Evolution of microstructures in hydrogenated silicon films prepared by diluted hydrogen and hydrogen atom treatment methods

KuoChiang Hsu, Hua Chang, and HueyLiang Hwang

Citation: J. Appl. Phys. 73, 4841 (1993); doi: 10.1063/1.353799

View online: http://dx.doi.org/10.1063/1.353799

View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v73/i10

Published by the American Institute of Physics.

Related Articles

Facile creation of bio-inspired superhydrophobic Ce-based metallic glass surfaces

How does spallation microdamage nucleate in bulk amorphous alloys under shock loading?
J. Appl. Phys. 110, 103519 (2011)

Unexpected short- and medium-range atomic structure of sputtered amorphous silicon upon thermal annealing
J. Appl. Phys. 110, 096104 (2011)

Enhanced amorphous stability of carbon-doped Ge2Sb2Te5: Ab Initio investigation

Structural study on amorphous and crystalline state of phase change material
J. Appl. Phys. 110, 083711 (2011)

Additional information on J. Appl. Phys.

Journal Homepage: http://jap.aip.org/

Journal Information: http://jap.aip.org/about/about_the_journal

Top downloads: http://jap.aip.org/features/most_downloaded

Information for Authors: http://jap.aip.org/authors

ADVERTISEMENT
Evolution of microstructures in hydrogenated silicon films prepared by diluted-hydrogen and hydrogen-atom-treatment methods

Kuo-Chiang Hsu, Hua Chang, and Huey-Liang Hwang

Department of Electrical Engineering, National Tsing Hua University, Hsin-Chu, Taiwan 30043, Republic of China.

(Received 19 October 1992; accepted for publication 29 January 1993)

Nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy, and Raman studies on microstructures of hydrogenated silicon films that were fabricated by diluted-hydrogen and hydrogen-atom-treatment methods are presented. The diluted-hydrogen samples tend to show a very sharp line shape in the NMR spectra at substrate temperatures higher than 300 °C, and the addition of atomic hydrogen treatment can produce the same NMR spectra at a lower temperature of about 250 °C. The Raman scattering spectra show that the atomic hydrogen treatment creates the microcrystalline phase while the diluted-hydrogen method produces amorphous phase plus a small quantity of microcrystalline phase. The infrared-absorption spectra also indicate an increase of SiH₂ bonding configuration and a hydrogen content reduction when atomic hydrogen treatment is employed. The relation between the origin of the sharp line shape in the NMR spectra and the formation of the microcrystalline phase is also discussed. Together with increase of dark conductivity and reduction of the photo-to-dark conductivity ratio, these samples indicate that with appropriate hydrogen incorporation during deposition, and with plasma hydrogen treatment, these films should possess a much more compact structure. These results suggest that the degree of crystallinity of hydrogenated silicon films can be systematically adjusted. A qualitative model based on our experimental data is presented to illustrate the formation procedures of microcrystalline-phase hydrogenated silicon under the influence of plasma hydrogen and hydrogen dilution.

I. INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) films are indispensable for many large area devices such as solar cells, contact image sensors, and thin-film transistors. The factors limiting their applications are the low electron mobilities and light-induced degradation of electrical conductivity of a-Si:II, which are generally related to the intrinsic network structure. In our early work, we reported that the Si—H bonding structure and the size of the micropores created during deposition are responsible for instability and other problems of the a-Si:H materials.

It is also known that hydrogen incorporation during deposition plays an important role in determining the structures of the Si—H bonding. Recently, we found that amorphous-microcrystalline mixed-phase hydrogenated silicon films can be deposited at a substrate temperature of T<sub>s</sub> < 300 °C by controlling the H<sub>2</sub>/SiH<sub>4</sub> gas mixture and the rf power, or by using alternative atomic hydrogen chemical annealing during each thin layer growth. It is desirable to explore in depth the nature of the microstructures when films are prepared under different hydrogen incorporation mechanisms. In this article we report the microstructures of hydrogenated silicon associated with hydrogen incorporation using several novel fabrication methods, including the diluted-hydrogen method and the hydrogen-atom-treatment method. Fourier transform nuclear magnetic resonance (FT NMR) and Fourier transform infrared spectroscopy (FTIR) were employed to analyze the silicon-hydrogen bonding configurations, and Raman scattering spectroscopy was used to identify the Si—Si bonding structures. These results were correlated with the studies of optical band gap and electrical conductivity for the above hydrogenated silicon samples.

