PHYSICAL REVIEW B **69**, 245203 (2004)

Site-dependent structural instability at the surroundings of the Si−H bond in hydrogenated amorphous silicon based wide-gap alloys

Hidetoshi Oheda
Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

(Received 11 December 2003; revised manuscript received 26 February 2004; published 22 June 2004)

A real-time change in the absorption strength of the Si−H stretching vibration in hydrogenated amorphous silicon (*a*-Si:H), so-called modulated IR-absorption, is observable when *a*-Si:H is illuminated with modulated band-gap light at low-temperature. This IR-absorption change should reflect a change in a structural configuration at the local surroundings of the Si−H bond, since the band-gap light does not directly affect the localized vibrational mode. We have utilized this phenomenon as a sensor for detecting the real-time structural instability in the vicinity of the bonded hydrogen. Following a previous study on a difference in the structural instability between the surroundings of Si−H and Si−H_2 bonds in updoped *a*-Si:H [H. Oheda, Phys. Rev. B **68**, 085206 (2003)], the present study extends the investigation to *a*-Si:H-based wide-gap alloys, such as *a*-SiN:H and *a*-SiO:H. In particular, it is concerned with how the structural instability around the Si:H bond is affected by a change in the structural configuration at the local surroundings of the Si:H bond due to neighboring of alloy atoms. It is found that the magnitude of the modulated IR-absorption, or the structural instability, is reduced as the number of neighboring alloy atoms increases. An examination of the spectral difference between the modulated IR-absorption and the corresponding normal IR-absorption shows that the structural instability takes place more effectively at the specific site where the Si−H bond is surrounded by two or three nearest-neighbor Si atoms. The change in strength of the local strain around the Si−H bond, due to the neighboring of alloy atoms, is a major cause of the site-dependent structural instability in the wide-gap alloys.

DOI: 10.1103/PhysRevB.69.245203 PACS number(s): 78.66.Jg, 78.30.Ly, 63.50.+x

I. INTRODUCTION

Since amorphous materials are not in the thermally equilibrated state, their characteristics in many aspects are easily affected by applying some perturbation. In hydrogenated amorphous silicon (*a*-Si:H), a well known phenomenon is the Staebler-Wronsky effect,[1] in which electronic properties degrade after exposing to an intense visible light as a result of creation of many Si dangling bonds. This change is almost irreversible at room temperature, and is closely related with the metastable nature of the network structures of *a*-Si:H.

In a previous paper,[2] we have studied a real-time structural change, or structural instability, that takes place at the surroundings of Si−H bond. When *a*-Si:H is illuminated at low temperatures with a modulated band-gap light, the absorption strength of the Si−H stretching vibration varies with time following the modulated excitation. We call this phenomenon "modulated IR-absorption." Since a localized vibrational mode is not directly affected by the band-gap light, the observed change in the IR-absorption should be indirectly induced by a change in a structural configuration at the just surroundings of the Si−H bond. Therefore, the observation of the modulated IR-absorption can be utilized as a technique for detecting a microscopic structural change around the Si−H bond. Preliminary measurements were performed in a previous paper for examining the difference in the structural instability between the surroundings of the monhydride (Si−H) and dihydride (Si−H_2) bonds in undoped *a*-Si:H samples prepared at different substrate temperatures (T_S).[2] Even when the 2100-cm^{-1} component due to the Si−H_2 configuration was dominant in the normal IR-absorption spectrum for samples with lower T_S, the modulated IR-absorption spectrum was dominated by the 2000-cm^{-1} component due to the Si−H confuguration irrespective of T_S: indicating that the structural instability occurs more effectively in the neighborhood of the Si−H bond than in that of Si−H_2 bond. Furthermore, it was found that the undoped sample prepared at $T_S = 300\,°\mathrm{C}$ with a good quality exhibited the most intense modulated IR absorption. In conjunction with reported studies concerning the elastic properties and internal stress in a series of undoped *a*-Si:H samples with different network structures,[3–6] it has been inferred that the local strain, which is inherently held in a disordered network, is the most probable cause for the structural instability, or the modulated IR absorption.[2] Under modulated band-gap excitation, the observed change in the IR-absorption reflects a change in a charge distribution in the region under strain by modification of the local strain and by a corresponding change in the bonding configuration that is needed for establishment of a new force balance.

