Spectral dependence of lifetime of excited Si-H stretching vibration in hydrogenated amorphous silicon

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A convenient method for evaluating the relative spectral dependence of the lifetime of a localized vibrational mode in an amorphous semiconductor is proposed. The energy relaxation of an excited vibrational population is analyzed on the basis of a two-level system when the system is perturbed by a weak thermal modulation. An equation is derived, which indicates that the vibrational lifetime, at an arbitrary vibrational energy, $h\nu$, is simply proportional to $[\Delta E(h\nu)/E(h\nu)]/\nu^4$, where $\Delta E(h\nu)$ and $E(h\nu)$ are spectra of the excess radiation power induced by the thermal modulation and the emissive power in thermal equilibrium, respectively. The method is applied to several undoped hydrogenated amorphous silicon films. The spectral dependence of the vibrational lifetime of the Si-H stretching mode is evaluated for these films which are prepared at different substrate temperatures. The resulting spectra exhibit a tendency for the vibrational localization to increase as $h\nu$ decreases.

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I. INTRODUCTION

Hydrogen in a crystalline semiconductor sometimes plays a crucial role in affecting its electronic properties. This is due to the migration of hydrogen within the lattice, and/or the formation of a complex with impurity atoms or vacancies.[1,2] Hydrogen that is incorporated in amorphous silicon plays an essential role[3] in the effective activation of doping by terminating the dangling bonds, which are inherent in a disordered network only of Si atoms. However, in contrast to this desirable effect, there is a well-known problem associated with hydrogenated amorphous silicon (a-Si:H). That is, the electronic quality of a-Si:H degrades after exposure to strong light. This is known as the Staebler-Wronski effect.[4] Many experimental and theoretical studies have focused on the role of hydrogen in this effect.

An interesting observation is that the degree of the light-induced degradation is reduced when deuterium replaces hydrogen in a-Si:H.[5–8] This difference in the reduction of the photo-degradation of a-Si:H and a-Si:D is presently understood as due to the difference between the rate of transfer of excess energy from the wagging vibration of the Si-H and Si-D band to the surrounding lattice phonons.[5–8] The Si-H vibration appears to be more localized than its Si-D counterpart. In other words, it is much harder for the former than the latter to transfer an accumulation of excess energy to its surroundings.

A more direct evaluation of the degree of localization of the Si-H stretching vibration in a-Si:H has been carried out by Xu *et al.*[9] and subsequently by Dijkhuis and co-workers.[10–12] These authors observed a transient change in the infrared absorption of the Si-H stretching vibration, after exciting it directly with a pulsed free-electron laser. At low enough temperature, they found the vibrational lifetime to be about 100 ps,[9–12] which was an order of magnitude longer than that of the corresponding Si-H vibration in a crystalline Si network.[13] This indicates that the localization of the Si-H stretching vibration is much stronger in a disordered network than in an ordered lattice. Furthermore, Dijkhuis and co-workers proposed a plausible path for relaxing the energy of the excited Si-H stretching vibration based on the observed temperature dependence of the vibrational lifetime. They concluded that the excess energy was transferred indirectly to the surroundings, after the vibrational mode changed to the wagging mode.[10–12] Thus a study of the microscopic dynamics of the localized Si-H vibration is expected to provide some advanced information on the structural characteristics of a-Si:H *vis à vis* the role of hydrogen in the photodegradation.

Because of the strong localization of the Si-H stretching vibration, its properties will be affected, within a limited range, by the local surroundings. In this sense, the vibration is sensitive to its immediate environment, which differs from site to site due to the disordered nature of the material. Therefore, the spectral dependence of the vibrational lifetime of this mode is expected to reflect such a variation in structures surrounding the Si-H bond. Such is the case of the Si-H infrared absorption, whose bandwidth is broadened by the inhomogeneity of the local environments. As noted above, a key factor for clarifying the microscopic dynamics of the light-induced degradation is concerned with knowing how closely the localized Si-H vibration is energetically coupled to its surroundings. It is useful to know how the degree of localization varies with the vibrational energy within the localized Si-H vibrational mode. Such information can be obtained on the basis of the spectral dependence of the lifetime of a focused vibrational mode.