II. EXPERIMENT

The diluted-hydrogen method employed rf glow discharge with a SiH<sub>4</sub>/H<sub>2</sub> ratio between 2/1 and 1/20 at substrate temperatures between 150 and 400 °C. The operating pressure was set between 0.5 and 1.1 Torr, and the rf power density was varied from 0.05 to 0.1 W/cm<sup>2</sup>. The hydrogen-atom-treatment method involves alternately exposing the growing film surface to hydrogen atoms which are generated by a rf plasma in the same deposition chamber. The typical growth time was 5–15 s with the same growth conditions as the diluted-hydrogen method, and the hydrogen treatment time was 30–180 s. The cycle was repeated 500–2000 times to deposit a film thick enough for the NMR measurements. The hydrogenated silicon samples were deposited on aluminum foils; these foils were etched away with dilute HCl solution and the powders were collected for the NMR measurements. A typical sample weighed about 0.1–0.2 g. The 1H NMR spectra of hydrogenated silicon films were measured with a Bruker MSL-200 FT NMR at a Larmor frequency of 200.13 MHz, and the Fourier transform of the free induction decay (FID) was obtained after a 90° pulse. The line shapes of the NMR spectra were deconvoluted to determine the configurations.
of the isolated Si—H bonding structures. Hydrogen con-
tents were determined from integration of the IR-
absorption coefficients of the SiH wagging mode around
640 cm⁻¹ with an integration constant of 1.6×10¹⁹
cm⁻². The silicon-hydrogen bonding structure of these
hydrogenated silicon samples was also checked by IR-
absorption spectroscopy in the range of 2000–2100 cm⁻¹
where the SiH and SiH₂ stretching modes were examined;
from the results of spectroscopy, the line shapes of the
FTIR spectra were also deconvoluted to determine the
SiH/SiH₂ concentration ratio.

The Raman spectra were obtained from the right-
angle-scattered light with an excitation of a 150 mW, 488
nm argon-ion laser. The optical band gaps were deter-
mixed from the Tauc’s plot using UV-VIS absorption spec-
trophotometry. The dark and photoconductivity were de-
termined from the silver coplaner electrode structure using
a HP4140B at a bias voltage of 50 V.

III. RESULTS AND DISCUSSION

The ¹H NMR spectra of several hydrogenated silicon
films deposited using different methods are shown in Fig. 1.
The deposition methods and conditions, the NMR data,
including the full width at half-maximum (FWHM), and
the relative intensity for the sharp, narrow, and broad line
shape spectra, are summarized in Table I. In Fig. 1 (a) we
show the NMR spectrum for a sample grown by the con-
ventional method, under typical growth conditions, at a
substrate temperature of $T_s=250 \,^oC$. The spectrum is sim-
ilar to the previously published data, in which a narrow
Lorentzian-shaped spectrum with FWHM of about 3.4
kHz and a broad Gaussian-shaped spectrum with FWHM
of about 23.5 kHz are superimposed. The narrow line
shape corresponds to the randomly distributed Si-H struc-
ture in the amorphous silicon network, and the broad spec-
trum corresponds to the region associated with clustered
hydrogen which may contain internal surface, poly-
hydride groups, and poly-silane chains. In Fig. 1 (b), the
line shape of the high-temperature sample, also grown by
the conventional method and deposited at $T_s=400 \,^oC$,
becomes narrower both in the narrow- and broad-shaped
spectra. These results are quite consistent with those of the
annealing experiment for a-Si:H films annealed at about
400 °C (Ref. 16), in which it was found that the amount of
hydrogen contained in the a-Si:H sample decreased and the
hydrogen-hydrogen separation increased. The NMR spec-
tra of the samples grown by the diluted-hydrogen method,