Following those results, the study is extended, in this paper, to *a*-Si:H based wide-gap alloys. Since a vibrational frequency of the Si−H stretching vibration in a wide-gap alloy varies with respect to the number of alloy atoms in the neighborhood of the Si−H bond, we can argue definitively as to how the structural instability around the Si−H bond is affected by the substitution of alloy atoms for some of the three nearest-neighbor Si atoms.

II. EXPERIMENT

Measurements were made on the *a*-Si:H-based wide-gap alloys *a*-SiN:H and *a*-SiO:H. Films of *a*-SiN:H and *a*

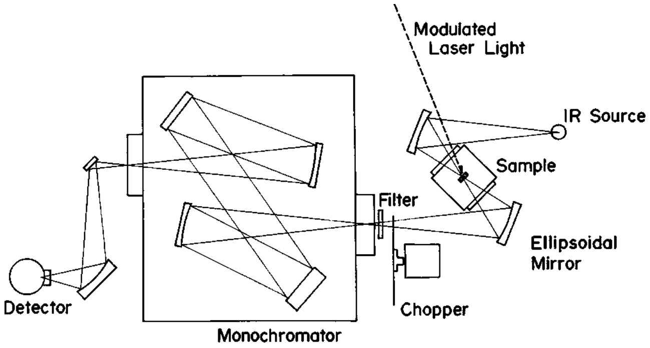

FIG. 1. Optical setup for the measurements of the modulated IR absorption.

-SiO:H, of various compositions, were prepared o intrinsic crystalline sililcon (*c*-Si) wafers by radio-frequency, glow-discharge decomposition of a gas mixture of SiH_4 and NH_3, and SiH_4 and O_2, respectively. The substrate temperature was held at 250 °C. The film thickness was about 7 μm. The alloy composition of each film was determined with x-ray photoelectron spectroscopy. The alloys are denoted as $a\text{-Si}_{1-y}X_y$:H (X=N or O), where the fractional values of y for the three *a*-SiN:H samples and the three *a*-SiO:H samples are given by 0.17, 0.25, 0.38, and 0.17, 0.49, 0.51, respectively.

An optical setup for the modulated IR-absorption measurement is shown in Fig. 1. While being maintained at 12 K within a cryostat, the sample was excited with a pump light modulated at 11 Hz. The change induced in the transmittance was monitored with a probe-light. The photon energy of the pump-light was adjusted to correspond approximately with the band-gap energy of the sample under consideration. Photodegradation of the sample, during pump-light illumination, was avoided by holding the intensity of the pump-light at a sufficiently low level such that the measurements could be made with a permissible signal-to-noise ratio. An IR probe-light was focused with an ellipsoidal mirror at the same area of the sample's surface as that illuminated by the pump-light. The transmitted probe-light was collimated in a liquid-nitrogen cooled Hg–Cd–Te detector after being dispersed with a monochromator. The 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 the photomodulation (PM) spectrum.

III. RESULTS

The PM spectrum is dominated by the optical transitions of photoexcited carriers between tail states adjacent to the valence- and conduction-band edges.[7] It is the photoinduced absorption (PA) spectrum that is normally observed. The modulated IR-absorption band of the Si–H stretching vibration is superimposed on the PA spectrum around 2000 cm^{-1} as a dip band. It is possible, in principle, to separate out a pure modulated IR-absorption band by subtracting a background PA spectrum from a measured PM spectrum. However, a PM spectrum for a thin film accompanies interference fringes, owing to the difference in the refractive index between a film sample and *c*-Si substrate. For alloy samples with large y values, the amplitude of the interference fringes becomes to be greatly pronounced. Furthermore, since a dispersion of the complex refractive index, $\tilde{n}$, accompanies a localized IR-absorption band, both amplitude and periodicity of the interference fringes are distorted in the spectral range where the Si–H stretching band is located. Thus, it is difficult, at first glance, to identify the presence of a modulated IR-absorption band in the PM spectrum for the alloy film. Therefore, an exact simulation of the distorted interference fringes in the background PA spectrum must be made in order to make accurate extraction of the modulated IR-absorption band.

