Temperature-dependent Raman studies of hydrogenated-amorphous-silicon films

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We report here the temperature-dependent Raman-scattering studies of the hydrogenated amorphous silicon (*a*-Si:H) films in the range 77–623 K. The bandwidth (Γ) of the optic phonon obtained from the measured Raman spectra was found to have a nonlinear behavior when plotted versus the temperature and displayed a minimum magnitude (Γ_{min}) when the Raman-measurement temperature equaled the deposition temperature. Furthermore, the Γ_{min} was found to be nearly independent of the H concentration. These results are therefore attributed to the postdeposition effect of an extrinsic stress that originates from the difference in thermal expansion of the film and substrate. The extrinsic stress is proposed to induce additional density of weak bonds, which may enhance the degradation of optoelectronic properties of *a*-Si:H. Furthermore, if the extrinsic stress effects are eliminated, the minimum width of the bond-angle deviation is expected to reduce to approximately $\pm 6°$.

INTRODUCTION

Hydrogenated amorphous silicon (*a*-Si:H) is of great interest for thin-film semiconductor device technology as well as for a basic understanding of the physics of the amorphous state.[1] In contrast to many other conventional glasses, its physical properties, e.g., optical band gap,[2] Urbach slope,[3] defect density of states,[4] are all observed to alter with the deposition as well as the postdeposition thermal annealing conditions. Additionally, vibrational probes such as Raman[5–7] and inelastic neutron scattering[8] also indicate corresponding substantial changes in the structural short-range-order (SRO) consistent with the radial distribution studies.[9] These studies indicate that the SRO in this material varies with the deposition conditions and it can have a direct influence on its optical, electronic, and vibrational properties.[10] The current interest in this material is, therefore, focused on the studies which can provide an accurate knowledge (and measure) of such SRO parameters as may be useful for the accurate description of amorphous networks and also assist in the search for the origin of various changes in the physical properties of the material.[10,11]

The SRO in the tetrahedral amorphous state is mainly described in terms of the statistical variation of the bond lengths (Δr), bond angles ($\Delta\theta$), and distances between the atoms that form second neighbors.[10] Among these variable parameters, the variations $\Delta\theta$ are found to have a large spread of about $\pm 10\%$, while the variations Δr are less than $\pm 1\%$ of their respective magnitudes in the crystalline state. The $\Delta\theta$ parameter, therefore, can alone distinguish between the various structural phases and predict the degree of disorder present in the material.[12] A higher degree of disorder is considered to be an indication of the presence of a high degree of intrinsic stress in the film. This stress can give rise to a larger density of strained bonds (weak bonds) which are considered to form the source of the variety of optoelectronic degradation phenomena displayed by these materials.[13,14] Therefore, the minimization of disorder or the formation of a highly metastable phase of minimum energy is of paramount importance for the device applications of such materials. Theoretical estimates[6,15] show that such a metastable phase in *a*-Si, the unhydrogenated material, would have the minimum energy as low as that of the crystalline state, when $\Delta\theta$ is as low as $\pm 7°$. In the case of *a*-Si:H, such low values of $\Delta\theta$ could easily be realized as a result of the additional role of H in relieving the strain in the amorphous network. The various Raman-scattering (RS) measurements so far reported on *a*-Si:H films have, however, revealed that the room-temperature value of $\Delta\theta$ is greater than $\pm 9°$, which raises a question about the long-term stability of these films. We believe that the contributions to $\Delta\theta$ from other factors such as the extrinsic stress have been ignored in the earlier work.

In general, the RS measurements are carried out principally at room temperature but on the samples essentially having the frozen postdeposition structural state which may differ from the state that actually prevails at the deposition temperature. The postdeposition state is expected to be the result of the total stress accumulated in the film "during" and "after" the deposition process, the former being the "intrinsic stress" and the latter being the "extrinsic stress."[16,17] The intrinsic stress is induced in the film as a result of local atomic structural and compositional (chemical) disorder conferred by the substrate temperature and other deposition conditions, whereas the extrinsic stress results mainly due to the difference in the thermal expansion of the substrate and *a*-Si:H film. During the deposition process at a given substrate temperature, the film grows essentially in equilibrium with the expanded substrate and, therefore, it may not experience the external stress. However, when the film-substrate union is cooled to room temperature, the film may experience extrinsic stress in the form of a compression (or tension) generated at the film-substrate interface. Thus the measured $\Delta\theta$ can differ from the actual SRO that would prevail at the given substrate temperature. Nevertheless, the extrinsic stress contributions to $\Delta\theta$ may become negligible when the temperature (T_m) for the Raman

