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Direct and highly sensitive measurement of defect-related absorption in amorphous silicon thin films by cavity ringdown spectroscopy

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Cavity ringdown spectroscopy has been applied to hydrogenated amorphous silicon (*a*-Si:H) showing that this fully optical method is suited for the detection of defect-related absorption in thin films with a minimal detectable absorption of 1×10^{-6} per laser pulse and without the need for a calibration procedure. Absolute absorption coefficient spectra for photon energies between 0.7 and 1.7 eV have been obtained for thin *a*-Si:H films (4–98 nm) revealing a different spectral dependence for defects located in the bulk and in the surface/interface region of *a*-Si:H. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1713047]

Due to the continuous advancement in thin film technologies a constant need exists for new or improved thin film diagnostic techniques. Especially in the optoelectronics and semiconductor industries there is a strong demand for these techniques because the decreasing device dimensions make the materials used more sensitive to low-concentration defects and impurities. In the case of hydrogenated amorphous silicon (*a*-Si:H) for example, low concentrations of defects determine to a large extent the optoelectronic performance of the material as used in solar cell, thin film transistor (TFT), and complementary metal oxide semiconductor (CMOS) technologies.[1] Presently used detection schemes for defect spectroscopy, such as photothermal deflection spectroscopy (PDS) or the constant photocurrent method are very sensitive but indirect,[2,3] which means that they require a calibration procedure and cannot be applied real-time during film growth. Therefore, new diagnostics which are preferably direct and "all optical" would be of great use for the field of *a*-Si:H and for thin film technologies in general. In this letter, we present defect-related measurements obtained with a fully optical absorption method based upon the well-known gas phase absorption technique of cavity ringdown spectroscopy (CRDS).[4] We will prove and discuss the validity of this direct technique and compare conventional subgap absorption measurements on a 1031 nm thick *a*-Si:H film with CRDS measurements. Furthermore, the potential of CRDS is demonstrated by measuring defect related absorption in *a*-Si:H films of 4–98 nm thickness.

After its introduction in 1988, CRDS has proven its role in direct detection of extremely low concentrations of gaseous species and the determination of their absolute number densities.[4,5] The extension of CRDS to the condensed matter was first proposed and demonstrated by Engeln *et al.*,[6,7] and was soon followed by others.[8–12] In principle, CRDS is similar to conventional absorption spectroscopy apart from the fact that the sample is placed inside a high finesse optical cavity to enhance the sensitivity of the measurement. After introducing a short light pulse into the cavity, the light intensity in the cavity decays exponentially with a ringdown time $\tau(\omega)$ that is directly related to the quality factor of the empty cavity as well as to the absorption αd of the sample (e.g., film with substrate), with α the absorption coefficient, and d the absorption path length. The enhancement of the sensitivity is achieved by an increased sampling length and by the fact that the measured ringdown time is insensitive to light source intensity variations.[4] Equation (1) gives the ringdown time in terms of the roundtrip time t_r for light in the cavity and the roundtrip losses $L_i(\omega)$ generated in the cavity[13]

$$\tau(\omega) = \frac{t_r}{\Sigma_i L_i(\omega)} = \frac{t_r}{L_{\text{cavity}}(\omega) + L_{\text{substrate}}(\omega) + L_{\text{film}}(\omega)}. \quad (1)$$

The losses have been divided into intrinsic losses due to the cavity L_{cavity} inherent to the mirrors finite reflectivity, absorption losses induced by the substrate $L_{\text{substrate}}$, and the absorption loss due to the film L_{film}. From Eq. (1) it follows that by measuring τ the losses can be directly calculated while differential measurements can be used to obtain the losses caused by the substrate or film separately.

The experiments have been carried out with the tunable idler output of an optical parametric oscillator (OPO), which is pumped by the third harmonic of a pulsed Nd:YAG laser operating at 30 Hz. The idler output of the OPO can be tuned over the photon energy range of 0.6–1.8 eV and the resulting pulse has a typical bandwidth of 10 cm^{-1}, a duration of 5 ns, and a pulse energy of 10 mJ. The pulse is injected into a stable optical cavity formed by two planoconcave highly reflecting ($R > 0.9997$) dielectric mirrors without using mode matching optics. The cavity is purged with dry nitrogen to reduce the effects of absorption lines of water. The decrease in light intensity inside the cavity has been detected with a photomultiplier tube or a photodiode depending on the photon energy used. Individual transients are sampled using a 12 bit, 100 MHz data acquisition system and fitted with a standard weighted linear regression technique to extract the ringdown time. Reported values of cavity loss and absorptions are typically deduced from averages over 400 laser shots.

