PHYSICAL REVIEW B **68**, 085206 (2003)

Photoinduced structural instability around the Si-H bond in undoped hydrogenated amorphous silicon

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(Received 22 January 2003; published 25 August 2003)

When hydrogenated amorphous silicon (a-Si:H) is illuminated at low temperature by a modulated band-gap light, a photoinduced bleaching band, which is superimposed on a usually observed photoinduced absorption spectrum, can be observed around 2000 cm^{-1}. The observation of such a photomodulated ir-absorption band shows that a real-time change in the absorption strength of the Si-H stretching vibration takes place in accordance with the modulated excitation. Since the Si-H stretching vibration is not affected directly by the band-gap light and is strongly localized in a-Si:H, the observed change in the vibronic absorption should be caused indirectly by some structural instability of local environment of the Si-H bond. Therefore, the localized Si-H oscillator can serve as a detector of a dynamic structural change in its vicinity. Preliminary measurements of the photomodulated vibrational absorption have been performed with undoped a-Si:H prepared at different substrate temperatures (T_S), in which bonded hydrogen takes on two different configurations, namely, monohydride (Si-H) and dihydride ($\mathrm{Si\text{-}H_2}$). Irrespective of T_S, it is found that the modulated vibrational absorption band is dominated by the 2000-cm^{-1} component due to the Si-H vibration. This disclosure includes even those cases where the 2100-cm^{-1} component due to the $\mathrm{Si\text{-}H_2}$ vibration dominates the usual ir-absorption band of the Si-H stretching mode. It follows that the structural instability takes place more effectively in the neighborhood of the Si-H bond than it does in the neighborhood of the $\mathrm{Si\text{-}H_2}$ bond. It will be argued that such a site-dependent structural instability is concerned to the nonuniformity of the local strain in the disordered a-Si:H network.

DOI: 10.1103/PhysRevB.68.085206 PACS number(s): 78.30.Ly, 63.50.+x, 78.66.Jg

I. INTRODUCTION

The incorporation of hydrogen in amorphous silicon achieves an effective activation of doping by terminating dangling bonds, which are inherent in a disordered network only of Si atoms. However, in contrast to this generally desirable effect, there is a drawback in the case of hydrogenated amorphous silicon (a-Si:H). Namely, the electronic quality of a-Si:H degrades after it is exposed to strong light.[1] Since an amorphous material is not in thermodynamic equilibrium, its photodegradation is a kind of structural instability: such a system can easily change its state among available metastable states. After the accumulation of many studies, there is a consensus that the incorporated hydrogen plays an important role in photodegradation, which is likely to take place around hydrogen during its migration within the network.[2–4] In order to establish more convincing evidence concerning this effect, it is desirable to detect directly a local structural change or instability at a region around hydrogen, which should be a precursor to the photodegradation.

It has been observed that ir absorption in a-Si:H due to the Si-H stretching vibration varies with time following a band-gap illumination of periodically modulated intensity.[5,6] This indicates that some properties of the Si-H oscillator vary with time following the modulated excitation. However, since the Si-H stretching vibration is hardly affected by the band-gap light, some characteristics of the oscillator should be altered indirectly by a change in the structural configuration in the neighborhood of the Si-H bond. Furthermore, the Si-H stretching vibration is more strongly localized in a-Si:H, as inferred from its much longer vibrational lifetime, than that of the corresponding vibration in crystalline Si.[7–9] Therefore, its properties will be affected, within a limited range, by the local surrounding of the Si-H bond. It follows that the Si-H localized oscillator can be used as a sensor for detecting a dynamic structural change in its vicinity. Based on this understanding, we investigate here the photoinduced structural instability in the disordered network of a-Si:H by observing a real-time change in the ir absorption of the localized Si-H vibration.

Short- and medium-range order, or macroscopic structure, in the disordered network of a-Si:H has been examined with various methods, such as Raman scattering,[10] extended x-ray absorption fine structure,[11] small-angle x-ray scattering,[12] or wide-angle x-ray scattering.[13] However, these techniques essentially survey the macroscopic properties of the network structure and provide a statistical average, or a distribution, of the quantity under consideration in each method. By way of contrast, the present method gives more direct, microscopic structural information concerning the neighborhood of the Si-H bond.

In a previous paper, we have tried to see how the photomodulated absorption band of the Si-H stretching vibration changes after light soaking or thermal annealing.[6] Concerning the photodegradation, it was found that the photomodulated ir-absorption spectrum did not change its shape after light soaking, although its intensity was reduced. A quantitative analysis of the change in strength of the photomodulation spectrum was made by regarding the real-time change in the Si-H stretching vibration simply as a result of modulation of a neighboring weak Si-Si bond following a modulated excitation. With the assumption that the weak Si-Si bonds were broken or reformed by light soaking or thermal annealing, respectively, the density of the weak Si-Si bonds or neighboring Si-H bonds responsible for the observed photomodulation was evaluated to be about 5×10^{17} cm^{-3}.[6] Since the density of the bonded hydrogen in the monohydride configuration was about the order of 10^{21} cm^{-3} in the samples studied, this result indicates that a very small fraction of the bonded hydrogen can participate in the photomodulation.

In this paper, we reconsider again the precise cause of the photomodulation of the Si-H vibration. In order to see how the structural instability around the Si-H bond varies from site to site in the a-Si:H network, detailed measurements of the photomodulated vibrational absorption of the Si-H stretching mode are performed with undoped a-Si:H films prepared at different substrate temperatures.

