

Photoinduced effects on infrared and near infrared absorption of amorphous and microcrystalline Si measured by photothermal bending spectroscopy

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Photothermal bending spectroscopy (PBS) technique has been extended to infrared region to measure low optical absorption spectra of thin film semiconductors. It is found that the sensitivity of the PBS is $\alpha d \sim 10^{-3}$. Using this technique, absorption coefficients of hydrogenated amorphous silicon (a-Si:H) and hydrogenated microcrystalline silicon (μ c-Si:H) films can be measured from band-to-band transition region to Si-H stretching mode at $\sim 2000 \text{ cm}^{-1}$. Correlation between photodegradation and any change in the spectrum of Si-H stretching mode in a-Si:H films has also been studied.

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The photothermal spectroscopy (PTS) technique is a powerful tool to measure absorption spectra of thin films because of the wide energy range from visible to infrared light. For example, the photothermal deflection spectroscopy (PDS) has high sensitivity. However, this method needs a liquid media around the sample. Hence, there are some difficulties to measure absorption spectra in infrared region due to absorption by the medium itself.

We have previously developed a new method [1] for measurements of optical absorption of thin films named photothermal bending spectroscopy (PBS). This technique utilizes a bending effect in a film/substrate bimorph structure with different thermal expansion coefficients. The bending in the film/substrate under light illumination is induced by temperature rises originating from non-radiative recombination of photoexcited carriers. Hence, magnitudes of the bending reflect the number of absorbed photons (*i.e.* absorption coefficients of the sample) at each wavelength. The bending can easily be detected using optical lever method [1]. Note that this method does not need any media around the sample.

In this paper, we have tried to extend the PBS technique to infrared region to detect Si-H stretching mode at $\sim 2000 \text{ cm}^{-1}$ in hydrogenated amorphous silicon (a-Si:H) and hydrogenated microcrystalline silicon (μ c-Si:H) films. We have also tried to improve the sensitivity of the PBS. Such studies can contribute to *in situ* monitoring the quality of these films during preparation and to investigations for the photodegradation in a-Si:H solar cells.

Experimental

Samples were prepared by the plasma enhanced chemical vapor deposition (PECVD) using SiH_4 and H_2 gases at an RF (13.56 MHz) powers of 18 \sim 40 W and at a substrate temperature of $\sim 250^\circ\text{C}$. For a-Si:H, H_2/SiH_4 dilution ratio to SiH_4 (H_2/SiH_4) was ~ 4 with a total gas pressure of ~ 1 Torr. And, for μ c-Si:H, H_2/SiH_4 was ~ 9 with a total gas pressure of ~ 1 Torr. The thickness of these films were 1 \sim 1.5 μm .

The samples for PBS measurements are a-Si:H and μ c-Si:H films deposited on sapphire with a thickness of 50 μm and crystalline Si with a thickness of 30 μm . Those sizes were 1 mm \times 20 mm and 1 mm \times 15 mm, respectively. Samples were also deposited on quartz substrates for measurements of the transmittance to check the absolute values of absorption

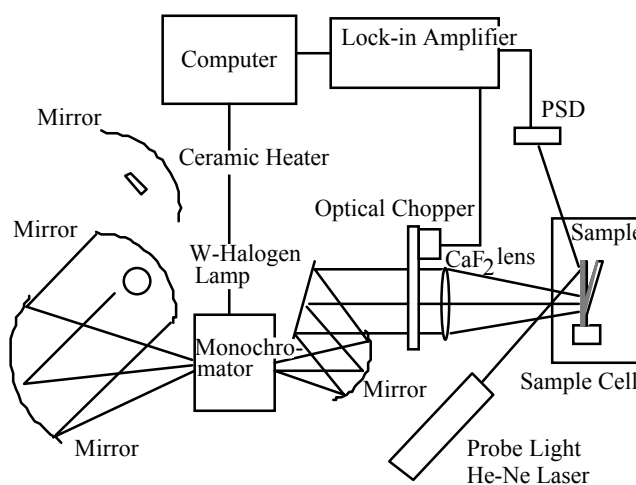


Figure 1. A schematic illustration of the PBS system used in this study. The W-halogen lamp and the SiC heater are set up on the x-stage and can be moved reversibly.

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coefficients.