It is of interest to determine exactly, the absolute value of the lifetime of each oscillator in a composite of oscillators that constitute a localized vibrational band. The best procedure for measuring the transient response of each oscillator, after selective excitation, is that followed by Xu *et al.*[9] and Dijkhuis and co-workers.[10–12] However, the particular light source as adopted by these authors is not so conveniently available. It suffices, for a qualitative analysis, to obtain the

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relative spectral dependence of the vibrational lifetime. In this paper, we propose an alternate method for evaluating the relative spectral dependence of the lifetime, without requiring any specific light source. To determine the usefulness of the method, it is applied to several undoped a-Si:H films that are prepared at different substrate temperatures.

II. PRINCIPLE OF EVALUATION OF VIBRATIONAL LIFETIME

The exploration of any kind of relaxation phenomenon usually requires that the system of interest be perturbed. Xu *et al.* and Dijkhuis and co-workers determined the lifetime of the Si-H stretching vibration by exciting an excess vibrational population with a wavelength tunable pulsed laser. Immediately thereafter, the induced transient bleaching of the infrared absorption was monitored.[9–12] Such an absorption quenching can be regarded as enhanced radiation during the energy relaxation of the excess vibrational population.

Theoretical consideration of the vibrational relaxation of the excited Si-H stretching mode will be given in terms of a two-level system consisting of a pair of bound states, as adopted in Einstein theory.[14] Here we analyze the case where a system is perturbed by thermal modulation rather than by direct optical excitation. The densities of vibrational population, at the ground and first excited states, are denoted as $N_1(T)$ and $N_2(T)$, respectively, where T is the thermal equilibrium temperature. The upward transition rate is expressed as $N_1(T)BW_B(T)$, where $W_B(T)$ is the blackbody radiative energy density at T, and B is the Einstein B coefficient. When stimulated emission is negligible, the downward transition rate can be expressed as $N_2(T)A$, where A is the Einstein A coefficient, and corresponds to the transition probability of spontaneous emission, $\tau_{\mathrm{IR}}(h\nu)^{-1}$. When the system is in thermal equilibrium, these transition rates are equal:

$$N_1(T)BW_B(T)=N_2(T)A. \tag{1}$$

When the vibrational population is perturbed with a weak thermal modulation, the induced change ΔN_2 in the population of the excited state can be described by the rate equation

$$\frac{d\Delta N_2(t)}{dt}=\Delta g(t)-\frac{\Delta N_2(t)}{\tau_{\mathrm{eff}}}, \tag{2}$$

where τ_{eff} is the effective relaxation time, defined as

$$\frac{1}{\tau_{\mathrm{eff}}}=\frac{1}{\tau_{\mathrm{IR}}(h\nu)}+\frac{1}{\tau(h\nu)}\approx\frac{1}{\tau(h\nu)}. \tag{3}$$

As the system deviates from thermal equilibrium, various relaxation processes, other than the direct radiative relaxation, become possible. This is because the condition of detailed balancing is no longer valid. It has been reported that the observed lifetime of the Si-H stretching vibration is much shorter than the radiative lifetime $\tau_{\mathrm{IR}}(h\nu)$.[12,13] This result suggests that the energy relaxation is dominated by some competitive indirect relaxation process characterized by a much shorter lifetime, $\tau(h\nu)$, in comparison with $\tau_{\mathrm{IR}}(h\nu)$. In the same sense, τ_{eff} can be approximated as $\tau(h\nu)$, as shown in Eq. (3). The quantity $\Delta g(t)$ is the change in the upward transition rate, due to thermal modulation. For a temperature change of ΔT, it can be expressed as

$$\Delta g(t)=N_1(T)B[W_B(T+\Delta T)-W_B(T)]. \tag{4}$$

Plank's distribution of emissive power, $W_B(T)$, is given as[14]

$$W_B(T)=\frac{8\pi\nu^3}{c^3}\frac{1}{\exp(h\nu/kT)-1}, \tag{5}$$

where ν is the photon frequency, and the other symbols in Eq. (5) have their usual meanings. Approximating $W_B(T+\Delta T)$ by terminating its Taylor expansion at the first nonequilibrium term, and using the condition $h\nu\gg kT$, as well as Eq. (1) and $A=\tau_{\mathrm{IR}}(h\nu)^{-1}$, we can describe $\Delta g(t)$ explicitly as follows:

$$\Delta g(t)=N_2(T)\tau_{\mathrm{IR}}(h\nu)^{-1}\frac{h\nu}{kT^2}\Delta T. \tag{6}$$