II. EXPERIMENT

Samples of undoped a-Si:H films were prepared by radio-frequency, glow-discharge decomposition of $\mathrm{SiH_4}$ on intrinsic crystalline silicon (c-Si) wafers at substrate temperatures (T_S) of 300, 100, and 50 °C. In the following, they are denoted as *A*, *B* and *C*, respectively. Film thickness varied from 4 to 6 μm. From the vibrational spectra, hydrogen-bonding sites can be identified. The ir-absorption band observed around 2000 cm^{-1} is due to the stretching vibration of a silicon-hydrogen bond, and can be decomposed into two components peaked at about 2000 and 2100 cm^{-1}. Although the 2000-cm^{-1} component can be attributed to the monohydride (Si-H) configuration,[14] there is some controversy concerning the assignment of the 2100-cm^{-1} component. It is associated with the dihydride ($\mathrm{Si\text{-}H_2}$) configuration, Si-H bonds on the surface of voids, or platelet like clustered Si-H bonds.[14–16] In the *B* and *C* samples, it was confirmed, from the conventional Fourier-transform infrared (FTIR) measurements, that the 890-cm^{-1} band due to the $\mathrm{Si\text{-}H_2}$ bending mode was present in accordance with the 2100-cm^{-1} band, so that the 2100-cm^{-1} component in those samples could be attributed to the $\mathrm{Si\text{-}H_2}$ configuration. A ratio between the hydrogen contents of the monohydride and dihydride configurations differs in its dependence on T_S. For the good-quality *A* sample, the 2000-cm^{-1} component due to the Si-H vibration dominates the ir-absorption spectrum, while for the *B* and *C* samples with low T_S, the magnitude of the 2100-cm^{-1} component due to the $\mathrm{Si\text{-}H_2}$ vibration is equal to or stronger than that of the 2000-cm^{-1} component.

A sample was maintained at 15 K within a cryostat for the measurements of the photomodulated vibrational absorption. It was excited with a modulated pump light, and an induced transmittance change in the sample was monitored with a probe light. The optical setup for the measurement was almost the same as that used for a conventional photoinduced absorption (PA) measurement.[17] The pump light was provided by the 647-nm line from a Kr^+ laser, which was modulated at 11 Hz with a mechanical chopper. In order to avoid photodegradation of the samples during pump-light illumination, the intensity of the pump light was held at a level sufficiently low for performing the measurements with a permissible signal-to-noise ratio: 1, 4, and 20 $\mathrm{mW\,cm}^{-2}$ for samples *A*, *B*, and *C* in the as-deposited state, respectively. When measuring the *B* and *C* samples, after thermal annealing, the intensity of the pump light was reduced by about a factor of 5 in each case. An ir-light source was used as the probe light and was focused with an ellipsoidal mirror onto the same area of the sample surface that was illuminated by the pump light. After passing through the sample, and after being dispersed with a monochromator, which has a 25-cm focal length combined with a cutoff filter, the probe light was collimated in a liquid-nitrogen-cooled Hg-Cd-Te detector. Transmission T and its modulated change ΔT were measured separately with a phase-sensitive detection technique. The ratio between ΔT and T was plotted as a photomodulation (PM) spectrum. In the measurement, the slit width of the monochromator was fixed at 2 mm irrespective of wavelength. At about 2000 cm^{-1}, the spectral resolution was about 16 cm^{-1}.

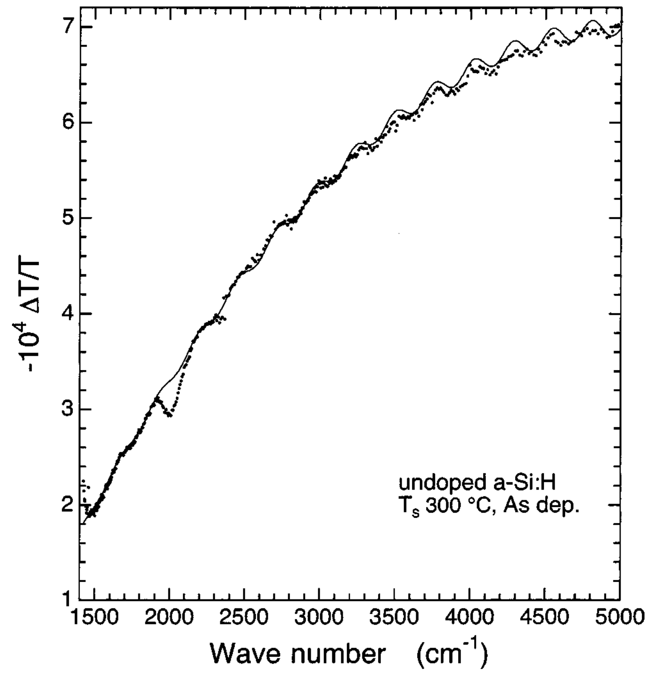

FIG. 1. Photomodulation spectrum of the *A* sample prepared at $T_S = 300$ °C. Data points are denoted by dots, and the interference fringes overriding the spectrum are simulated with a sine curve, as shown by the solid line.

