since e_s is the same for all samples). This can be explained by a smaller thermal conductivity, which can be related to the increased heterogeneity of the samples deposited with high H_2 (D_2) dilution.[38] It is im-

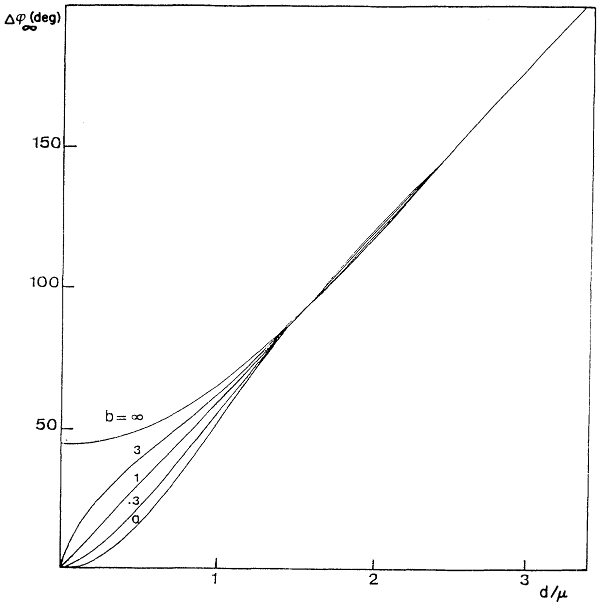

FIG. 6. Theoretical variations of the difference $\Delta\varphi_\infty$ between the values of the phase of the surface temperature computed for front and rear illumination with $\alpha d \rightarrow \infty$, as a function of the film thickness to thermal diffusion length ratio d/μ, for different values of the substrate to film effusivity ratio b.

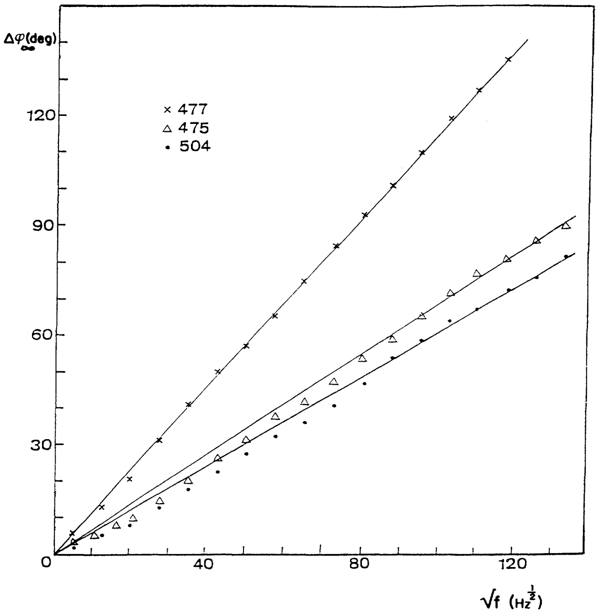

FIG. 7. Experimental variations of the difference $\Delta\varphi_\infty$ between the phase of the PDS signals measured for strongly absorbed light ($\alpha d \to \infty$) for front and rear illumination, as a function of the square root of the modulation frequency f, for two thick undoped a-Si:H films: one deposited under optimized conditions, $d = 7.5$ μm (△), and one deposited under high D_2 dilution, $d = 7.06$ μm (●), and for a thick P-doped a-Si:H film deposited under optimized conditions, $d = 9.9$ μm (×).

portant to notice that in all cases, b is close to 1; in the following, we will assume $b = 1$, which implies that the interface between the film and its substrate has no influence in the thermal wave propagation.