Furthermore, when ΔT oscillates with time, as expressed by $\Delta T(t)=\Delta T_m\exp(i\omega t)$, the corresponding change in $\Delta N_2(t)$ will also reflect the same time dependence. Thus

$$\Delta N_2(t)=N_{2ac}\exp(i\omega t), \tag{7}$$

where ΔT_m and N_{2ac} are the amplitudes of $\Delta T(t)$ and $\Delta N_2(t)$, respectively. Combining with Eqs. (3), (6), and (7), we can then solve the rate equation (2), and the expression for N_{2ac} follows as

$$N_{2ac}=N_2(T)\tau_{\mathrm{IR}}(h\nu)^{-1}\frac{h\nu}{kT^2}\frac{\tau(h\nu)}{\sqrt{1+(\omega\tau)^2}}\Delta T_m\exp(-i\phi), \tag{8}$$

where $\phi=\tan^{-1}(\omega\tau)$. When $\omega\tau\ll1$, the absolute magnitude of N_{2ac} can be approximated as

$$|N_{2ac}|\approx N_2(T)\frac{h\nu}{kT^2}\Delta T_m\frac{\tau(h\nu)}{\tau_{\mathrm{IR}}(h\nu)}. \tag{9}$$

As explained at the beginning of this section, when the system deviates from thermal equilibrium, only part of the excess vibrational population of the excited state returns to the ground state radiatively. The excess radiation power induced by the thermal modulation can be written as

$$\Delta E(h\nu)=h\nu|N_{2ac}|\tau_{\mathrm{IR}}(h\nu)^{-1}. \tag{10}$$

On the other hand, the radiation power of the system, in thermal equilibrium at T, is described as

$$E(h\nu)=h\nu N_2(T)\tau_{\mathrm{IR}}(h\nu)^{-1}. \tag{11}$$

Using Eqs. (9) and (11), we can rewrite $\Delta E(h\nu)$ of Eq. (10) as

$$\Delta E(h\nu)=E(h\nu)\frac{h\nu}{kT^2}\Delta T_m\frac{\tau(h\nu)}{\tau_{\mathrm{IR}}(h\nu)}. \tag{12}$$

By rearranging this equation, we develop an expression for $\tau(h\nu)$, namely,

$$\tau(h\nu)=\frac{\Delta E(h\nu)}{E(h\nu)}\frac{1}{h\nu}\frac{kT^2}{\Delta T_m}\tau_{\mathrm{IR}}(h\nu). \tag{13}$$

The quantity $kT^2/\Delta T_m$ is independent of $h\nu$. Since $\tau_{\mathrm{IR}}(h\nu)^{-1}$ is equivalent to the Einstein A coefficient, it is proportional to $|M|^2\nu^3$, where M is the transition matrix element between the ground state and excited state.[14] It follows that, if $|M|^2$ has no vibrational energy dependence, a simplified expression for $\tau(h\nu)$ can be obtained in the form

$$\tau(h\nu)\propto\frac{\Delta E(h\nu)}{E(h\nu)}\frac{1}{\nu^4}. \tag{14}$$

This indicates that the relative spectral dependence of the lifetime of a localized vibrational band can be determined from the spectral dependence of $\Delta E(h\nu)$ and $E(h\nu)$.

III. EXPERIMENT

Specimens used for the measurements were thin films of undoped *a*-Si:H. These films were prepared by radio-frequency, glow-discharge decomposition of SiH_4 on intrinsic crystalline silicon (*c*-Si) wafers at substrate temperatures of 50, 100, and 300 °C. The thickness of the thin films and wafers was 4–6 μm and 0.5 mm, respectively.