| Table I. Summary of the deposition conditions and the NMR results for the hydrogenated silicon samples. Conv.: conventional method; Dilu.: diluted-hydrogen method; H.tr.: hydrogen-atom-treatment method, deposition time= 10 s, H.tr. time=50 s; $T_s$: substrate temperature; $rf$: rf power; $Pr.$: deposition vacuum pressure. |
|---|---|---|---|---|---|---|
| Method | $T_s$ (°C) | SiH₄/H₂ | $rf$ (W/cm²) | $Pr.$ (Torr) | FWHM (kHz) | Relative intensity (%) |
| | | | | | sharp | narrow | broad | sharp | narrow | broad |
| Conv. | 250 | 3/2 | 0.05 | 0.5 | ... | 3.4 | 23.5 | 0 | 97 | 3 |
| Conv. | 400 | 3/2 | 0.05 | 0.5 | ... | 3.4 | 23.5 | 0 | 98 | 2 |
| Dilu. | 250 | 1/10 | 0.1 | 1.1 | 0.765 | 3.4 | 23.5 | 100 | 0 | 0 |
| Dilu. | 300 | 1/10 | 0.1 | 1.1 | 0.399 | ... | ... | 100 | 0 | 0 |
| Dilu. | 350 | 1/10 | 0.1 | 1.1 | 0.397 | ... | ... | 100 | 0 | 0 |
| Dilu. | 400 | 1/10 | 0.1 | 1.1 | 0.398 | ... | ... | 100 | 0 | 0 |
| H.tr. | 250 | 1/10 | 0.1 | 1.1 | 0.394 | ... | ... | 100 | 0 | 0 |
| H.tr. | 400 | 1/10 | 0.1 | 1.1 | 0.500 | ... | ... | 100 | 0 | 0 |
with a gas ratio of SiH$_4$/H$_2$ = 1/10, are shown in Figs. 1(c) and 1(d). The diluted-hydrogen sample, with a substrate temperature $T_s$ = 250 °C is shown in Fig. 1(c). It shows that a sharp line-shaped spectrum with FWHM $\approx$ 0.77 kHz is inserted onto a narrow Lorentzian-shaped spectrum with FWHM $\approx$ 3.4 kHz and onto a broad Gaussian-shaped spectrum with FWHM $\approx$ 23.5 kHz. The latter two spectra are almost the same as the conventional ones except that the relative intensity of the narrow line shape is smaller. This result indicates that the diluted-hydrogen method adds an extra sharp line shape to the conventional NMR spectra. As the temperature is elevated, the narrow Lorentzian line shape and broad Gaussian line shape disappear and the sharp line shape in the NMR spectra tends to dominate. The NMR spectra of samples with substrate temperatures $T_s$ > 300 °C exhibit a very sharp line shape spectrum with neither apparent narrow Lorentzian nor broad Gaussian line shapes. Figure 1(d) shows an example for the high-temperature diluted sample with $T_s$ = 400 °C. These sharp line shape spectra can also be analyzed to be Lorentzian line shape with a FWHM of about 0.389–0.399 kHz. The above results indicate that the diluted-hydrogen growth method tends to create Si—H bonding structure having a sharp line shape spectrum at elevated substrate temperatures.

Figure 1(e) shows the NMR spectrum of the hydrogen-atom treated sample, deposited at $T_s$ = 250 °C. It exhibits a line shape similar to that of the diluted-hydrogen sample deposited at $T_s$ > 300 °C, but quite different from that of the 250 °C diluted-hydrogen sample. This indicates that the atomic hydrogen treatment in between each alternative deposition did affect the Si—H structure on the growing surface of the film even at a substrate temperature as low as 250 °C.

The hydrogen content of the hydrogenated silicon samples, determined from the integrated IR absorption, shows that the hydrogen content of our diluted-hydrogen sample deposited at a substrate temperature of $T_s$ = 250 °C is about 16.3% (atomic percent) which is very close to that of the conventional samples deposited at $T_s$ = 250 °C (15.5%); but, when the substrate temperature was increased to $T_s$ = 400 °C, the hydrogen content decreased to 9.3%. The hydrogen-atom-treated sample, deposited at $T_s$ = 250 °C, also shows a hydrogen content of about 9.5% as does the high-temperature diluted-hydrogen sample. The hydrogen content in the samples which show a sharp NMR linewidth does not agree with those reported for the dipolar interaction, for which its FWHM of Lorentzian line shape is proportional to the hydrogen content. This suggests that some other mechanisms might exist.

