Structural order in anneal-stable amorphous silicon

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Raman scattering is reported on anneal-stable *a*-Si films prepared by chemical-vapor deposition (CVD). In contrast to earlier work, substantial changes are observed in the phonon spectrum and Raman matrix elements relative to *a*-Si deposited by other techniques. The results indicate improved short-range order associated with a decrease in bond-angle fluctuations in CVD *a*-Si. While the CVD *a*-Si spectra are similar to those of glow discharge *a*-$Si_{0.92}H_{0.08}$, small differences suggest enhanced order in the H alloy. The results indicate that small changes in short-range order may appreciably modify the properties of *a*-Si.

To what extent the structural order of noncrystalline solids can be modified, as well as the degree to which such order influences the properties of amorphous materials, is of considerable current interest. Of basic importance are the extent to which short- or intermediate-range order may be enhanced, either by deposition methods or chemical modification. While it is well known that the electrical and optical properties of thin-film amorphous solids such as *a*-Si and *a*-Ge may be substantially modified by preparation conditions,[1,2] it has been unclear as to the role of changes in the "intrinsic" structural network versus "extrinsic" effects associated with microvoids or micromorphology in general. Detailed x-ray diffraction measurements in *a*-Ge have shown that considerable changes in physical properties may be a consequence of either or both small changes in network structure or modifications of the microvoid distribution.[1] Other measurements that might be sensitive to the network structure, such as Raman scattering, were found to be apparently insensitive to preparation conditions,[3] so that the importance of microvoid effects has been considered a significant factor in influencing physical properties. Recent studies in hydrogenated alloys of amorphous silicon have found that more substantial modifications of the amorphous state are possible, e.g., leading to the potential for doping. Aside from saturating dangling bonds, limited *direct* evidence for the network-structural role of hydrogen has been provided, however, though some small modifications of the radial distribution function at ~ 4.5 Å have suggested possible changes in the dihedral angle distribution.[4] It has, for example, been suggested that H, in addition to saturating dangling bonds, also reduces "microstrains" in the amorphous network.[5-6] The precise meaning and role of such strains, their central and noncentral nature, and degree of locality has been unclear, however. More recent interest has also occurred in *a*-Si prepared by high-temperature chemical-vapor deposition (CVD) by thermal decomposition of SiH_4 molecules. This process has been found to yield material that has very little hydrogen, with physical properties such as a large optical gap (~ 1.5 eV), thermal stability, and the potential for doping.[7,8] As high-temperature CVD material corresponds to the anneal-stable state of relatively pure *a*-Si, its properties are of intrinsic interest to theoretical models of amorphous solids.

In the present study, Raman-scattering measurements are reported on CVD *a*-Si, which in contrast to earlier work on *a*-Si prepared by other methods, indicates considerable modifications of the vibrational spectrum. The results imply improved short-range order in the amorphous network in CVD material that is interpreted as a primary consequence of reduced bond-angle variations within the first coordination sphere. It is also found that the CVD spectra are similar in form to those of *a*-$Si_{1-x}H_x$ alloys. This implies that the role of H in the network regions of *a*-$Si_{1-x}H_x$ alloys is to improve the short-range order in a manner similar to that of films prepared by the CVD process. The present results emphasize that small modifications of short-range order may play an important role in the physical properties of *a*-Si and its alloys.

Thin-film CVD *a*-Si material was obtained from

Professor B. O. Seraphin. Extensive characterization of this material by optical and structural means has been previously performed.[8] Films prepared on substrates at temperatures, T_s, between ~ 525 and 650 °C are found to exhibit relatively similar optical spectra in the visible and near infrared, while surfaces roughness and void distribution vary with T_s and modify the ultravoilet optical properties.[8,9] The H content of the films is in the heavily doped range and varies from ~ 0.2 at.% to ~ 0.7 at.% as T_s decreases. The Raman spectra on films prepared under conditions of variable T_s are very similar within the signal-to-noise and background-level estimates. The spectra were obtained on a Spex third-monochromator system using an Apple II microcomputer system for improved signal averaging. The Raman spectra also directly confirm that the films are fully amorphous with no indications of crystallites. Measurements were made at 300 K using 200 mW power of an argon laser at 5145 Å. This corresponds to a photon energy where resonant enhancement changes are expected to be gradual.[10]

In Fig. 1 the two Raman components I_{VH} and I_{HH} of CVD *a*-Si are compared to the corresponding spectra of *a*-Si prepared by rf sputter deposition. The latter film was prepared at a sputtering pressure of 7 mTorr of Ar with T_s of 120 °C measured directly by a thin-film Ag-Al thermocouple. As is clear from these spectra the form of the Raman scattering is significantly modified in these two rather differently prepared *a*-Si films. This is primarily indicated by the full width at high maximum Δ of the high-frequency TO-like band which decreases by factors of 2.4 and 1.7 in the CVD material for the *HH* and *VH* components, respectively. In addition, the relative intensity of the low-frequency TA-like region decreases by a factor of 0.65 – 0.7 in the CVD material, with a larger decrease for the *VH* component. Earlier measurements[3] in *a*-Si have suggested that the Raman spectra for films deposited at low T_s values were relatively insensitive to the technique of preparation, however, the present results clearly emphasize that considerable modifications of the spectra are possible in CVD *a*-Si.