In the measurement, a specimen was installed within a cryostat, and its temperature was controlled in order to maintain an ambient value of 296 K. In this context, a periodic, weak, thermal modulation was added to the specimen by illuminating it from the *c*-Si side with the 647-nm line of a Kr laser, which was modulated at 6 Hz with a mechanical chopper. The laser light illuminated an area of 7.1×10^{-2} cm^2 with 300 mW of power. The incident light was partially reflected at the surface, while the remainder was converted to heat by absorption near the surface of the *c*-Si substrate. Under these conditions, the thermally modulated radiation from the *a*-Si:H film could be observed concurrently with the thermal modulation. After collecting the emitted radiation with an ellipsoidal mirror, and after passing it through a grating monochromator in combination with an optical cutoff filter, it was detected with a cooled mercury cadmium telluride detector. The detector signal was fed into a lock-in amplifier where the amplitude of the fundamental component of the Fourier series of the modulated signal was measured.

In order to examine the thermodynamic state of the specimen during the modulation period, it is necessary to observe a transient change in the specimen's temperature. This change can be estimated approximately by monitoring the time dependence of the thermally modulated radiation. However, it was difficult to trace directly a wave form of the modulated signal of the thermally modulated radiation, because the detector signal was too weak. In principle, the lock-in amplifier can measure a magnitude and phase of each component of the Fourier series of some given periodic signal. The time dependence of the wave form of the modulated signal was synthesized after separate measurements of the corresponding magnitude and phase of the fundamental component and the higher harmonics (up to the ninth higher harmonics) were made with the lock-in amplifier. It was found

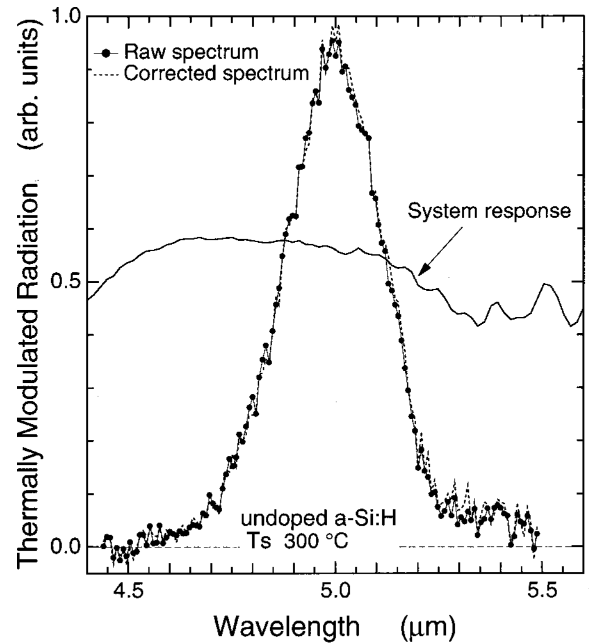

FIG. 1. Spectrum of the thermally modulated radiation from the Si-H stretching vibration in the undoped *a*-Si: H film, which was prepared on a *c*-Si wafer with a substrate temperature (T_s) of 300 °C. The spectrum was measured at 296 K by illuminating the specimen from the *c*-Si side with the 647-nm line of a Kr laser modulated at 6 Hz. The incident power of the laser was 360 mW at an area of 7.1×10^{-2} cm^2. The solid circles connected with the thin solid line represent the measured spectrum. The dashed line is the spectrum after correcting with the spectral response of the optical system, which is shown by the solid line.

that the specimen's temperature could not follow instantaneously a modulated illumination of constant intensity, but exhibited the $t^{0.5}$-type time dependence. Such a time dependence is expected for a transient response in one-dimensional thermal conduction.[15] Thus, since the specimen's temperature continued to vary during the modulation period, even though a constant amount of heat was applied to the specimen during each half period of the modulation, it can be said that the specimen could not attain thermodynamic equilibrium within the modulation period. The temperature rise within the *a*-Si:H film, during the heating period of the modulation (83.3 ms), was estimated to be about 0.8 K.[15]

IV. RESULTS AND DISCUSSION

A measured spectrum of the thermally modulated radiation from the Si-H stretching vibration is shown in Fig. 1 by solid circles connected with the thin solid line. This undoped *a*-Si:H specimen was prepared with a substrate temperature of 300 °C. Under the present experimental conditions, the modulated radiation emitted from the specimen was very weak, and it took almost 24 h to obtain the entire spectrum. Since the optical system, including the detector, has its own spectral response, the raw spectrum in Fig. 1 must be corrected accordingly. A way of evaluating the spectral response of the optical system will be reported in a separate paper.[16] Suffice it to say here that the spectral response of the optical