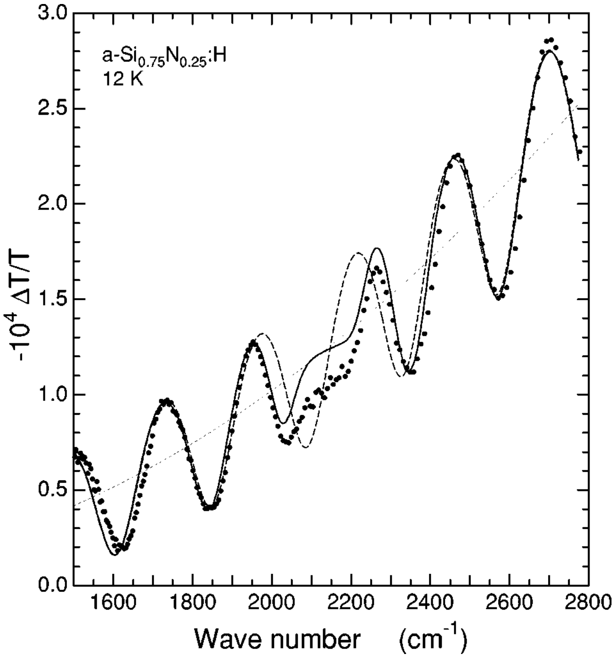

FIG. 2. The photomodulation spectrum for $a\text{-Si}_{0.75}N_{0.25}$:H. Dots denote data points. The exact simulation of the background PA spectrum, including the distorted interference fringes, is shown by the solid line. The broken line is the spectrum that is simulated with a sine wave of constant periodicity. The dotted line represents the real PA spectrum after washing out the interference fringes.

A practical procedure for simulating distorted interference fringes is explained in detail in a previous paper.[2] In the simulation, it requires spectral values for both the real and imaginary parts of $\tilde{n}$. A dispersion spectrum of the imaginary part of $\tilde{n}$ can be obtained experimentally as an absorption-coefficient spectrum of the Si–H stretching mode from the normal transmission measurement. On the other hand, a dispersion spectrum of the refractive index, n, can be evaluated with the absorption-coefficient spectrum by using the Kramers-Kronig relation, or, alternatively, by employing our experimental method[8] that is based on thermal radiation measurements.

When the spectral values of α and n are at hand, the simulation of the background PA spectrum including the interference fringes can be completed. As a typical example, the PM spectrum for the $a\text{-Si}_{0.75}N_{0.25}$:H sample is demonstrated in Fig. 2 by the dots. The solid line in the figure represents the PA spectrum that is exactly simulated by using the proposed procedure. It is clear from the figure that the periodicity of the exactly simulated interference fringes (solid line) increases in the region of interest as compared to the constant periodicity of the simple sine wave (broken line). Both distortions of the amplitude and periodicity of the interference fringes are reproduced well by the exact simulation. The remaining spectral difference between the measured and the exactly simulated spectra, as observed around $2000-2300\ \mathrm{cm}^{-1}$, comes from the modulated IR-absorption band of the Si–H stretching mode. The thick-solid line Fig. 3 depicts the extracted spectrum of the modulated IR-absorption band. When a PM spectrum is accompanied by intense interference fringes, as shown in Fig. 2, simulation of the interference fringes cannot be done perfectly. The incompleteness in the simulation of the distorted interference fringes is a cause of the unexpected large errors and incorrect structures in the resulting modulated IR-absorption spectrum. The apparently inaccurate parts of the extracted spectrum in Fig. 3 are represented by the thick-dotted line. In the same figure, the absorption-coefficient spectrum is also shown by the thick-dashed line for the sake of comparison. The spectral shape of the modulated IR-absorption band is different from that of the absorption-coefficient spectrum: the peak position of the modulated IR-absorption spectrum is shifted towards a lower frequency as compared to that of the absorption-coefficient spectrum.