III. RESULTS

Figure 1 shows the PM spectrum of the *A* sample, which is dominated mainly by the usual PA due to the excess carriers trapped at the tail and dangling-bond states.[17] The PM spectrum shows weak interference fringes due to a slight difference in the refractive index between the *A*-sample film and the c-Si substrate. By simulating the interference fringes with a sine curve, as shown in Fig. 1 by the solid line, the presence of a dip band can be noticed clearly at 2000 cm^{-1}. An enlargement of the spectrum around 2000 cm^{-1} is shown

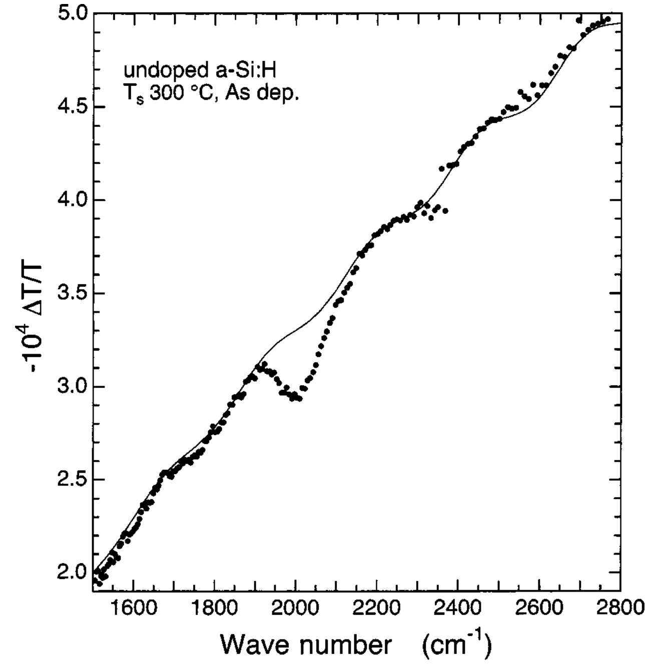

FIG. 2. An enlargement of the spectrum in Fig. 1 in the neighborhood of 2000 cm^{-1}. Solid circles denote data points. Interference fringes in the background PA spectrum are simulated with a sine curve, as shown by the solid line.

in Fig. 2. Since the dip band is directed downward in the spectrum, it is a photoinduced-bleaching (PB) band. The net dip band can be separated from the measured PM spectrum (solid circles) in Fig. 2 by subtracting the simulated background PA spectrum (solid line). Figure 3 shows a comparison between the spectra of the separated dip band (solid circles connected with the thin solid line) and the ir-absorption band (thick dashed line) of the Si-H stretching vibration in this sample. Both spectral dependences are practically the same. Since the ir-absorption band of the *A* sample is dominated mainly by the monohydride Si-H stretching vibration, which peaks at about 2000 cm^{-1}, the dip band can be considered as resulting from a real-time change in the ir absorption of the monohydride vibration. Such a change in the ir absorption of the Si-H stretching mode under a modulated excitation is referenced here as the modulated ir absorption.

The PM spectrum measured with the *C* sample, in the as-deposited state, is shown in Fig. 4 by dots. Because this sample contained numerous dangling bonds, the signal intensity of ΔT is reduced regardless of the enhancement of the pump-light intensity. The amplitude of the interference fringes is enlarged by the rather significant difference between the refractive indices of the *C*-sample film and the *c*-Si substrate. Again, after simulating the interference fringes in the background PA spectrum with a sine curve, as shown in Fig. 4 by the solid line, we can notice the presence of the dip band around 2000 cm^{-1}. When the film is not thick enough, simulation of the interference fringes must be made in a spectral range as wide as possible in order to find the correct periodicity of the interference fringes.[18]

When the amplitude of the interference fringes is large and, in addition, some localized ir-absorption band, such as the Si-H stretching band, exists in the spectral range under consideration, it takes some care to simulate a background PA spectrum combined with interference fringes. Here we

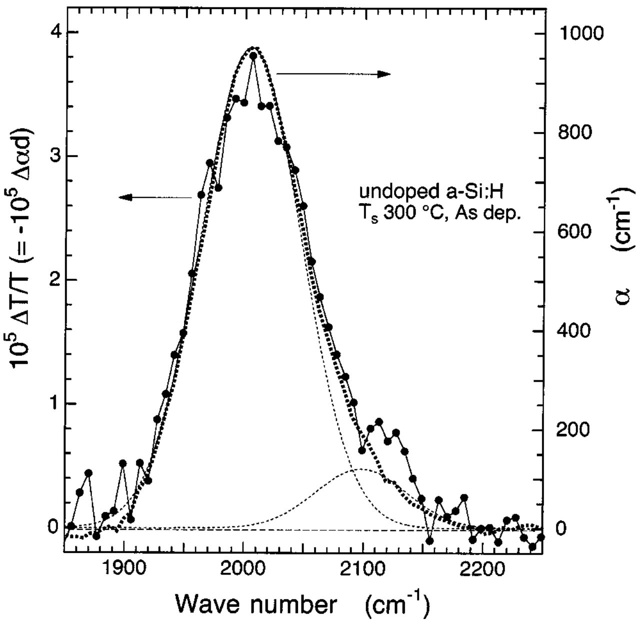

FIG. 3. The modulated ir-absorption spectrum of the Si-H stretching vibration in the *A* sample is shown by the solid circles connected with the thin solid line. The thick dashed line represents the absorption-coefficient spectrum of this sample. The thin dashed lines show the decomposition of the absorption-coefficient spectrum into its 2000- and 2100-cm^{-1} components.