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measurement is raised to equal the value of T_s the temperature at which deposition was done.[16,17] We have, therefore, attempted here to resolve the intrinsic and extrinsic contributions to $\Delta\theta$ by performing the systematic temperature-dependent Raman measurements at various values of T_m in the range 77–623 K on the *a*-Si and *a*-Si:H samples deposited at different T_s values keeping all other deposition parameters constant. These results are used to predict the room-temperature $\Delta\theta$ values which may be considered as truly representative of the real intrinsic stress. Our analysis shows that such $\Delta\theta$ values for *a*-Si:H can be as low as $\pm 6°$.

EXPERIMENT

The *a*-Si:H films were deposited on the crystalline silicon (*c*-Si) $\langle 111 \rangle$ substrate (2×1 cm). These substrates were cut from a 2-in.-diameter wafer (having one side optically polished) such that the reference mark, a side-cutoff portion, provided on the wafer was parallel to the length of the substrate. The deposition of *a*-Si:H was carried out in a modified radio frequency (rf) glow-discharge reactor[18] with the following deposition conditions: SiH_4 gas pressure ~ 500 mTorr, rf power 0.05 W/cm^2, and deposition temperatures (T_s) of 200, 230, 250, and 300 °C. The *a*-Si films were sputter deposited in the absence of hydrogen in the Materials Research Corporation system (Model 8620) with the following deposition conditions: rf power 100 W, Ar gas pressure 8 mTorr, rms peak voltage 2000 V, and values of T_s the same as those used for *a*-Si:H films.

The *a*-Si:H films displayed the IR absorption spectra characteristic of monohydride (-Si-H) bonding configuration (except for the one deposited at 200 °C). The H-concentration values calculated by following Brodsky, Cardona, and Cuomo[19] are given in Table I.

The RS data at various temperatures $T_m > 300$ K were acquired in the backscattering geometry from the *a*-Si and *a*-Si:H films with their supporting substrates placed in close contact with the variable temperature cold finger of a Dewar evacuated to 10^{-6} Torr. For the RS data collection at 77 and 195 K, the Dewar was filled, respectively, with the liquid nitrogen or a mixture of dry ice plus acetone. The argon-ion-laser radiation of wavelength 514.5 nm in the line-focused geometry (an area approximately 0.8×0.005 cm^2) was used as the excitation source. The vertical polarization electric wave vector of the laser was rotated through 90° with the help of a Babinet compensator. The rectangular *c*-Si substrate was then oriented such that its longer side was fixed perpendicular to the polarization vector. Furthermore, the line focus of the excitation laser was adjusted to lie parallel to the longer side of the wafer. The total power incident on the sample was approximately 200 mW. The details of the Raman apparatus and experimentation are the same as described elsewhere.[7] The RS measurements at various temperatures were carried out by maintaining undisturbed the overall optical path and geometry. No polarization analyzer was placed between the spectrometer and sample. Since we have used a spectral slit width of ~ 2 cm^{-1}, the error in frequency measurement is less than ± 1 cm^{-1}. During the Raman measurements, the temperature of the sample was controlled to within ± 2 °C. The surface temperature of the sample was measured by a Chromel-Alumel thermocouple which was calibrated by measuring the ratio of anti-Stokes to Stokes intensities in the Raman spectra of crystalline silicon $\langle 111 \rangle$ on which the *a*-Si:H films were deposited.

RESULTS AND DISCUSSION

In Fig. 1, we show the typical anti-Stokes and Stokes Raman spectra recorded at $T_m = 77$, 300, and 503 K for *a*-Si:H films deposited on a partially covered *c*-Si$\langle 111 \rangle$ substrate with the substrate (or deposition) temperature $T_s = 503$ K and whose H content was approximately 13 at. %. The strong bands corresponding to the transverse-acoustic (TA) and transverse-optical (TO) phonons and the weak bands corresponding to the longitudinal-acoustic (LA) and longitudinal-optical (LO) phonons are appropriately labeled in the figure. With the changes in Raman-measurement temperature (T_m), the Stokes component shows substantial changes in the scattered intensity of various bands as well as in the bandwidth, in particular of the TO phonon. The anti-Stokes component, on the other hand, diminishes at 77 K particularly for higher phonon frequencies. Some of this temperature-dependent scattering may be accounted for by considering the basic Raman-scattering process in amorphous solids as follows.