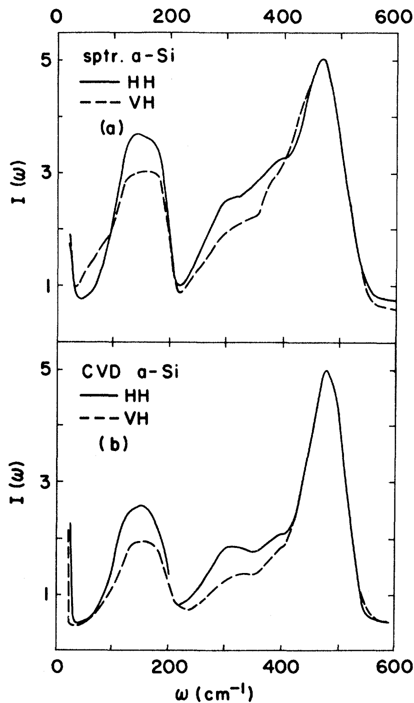

FIG. 1. Comparison of the *VH* and *HH* Raman spectra of sputtered *a*-Si in (a) and CVD *a*-Si in (b). The spectra have been normalized to the peak intensity in arbitrary units. The zero levels correspond to the intensity at $\omega = 1200$ cm^{-1}.

For first-order Stokes-Raman scattering, which in the present case extends to ~ 600 cm^{-1}, the scattering intensity is related to a coupling-parameter weighted-phonon density of states $\rho(\omega)$ by the relation

$$I^{\gamma}(\omega) \sim \omega^{-1}(n+1)\bar{C}^{\gamma}(\omega)\rho(\omega) \, .$$

The factor $\bar{C}^{\gamma}(\omega)$ represents the average coupling parameter for $\gamma = VH$ or HH components. The variation in the form of the Raman spectra between the sputtered and CVD *a*-Si films in Fig. 1 thus indicates that either or both the phonon density of states or coupling parameters are a function of deposition conditions. At high frequencies the TO-like band which peaks at ~ 480 cm^{-1} is primarily associated with induced polarizability from stretching like vibrational modes. Theoretical studies[11] in *a*-Si and *a*-Ge indicate that the broad peaks in the Raman spectra correspond to those of the phonon density of states as $\bar{C}^{\gamma}(\omega)$ is smoothly varying to first order. It may be further argued that the shape of the high-frequency *VH* spectrum is expected to be more similar than the *HH* component to that of $\rho(\omega)$.[12] This implies that the broadening of the high-frequency *VH* width is primarily indicative of a similar modification of the phonon density of states. The origin of this broadening, which is also exhibited by the *HH* component, is attributed to variations in bond-angle distribution with deposition conditions. Such modifications in short-range order have been shown in theoretical calculations of Meek, for

model networks of a-Ge, to result in an increased TO-like phonon width as the root-mean-square bond-angle variation $\Delta\theta_{rms}$ is increased.[13] As the vibrational and Raman spectra of a-Ge and a-Si are rather similar,[11,14] and approximately scale as $m^{-1/2}$, these conclusions also apply to a-Si whose $\Delta\theta_{rms}$ of $\sim\pm 10°$ is similar to that of a-Ge.[2]

As the integral over the phonon spectrum is essentially conserved, a broadening of the high-frequency phonon spectrum results in a general redistribution of states to lower frequencies. While this trend of increased intensity is observed experimentally in the sputtered a-Si Raman spectra of Fig. 1, some modifications of $\bar{C}^{\gamma}(\omega)$ may also arise due to structural changes. The relative decrease in the depolarization ratio, $I_{VH}(\omega)/I_{HH}(\omega)$, in the CVD material indicates changes in $\bar{C}^{\gamma}(\omega)$ at lower frequencies. The increase in polarized character of these states may be reasonably attributed to a decrease in the bond-bending induced-polarizability term[11] α_2, as a consequence of increased short-range order γ in the network. That is, in the limit of a narrow distribution of bond angles, the depolarized *VH* Raman scattering is expected to be reduced, since at low frequencies it is primarily a function of bond-bending modes. In particular, in the limit of perfect tetrahedral symmetry α_2 vanishes.[11]

In Fig. 2 the Raman spectra of CVD a-Si are compared to that of a glow-discharge-deposited a-$Si_{0.92}H_{0.08}$ alloy obtained by Tsai and Nemanich.[15] As Fig. 2 clearly indicates, these spectra are rather similar in form relative to the lower T_s-sputtered a-Si spectra. While some variations in background level probably exist between the thin-film CVD spectra and the glow-discharge results obtained using interference enhancement on very thin films, there are small differences in the spectra that are a consequence of enhanced hydrogen concentration. In particular, Δ_{VH} and Δ_{HH} of the glow-discharge spectra are $\sim 10\%$ lower than in CVD a-Si. Similarly, the relative intensity of the *VH* peak in the TA-like band of the CVD film is approximately 50% greater than that of the glow-discharge alloy. These changes may be either a consequence of modifications in the vibrational spectrum with hydrogen and changes in the Raman-coupling parameters. The decrease in Δ_{VH} *and* Δ_{HH} suggest that modifications of $\rho(\omega)$ have occurred which, based on the results of Fig. 1, would imply a reduced bond-angle variation. The simultaneous decrease of the TA-like peak of the *VH* component in the glow-discharge alloy is consistent with this, as a