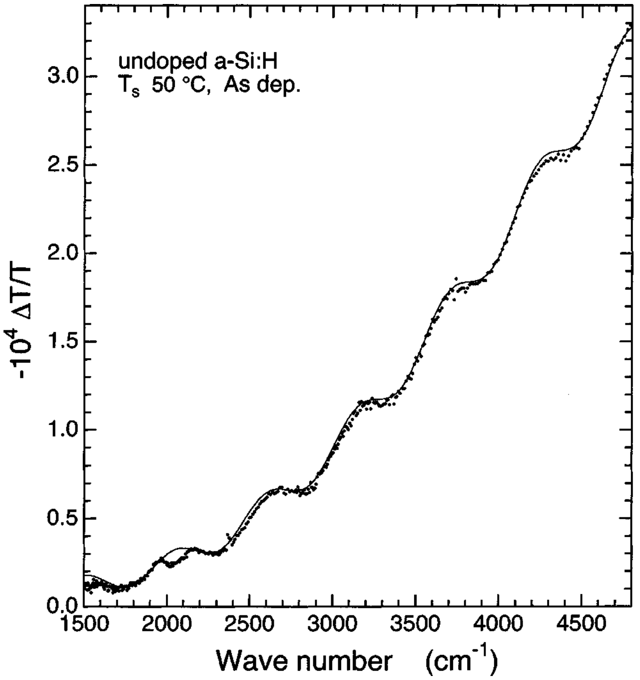

FIG. 4. Photomodulation spectrum of the *C* sample prepared at $T_S = 50\,^{\circ}\mathrm{C}$. Data points are denoted by dots. The interference fringes in the background PA spectrum are simulated with a sine curve, as shown by the solid line.

adopted a practical procedure for that purpose, as explained below.

The PM signal, which is defined as the ratio between the modulated and steady-state transmittance signals, can be expressed as

$$\Delta T/T \approx f_\alpha \Delta \alpha d, \tag{1}$$

where d is the film thickness. The factor $\Delta\alpha$ represents the genuine spectrum of the photoinduced change in the absorption coefficients. This quantity is the PM spectrum after washing out the interference fringes. The f_α factor is defined as

$$f_\alpha = (1/T)(1/d)(\partial T/\partial \alpha). \tag{2}$$

When there are internal reflections within a film that has been deposited on a substrate, the analytical expression for T is expressed as[6]

$$\begin{aligned} T = {} & (1+\kappa^2/n^2)(1-R_{01})(1-R_{21})\exp(-\alpha d) \\ & \times [1-2(R_{01}R_{21})^{1/2}\exp(-\alpha d)\cos(2kd+\phi_{01}+\phi_{21}) \\ & + R_{01}R_{21}\exp(-2\alpha d)]^{-1}, \end{aligned} \tag{3}$$

where $k=2\pi n/\lambda$ is the magnitude of the wave vector (λ is the wavelength in vacuum). The quantities R_{01} and R_{21} are the reflectivity of the vacuum-film and film-substrate interfaces, respectively,

$$R_{i1} = [(n_i-n)^2+\kappa^2]/[(n_i+n)^2+\kappa^2], \tag{4}$$

with i referring either to vacuum (0) or the substrate (2). The phase shifts ϕ_{01} and ϕ_{21} are due to the absorption coefficient of the film and are expressed as

$$\phi_{i1} = \arctan[2n_i\kappa/(n^2+\kappa^2-n_i^2)], \tag{5}$$

where $\kappa=\alpha\lambda/4\pi$. An analytical expression for the numerical calculation of f_α can be obtained from Eqs. (2) and (3).

When there is no ir-absorption band in the spectral range under consideration (i.e., $\alpha=0$ and $n=\text{const}$), f_α varies almost sinusoidally with wave number around -1, while maintaining constant amplitude and regular periodicity.[6] In this case, f_α can be expressed as

$$f_\alpha = -(1+\Delta f),$$

where Δf represents the oscillating part of f_α that varies with wave number. Then, according to Eq. (1), the expression $\Delta f \Delta \alpha d$ corresponds to the interference fringes of the PM spectrum. This indicates that the amplitude of the interference fringes is expected to be proportional to $\Delta\alpha$. On the other hand, when some ir-absorption band is present, the constancy of Δf's amplitude, as well as the regularity of its periodicity, is no longer valid. This is because f_α depends on both α and n through T as indicated in Eq. (2). In other words, since an ir-absorption band is inherently accompanied by the dispersion of a complex refractive index, $\tilde{n}$, Δf should be affected by the dispersion.

The f_α spectrum for the C sample, in the as-deposited state, is shown in Fig. 5 by the solid line. It is calculated with the absorption coefficients of the Si-H stretching band in this sample and with the values $n_2=3.42$ for c-Si and $n_0=1$. Here, only the dispersion of the imaginary part of $\tilde{n}$, i.e., the absorption coefficient, is taken into account. This is because the dispersion of the real part of $\tilde{n}$ does not have a significant effect on the present results when the interference fringes are rather weak as in the C sample. In Fig. 5, a simple sine curve with constant amplitude (i.e., $\alpha=0$) is represented by the broken line for comparison. It is clear from this figure that the amplitude of the f_α spectrum is reduced around 2000 cm^{-1} by the presence of the ir-absorption band. Although the results are not shown here, when the refractive index difference between the film sample and the c-Si substrate is significantly large, the dispersion of the real part of $\tilde{n}$ must be taken into account, since the periodicity of the interference fringes will be too severely distorted to be ignored.

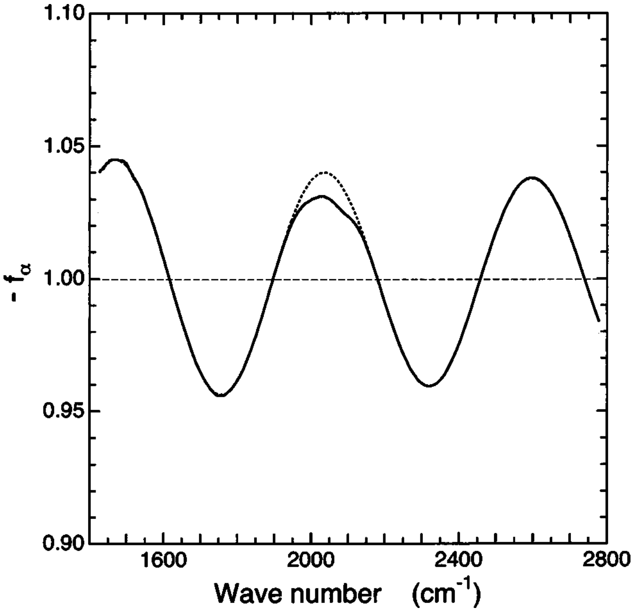

FIG. 5. The calculated f_α spectrum of the C sample (solid line). For comparison, the broken line shows a simple sine curve with the same periodicity as the f_α spectrum.