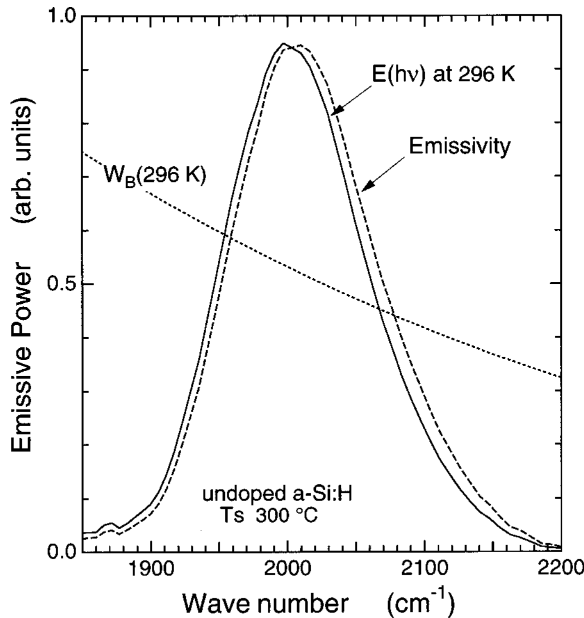

FIG. 2. The solid line represents the spectrum of emissive power, $E(h\nu)$, at 296 K of the undoped a-Si:H film prepared at $T_s = 300\,°\mathrm{C}$. It was calculated by multiplying the emissivity at every $h\nu$ times Plank's distribution of emissive power, $W_B(T)$, at 296 K. For reference, the emissivity and $W_B(T)$ spectra are shown by the dashed and dotted lines, respectively.

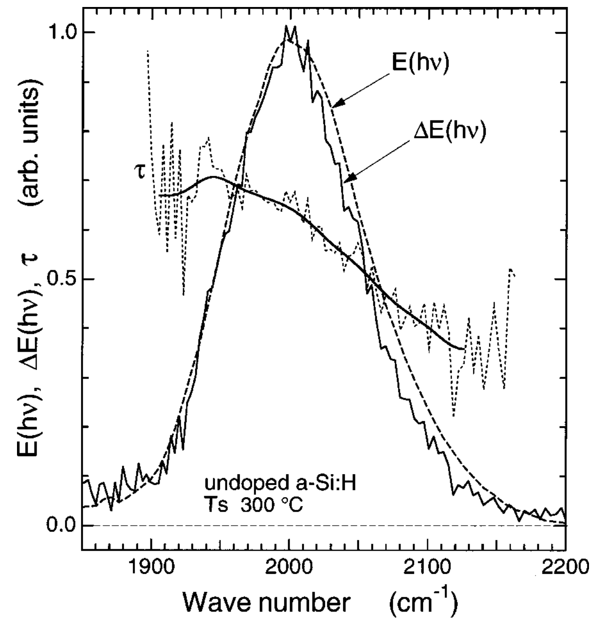

FIG. 3. Relative spectral dependence of the lifetime of the Si-H stretching vibration in the undoped a-Si:H film prepared at $T_s = 300\,°\mathrm{C}$. It was obtained according to Eq. (14), from the ratio of $\Delta E(h\nu)$ to $E(h\nu)$, with a ν^{-4} correction at every $h\nu$. The dotted and thick solid lines are the measured and smoothed out lifetime spectra, respectively. $\Delta E(h\nu)$ and $E(h\nu)$ spectra are shown by the solid and dashed lines, respectively. The maximum values of both spectra are made to coincide.

system had very weak wavelength dependence within the measured wavelength range, as shown in Fig. 1 by the solid line. The corrected $\Delta E(h\nu)$ spectrum is shown by the dashed line in Fig. 1, where it is seen that the difference between the raw and corrected spectra is very slight.