The modulated IR-absorption spectra for other samples are also evaluated with the same procedure. Figures 4 and 5 show the results for the $a\text{-Si}_{0.83}\text{N}_{0.17}\text{:H}$ sample with the lowest N content and for the $a\text{-Si}_{0.83}\text{O}_{0.17}\text{:H}$ sample with the lowest O content, respectively. Comparing with the corresponding absorption-coefficient spectrum included in each figure, it is observed a slight shift of the modulated IR-absorption spectrum toward a low frequency. The modulated IR-absorption spectrum as well as the absorption-coefficient spectrum for the $a\text{-Si}_{0.49}\text{O}_{0.51}\text{:H}$ sample with the highest O content is shown in Fig. 6. In this case, although the absorption-coefficient spectrum is distinctively peaked at about $2260\ \mathrm{cm}^{-1}$, the modulated IR-absorption spectrum exhibits a very different spectral shape. Surprisingly, the modulated IR-absorption band appears only at the low-frequency region around $2050\ \mathrm{cm}^{-1}$, and is almost absent at the range where the absorption-coefficient spectrum shows a maximum.

The remaining samples of $a\text{-Si}_{0.62}\text{N}_{0.38}\text{:H}$ and $a\text{-Si}_{0.51}\text{O}_{0.49}\text{:H}$ exhibit almost the same modulated IR-absorption spectra as the $a\text{-Si}_{0.75}\text{N}_{0.25}\text{:H}$ and $a\text{-Si}_{0.49}\text{O}_{0.51}\text{:H}$ samples, respectively.

IV. DISCUSSION

It has been known well that an absorption-coefficient spectrum of the Si–H stretching vibration in a-SiN:H and a-SiO:H alloys can be separated into four absorption components.[9–13] Each component is characterized with a distinct peak frequency, and is associated with a $\text{HSi}-\text{Si}_{3-m}X_m$ unit ($X=N$ or O) with a specific value of $m(m=0-3)$. The peak frequency shifts to higher values as the value of m increases. Those four absorption components can be simulated with Gaussian curves with different central frequencies as shown in Figs. 3–6 by the thin-dashed lines. As observed in each figure, there exists a spectral difference between the absorption coefficient and modulated IR-absorption band,

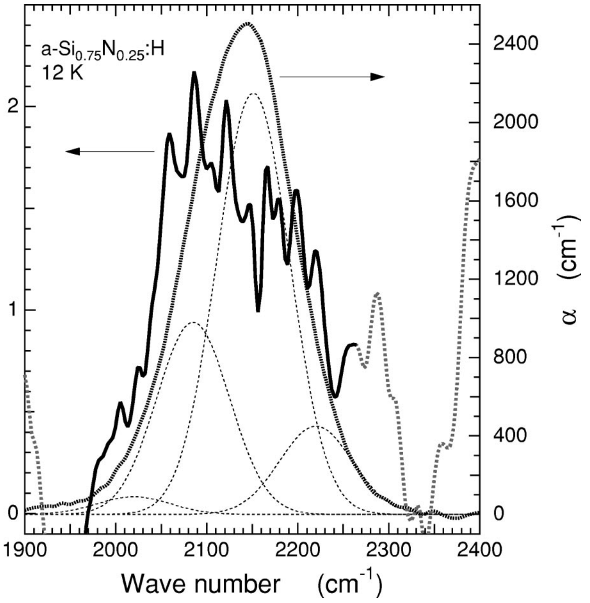

FIG. 3. The thick-solid line shows the modulated IR-absorption spectrum of the Si–H stretching mode in $a\text{-Si}_{0.75}\text{N}_{0.25}\text{:H}$. The corresponding absorption-coefficient spectrum and its individual components, each of which is associated with a $\text{HSi}-\text{Si}_{3-m}\text{N}_m$ unit with a specific value of $m(m=0-3)$, are also shown by the thick- and thin-dashed lines, respectively.