Using the f_α spectrum of Fig. 5, we now proceed to simulate the background PA spectrum, including the interference fringes of Fig. 4. In view of Eq. (1), it may be thought that such a simulation is done simply by evaluating the product of $f_\alpha \Delta\alpha$ at each wave number, while also assuming a smoothed background PA spectrum as the genuine $\Delta\alpha$ spectrum. However, contrary to expectation, this approach does not work well, because the absolute magnitude of the ratio between the observed amplitude of the interference fringes, which is expected theoretically to be $\Delta f \Delta \alpha d$, and $\Delta\alpha$ is not constant, but actually is a function of wave number. Although an exact explanation of this discrepancy is not presently known, a practical procedure is adopted here for avoiding this difficulty. For this purpose, Eq. (1) is modified to read as

$$\Delta T/T = -(1+b\Delta f)(\Delta\alpha d + c) + c, \tag{6}$$

where b and c are introduced as adjustable parameters. The best combination of values for b and c can be determined by fitting the interference fringes of both spectral branches in

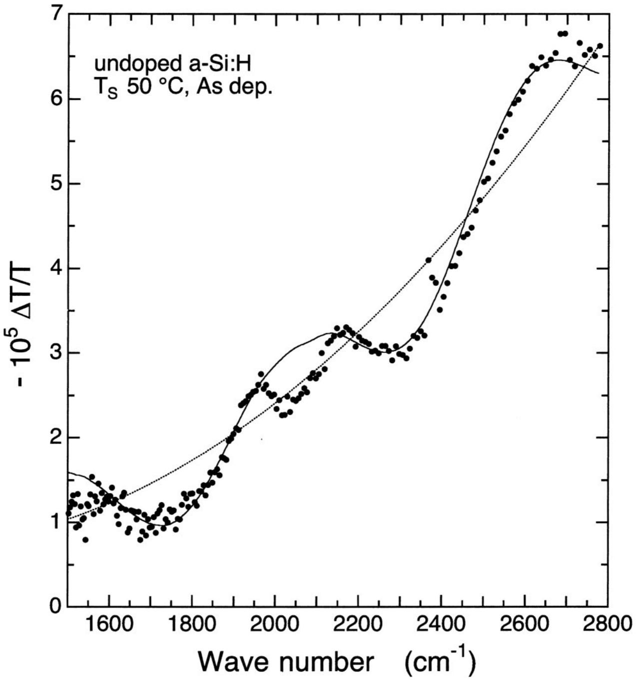

FIG. 6. An enlargement around 2000 cm^{-1} of the spectrum in Fig. 4. The solid circles show data points. The dotted line represents the averaged background PA spectrum, $\Delta\alpha$. Only the dispersion of the imaginary part of the complex refractive index (i.e., absorption coefficients of the Si-H stretching vibration) of the C sample is taken into account in the calculation of the simulated background PA spectrum (solid line).

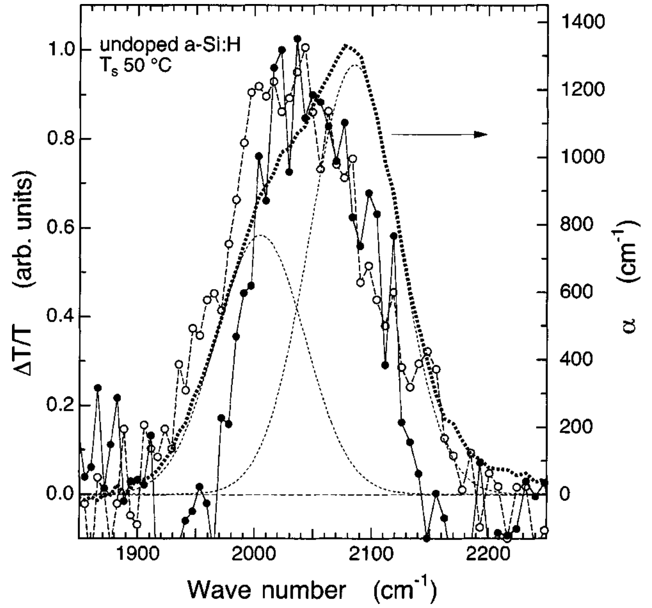

FIG. 7. Modulated ir-absorption spectra of the Si-H stretching vibration in the C sample. Spectra in the as-deposited state and in the state after thermal annealing are shown by the solid circles connected with the thin solid line and the open circles connected with the broken line, respectively. The maximum values of both spectra are made to coincide. The thick dashed line represents the absorption-coefficient spectrum of this sample. The decomposition of the absorption-coefficient spectrum into its 2000- and 2100-cm^{-1} components are shown by the thin dashed lines.

the neighborhood of the 2000-cm^{-1} band (in the measured PM spectrum in Fig. 4) with a spectrum calculated from Eq. (6) with $\alpha=0$ and $n=\text{const}$. Then, we can insert the $\Delta f\ (=-f_\alpha-1)$ spectrum of Fig. 5 into Eq. (6) for an exact simulation of the background PA spectrum that accompanies the interference fringes.