The high-frequency PDS experiments were performed on four undoped thick samples, with thicknesses ranging from 7.5 to 10 μm; three of them were deposited under standard conditions on Corning glass and silica substrates, the fourth one was prepared from SiH_4 diluted in D_2. Figure 8 shows that, compared to the "standard" films, this last sample has a larger optical gap, probably related to its higher hydrogen content: $E_{04} = 1.95$ eV, a larger Urbach parameter $E_0 = 62$ meV, and a significantly higher sub-band-gap absorption, with a bump centered at 1.2 eV characteristic of a higher dangling bond density; the optical spectra tend, however, to coincide at the lowest energies. For the phase measurements, we successively used three wideband filters, as explained above. Filter A ($2.25 \lesssim \hbar\omega \lesssim 2.75$ eV) corresponds to a very high absorption range (α of the order of 10^5 cm^{-1}), which ensures that all the incident electromagnetic energy is deposited in the immediate vicinity of the illuminated surface (free surface and film-substrate interface for front and rear illumination, respectively). Filter B ($1.45 \lesssim \hbar\omega \lesssim 1.77$ eV) corresponds to the bottom of the Urbach edge, with α comprised between 10 and 10^3 cm^{-1} (i.e., αd varying from 10^{-2} to 1). Filter C ($\hbar\omega \lesssim 1.10$ eV) corresponds roughly to the low absorption range ($\alpha \lesssim 1$ cm^{-1}) where the CPM-derived absorption spectra depart from the PDS-derived one in Fig. 2. The measured phase values are summarized in Table II; the value obtained with filter A for front illumination has been taken as the phase origin for each film. The uncertainties on the φ_F and φ_R values are estimated of the order of a few degrees for filters A and B, a little larger for filter C. It is first interesting to note that the values of $\Delta\varphi = \varphi_F - \varphi_R$ measured with filter A (strongly absorbed light) for samples 475 and 477 are in very good agreement with those corresponding to $f = 5$ kHz in Fig. 7, which provides a cross-check of the validity of the measurements. On the other hand, it can be seen that the corresponding $\Delta\varphi$ values obtained for samples 629A and 629B scale well with their respective thickness, as expected from expression (3).

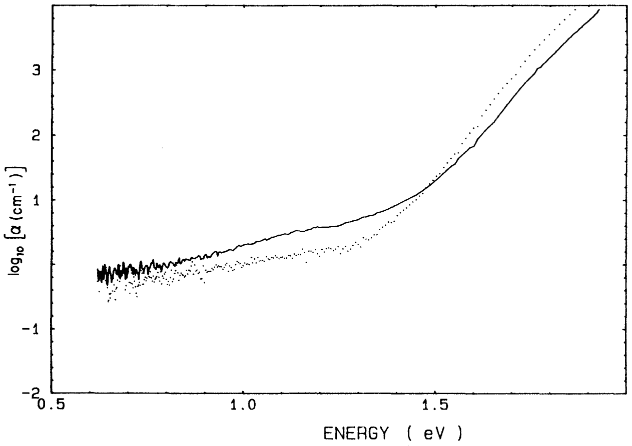

FIG. 8. Comparison between the optical-absorption coefficient spectra deduced from PDS experiments for two thick undoped a-Si:H films deposited on glass substrates, respectively, under optimized conditions, $d = 7.5$ μm (dots), and with high D_2 dilution, $d = 9.9$ μm (continuous line).

TABLE I. Experimental values of the thermal diffusivity D and of the ratio b of the substrate (e_s) and film (e) effusivities for three a-Si:H films (with thickness d) deposited on Corning glass under standard conditions (undoped and P-doped) and with SiH_4 diluted in D_2 (undoped).

Sample	Deposition	d (μm)	D (10^{-6} m^{2}s^{-1})	$b = e_s/e$
475 undoped	standard	7.5	1.22	0.7±0.1
504 P-doped	standard	7.06	1.36	0.7±0.1
477 undoped	D_2 dilution	9.9	0.74	1

We now compare the φ_F and φ_R values measured for each film with the different filters. In all cases, the φ_F and φ_R values obtained with filter B are close to each other, and intermediate between the φ_F (=0) and φ_R values obtained with filter A which, as emphasized above, are the reference phase values for an optical absorption localized at the free surface and at the film-substrate in-

TABLE II. Experimental values of the phase φ of the PDS signal for front (F) and rear (R) illumination in the spectral ranges corresponding to filters A, B, and C (see text) for four undoped a-Si:H thick films; the φ_F value obtained with filter A has been taken as the phase origin for each film. The deposition conditions and the nature of the substrate, as well as the film thickness d and the ratio of the thickness to the thermal diffusion length μ, are indicated in each case.