It is well known that in the absence of long-range ordering in the amorphous state, long-range correlations are not possible and therefore the concept of well-defined crystal momentum (or wave-vector quantum number) becomes meaningless. This introduces a breakdown of the $\mathbf{q} = \Delta\mathbf{k} \sim 0$ selection rule valid for the crystalline state, where $\mathbf{q}$ is the phonon wave vector and $\Delta\mathbf{k}$ is the difference between incident and scattered photon wave

TABLE I. The observed and calculated values of the TO bandwidth [$\Gamma(T)$] for various measurement temperatures and the values of RMS bond-angle deviation ($\Delta\theta$) are given as a function of substrate temperature (T_s).

T_s (°C)	[H] (at. %)	$\Gamma(T_s)$ (cm^{-1}) Obs.	$\Gamma(0)$ (cm^{-1}) Calc.	$\Gamma(300)$ (cm^{-1}) Obs.	$\Gamma(300)$ (cm^{-1}) Calc.	$\Delta\theta(300)$ (deg) Obs.	$\Delta\theta(300)$ (deg) Calc.
200	16	66	50	76	55.5	10.16	6.75
230	12.8	62	46	72	51.1	9.5	6.01
250	11.5	64	46.6	76	51.8	10.16	6.13
300	9.2	68	47.2	76	52.4	10.16	6.23

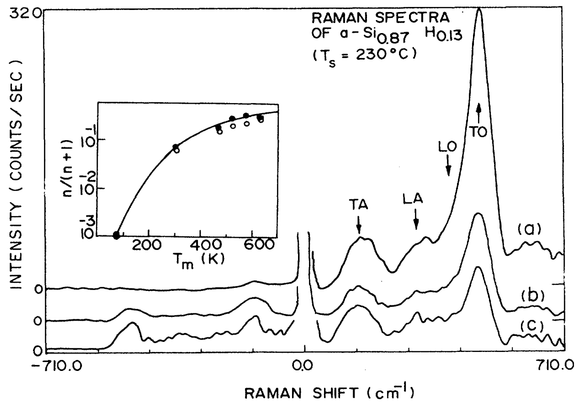

FIG. 1. The anti-Stokes and Stokes Raman spectra of an a-Si:H sample (deposited at $T_s=230\,^\circ\mathrm{C}$) recorded at temperature (T_m) (a) 77 K, (b) 300 K, and (c) 503 K. The inset shows the variation of ratio I_A/I_S with T_m for a-Si:H (●) and c-Si (○) compared with the calculated ratio $n/(n+1)$ (solid-line curve).

vectors. That is the correlation length which characterizes the spatial extent of a normal-mode vibrational state, and becomes negligibly small compared to the incident-photon wavelength. All the vibrational modes, therefore, may be presumed to be nearly localized and thus become first-order Raman active. The expression that relates Raman-scattered intensity $[I(w)]$ to the vibrational density of states $g_b(w)$ for phonon frequency w has been developed by Shuker and Gamon,[20] viz.,

$$I(w)=C_b(1/w)[1+n(w,T_m)]g_b(w)+C_b(1/w)[n(w,T_m)]g_b(w)\ . \quad (1)$$

The first and second term correspond to the Stokes and anti-Stokes Raman component, respectively. Each band of the vibrational states having vibrational density $g_b(w)$ is presumed to have the coupling parameter (C_b) reasonably constant inside the band, though it may differ from band to band. The temperature-dependent phonon population of the vibrational states is given by the Bose-Einstein distribution function, viz.,

$$n(w,T_m)=[\exp(\hbar w/K_BT_m)-1]^{-1}\ . \quad (2)$$

Thus the vanishingly small value of $n(w,T_m)$ for the low temperature ($T_m=77$ K) and $w>400\ \mathrm{cm}^{-1}$ seems to take care of the vanishing of high-frequency TO band from the anti-Stokes spectrum. We have used this property to calibrate our temperature measurements. The inset in Fig. 1 shows the $n/(n+1)$ values obtained from the ratio of anti-Stokes to Stokes TO-band intensity (I_A/I_S) measurements on c-Si as well as on a-Si:H samples. The continuous curve shows calculated values of $n/(n+1)$ which appear to match well with the I_A/I_S ratio values obtained for a-Si:H, though they deviate slightly at high T_m for c-Si, a result which was also observed by earlier workers.[21,22] Therefore, we infer that our temperature measurements are free from any serious errors.