On the other hand, the spectrum of emissive power $E(h\nu)$, in thermal equilibrium at 296 K, can be calculated by multiplying the emissivity at every $h\nu$ times $W_B(T)$ at room temperature.[17] The emissivity of a body is a measure of how well it can emit radiation power in comparison with that of a blackbody.[18] The detailed experimental procedure for evaluating the emissivity spectrum will be reported elsewhere.[16] However, since Kirchhoff's law equates emissivity and absorptivity at any $h\nu$,[17,18] the spectral dependence of the emissivity can be obtained alternatively from a spectrum of infrared absorption coefficients. This is accomplished in accordance with the absorption expression, 1-exp(-αd), under the assumption of a constant reflectivity at the surface of the a-Si:H film irrespective of the value of $h\nu$. In this expression, α and d are the absorption coefficient and the thickness of the specimen, respectively. We have confirmed that the spectral dependence of the resulting absorptivity actually coincides with that of the emissivity evaluated with our proposed method.[16] Figure 2 shows the $E(h\nu)$ spectrum that was obtained from the corresponding emissivity spectrum at 296 K. For reference, the spectral curves of the emissivity and of $W_B(T)$, at the same temperature, are also shown in this figure.

The $E(h\nu)$ and $\Delta E(h\nu)$ spectra are compared in Fig. 3, where the maximum values of both spectra are made to coincide. Although the $\Delta E(h\nu)$ spectrum is still quite noisy, even after the long accumulation time, a difference in shape between these two spectra is clearly evident. On the basis of these results, the relative spectral dependence of the lifetime of the Si-H stretching vibration can be obtained according to Eq. (14), from the ratio of $\Delta E(h\nu)$ to $E(h\nu)$, with the ν^{-4} correction at every $h\nu$. The outcome is shown in Fig. 3 by the dotted line. The thick solid curve through this line shows the smoothed out lifetime spectrum. Identical measurements were performed for other specimens that were prepared at 100 and 50 °C. The corresponding results are summarized in Figs. 4(a) and 4(b).

Although the $\Delta E(h\nu)$ spectrum of Fig. 1 was corrected for the spectral response of the optical system, it should be noted that this correction has no influence on the resulting lifetime spectrum. Although the details will be explained elsewhere,[16] the present optical setup was used for the determination of the emissivity spectrum. The same correction due to the spectral response of the optical system was applied to the emissivity spectrum. Since $E(h\nu)$ is proportional to the emissivity, the influence of this correction on $\Delta E(h\nu)$ and $E(h\nu)$ cancels out of their ratio in Eq. (14).

Looking at the smoothed out lifetime spectra in Figs. 3 and 4, we can see that the vibrational lifetime exhibits a tendency to decrease almost monotonically with increasing vibrational energy. Furthermore, the spectra show some distinctive structures: (1) a bump is likely to be located commonly at around 1950 cm^{-1}, and (2) a shoulder appears at either 2000 or 2100 cm^{-1}, depending on the particular specimen. Such a spectral dependence of the lifetime at 296 K is consistent qualitatively with the result reported by Rella