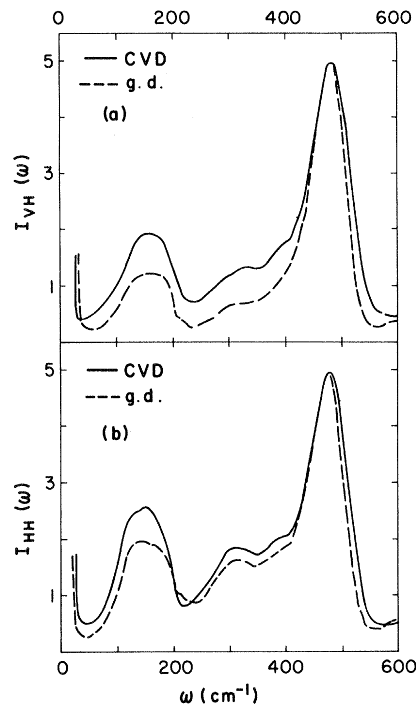

FIG. 2. Comparison of the Raman spectra of CVD a-Si (solid) and glow discharge deposited a-$Si_{0.92}H_{0.08}$ of Ref. 15 (dashed). (a) indicates the *VH* and (b) the *HH* normalized spectra.

reduction of $\Delta\theta_{rms}$, as noted above, reduces α_2. The $\sim 30\%$ smaller *HH*, TA-like peak intensity of the glow-discharge film is also similar to the trend observed in Fig. 1 associated with increasing short-range order. Modifications of the *HH* spectra of the glow-discharge film with H evolution are consistent with this conclusion,[15] as are changes in the spectra of sputtered a-$Si_{1-x}H_x$.[10]

Of particular interest is the quantitative degree of modification of short-range order in the films of Figs. 1 and 2. A comparison with detailed radial-distribution studies in sputtered a-Ge deposited at low- and high-substrate temperatures indicates an $\sim 7\%$ change in $\Delta\theta_{rms}$.[1] The difference in structural order between the films of Fig. 1 is thus likely to be roughly $\sim 10\%$, assuming a scaling of phonon frequencies and disorder between a-Si and a-Ge. For the glow-discharge film an extrapolation of Meek's a-Ge model calculations,[13] which indicate the variation of the TO-like phonon width, suggest perhaps a possible increase of $\sim 2-4\%$ in the bond-angle order of the H alloy relative to the CVD a-Si material. While these estimates of changes in the short-range order are very approximate and serve at present as a semiquantitative

gauge, they do clearly emphasize that rather small variations in local order may have a substantial effect on the phonon density of states and Raman spectral components of a-$Si_{1-x}H_x$.

The observation of reduced fluctuations in bond-angle distribution in both the CVD a-Si and glow-discharge a-$Si_{0.92}H_{0.08}$ alloy result in increased local order in a-Si relative to other preparation procedures studied to date. The reduced bond-angle variations result in a decrease in local strain energy for the system and thus a lower free energy. Such local strains are primarily associated with noncentral, bond-bending forces. This contrasts with central interaction effects which modify bond lengths, and which dominate in metallic films. The latter interactions have alternatively been suggested to be the origin of nonlocal strains in a-$Si_{1-x}H_x$ that influence film growth and morphology.[5,6]

In addition to modifications of the phonon density of states, it is quite possible that improved short-range order in CVD a-Si results in both a larger optical gap as well as a reduction of states in the gap due to a modification of the bond-angle distribution. In particular, states for which the local bond-angle variations are large may yield deep defect states, which in turn are removed with increasing short-range order. Alternatively, increased bond-angle fluctuations may allow configurations that have a defect character. As CVD a-Si may be doped, this suggests the possibility that improved short-range order has reduced certain states in the gap. While the CVD material does contain some hydrogen, its relatively low value suggests that network-structural order may also be of some significance in determining the number of gap states. Even in the most ordered a-$Si_{1-x}H_x$ material the width of the TO-like Raman band implies a bond-angle variation greater than $\pm 9°$. This intrinsic limit on $\Delta\theta_{rms}$ may be a consequence of local noncentral strain contributions to the free energy which have been suggested to arise due to dimensional constraints in tetrahedral systems.[16] While such strains may influence the micromorphology[16] and defect geometry on a scale < 10 Å, the present results suggest that intrinsic network order may also influence defect states. The results clearly emphasize that small modifications of bond-angle distribution play a significant role on the vibrational properties of a-Si and its alloys.

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