Sample	Deposition	d (μm)	d/μ	φ (deg)	Filter A	Filter B	Filter C
475	standard	7.5	0.85	F	0	−22	−3
	glass			R	−42	−26	−6
629A	standard	8.1	0.92	F	0	−21	+3
	glass			R	−47	−30	−10
629B	standard	8.9	1.01	F	0	−25	+5
	silica			R	−56	−34	−9
477	D_2 dilution	9.9	1.43	F	0	−34	−12
	glass			R	−81	−37	−20

terface, respectively. This is consistent with a rather uniform distribution of the heat sources across the film thickness, which corresponds to bulk absorption. One can notice that the $|\varphi_F|$ values are systematically slightly smaller than the $|\varphi_R|$ values. We checked the consistency of our measurements by comparing, for front and for rear illumination, the difference $\delta\varphi_{\text{ex}}$ between the phase values measured with filter A and filter B, and the difference $\delta\varphi_{\text{th}}$ between the phase values computed for $\alpha d \rightarrow \infty$ and $\alpha d = 0$ (under the assumption $b = 1$);[35] the results are summarized in Table III. The agreement between $\delta\varphi_{\text{ex}}$ and $\delta\varphi_{\text{th}}$ is very good for front illumination, less good for rear illumination. This may be explained by the fact that the computations do not include the effect of multiple reflections in the substrate.

If now we consider the φ_F and φ_R values measured with filter C, we can see that, for each film, both of them are very close to the reference value relative to free-surface absorption (i.e., 0). We have already emphasized that the experimental uncertainties are larger in the case of filter C, due to the low absorption level, which explains the scattering of the data. However, there is no doubt that, in this spectral range below 1.1 eV, the "apparent" optical absorption is dominated by an absorption localized very close to the free surface in all samples. The slightly higher $|\varphi_F|$ and $|\varphi_R|$ values obtained for sample 477 may indicate either that the "surface absorption" region extends deeper into the film due to its particular deposition conditions, or that there is a non-negligible contribution of "bulk absorption" even in this low-energy range. This last interpretation prevails for the doped thick sample 504, the optical-absorption spectrum of which is presented in Fig. 4, since in this case both the φ_F and φ_R values measured with filter C are almost identical to those measured with filter B, indicating the predominance of "bulk" absorption down to low energies.

TABLE III. Comparison of the differences between the phase values measured with filter A and filter B (expt.) and computed for $\alpha d \rightarrow \infty$ and $\alpha d \simeq 0$ (theor.), for front (F) and rear (R) illumination, for the same undoped a-Si:H films as in Table II (the thickness to thermal diffusion length ratio d/μ is indicated in each case).

Sample		475	629A	629B	477
d/μ		0.85	0.92	1.01	1.43
(F)	expt.	−22	−21	−25	−34
	theor.	−22	−23	−25	−33
(R)	expt.	16	17	22	44
	theor.	30	33	37	54

V. CONCLUSION

In the first part of this paper, we have used "conventional" PDS experiments at low modulation frequency performed as a function of film thickness, to confirm the existence of surface and/or interface absorption in device-quality undoped a-Si:H samples. We have also shown that the CPM-derived absorption spectra obtained for the same samples exhibit very little, if any, surface-interface effect, and that they coincide within experimental uncertainties with the PDS-derived spectra characteristic of thick films down to about 1.1 eV. At lower energies, however, the CPM-derived absorption coefficients decrease rapidly, while the PDS-derived ones remain roughly constant down to 0.6 eV.

In the second part of this paper, we have proposed a method which is able to discriminate between bulk, surface, or interface absorption in a film. This method is based on PDS experiments at high frequency (thermal diffusion length of the order of the film thickness), in which we compare the values of the phase of the PDS signal measured for front and rear illumination, the probe-beam–sample geometry remaining identical in both cases. This method allowed us to demonstrate unambiguously that, for our a-Si:H films deposited either on Corning glass or on silica, the optical absorption measured by PDS at energies smaller than 1 eV comes essentially from the free-surface region.

It can be inferred from the variations with film thickness of the apparent optical-absorption coefficient deduced from our conventional low-frequency PDS experiments that this surface absorption extends to higher energies, i.e., in the 1–1.5 eV spectral range where it coexists with bulk absorption. It can be associated with the presence of a surface layer exhibiting more disorder and more defects, and possibly more hydrogen, than the bulk, and resulting from the growth mechanisms themselves. A reasonable assumption is that the surface defects introduce a high density of gap states with a wide and nearly flat distribution in energy since they are likely to take a variety of configurations in this strongly perturbed region, and that the surface disorder creates large potential fluctuations responsible for a significant modulation of the band-edge energies; a nonuniform incorporation of hydrogen could play a similar role. This would explain why the surface layer contributes to the optical absorption over a large spectral range.

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