A schematic illustration of the PBS system is shown in Fig. 1. A W-halogen lamp (250 W, 28 V) and a SiC heater (60W, 120 V for $\sim 1200^\circ\text{C}$) were employed as a light source from visible to near-infrared light and infrared light region, respectively. The excitation light is chopped at a frequency of ~ 3.4 Hz [1] for computer-controlled lock-in detection of PBS signals after passing through a monochromator with a focal length of 100 mm. And, the light was focused by a CaF_2 lens with a focal length of 100 mm to increase the magnitude of the PBS signal. The sample was held by super-invar metal which has a low thermal expansion coefficient at room temperature (as same as that of quartz of $\sim 0.4 \times 10^{-6} \text{ K}^{-1}$ [2]) to remove thermal strain of the system during measurements. The sample and the holder were set in a cell with CaF_2 windows.

The method for detecting PBS signals is described. A He-Ne laser (633 nm, 10 mW) was employed as a probe beam. The beam was illuminated at a free edge of the sample. The displacement of the reflected beam was measured using a position sensitive detector as a PBS signal, S .

The absorption coefficients α (cm^{-1}) [3] of the film with a thickness of d (cm^{-1}) at each photon energy $\hbar\omega$ were estimated using the PBS signal S ($\hbar\omega$) as;

$$\alpha(\hbar\omega) = -\ln[1 - \{S(\hbar\omega)/S_{\text{sat}}\}]/d \quad (1)$$

,where S_{sat} is the PBS signal in the saturated region. The absorption coefficient determined by the PBS was fitted to the absolute absorption coefficient around only visible light obtained by the transmittance measurement in order to make sure.

To investigate the correlation between the photodegradation in a-Si:H films [4] and an absorption by Si-H stretching mode at $\sim 2000 \text{ cm}^{-1}$ [4,5], PBS spectra were measured around this wavenumber before and after light illumination. A 500 W Xe lamp with an IR-cut filter was employed for a light source with an intensity of $\sim 400 \text{ mW/cm}^2$.

All experiments were performed at room temperature and in air.

Results and Discussion

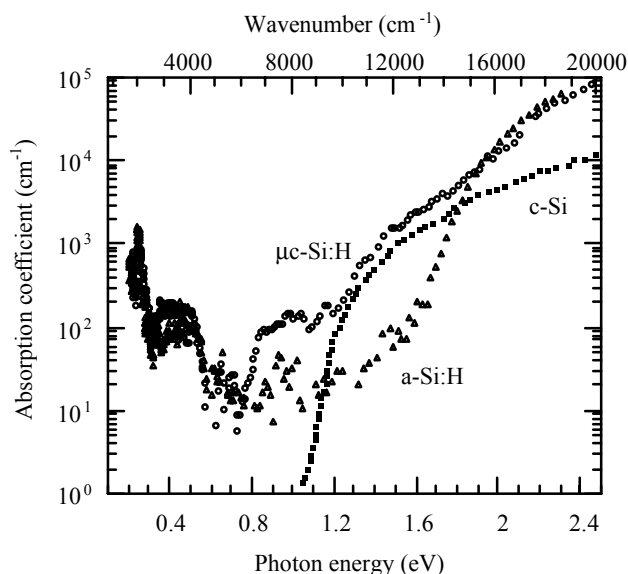


Figure 2. Absorption spectra of a-Si:H (solid circles) and $\mu\text{c-Si:H}$ (open circles) films measured by the PBS technique. An absorption coefficient of c-Si [6,7] is also plotted for comparisons.

The sensitivity of the PBS is described. We obtained the sensitivity of $\alpha d \sim 10^{-3}$ at $\hbar\omega \leq 1.0 \text{ eV}$. In the photon energy region over 1.0 eV, the established sensitivity was $\alpha d \sim 5 \times 10^{-4}$. This value is comparable to that of our previous result in Ref. [1]. Note that the output signal of the PBS became ~ 1.5 times greater when a mirror was put at backside of the sample.

Figure 2 shows absorption spectra ranging from 0.2 eV (1600 cm^{-1}) $\sim 2.5 \text{ eV}$ (20000 cm^{-1}) for a-Si:H and $\mu\text{c-Si:H}$ films deposited on a sapphire substrate. An absorption coefficient of crystalline Si (c-Si) [6,7] is also plotted for comparing with those of $\mu\text{c-Si:H}$ films. Some characteristics of the absorption coefficient for these films at each spectrum range are described below.