FTIR-absorption coefficients for the conventional, diluted-hydrogen and hydrogen-atom-treated samples are shown in Fig. 2. The absorption spectra are deconvoluted into two Gaussian line shapes centered at the SiH and SiH$_2$ stretching frequency of 2000 and 2090 cm$^{-1}$, respectively, and the SiH/SiH$_2$ concentration ratio is determined from the integration of these Gaussian line shapes. It is found that the ratio of SiH/SiH$_2$ is about 13 for the conventional samples deposited at $T_s$ = 250 °C, and the ratio of SiH/

SiH$_2$ decreases to 10 and 5 for the diluted-hydrogen samples deposited at $T_s$ = 250 and 400 °C, respectively. These results show that an appreciable amount of SiH was present in all the diluted hydrogen samples despite their differences in the NMR spectra; but, the IR absorption spectra of the hydrogen-atom-treated sample, deposited at $T_s$ = 250 °C, exhibits a drastic reduction of SiH, with a SiH/SiH$_2$ ratio of about 0.85, which indicates the existence of microcrystalline phase in the hydrogenated silicon samples.

The Raman spectra of the conventional samples are shown in Fig. 3. In Fig. 3(a) the Raman spectra of the sample deposited at $T_s$ = 250 °C shows a broad band with FWHM of 60 cm$^{-1}$ and a peak centered at 475 cm$^{-1}$ while the sample deposited at $T_s$ = 400 °C shows a broad band with the same FWHM and a peak shift to about 480 cm$^{-1}$ [Fig. 3(b)]. Figures 4(a), 4(b), and 4(c) show the Raman spectra of the diluted-hydrogen samples with $T_s$ = 300, 350, and 400 °C, respectively; these three spectra are all broad band with FWHM of 60 cm$^{-1}$ and peak centered at 480 cm$^{-1}$, but a small band with peak centered at around 520 cm$^{-1}$ is growing up as the temperature is elevated and it reaches a maximum when $T_s$ = 400 °C. This result indicates that a mixed structure exists in which a small quantity of the microcrystalline phase is produced in the diluted-hydrogen samples, and the volume fraction of the microcrystalline phase is increased as the substrate temperature is increased.

Figures 5(a) and 5(b) show the Raman spectra of the hydrogen-atom-treated samples with $T_s$ = 250 and 400 °C, respectively, which are relatively sharp bands with FWHM of 15 cm$^{-1}$ and peak at 520 cm$^{-1}$. This indicates that a large volume fraction of microcrystalline phase is created, which becomes dominant in the Raman spectra for sami
The Raman scattering spectra of hydrogenated silicon samples deposited by the conventional method at (a) $T_s = 250^\circ C$ and (b) $T_s = 400^\circ C$.

The Raman results verify that the microcrystalline-phase formation is strongly enhanced by the atomic-hydrogen-treatment on the growing surface of the film in between each alternative deposition at a substrate temperature even as low as $250^\circ C$. At this temperature, the microcrystalline-phase formation by the diluted-hydrogen method with the $\text{SiH}_4/\text{H}_2 = 1/10$ gas ratio at $T_s > 300^\circ C$ is still low, although the NMR spectra from both methods show almost the same line shape.

In Table II we summarize the Raman peak and its FWHM, $\text{SiH}/\text{SiH}_2$ ratio, hydrogen content, optical band gap, and the conductivities of the hydrogenated silicon samples deposited by different methods and conditions. The optical band gap of the sample grown by the conventional method with $T_s = 250^\circ C$ is 1.69 eV, the dark conductivity is $1 \times 10^{-10}$ S/cm, and the photo-to-dark conductivity ratio is $1.5 \times 10^3$. The optical band gap of the sample grown by the conventional method with $T_s = 400^\circ C$ is a bit narrower, at 1.62 eV, the dark conductivity is larger, $2 \times 10^{-9}$ S/cm, and the photo-to-dark conductivity ratio is only $2 \times 10^1$. The optical band gap of the diluted-hydrogen sample with $T_s = 300^\circ C$ is even narrower, 1.59 eV, and it shows a dark conductivity of $5 \times 10^{-9}$ S/cm with a photo-to-dark conductivity ratio of $5 \times 10^0$. When the substrate temperature is raised to $T_s = 400^\circ C$, the optical band gap of the diluted-hydrogen sample is only 1.48 eV, the dark conductivity is greater, up to $1 \times 10^{-7}$ S/cm, and it shows a unity photo-to-dark conductivity ratio.

The optical band gap of the hydrogen-atom-treated sample with substrate temperature of $T_s = 250^\circ C$ is 1.56 eV, and the dark conductivity is $2 \times 10^{-8}$ S/cm with a unity photo-to-dark conductivity ratio. When the substrate...
TABLE II. Summary of the Raman data, SiH/SiH₂ ratio, hydrogen content, optical band gap and conductivities of the hydrogenated silicon samples. Conv.: conventional method; Dilu.: diluted-hydrogen method; H.tr.: hydrogen-atom-treatment method, deposition time = 10 s, H.tr. time = 50 s; Tₛ: substrate temperature.