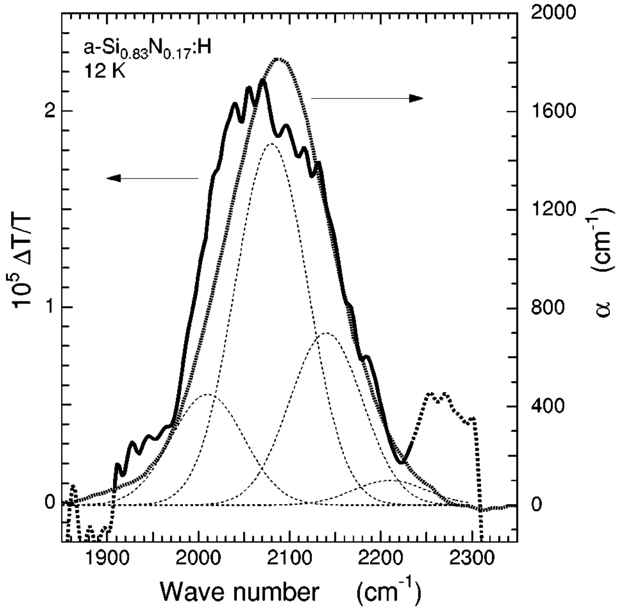

FIG. 4. The thick-solid line shows the modulated IR-absorption spectrum of the Si–H stretching mode in $a\text{-Si}_{0.83}\text{N}_{0.17}\text{:H}$. The corresponding absorption-coefficient spectrum and its individual components, each of which is associated with a $\text{HSi}-\text{Si}_{3-m}\text{N}_m$ unit with a specific value of $m(m=0-3)$, are shown by the thick- and thin-dashed lines, respectively.

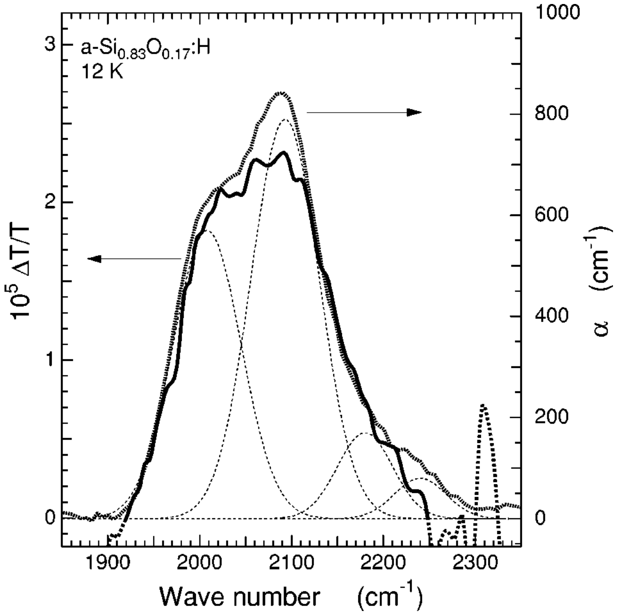

FIG. 5. The thick-solid line shows the modulated IR-absorption spectrum of the Si–H stretching mode in a-Si$_{0.83}$O$_{0.17}$:H. The corresponding absorption-coefficient spectrum and its individual components, each of which is associated with a HSi–Si$_{3-m}$O$_m$ unit with a specific value of $m(m=0-3)$, are shown by the thick- and thin-dashed lines, respectively.