The measured and simulated PA spectra,[18] especially around 2000 cm^{-1}, are shown in Fig. 6 by the solid circles and the solid line, respectively. The dotted line in this figure represents the averaged background PA spectrum, i.e., the genuine $\Delta\alpha$ spectrum. Simulation of the PM spectrum over the whole spectral range, except for the region around 2000 cm^{-1}, is not very successful, because of the scattering of the data points in the as-deposited state, and/or because of the neglect of the dispersion of the real part of $\tilde{n}$. The separated dip-band spectrum and the corresponding absorption-coefficient spectrum of the Si-H stretching vibration in the C sample, in the as-deposited state, are shown in Fig. 7 by the solid circles connected with the thin solid line and the thick dashed line, respectively. The thin dashed lines show the results of decomposition of the absorption-coefficient spectrum into the 2000- and 2100-cm^{-1} components. Although the magnitude of the latter is much larger than that of the former in the absorption-coefficient spectrum, the relative intensity between the two components is reversed in the modulated ir-absorption spectrum.

For further insight into the structural instability, the effect of thermal annealing on the modulated ir absorption, or the dip-band spectrum, was examined with a C-type sample that was used in a previous study.[6] That sample was vacuum-annealed at several temperatures below 230 °C for 3 h at each step. After this treatment, the sample's defect density was evaluated with the electron-spin-resonance spectroscopy and found to be reduced by about two orders of magnitude.[6] It is shown in Ref. 6 that the intensity of the modulated ir-absorption band as well as that of the background PA was enhanced after the annealing. In the present work, it was confirmed that the absorption-coefficient spectrum itself does not show any change during the annealing treatment.[18]

The PM spectrum after the thermal annealing is shown in Fig. 8 by the solid circles. Comparing this spectrum with that in Fig. 6, we find that the peak positions of the interference fringes are shifted and their relative amplitudes are weakened. This indicates that the thermal annealing changed the refractive index. The spectrum simulation, taking into account only the ir-absorption band of the Si-H stretching mode, is represented by the solid line in Fig. 8. The averaged background PA spectrum is shown by the dotted line in the same figure. The modulated ir-absorption spectrum in the annealed state can be separated from these results, and the outcome is shown in Fig. 7 by the open circles connected with the broken line. In this figure, the maximum values of both spectra before and after the thermal annealing are made to coincide with each other. At first glance, it seems as if a difference exists between two modulated ir-absorption spectra in the lower-wave-number region. However, by considering the incompleteness of the simulation of the background PA spectrum in the as-deposited state (Fig. 6), it can be stated

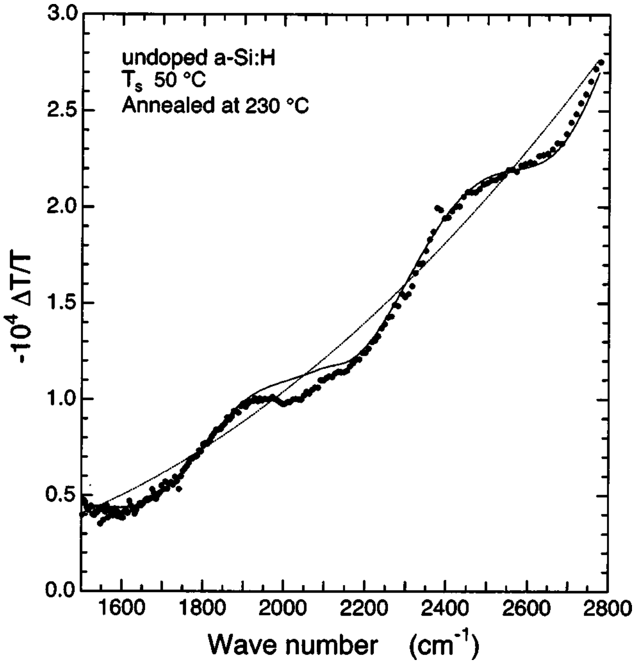

FIG. 8. Photomodulation spectrum of the *B* sample prepared at $T_S = 100\,°\mathrm{C}$. Solid circles denote data points. The dotted line is the averaged background PA spectrum, $\Delta\alpha$. Only the dispersion of the imaginary part of the complex refractive index (i.e., absorption coefficients of the Si-H stretching vibration) of the *B* sample is taken into account in the calculation of the simulated background PA spectrum (solid line).

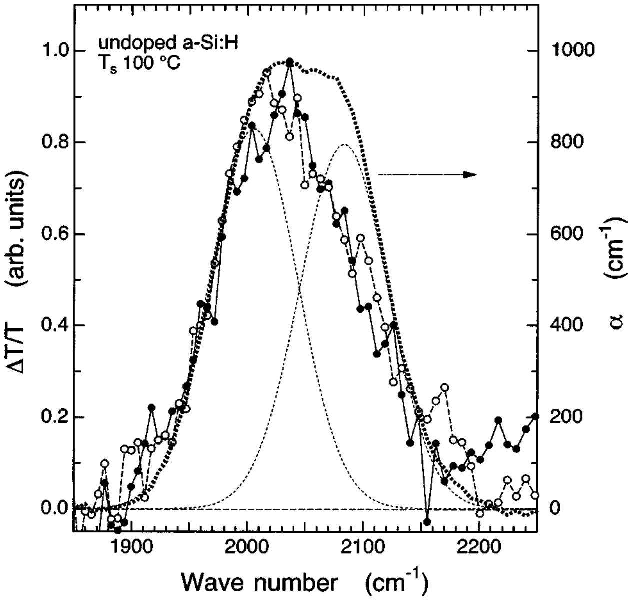

FIG. 9. Modulated ir-absorption spectra of the Si-H stretching vibration in the *B* sample. Spectra in the as-deposited state and in the state after thermal annealing are shown by the solid circles connected with the thin solid line and the open circles connected with the broken line, respectively. The maximum values of both spectra are made to coincide. The thick dashed line represents the absorption-coefficient spectrum of this sample. The thin dashed lines show the decomposition of the absorption-coefficient spectrum into its 2000- and 2100-cm^{-1} components.

approximately that the spectral shape of the modulated ir absorption is almost invariant against the thermal annealing up to 230 °C. The 2000-cm^{-1} component still dominates the modulated ir-absorption spectrum even after the thermal annealing.