<table>
<thead>
<tr>
<th>Sample Method</th>
<th>Tₛ °C</th>
<th>Peak (cm⁻¹)</th>
<th>FWHM (cm⁻¹)</th>
<th>SiH/SiH₂ ratio</th>
<th>H content (at. %)</th>
<th>Optical band gap (eV)</th>
<th>Dark conductivity (S/cm)</th>
<th>Photo-to-dark conductivity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conv.</td>
<td>250</td>
<td>475</td>
<td>60</td>
<td>13</td>
<td>15.5</td>
<td>1.69</td>
<td>1.0×10⁻¹⁰</td>
<td>1.5×10⁴</td>
</tr>
<tr>
<td>Conv.</td>
<td>400</td>
<td>480</td>
<td>60</td>
<td>...</td>
<td>...</td>
<td>1.62</td>
<td>2.0×10⁻⁹</td>
<td>2.0×10¹</td>
</tr>
<tr>
<td>Dilu.</td>
<td>250</td>
<td>...</td>
<td>...</td>
<td>10</td>
<td>16.3</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Dilu.</td>
<td>300</td>
<td>480</td>
<td>60</td>
<td>...</td>
<td>10.3</td>
<td>1.59</td>
<td>5.0×10⁻⁹</td>
<td>5.0×10⁶</td>
</tr>
<tr>
<td>Dilu.</td>
<td>400</td>
<td>480</td>
<td>60</td>
<td>3</td>
<td>9.3</td>
<td>1.48</td>
<td>1.0×10⁻⁷</td>
<td>1.0×10⁶</td>
</tr>
<tr>
<td>H.tr.</td>
<td>250</td>
<td>520</td>
<td>15</td>
<td>0.85</td>
<td>9.5</td>
<td>1.56</td>
<td>2.0×10⁻⁸</td>
<td>1.0×10⁶</td>
</tr>
<tr>
<td>H.tr.</td>
<td>400</td>
<td>520</td>
<td>15</td>
<td>...</td>
<td>8.4</td>
<td>1.44</td>
<td>1.0×10⁻⁷</td>
<td>1.0×10⁶</td>
</tr>
</tbody>
</table>

The temperature is increased to Tₛ = 400 °C and it shows an optical band gap of 1.44 eV and the dark conductivity increases to 1×10⁻⁷ S/cm with a unity photo-to-dark conductivity ratio. It is noted that the room-temperature band gap of crystalline silicon is 1.1 eV, and the optical band gap of hydrogenated silicon films can be systematically changed as depicted in Table II.

The relation between the optical band gap and the hydrogen content of hydrogenated silicon films fabricated by different methods and conditions was found to follow the following relationship: The optical band gap decreases as the hydrogen density per unit length decreased.

It is interesting to explore the relationship between the origin of the sharp line shape in the NMR spectra and the formation of the microcrystalline phase. The narrowing phenomena of the line shape was also reported in the spectra of both the μc-Si:H (Refs. 9, 20, and 21) and high-rf-power-prepared α-Si:II samples which showed a sharp line shape with FWHM of about 0.5 kHz and a broad line shape with FWHM of about 25 kHz. However, our diluted-hydrogen samples deposited at Tₛ > 300 °C presented an even sharper line-shape spectrum of about 0.4 kHz as compared to the μc-Si:H results in the 90 MHz Larmor frequency NMR measurement. The sharp line shape in the μc-Si:II samples was designated to come from the moving hydrogen in SiH₂ chain or molecular hydrogen (H₂) in a motional narrowing state.