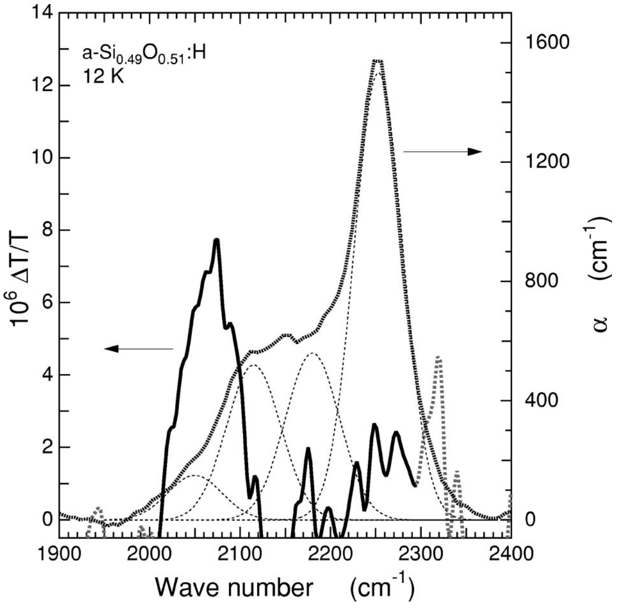

FIG. 6. The thick-solid line shows the modulated IR-absorption spectrum of the Si–H stretching mode in a-Si$_{0.49}$O$_{0.51}$:H. The corresponding absorption-cofficient spectrum and its individual components, each of which is associated with a HSi–Si$_{3-m}$O$_m$ unit with a specific value of $m(m=0-3)$, are shown by the thick- and thin-dashed lines, respectively.

saying that the relative contribution of each absorption component in the modulated IR-absorption spectrum is different from that in the absorption-coefficient spectrum. Contribution of the absorption components with lower peak frequencies is more enhanced in the modulated IR-absorption spectrum. The most extreme case is the a-Si$_{0.49}$O$_{0.51}$:H sample as demonstrated in Fig. 6. The absorption component associated with the HSi–O$_3$ unit is absent from the modulated IR-absorption spectrum, even though that component dominates the absorption-coefficient spectrum.

Looking over the results of both types of wide-gap alloys, it is roughly said that the modulated IR-absorption spectra are dominated by the absorption components associated especially with the $m=0$ and $m=1$ units of HSi–Si$_{3-m}X_m$. As the number of alloy atoms in the neighborhood of the Si–H bond increases, the contribution of the corresponding absorption components to the modulated IR-absorption spectrum decreases. In other words, the structural instability around the Si–H bond in the wide-gap alloys is greatly affected by the replacement of the nearest-neighbor Si, i.e, those adjacent to the Si–H bond, with alloy atoms of lower coordination number, such as N or O atoms.

As pointed out previously,[2] the most intense modulated IR-absorption band can be observed in the undoped a-Si:H with a good quality. Since such good-quality undoped a-Si:H has been evidenced to have an ideally homogeneous, continuous-random-network structure,[3] we have inferred that the local strain is the essential factor for producing the structural instability, or the modulated IR absorption.[2] In contrast with such a network nature of the good-quality undoped a-Si:H, the substitution of N or O atoms for some of the three nearest-neighbor Si atoms will produce a structurally flexible bonding configuration at the boundary between the HSi–Si$_{3-m}X_m$ unit and its surrounding network. Hence, it can be considered that the HSi–Si$_{3-m}X_m$ unit with $m>1$ will not be capable of sustaining a local strain in its immediate neighborhood.

However, this effect alone is not a sufficient explanation of the characteristic nature of the structural instability in the wide-gap alloys. In addition to the difference in the structural configuration just around the Si–H bond, a change in the network structure itself, far from the Si–H bond, seems to have a non-negligible effect on the structural instability.

In order to make a quantitative comparison of this additional effect among the samples, a new quantity called R_{mod} is introduced. It is defined as the ratio between the magnitude of the modulated IR-absorption and the combined intensities of the two components in the absorption-coefficient spectrum, which are associated with the $m=0$ and $m=1$ units of HSi–Si$_{3-m}X_m$. However, prior to evaluating R_{mod}, it is necessary to correct the observed magnitude of the modulated IR-absorption band, since the intensity of the pump-light was not the same in the measurements for all samples. This correction can be carried out by using the observed dependence of $\Delta\alpha$ on G, i.e., $\Delta\alpha \propto G^{0.9}$, where G is the pump-light intensity, and $\Delta\alpha$ is the magnitude of the modulated IR-absorption, defined as $\Delta\alpha=-(1/d)(\Delta T/T)$, where d is the film thickness. The values of $\Delta\alpha$ estimated at $G=0.1$ mW are chosen here for the evaluation of R_{mod}.