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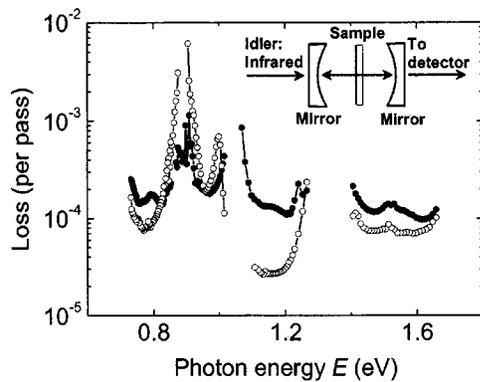
FIG. 1. Inherent optical loss of the empty cavity L_{cavity} (●) and the optical loss induced by the substrate $L_{substrate}$ (○) when placed inside the cavity (see inset). The sum of the two losses $L_0 = L_{cavity} + L_{substrate}$ defines the total intrinsic loss. L_{cavity} shows signatures of OH absorptions due to strong optical transitions of remaining water, while $L_{substrate}$ shows absorption peaks related to vibrational modes of SiO_4 and OH present in the substrate material.

Figure 1 shows the inherent loss of the cavity L_{cavity} as a function of the photon energy. To cover the complete photon energy shown, four sets of mirrors have been used while several parts of the spectrum could not be measured due to strong optical transitions of water. Also shown in Fig. 1 are the losses $L_{substrate}$ due to the quartz substrate material onto which the a-Si:H films have been deposited. $L_{substrate}$ has been deduced from the intrinsic loss $L_0 = L_{cavity} + L_{substrate}$ measured with the substrate inside the cavity and the cavity loss L_{cavity}.

Prior to the measured loss of the film or substrate can solely be attributed to absorption losses, several important issues inherent to the technique must be discussed.[14] In our experiments the substrate has been placed perpendicular to the incident light pulse (see inset Fig. 1), as other reported configurations such as using the mirror as a substrate or placing the substrate at the Brewster angle are in the present case not options.[8,9] For instance, the Brewster angle scheme has the disadvantage that a single Brewster angle is "ill-defined" for a substrate-film configuration, while this scheme is also only sensitive for one polarization direction. Alternatively, the perpendicular position of the substrate is generally applicable without clear disadvantages: The sample's reflectivity induces distortions in the buildup of a homogenous light intensity inside the cavity when the pulse is coupled into the cavity. However, by calculating the response of a cavity with a finite absorbing sample using Fresnel coefficients and allowing multiple reflections to occur (both in the cavity and in the sample), it has been shown that Eq. (1) remains valid if the reflectivity of the sample's surfaces is less than 0.9 and absorption losses are less than 0.01 per pass.[14] Furthermore, the very important aspect and influence of light scattering losses induced by the surface roughness of the substrate or film has been evaluated. The amount of light scattering has been calculated by applying scalar scattering theory[15] using information on the surface roughness and lateral correlation length of the substrate and film as obtained by atomic force microscopy. Taking into account that most of the scattered light (i.e., at small scattering angles) remains stable in the cavity, the scattering losses have been found to be less than the absolute sensitivity of our experimental configuration. We note that this would not be the case for the Brewster
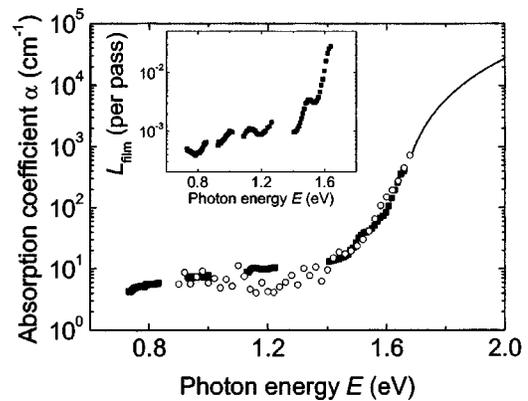