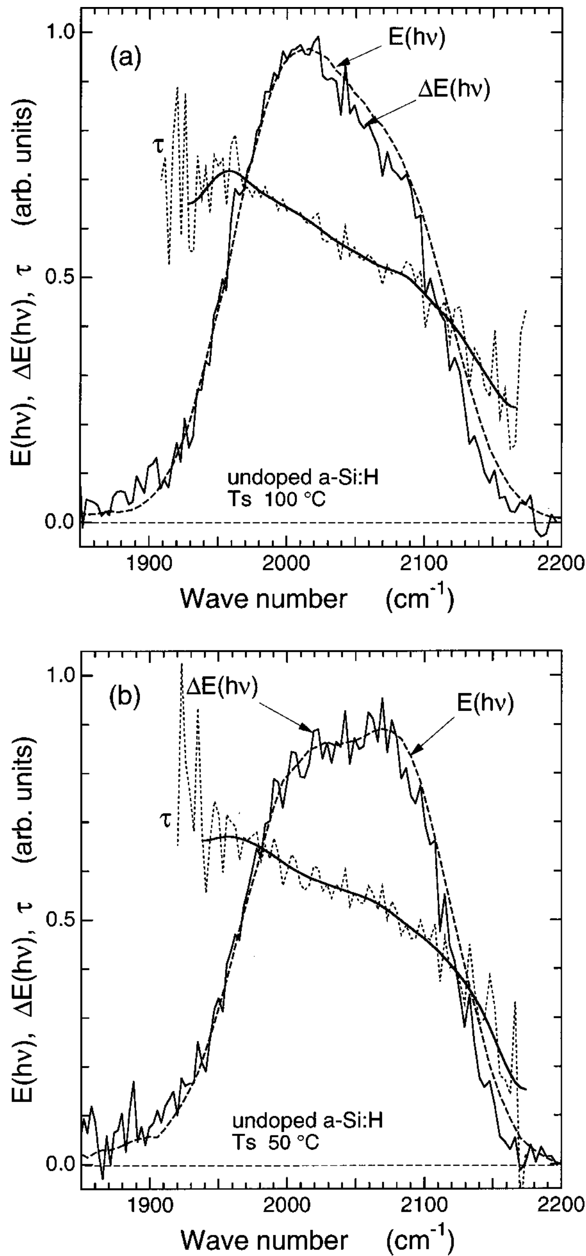

FIG. 4. Relative spectral dependences of the lifetime of the Si-H stretching vibration in other undoped *a*-Si:H films: (a) is for the specimen prepared at $T_s = 100\,°C$, and (b) for the specimen prepared at $T_s = 50\,°C$. The dotted and thick solid lines in each figure are the measured and smoothed out lifetime spectra, respectively. $\Delta E(h\nu)$ and $E(h\nu)$ spectra are also shown.

et al.[10] The spectrum in Ref. 10 refers to the geometric mean lifetime measured at 10 K, and exhibits a maximum at around 2000 cm^{-1} with a tendency to decrease in value slightly in the energy ranges beyond the maximum.

The observation that the smaller the vibrational energy the longer the vibrational lifetime indicates that the localization of the Si-H stretching mode becomes stronger at lower vibrational energies. At present, only a few reports deal with the problem of the degree of the vibrational localization. Recently, Zhao *et al.*[19] reported on an induced change in the infrared, absorption coefficients $\Delta\alpha$ of the Si-H stretching vibration, that resulted after exposing the material to strong light. They deconvoluted the $\Delta\alpha$ spectrum into three Gaussian components with peaks at 1935, 2000, and 2068 cm^{-1}. After normalizing these deconvoluted bands with their respective peak absorption coefficients, it was found that the 1935 component was the largest.[20] This indicates that the light-induced change does not take place uniformly within the absorption band, since there is a preference for the induced change to be enhanced at the lower vibrational energies. This result is consistent with the properties of the $\tau(h\nu)$ spectra in Figs. 3 and 4.

We now consider several uncertainties and problems related to the foregoing theoretical analysis. First, we look again at Eq. (14). According to this equation, the ν^{-4} term appears to dominate the spectral dependence of $\tau(h\nu)$. However, there exists a clear difference in the spectral shapes of $\Delta E(h\nu)$ and $E(h\nu)$, as illustrated in Fig. 3. Therefore, the $\Delta E(h\nu)/E(h\nu)$ ratio in Eq. (14) makes a meaningful contribution to $\tau(h\nu)$, and causes notable structures in the $\tau(h\nu)$ spectra. A vibrational feature of hydrogenated As_2S_3 glass has been observed, which contrasts with the present result for *a*-Si:H. It has been reported that the vibrational lifetime of the S-H stretching mode in As_2S_3 glass increases with increasing vibrational energy.[21,22] Finally, this finding demonstrates that the ν^{-4} term does not dominate the spectral dependence of $\tau(h\nu)$.

In reference to the basic assumption made in the theoretical analysis, namely, that the system is not in an equilibrium state during the thermal modulation, it may be argued that an equilibrium condition is established within each half period of the modulation, because the relaxation time $\tau(h\nu)$ is expected to be much shorter than the modulation period. However, the difference between the spectra of $\Delta E(h\nu)$ and $E(h\nu)$ surely indicates that the system does not equilibrate within the modulation period. As a result, the condition of detailed balancing of Eq. (1) is no longer valid, within the thermal modulation, as one of the experimental parameters.