Next, the broad nature of all Raman bands as seen in Fig. 1 has been well explained[23] by appropriate Gaussian broadening of the corresponding bands in the $g_b(w)$ curve. This broadening is due to the structural disorder that may be described in terms of the intrinsic stress-induced deviations in the tetrahedral bond angles ($\Delta\theta$) and bond lengths. The theoretical model calculations of $g(w)$ have shown that the TO bandwidth (Γ) at half maximum is considerably sensitive to the variations in $\Delta\theta$, and obeys a relation,[24] viz.,

$$\Gamma=15+6\Delta\theta\ . \quad (3)$$

Following Beeman, Tsu, and Thorpe,[24] we have obtained the $\Gamma(T)$ values of TO bands from measured Raman spectra for a-Si:H and estimated the $\Delta\theta$ values at various temperatures T. In contrast to c-Si, the variation of $\Gamma(T)$ for various a-$Si_{1-x}H_x$ films (plotted in Fig. 2) appears to be nonlinear with a minimum at $T=T_m=T_s$. In c-Si, the temperature effects[21,22] which enhance the anharmonicity of the interatomic forces, broaden the amplitudes of vibrations and increase the phonon population of higher vibration levels, result in the broadening of $\Gamma(T)$ and simultaneously in the lowering of TO-phonon frequency (w_{TO}) linearly with the rise in crystal temperature. This temperature dependence of $\Gamma(T)$ of c-Si is given by the relation (4) theoretically developed by Cowley[25] and experimentally verified by Cerderia and Cardona:[26]

$$\Gamma(T)=\Gamma(0)\{1+1/[\exp(x)-1]\}\ , \quad (4)$$

where $x=h\nu/(K_BT)$, $\nu=Cw$ with $K_B=1.38\times10^{-16}$

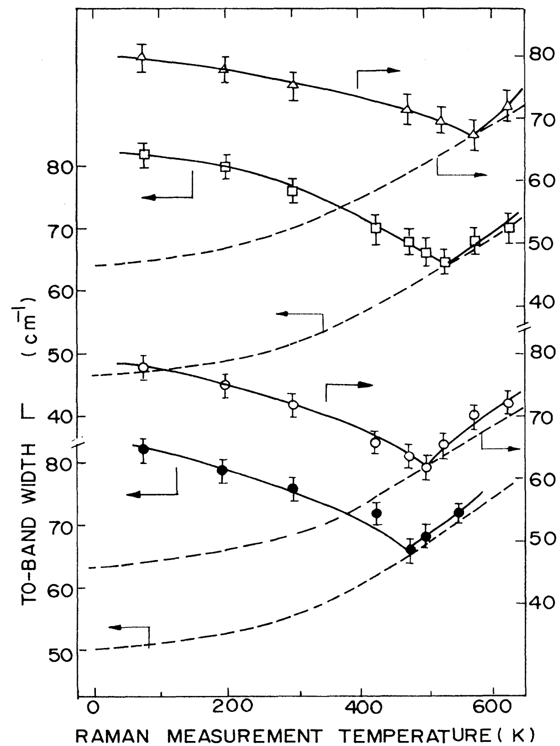

FIG. 2. The variation of the TO bandwidth (Γ) with Raman measurement temperature (T_m) for the four a-Si:H samples deposited at $T_s=200\,^\circ\mathrm{C}$ (●), $230\,^\circ\mathrm{C}$ (○), $250\,^\circ\mathrm{C}$ (□), and $300\,^\circ\mathrm{C}$ (△). The broken-line curve represents calculated Γ values.

ergs/deg, $\hbar = h/2\pi$, $h = 6.625\times10^{-27}$ ergs/sec, $C = 2.998\times10^{10}$ cm/sec, or $x = w/0.6948\ T$ for w in cm^{-1}.