FIG. 2. Absorption coefficient α of a 1031 nm thick a-Si:H film as a function of the photon energy as obtained by CRDS (■), photothermal deflection spectroscopy (○), and transmission-reflection spectroscopy (—). For CRDS, the absorption coefficient has been determined from the optical loss caused by the a-Si:H (inset) after a correction for interference in the film. The absolute scale of the PDS results has been determined by linking the PDS data to the transmission-reflection data at a transmission value of 10%.

angle geometry.[8] A last important issue to be examined is the achievable minimal detectable absorption $(L_{abs})_{min}$ of CRDS for the measurements of thin films. $(L_{abs})_{min}$ is generally calculated using the equation $(L_{abs})_{min} = L_0(\Delta\tau/\tau)_{min}$, which states that the intrinsic loss $L_0 = L_{cavity} + L_{substrate}$ should be as low as possible while the uncertainty in the determination of the ringdown time should be minimized. Based upon the results shown in Fig. 1 and a measured relative uncertainty in the ringdown of less than 1%, we have found that for our experimental configuration $(L_{abs})_{min} = 10^{-6}$ per laser pulse, resulting in a $(L_{abs})_{min}$ of 5×10^{-8} when averaging 400 ringdown times. Taking the abovementioned aspects into account, it is established that the losses measured with CRDS can be directly related to absorption losses in the substrate or film with the benefit of an enhanced sensitivity and no need for calibration procedures.

We have measured the optical loss L_{film} of a 1031 nm thick radio frequency plasma deposited a-Si:H film with CRDS. The result is depicted in the inset of Fig. 2 and clearly shows a periodic modulation of L_{film} as a function of the photon energy. This modulation is caused by interference effects that enhance and reduce the average electric field in the a-Si:H film and consequently affect the amount of light absorbed within the film. Corrections for these interference effects have been made by calculating the light intensity distribution in the a-Si:H film as a function of thickness and wavelength using Fresnel equation.[14,16,17] The resulting absorption coefficient of the 1031 nm thick film is depicted in Fig. 2 together with results obtained by PDS and transmission-reflection measurements. The agreement between CRDS and PDS is within the experimental accuracy of the PDS data calibration. The reproducibility of the CRDS measurement is close to the calculated value for $(L_{abs})_{min}$.

The potential of the method in terms of the sensitivity is demonstrated by measuring the absolute absorption coefficient α for a-Si:H films of 4, 9, 30, and 98 nm thickness at subgap energies. As can be seen in Fig. 3, the absorption coefficient decreases with increasing film thickness. This trend can be attributed to the existence of a relatively defect-
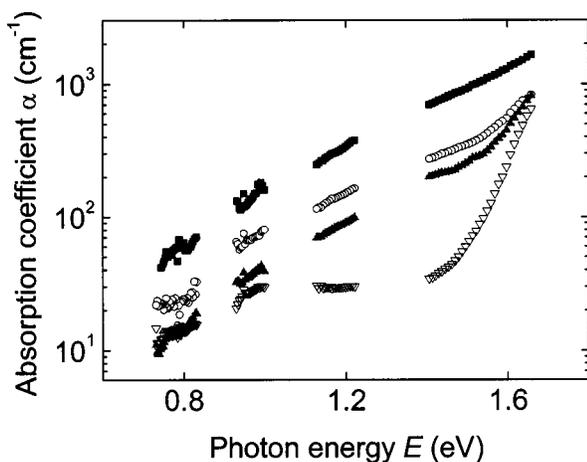
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FIG. 3. Subgap absorption spectra showing the absorption coefficient (after interference corrections) for *a*-Si:H thin films with a thickness of 4 nm (■), 9 nm (○), 30 nm (▲), and 98 nm (▽).

rich surface and/or interface layer, as reported but only by indirect techniques and not for such thin *a*-Si:H films.[17,18] Another important observation in Fig. 3 is that α at subgap energies decreases much more rapidly at photon energies between 1.0 and 1.4 eV for the 4 nm film than for the 98 nm film. It is likely that this spectral dissimilarity is caused by a different density of states, possibly caused by a difference in the local environment of the defects and/or by a difference in the defects probed.[19]

In conclusion, we have proven that CRDS can be used for ultrasensitive detection of defect-related absorptions in thin films with a sensitivity of 1×10^{-6} per laser pulse and without the need for a calibration procedure. The absorption coefficients of *a*-Si:H films with a thickness down to 4 nm have been determined revealing a distinct spectral dependence compared to thick films which illustrates the broad potential of the method for defect spectroscopy.

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