R_{mod} for all alloy samples is displayed in Fig. 7, as a function of the alloy composition, y. For several of the alloy samples, two specimens of a given sample were measured in order to see how completely the interference-fringe effect could be removed in the simulation. Figure 7 also includes

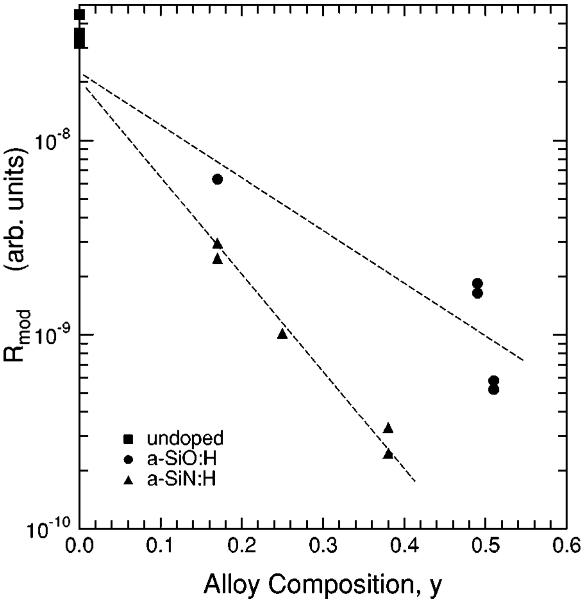

FIG. 7. R_{mod} for all wide-gap alloys, including undoped *a*-Si:H with $T_S=300\,°\mathrm{C}$, is plotted as a function of the alloy composition, y. R_{mod} is defined as the ratio between the corrected magnitude of the modulated IR-absorption ($\Delta\alpha$), and the combined intensities of the absorption components that are associated with the $\mathrm{HSi{-}Si}_{3-m}X_m$ units with $m=0$ and 1 in the absorption-coefficient spectrum. Since the intensity (G) of the pump-light was not the same in the measurements for all samples, the values of $\Delta\alpha$, which are estimated at $G=0.1$ mW by using the observed dependence of $\Delta\alpha$ on $G(\Delta\alpha\propto G^{0.9})$, are used for the evaluation of R_{mod}.

the R_{mod} for three undoped samples at $y=0$, which were prepared independently at $T_S=300\,°\mathrm{C}$. With reference to Fig. 7, we note that the lifetime of the photogenerated carriers has the same value of 1 ms at 12 K for all samples, a fact that was confirmed by the measurements of a lifetime distribution of photoluminescence.[14,15] Thus, the comparison made in Fig. 7 is subject to the condition that the same amount of excess carries is induced in all samples.

It is apparent from Fig. 7 that R_{mod} decreases with increasing alloy composition. This trend indicates that, even at the surroundings of the same $\mathrm{HSi{-}Si}_{3-m}X_m$ unit with $m=0$ or 1, some degree of the structural instability is reduced as the content of the N or O atoms increases in the network structure. In other words, a change in the nature of the network structure from being rigid to being loose, even in a region far from the Si–H bond, could affect the structural instability that takes place in the immediate surroundings of the Si–H bond. Here, it must be noted that dangling bonds, a density of which increases with the alloy composition,[16,17] may also affect the network rigidity. The dangling bonds work to disconnect a network structure, so that the requirement of holding the local strain within a disordered network will be relaxed with increasing alloy-composition. Those findings in the wide-gap alloys give further support to the speculation made in a previous paper,[2] namely, that the strength of the modulated IR-absorption is closely dependent on the rigidity of the network structure.

Furthermore, it is evident in Fig. 7 that R_{mod} for the *a*-SiN:H alloys decreases more rapidly with y than that for the *a*-SiO:H alloys. As a result, the value of R_{mod} for the *a*-SiO:H alloys is much larger than that for the *a*-SiN:H alloys for a same value of y. Such a difference in the y-dependence of R_{mod} between the two alloys seems strange at first sight, since the network containing N atoms can be thought to be more rigid than that containing O atoms, on account of the difference in the coordination number between N and O atoms. However, this difficulty can be removed by remembering that the N–H bonds are known to exist in the network of the *a*-SiN:H alloys in an amount that rapidly increases with increasing the N content.[18] In addition, it has been found that the internal stress in the *a*-SiN:H alloy is gradually reduced by increasing the N–H content in the Si-rich region.[19] As a result, the network rigidity, or the structural instability, around the Si–H bond can be more easily reduced in the *a*-SiN:H alloys than in the *a*-SiO:H alloys.