The same measurements and the simulation of the background PA spectrum were made using two *B*-type samples with $T_S = 100\,°\mathrm{C}$, as in the case of the *C* sample. The 2000- and 2100-cm^{-1} components contribute almost equally to the absorption-coefficient spectrum of the Si-H stretching vibration in the *B*-type samples, as shown in Fig. 9 by the thin dashed lines. The modulated ir-absorption bands, in the as-deposited state and in the state after the thermal annealing up to 250 °C, are compared in Fig. 9. These cases are represented by the solid circles connected with the thin solid line and the open circles connected with the broken line, respectively. As in the *C*-sample case, these results show that the spectral dependence of the modulated ir absorption, as well as the usual ir-absorption spectrum of the Si-H stretching vibration, does not suffer any change through thermal annealing, although the intensity of the modulated ir absorption is enhanced. From the results summarized in Figs. 7 and 9 for the low-T_S samples, it can be concluded that the 2000-cm^{-1} component is more dominant in the modulated ir-absorption spectrum than the 2100-cm^{-1} component, irrespective of T_S.

IV. DISCUSSION

The modulated ir absorption under consideration is the real-time change in magnitude of the Si-H stretching vibrational absorption following the modulated band-gap excitation. The most probable cause for this change would be the change in the effective charge of the Si-H oscillator under the band-gap excitation. However, the nature of the Si-H oscillator is not affected directly by the band-gap illumination, so the change in question must be induced indirectly. In the absence of illumination, charge fluctuations, which are inherent in a disordered network, produce net atomic charges on the silicon,[19] in addition to positive charge accumulation on the silicon due to the inductive effect of neighboring hydrogen.[20] The atoms in crystalline silicon have no charge at their equilibrium positions owing to their symmetrical configuration, but, in amorphous silicon, they carry charges due to the geometric distortions: bond-angle or bond-length distortion in a disordered network will result in nonzero atomic net charges. It is usually thought that most of the local strain in such a distorted network is concentrated in the bond-bending interaction, since the force constant of bond stretching is much larger than for bending in the Keating formulation.[21,22] Several experimental and theoretical works[23–26] have dealt with the charge fluctuations in the *a*-Si:H network. Quantum-chemical calculations by Kugler, Surjan, and Naray-Szabo[26] have demonstrated that atomic net charges have a close linear relationship with bond-angle distortions that involves first and second neighbors: the charge fluctuation in amorphous silicon is a three-atom effect and can be traced to bond-angle distortions.

When such a distorted network is excited by the band-gap light, the charge distribution undergoes a change, which is accompanied by a change in the bonding configuration around the strained region in order to establish a new force balance. Since the absorption strength of the Si-H stretching vibration is reduced under the band-gap excitation, as observed in the present study, the effective charge of the Si-H oscillator should be reduced under illumination. The magnitude of the induced change in the atomic charges depends on how deeply the structural distortion is modified under illumination. A simulation study for real-time local structural changes in such a situation has been given by Yonezawa, Sakamoto, and Hori.[27] It was found, after band-gap excitation, that the length of a weak Si-Si bond in the vicinity of the Si-H bond varies with time as if in a breathing mode.

In view of the above considerations, we understand that the modulated ir absorption reflects a change in the atomic charges under the modulated band-gap excitation through modification of the bond-angle and bond-length distortion which is expected to take place in the neighborhood of the Si-H oscillator. Therefore, observation of the modulated ir absorption provides a means for detecting directly a photoinduced real-time change in a structural configuration at a specific site, especially that around the silicon-hydrogen bond. Modulated ir-absorption measurements reveal how the structural instability around the silicon-hydrogen bond in undoped *a*-Si:H and related alloys differs in accordance with the local environment. In this regard, we have focused here on the difference in the structural instability related to the surroundings of the Si-H and Si-H_2 bonds in undoped *a*-Si:H. The main conclusion of the present study is that the 2000-cm^{-1} component due to the monohydride configuration is dominant in the modulated ir-absorption spectrum. This result is evident even for the cases in which the 2100-cm^{-1} component due to the dihydride configuration dominates the usual ir-absorption spectrum. The photoinduced structural instability seems to occur more effectively around the Si-H bond.