First, it is found that absorption coefficients of a-Si:H and $\mu\text{c-Si:H}$ films in the spectrum range of $> 1.8 \text{ eV}$ are greater than those of c-Si. This result is consistent with previous results in Refs. [6-9].

Second, the absorption coefficient of a-Si:H in the spectrum range of 1.2 $\sim 1.8 \text{ eV}$ rapidly decrease compared to those of c-Si and $\mu\text{c-Si:H}$. Consequently, it becomes smaller than those of c-Si and $\mu\text{c-Si:H}$. This is also consistent with the result in Refs. [6-9].

Third, the shape of absorption coefficients of $\mu\text{c-Si:H}$ films in the spectrum range of 1.2 $\sim 1.8 \text{ eV}$ is almost comparable to those of c-Si. The shape indicates the indirect optical transition in c-Si.

Furthermore, an absorption from 0.7 eV to 1.2 eV in $\mu\text{c-Si:H}$ film can be observed, in our knowledge, for the first time. This absorption may originate from Si dangling bonds.

Finally, the absorption peak can clearly be observed at $\sim 2000 \text{ cm}^{-1}$ in a-Si:H and $\mu\text{c-Si:H}$ films using PBS technique. This absorption peak originates from Si-H stretching mode [5] in these films. Note that this peak can also be detected by the conventional infrared spectroscopy because our sample contains hydrogen $\sim 10 \text{ at. \%}$.

Figure 3 shows absorption spectra of Si-H stretching mode in an a-Si:H film at $\sim 2000 \text{ cm}^{-1}$ before and after light illumination. The illumination time was ~ 24 hours. Note that the photodegradation should occur [4,10] in a-Si:H films during

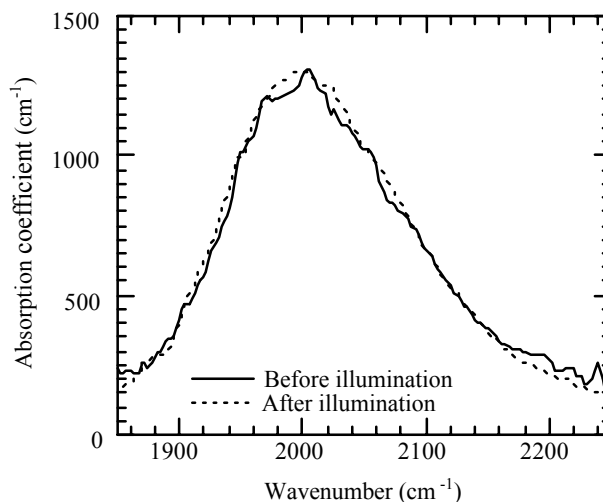


Figure 3. Absorption spectra of an a-Si:H film at Si-H stretching mode before (solid line) and after (dashed line) light illumination of $\sim 400 \text{ mW/cm}^2$ for ~ 24 hours. mode after light illumination.

this illumination time. Also note that crystalline silicon was employed as a substrate in this experiment. It is found that no change between these spectra was observed within the sensitivity of our PBS system.

This result seems to be inconsistent with results described in Ref. [5]. However, their method based on the conventional infrared absorption measurements but was differential technique. The sensitivity of our PBS is less than the technique described in Ref. [5] at present, which might hide the change of the spectrum. Note that the detection limit of spectrum change in our PBS technique was $\sim 10\%$.

The change of the absorption peak due to Si-H stretching has attracted a great deal of attention because of the possibility for interpretations of the photoinduced defect creation [4,5] and the photoinduced volume expansion [2] in a-Si:H, just like the prediction by hydrogen collision model [11].

In conclusions, we have extended the PBS technique to infrared region and established the sensitivity of $\alpha d \sim 10^{-3}$ around at 0.2 eV (wavelength $\lambda \sim 5\mu\text{m}$). Using this technique, the Si-H stretching mode at $\sim 2000\text{ cm}^{-1}$ can be observed in a-Si:H and $\mu\text{c-Si:H}$ films. It is found that there is no photoinduced effect in the Si-H stretching mode within the experimental condition and the sensitivity of the PBS. Further improvements of the sensitivity at infrared region will be promising for the precise measurements of the absorption related hydrogen, defects and impurities in films estimated from Si-O, O-H, Si-N, N-H infrared mode.

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