The next point to consider is the neglect of stimulated emission in the energy relaxation process. As for the direct radiative relaxation between the excited and ground states of the Si-H stretching mode, it is reasonable to assume that the thermally stimulated emission is negligible in comparison with the spontaneous emission at room temperature.[14] However, according to results reported by Dijkhuis and coworkers, the excited Si-H stretching vibration relaxes into a combination of the Si-H bending vibrations and Si lattice phonons. Meanwhile, the relaxation rate at 300 K is enhanced by a factor of about 2 as compared to the zero-temperature relaxation rate.[11,12] The $\tau(h\nu)^{-1}$ discussed in Sec. II corresponds to the zero-temperature relaxation rate. Strictly speaking, when such a multiphonon relaxation process is operative, it is necessary to take into account the stimulated emission of the receptor modes and phonons in the theoretical analysis, since our measurement was performed at 296 K. However, keep in mind that here we are considering the relative spectral dependence of $\tau(h\nu)$, rather than the absolute values of $\tau(h\nu)$. Therefore, in so far as the

same combination of receptor modes and lattice phonons participates in the relaxation process, irrespective of the value of $h\nu$ within the Si-H stretching band,[12] neglect of stimulated emission will have little effect on the resulting spectra.

A limitation of the present method should be noted. Measurement of the temperature dependence of the lifetime of an excited Si-H stretching vibration is of principal interest here, because it may refer to a possible path by which this localized excitation loses its excess energy during relaxation. However, the determination of $\tau(h\nu)$ by our method is based on the measurement of $\Delta E(h\nu)$, whose value depends on the emissive power of $E(h\nu)$ in thermal equilibrium, as Eq. (12) indicates. Consequently, detection of the thermally modulated radiation with good accuracy is impossible when the temperature of the specimen is lowered. In this case, there is a significant reduction of $\Delta E(h\nu)$, that accompanies the reduction of $E(h\nu)$ as the temperature is lowered.

Finally, we address the constancy of the transition probability $|M|^2$. The hydrogen content in an *a*-Si:H film is often estimated from the integrated infrared absorption of the Si-H vibrational modes in conjunction with appropriate proportionality constants, which are inversely proportional to the transition probabilities.[23] The Si-H stretching band consists of the 2000- and 2100-cm^{-1} modes, whose respective constants have been treated as fixed. There is disagreement concerning whether these constants for the two Si-H stretching modes are equal or not.[24,25] However, Beyer and Abo Ghazala[25] recently performed a detailed study of the ratios of the proportionality constants of the Si-H stretching modes to that of the Si-H wagging mode and concluded that the constants in question are essentially equal. These authors give 0.97 ± 0.12 as the value for the ratio of $|M|^2$ between the 2000- and 2100-cm^{-1} modes.

V. CONCLUSION

A convenient method for evaluating the spectral dependence of the lifetime of an excited localized vibrational mode is proposed. Analytical consideration of the thermally modulated radiation $\Delta E(h\nu)$ in terms of a two-level system reveals that the lifetime is proportional to $[\Delta E(h\nu)/E(h\nu)]/\nu^4$, providing that transition probability is independent of $h\nu$. The relative spectral dependence of the vibrational lifetime can be obtained from the spectral dependence of $\Delta E(h\nu)$ and $E(h\nu)$. The essence of the method is the measurement of $\Delta E(h\nu)$, which is induced in the specimen by the application of a weak thermal modulation. The relative spectral dependence of the lifetime of the Si-H stretching mode, of several undoped *a*-Si:H films, can be obtained on the basis of an analytical expression. The resulting lifetime spectra exhibit some distinctive features: a bump commonly appears in the spectra at around 1950 cm^{-1}, and the lifetime decreases monotonically as a function of increasing vibrational energy, with accompanying a shoulder at about 2000 or 2100 cm^{-1}, depending on the specimen. The vibrational localization of the Si-H stretching mode appears to be enhanced at lower values of $h\nu$. Furthermore, because of the strong localization of the vibrational mode, such a spectral dependence of the vibrational lifetime will reflect the difference, from site to site, of the local structures surrounding the Si-H bond. We plan to apply the present method to *a*-Si:H related alloys in order to discuss how the Si-H stretching vibration is affected by its local environment, such as the presence of alloying elements in the neighborhood of the Si-H bond.

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