Spatial locations of the two configurations of the silicon-hydrogen bond are different in the network of *a*-Si:H. It has been confirmed experimentally that the Si-H bonds are dispersed in the network, whereas the Si-H_2 bonds are likely to be clustered as forming a void.[28] It is thought that the overall strain in a rigid disordered network of Si atoms can be released by incorporating hydrogen. The Si-H_2 bonds are more efficient at releasing the local strain, because of the lower effective coordination of such Si atoms. With reference to the local strain residing at some distorted bonding configuration, several authors have performed experiments on the internal stress in *a*-Si:H, a property which manifests the macroscopic nature of *a*-Si:H. Spanakis, Stratakis, and Tzanetakis[29] have studied the elastic properties of several kinds of undoped *a*-Si:H films, with different hydrogen contents, and have indicated that high-quality *a*-Si:H, characterized by a nearly continuous, random-network structure and containing bonded hydrogen mainly in the monohydride configuration, can support the highest internal stress; in the as-deposited state, by impeding the stress relaxation which is accumulated during deposition. Related studies have been conducted on the dilatation of the disordered *a*-Si:H network, which is induced after strong light soaking.[30,31] Such studies show that the highest-quality *a*-Si:H film also exhibits the largest photoinduced volume change or compressive stress. Furthermore, Hishikawa[32] has reported interesting correlations between the mechanical stress and the hydrogen content of the two hydrogen bonding configurations in undoped *a*-Si:H, namely, the compressive stress enhances (reduces) with hydrogen atoms in the monohydride (dihydride) configuration. All these experimental results suggest strongly that a much stronger internal stress will be induced into the disordered lattice, as more and more bonded hydrogen takes on the monohydride configuration with the accompanying exclusion of inhomogeneity and an enhancement of the network rigidity. In conjunction with these published results, the present work suggests that a much stronger local strain will reside preferentially around the Si-H bond as compared to that around the Si-H_2 bond. The local strain will be relaxed to some degree under the band-gap illumination, thereby leading to the observed modulated ir absorption. Here, it must be noted that, when plateletlike clustered Si-H bonds happen to exist in the network, the modulated ir-absorption band may have an effective contribution from the 2100-cm^{-1} component, since the H pushes the Si network apart and, as a result, a large strain field will be introduced there.[16]

By following the above arguments, it was thought that the structural instability observed under the band-gap illumination, or the structural distortion in the dark, would be affected by the annealing treatment. The effect of thermal annealing was expected to be site dependent, in accordance with the difference in degree of the structural instability between the surroundings of the Si-H and Si-H_2 bonds. It turns out that we could observe almost no change in the spectral shape of the modulated ir absorption after the thermal annealing up to 230 °C and 250 °C for the *C* sample and *B* sample, respectively, thereby showing that the thermal annealing has no influence on the local structure around the silicon-hydrogen bonds.

However, since the dangling-bond density was actually reduced by the thermal annealing,[6] structural relaxation surely took place somewhere in the network. On the other hand, in spite of the absence of a spectral change, the intensity of the modulated ir absorption was enhanced after the thermal annealing. This probably means that the modulated ir absorption is a phenomenon related to excess carriers, as commonly observed in other quantities, such as photoconductivity or photoluminescence.[28] With the same excitation intensity, quality or signal intensity of these phenomena is improved with an increase in excess carriers through the reduction of the dangling-bond density by the annealing treatment. If the modulated ir absorption is a phenomenon initiated by the excess carriers as in these other cases, the recovery of its intensity after the thermal annealing can be understood in the same way. Furthermore, it is speculated that the structural relaxation induced by the thermal annealing will take place in a region far from the silicon-hydrogen bonds, where bonded hydrogen in scarce.

This work has focused on the structural instability that is related especially to the Si-H stretching vibration. This limitation is due to the characteristics of the optical components used in the experimental setup. It is of interest to extend the spectral range of the measurement to a different wavelength range where other vibrational modes connected with bonded hydrogen, such as the wagging and bending modes, or some impurity-related vibrational modes, or, even a vibrational modes resulting from paired hydrogens are observable. Recently, an interesting possibility involving paired hydrogen atoms in photodegradation has been pointed out from an NMR study.[33] The present method is the only known practical technique for confirming the presence of such a microscopic structure. However, if it is the case that modulated ir absorption is a phenomenon closely related to excess carriers, then coexistence of the electronic PA band with large intensity and severe interference fringes is inherent. In this case, an effective suppression of the background PA band would have to be achieved by a rather smart device.

V. CONCLUSION

From the fact that the Si-H stretching vibration is strongly localized in *a*-Si:H, and from the fact that the band-gap light does not affect directly the vibrational properties of the Si-H stretching mode, the modulated ir absorption can be considered as resulting from an induced change in the atomic charges on the silicon atom of the Si-H oscillator under the band-gap illumination through modification of the bonding configuration adjacent to the Si-H bond. Therefore, the modulated ir absorption of the Si-H stretching vibration can be utilized as a tool for detecting a real-time structural fluctuation in the immediate surroundings of the silicon-hydrogen bond.

Preliminary measurements are performed for undoped *a*-Si:H films prepared at different substrate temperatures for examining the site-dependent, structural-instability difference between the surroundings of the Si-H and Si-H_2 bonds. Irrespective of T_S, the modulated ir-absorption spectrum is found to be dominated by the 2000-cm^{-1} component due to the Si-H configuration, even when the 2100-cm^{-1} component due to the Si-H_2 configuration dominates the usual ir-absorption spectrum. It can be said that the structural instability occurs more effectively in the neighborhood of the monohydride Si-H bond. In conjunction with reported studies[29–32] concerning the compressive stress in undoped *a*-Si:H with different network structures, it is inferred that the local strain resides preferentially in the surroundings of the Si-H bond. Alternatively, it may be said that inclusion of the silicon-hydrogen bond itself in the disordered network of *a*-Si:H produces a distorted bonding configuration around it, which is modified with ease under the band-gap excitation.

Thermal annealing was introduced with the expectation that it would affect the structural instability in a site-dependent way, but no change could be observed in the spectral shape of the modulated ir absorption after the thermal annealing up to around 250 °C. However, the modulated ir absorption can be considered as a phenomenon closely related with excess carriers, because its intensity is recoverable after thermal annealing.

ACKNOWLEDGMENT

The author is grateful to Dr. G. Ganguly for kindly preparing the specimens.

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