At present, however, there exists no experimental or theoretical information on the temperature dependence of $\Gamma(T)$ of a-Si:H or a-Si. Since the $g(w)$ spectrum for the amorphous Si network is primarily determined by the tetrahedral SRO (sp^3 bonding) and the force constants which are nearly similar to those of c-Si, the temperature dependence of $\Gamma(T)$ for a-Si:H or a-Si may be presumed to obey relation (4), and thus it should be possible to calculate approximate values of $\Gamma(0)$ at $T_m = 0$ K or $\Gamma(300)$ at $T_m = 300$ K for a-Si and a-Si:H. For this purpose, on the basis of results in Fig. 2, we assume that, at $T_m = T_s$, the extrinsic stress effects become negligible and thus the $\Gamma(T_s)$, which is the minimum in $\Gamma(T)$ vs T curve, can be inserted in relation (4) to obtain $\Gamma(0)$. In Table I, we have listed the values of $\Gamma(0)$ and $\Gamma(300)$ calculated for a-Si:H films deposited at various values of T_s by substituting the respective observed $\Gamma(T_s)$ values, and compared them with the corresponding observed values of $\Gamma(300)$. In Fig. 2, the broken-line curves show the corresponding estimated values of $\Gamma(T)$ at various T_m. The difference in observed and calculated $\Gamma(T)$ values for all films is seen to increase drastically with the lowering of T_m, and indicates that the shrinkage of the substrate has pronounced effect on the $\Gamma(T)$ of the films and, therefore, on the distortion in bond angles. In Fig. 3, we show the variations of w_{TO} as a function of T_m as well as of $\Gamma^2_{(\text{calc})}$. The w_{TO} vs $\Gamma^2_{(\text{calc})}$ indicates approximately linear behavior, as is expected from the relation developed by Tsu,[27] and confirms that the $\Gamma_{(\text{calc})}$ values are in reasonable agreement with the expected effects of the intrinsic stress. Thus the extrinsic stress does appear to influence the SRO in a-Si:H films at room temperature.

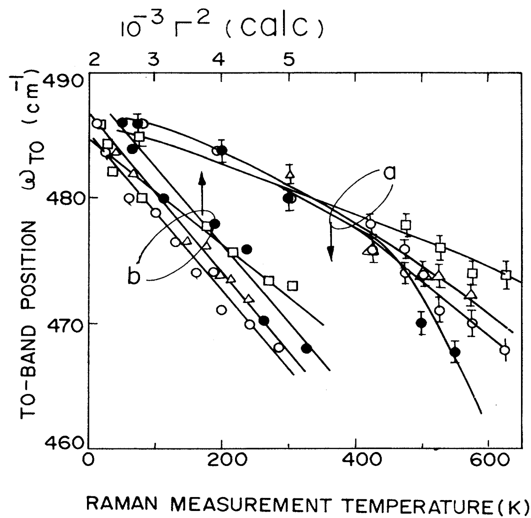

FIG. 3. The changes in the TO-band position (w_{TO}) with the Raman-measurement temperature (T_m) (shown by curves a) and with the square of the calculated TO bandwidth (Γ^2_{cal}) (shown by curves b) for the a-Si:H samples deposited at $T_s = 200\,^\circ\text{C}$ (●), 230 °C (○), 250 °C (△), and 300 °C (□).

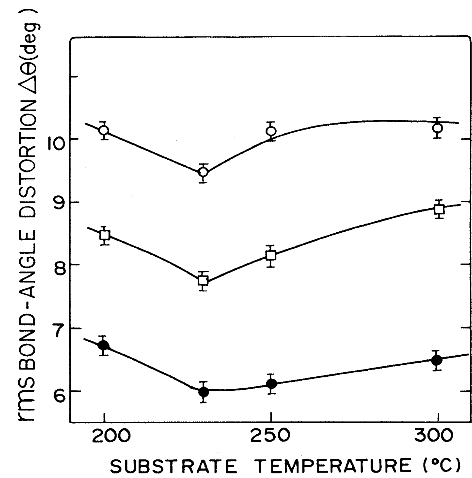

FIG. 4. The variations in the RMS bond-angle deviation ($\Delta\theta$) in a-Si:H with the substrate temperature (T_s). ○ is the observed values at $T_m = 300$ K, □ the observed values at $T_m = T_s$, and ● the calculated values at 300 K.