V. CONCLUSION

Structural instability in the *a*-SiN:H and *a*-SiO:H alloys is examined for the purpose of disclosing how the structural instability is affected by a change in the structural configuration at the local surroundings of the Si–H bonds due to the neighboring of alloy atoms. From measurements of the modulated IR-absorption in wide-gap alloys, with various alloy compositions, it is found that magnitude of the modulated IR-absorption band is reduced as the content of N or O is increased. On the basis of an examination of the contributions made by the individual absorption components to the modulated IR-absorption spectrum, it is inferred that the modulated IR-absorption takes place preferentially in the neighborhood of the $m=0$ and $m=1$ units of $\mathrm{HSi{-}Si}_{3-m}X_m$. In other words, a more effective structural instability occurs at the specific site where the Si–H bond is surrounded by two or three nearest-neighbor Si atoms.

As inferred previously,[2] the local strain held around the Si–H bond is the most probable cause for the structural instability. In this way, it can be understood that N or O atoms in the neighborhood of the Si–H bond, as well as their inclusion in the Si-network, tends to weaken the local strain around the Si–H bond, mainly because of the lower coordination number of the N, or O atoms.

ACKNOWLEDGMENTS

The author would like to express his gratitude to C. Ogihara of Yamaguchi University, S. Hasegawa and M. Futatsudera of Kanazawa University, and to M. Kumeda of Kanazawa University for kindly preparing the *a*-SiN:H alloys and the *a*-SiO:H alloys, respectively.

[1] D. L. Staebler and C. Wronski, Appl. Phys. Lett. **31**, 292 (1977).
[2] H. Oheda, Phys. Rev. B **68**, 085206 (2003).
[3] E. Spanakis, E. Stratakis, and P. Tzanetakis, J. Appl. Phys. **89**, 4294 (2001).
[4] S. Nonomura, N. Toshida, T. Gotoh, T. Sakamoto, M. Kondo, A. Matsuda, and S. Nitta, J. Non-Cryst. Solids **266-269**, 474 (2000).
[5] E. Stratakis, E. Spanakis, P. Tzanetakis, H. Fritzsche, S. Guha, and J. Yang, Appl. Phys. Lett. **80**, 1734 (2002).
[6] H. Hishikawa, J. Appl. Phys. **62**, 3150 (1987).
[7] H. A. Stoddart, Z. Vardeny, and J. Tauc, Phys. Rev. B **38**, 1362 (1988).
[8] H. Oheda, J. Appl. Phys. **92**, 195 (2002).
[9] G. Lucovsky, Solid State Commun. **29**, 571 (1979).
[10] E. Bustarret, M. Bensouda, M. C. Habrard, J. C. Bruyere, S. Poulin, and S. C. Gujrathi, Phys. Rev. B **38**, 8171 (1988).
[11] G. N. Parsons and G. Lucovsky, Phys. Rev. B **41**, 1664 (1990).
[12] D. V. Tsu, G. Lucovsky, and B. N. Davidson, Phys. Rev. B **40**, 1795 (1989).
[13] L. He, Y. Kurata, T. Inokuma, and S. Hasegawa, Appl. Phys. Lett. **63**, 162 (1993).
[14] H. Oheda, Phys. Rev. B **52**, 16 530 (1995).
[15] H. Oheda, J. Non-Cryst. Solids **198-200**, 284 (1996).
[16] A. Morimoto, H. Noriyama, and T. Shimizu, Jpn. J. Appl. Phys., Part 1 **26**, 22 (1987).
[17] S. Hasegawa, M. Matsuda, and Y. Kurata, Appl. Phys. Lett. **58**, 741 (1991).
[18] S. Hasegawa, M. Matsuda, and Y. Kurata, Appl. Phys. Lett. **57**, 2211 (1990).
[19] S. Hasegawa, Y. Amano, T. Inokuma, and Y. Kurata, J. Appl. Phys. **72**, 5676 (1992).