In our experiments, the sharp line shape in the NMR spectra appears in the diluted-hydrogen samples with a gas ratio of SiH₄/H₂ = 1/10, at a substrate temperature of 250 °C; however, narrow and broad line shapes also appear as in conventional samples. Comparing the hydrogen content and the SiH/SiH₂ concentration ratio between those two categories of samples, it is noted that the sharp line shape could be associated with the transition of Si-H bonding since the hydrogen content in the films indicated from the infrared measurement are nearly unchanged as the SiH/SiH₂ concentration ratio is decreased. The existence of a large amount of molecular hydrogen is also a possible origin for the sharp line-shape formation, which cannot be detected in the infrared-absorption spectrum. Then, as the substrate temperature is elevated beyond 300 °C, the sharp line shape dominates and the narrow and broad line shapes disappear. In this case the hydrogen content decreases, which indicates that some components of the SiH/SiH₂ bonding structures are missing or some of their formations might be changed into molecular hydrogen such that only the components contributing to the sharp line shape are left behind. However, from the IR-absorption spectra as shown in Fig. 2, though the SiH/SiH₂ ratio is further decreased, there still exists an appreciable amount of SiH bonding structure in the high-temperature diluted-hydrogen samples. Even in the microcrystalline phase, the SiH/SiH₂ concentration ratio of hydrogenated silicon samples prepared by the hydrogen-atom-treatment method is less than unity, which indicates that when the SiH₂ bonding structure becomes dominant, an appreciable amount of SiH bonding structure still exists. These results indicate that the sharp line shape of the NMR spectrum should come from molecular hydrogen and higher-order silicon hydrides in a form different from that of the conventional samples. The formation of the two species somehow suppress the narrow line shape in the NMR spectrum. Furthermore, since molecular hydrogen can only be detected in the NMR spectra, while an appreciable amount of higher-order silicon hydrides [SiH₂ or (SiH₂)₅] can be revealed in both NMR and FTIR spectra, this can then explain why the sharp line shape is created by the diluted hydrogen before the formation of a microcrystalline phase.

In view of the fact that the Raman peak position shifts to 520 cm⁻¹ and the SiH/SiH₂ ratio decreases to less than unity, and because of the decrease in the optical band gap, increase of the dark conductivity, and reduction of photodecay conductivity ratio, it is concluded that the samples prepared using the hydrogen-atom-treatment method with a substrate temperature as low as 250 °C are already constructed into the microcrystalline phase. For the microcrystalline-phase hydrogenated silicon samples, the hydrogen content is typically lower, less than 10%, and the NMR spectra show only a sharp line shape.

For the diluted-hydrogen samples, since the Raman peak locates at around 480 cm⁻¹ and the SiH/SiH₂ has a...
ratio of about 10, no apparent microcrystalline phase is formed. Although the high-temperature samples, with $T_s > 300^\circ\text{C}$, have a narrower optical band gap, less than 1.5 eV, a higher dark conductivity of about $1 \times 10^{-7} \text{ S/cm}$, and their hydrogen contents are lower, less than 10%, we still have the sharp NMR line spectra similar to those of the hydrogen-atom-treated samples. At this condition, the microcrystalline phase just begins to form.

These results indicate that when samples are prepared using hydrogen incorporation with a gas ratio of $\text{SiH}_4/\text{H}_2 = 1/10$, and/or with plasma hydrogen treatment, at elevated substrate temperatures during the deposition, the films possess a structure different from those prepared by the conventional method. When diluted hydrogen is employed at a substrate temperature of 250°C, the NMR spectra will first show a sharp line shape while other measurement results remain essentially unchanged. When the substrate temperature is elevated, NMR spectra are dominated by the sharp line shape, while the hydrogen content and the $\text{SiH}/\text{SiH}_2$ ratio starts to decrease, dark conductivity starts to increase, and the photo/dark conductivity ratio decreases. Under these conditions, the Raman spectra remain unchanged except that a very small peak at around 520 cm$^{-1}$ emerges. However, when the hydrogen-atom treatment is added to the diluted-hydrogen procedures at a substrate temperature of 250°C, all measurement results are drastically changed and creation of large volume fraction of microcrystalline phase is revealed. The results suggest that with appropriate hydrogen incorporation or atomic-hydrogen treatment during the deposition, the creation of a large volume fraction of microcrystalline phase is made possible and the degree of crystallinity of hydrogenated silicon film could be systematically adjusted as desired.

A few models that deal with the microcrystalline hydrogenated silicon growth have been reported. The etching model proposed by Tsai, Anderson, and Thompson suggested that the energetically less stable disordered structure is preferentially eliminated by the hydrogen plasma, and the optimal balance between the deposition and etching can produce microcrystalline or epitaxial silicon film at very low substrate temperature. This model describes the microcrystalline phase growth very well but is not yet able to explain the absorption intensity change of $\text{SiH}/\text{SiH}_2$. Today there is some experimental evidence against the "etching" mechanism to the effect that the growth rate per cycle in the alternative hydrogen treatment is independent of the treating time, another group found that a longer hydrogen treatment period resulted in no film growth. Shiurai, Hanaa, and Shimizu also developed a growth model involving structure relaxation during the hydrogen treatment. In their model, hydrogen atoms cause a dangling bond in the top surface to link with the Si network and diffuse into the growth zone; hydrogen atoms thus passivate the dangling bond and break the weak Si–Si bonds to rearrange the Si network; but the $\text{SiH}/\text{SiH}_2$ change could not be well explained either.