The values of $\Delta\theta$ obtained by conversion of Γ values through relation (3) are tabulated appropriately in Table I. The observed values of $\Delta\theta$ ($\Delta\theta_{(\text{obs})}$) at room temperature appear, as expected, to be higher than those obtained for calculated Γ values ($\Delta\theta_{(\text{calc})}$). The minimum value of $\sim\pm6°$ (see Fig. 4) appears to be the characteristic of the

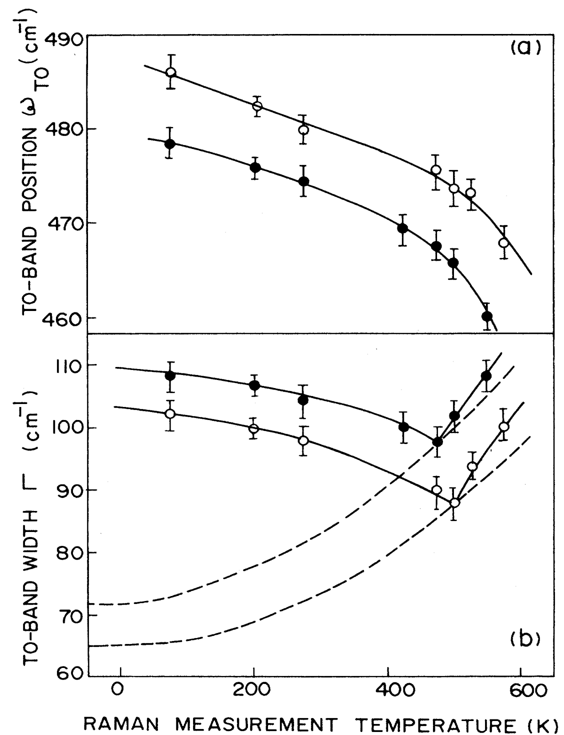

FIG. 5. The variations of (a) the TO-band position (w_{TO}) and (b) the TO bandwidth (Γ) with the Raman-measurement temperature (T_m) for a-Si (unhydrogenated) samples deposited at $T_s = 200\,^\circ\text{C}$ (●) and 230 °C (○). The broken-line curves represent calculated Γ values.

least disordered films deposited at 230 °C, which happens to coincide with the temperature of deposition employed for obtaining the highest efficiency of solar cells ever attained. However, the H concentration of the film appears to have no perceptible effect on the location of the minimum in $\Delta\theta$ vs T_m behavior.

Recently, Stutzmann[28] has postulated that Si-Si bonds weakened by stress would break more easily under light soaking, thus generating more light-induced defects that degrade the solar-cell efficiency with time. Since any applied stress would result mainly in the bending of bonds, the extrinsic stress imposed at the film-substrate interface can also enhance the weak-bond density in the film. Our results, therefore, indicate that a proper choice of a substrate having matched thermal properties with those of *a*-Si:H would result in a decrease in weak-bond density in the film and, therefore, possibly would reduce the light-induced degradation of the solar-cell output.

In the course of this study we have also meticulously watched for any anomalous changes in the TO bandwidth at the temperature which is reported as "equilibrium temperature"[14] (or glass transition temperature), T_E, of *a*-Si:H. Above $T_E \sim (180-200\,°C)$, the electronic properties are independent of the prior thermal history of the sample, while below T_E a nonequilibrium electronic and atomic structure is believed to relax towards the equilibrium with a thermally activated relaxation time. However, the results of Fig. 2 and those on sputtered unhydrogenated *a*-Si (Fig. 5) indicate that subtle changes in SRO occur only at $T_m = T_s$ and not at $T_m = T_E$. The absence of a minimum in disorder in *a*-Si:H at $T_m = T_E$ (Fig. 2) suggests that the glass transition in *a*-Si:H has no relevance to the relaxation of the amorphous Si-Si network as a whole and, therefore, the various electronic degradation phenomena observed in *a*-Si:H can rightly be investigated in terms of the dispersive diffusion of H and the defect distribution in equilibrium with such dispersed H.

Furthermore, a few sets of RS measurements at various temperatures on *a*-Si:H films were repeated after rotating the substrate by 90° so that its breadth was fixed parallel to the line focus. However, no perceptible changes compared to those of the earlier orientation were observed either in the TO bandwidth or intensity. It appears that the biaxial nature of the extrinsic stress exerted by the substrate does not have an appreciable effect on the temperature-dependent RS measurements on *a*-Si:H films. Thus this result leads to the conclusion that probably the silicon wafer responds elastically uniformly in all directions perpendicular to the $\langle 111 \rangle$ axis. Similar results on stress measurements on the SiO_2/Si interface have been already observed by Glang, Holmwood, and Rosenfeld.[29]

In summary, we find that the extrinsic stress influences considerably the width to the minimum bond-angle deviation in *a*-Si:H films. When such extrinsic stress effects are removed, the minimum bond-angle deviation would reduce to approximately $\pm 6°$.

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