We will in a future publication propose a unified model that can quantitatively illustrate the structure change in coincidence with our measurements. Our hypothesis is that with increasing dilution of hydrogen in the $\text{SiH}_4/\text{H}_2$ gas mixture, a small volume fraction of microcrystalline phase begins to be formed due to the fact that more hydrogen dilution initiates the "etching" process. The populations of molecular hydrogen and $\text{SiH}_2$ are relatively increased because more hydrogen in the gas mixture favors their formation. The $\text{SiH}_2$ structure is presumably more stable if its binding energy is larger and it might stand the etching process more easily than the SiH bonding structure. We also think that the $\text{SiH}_2$ bonding structure might be located around the outer surface of the small microcrystalline phase and it exhibits a sharp NMR line shape, different from the dipolar interaction line shape, while the SiH bonding structure is distributed in the amorphous phase as in the conventional amorphous hydrogenated silicon. This explains the appearance of the sharp NMR line shape deposited at a low substrate temperature of $T_s=250^\circ\text{C}$. As the temperature is elevated, higher surface mobility enhances the growth of a larger microcrystalline phase, together with the etching process, and hydrogen in the form of SiH bonding structure is driven out, which results in the reduction of the hydrogen content and a higher $\text{SiH}_2$ population. The increase of molecular hydrogen content and $\text{SiH}_2$ population together with the reduction of SiH population somehow suppresses the formation of the narrow line shape of the NMR spectra and the sharp line shape then becomes dominant. When the hydrogen atoms are increased to an extreme amount in the hydrogen-atom-treatment process, only the etching mechanism takes place, instead of deposition. Again, since the $\text{SiH}_2$ structure is more stable in the hydrogen plasma, it might survive from the etching process while the SiH bonding structure might not. This would result in the drastic $\text{SiH}/\text{SiH}_2$ change when a large volume fraction of the microcrystalline phase is formed.

IV. CONCLUSIONS

The Raman scattering spectra show that the atomic hydrogen treatment creates the microcrystalline structure while the diluted hydrogen method basically produces an amorphous phase with a small quantity of microcrystalline phase. The infrared-absorption spectra also indicate a bonding configuration change and a hydrogen content reduction when atomic hydrogen treatment is employed. The hydrogenated silicon films deposited both by the diluted-hydrogen method and hydrogen-atom-treatment method show very similar NMR results with a sharp line shape as the substrate temperature is increased beyond 300 and 250°C, respectively.

In view of the Raman shift and the $\text{SiH}/\text{SiH}_2$ ratio decrease, the optical band-gap decrease, dark conductivity increase, and photo-to-dark conductivity ratio reduction, the samples prepared by the hydrogen-atom-treatment method with $T_s=250^\circ\text{C}$ create the microcrystalline phase, while those prepared by the conventional method form only the amorphous phase. In the diluted-hydrogen sam-
amples, the Raman peak is located at 480 cm$^{-1}$ and the SiH/SiH$_2$ ratio shows that no apparent microcrystalline phase was formed.

Samples prepared by the above methods showing microcrystalline characteristics like the Raman shift, optical band-gap reduction, increase of dark conductivity, and reduction of photo-to-dark conductivity ratio, suggest that the treated film should possess a more compact structure than the conventional ones. These results suggest that with appropriate hydrogen incorporation or atomic hydrogen treatment during the deposition, the degree of crystallinity of hydrogenated silicon films can be systematically adjusted. A qualitative model based on our experimental data is presented to illustrate the formation of microcrystalline hydrogenated silicon under the influence of plasma hydrogen and hydrogen dilution. This model can explain the change of SiH/SiH$_2$ ratio and the appearance of the sharp NMR line shape.

ACKNOWLEDGMENTS

The authors acknowledge the assistance and support of Sinorxar Corporation in the sample preparation, and the financial support from National Council of Science under Contract No. NSC82-0404-E007-120.