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Variable structural order in amorphous silicon

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Raman scattering and optical-absorption spectra in low-pressure, rf-sputtered *a*-Si are shown to exhibit a continuous variation with deposition temperature. A direct correspondence between changes in the inverse width of the TO-like phonon band and the optical gap is observed in sputtered and chemical-vapor-deposited *a*-Si. The results are interpreted in terms of intrinsic changes in network short-range order of *a*-Si with temperature which yield substantial modifications of the vibrational and electronic states.

A number of physical properties of amorphous (*a*-) Si and Ge, such as optical absorption and electrical conductivity have been found to be highly sensitive to deposition conditions, whereas studies such as x-ray diffraction have indicated small changes in structural order.[1] Similarly, early Raman scattering measurements[2] in *a*-Si suggested insensitivity to deposition conditions. These results have left unclear[3] the role of "intrinsic" network order on physical properties versus "extrinsic" effects such as voids, which, for example, have been considered an important factor in determining the absorption spectra near the "optical gap."[4]

In this work we report on a systematic Raman scattering and optical-absorption study of *a*-Si prepared by rf sputtering under conditions of variable substrate temperature. In accord with a recent report[5] on chemical-vapor-deposited (CVD) *a*-Si, the results indicate that the Raman scattering spectra can be substantially modified. Moreover, the variation may be monotonic with temperature for appropriate deposition conditions. A similar variation of the optical gap is also observed that indicates a correspondence between changes in the electronic and vibrational states of *a*-Si. The results thus strongly suggest that changes in structural order may substantially modify *both* the vibrational and electronic states of *a*-Si and that the optical gap in the present films, is predominantly determined by intrinsic structural order. In an analogous manner it has recently been suggested that the optical gap of *a*-P is a function of intermediate- and short-range order.[6]

Films of *a*-Si were prepared by rf diode sputtering of a 5-in. target under conditions of fixed Ar pressure of 7×10^{-3} Torr and constant external power of 100 W. The potential of the plasma relative to the substrate was measured with an electrostatic probe to be $V_s \simeq 50$ V. Substrate temperature, T_s, was the major variable of interest in this study. For rf plasmas this temperature may differ significantly ($\sim 100\,^\circ\mathrm{C}$) from the thermocouple determined plate temperature, T_p. Detailed measurements of the substrate temperature are currently under study; thus only T_p values are reported here. Raman scattering measurements in the pseudo backscattering geometry were performed on a Spex third monochromator system at 5145-Å laser excitation wavelength. Optical transmission measurements on sputtered and CVD films were performed on a Cary 17 and reflectance on a Beckman DK-2A system.[6] Ellipsometry and scanning electron microscopy (SEM) measurements showed the sputtered films to be of high density with smooth morphology, and no indication of columnar or void structure. Microprobe analysis for films of $T_p = 300\,^\circ\mathrm{C}$ yielded O concentrations of $<\frac{1}{2}$ at. %. The chemical-vapor-deposited (CVD) *a*-Si films prepared at $T_s \simeq 525-650\,^\circ\mathrm{C}$, where obtained from Professor B. O. Seraphin and have been extensively characterized.[7]

In Fig. 1 variations in the Raman spectra at 300 K of rf sputtered and CVD *a*-Si for the *VH* and *HH* components are shown as a function of T_p. For purposes of discussion the spectra may be divided into three approximately distinct spectra regions: low-frequency scattering below $\sim 200\ \mathrm{cm}^{-1}$, corresponding to the transverse-acoustic (TA) band in *c*-Si; intermediate frequencies, from $\sim 200-420\ \mathrm{cm}^{-1}$, corresponding to the LA and LO peak range in *c*-Si; and a high-frequency regime extending to $\sim 600\ \mathrm{cm}^{-1}$ which has a TO correspondence in *c*-Si. As Fig. 1 clearly indicates the relative intensity and shape of the spectra in these regimes is a distinct function of substrate temperature. The general trend in both the *VH* and *HH* spectra is a broadening of the TO-like band as T_p decreases as well as an increase in the relative intensity of the TA- and LA-like peaks. In the case of the *HH* spectra the broadening at high-frequencies results in an overlap with the LA-like peak such that the spectra are highly asymmetric to

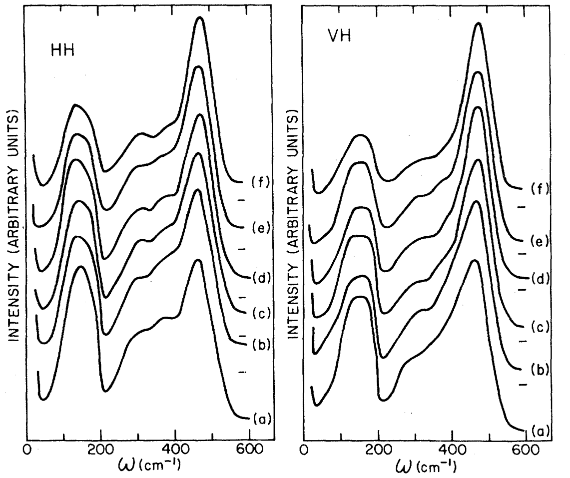

FIG. 1. Variation of the 300-K Raman spectra (normalized at 475 cm^{-1}) with T_p for sputtered and T_s for CVD a-Si for the *VH* and the *HH* components. The horizontal zero bars are taken at $\omega = 1200$ cm^{-1}. T_p: (a) = 30 °C, (b) = 200 °C, (c) = 400 °C, (d) = 500 °C, (e) = 560 °C; T_s: (f) = 525 °C.

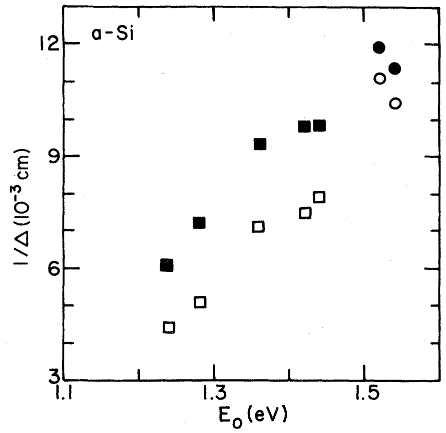

FIG. 2. Comparison of the inverse Raman full widths, Δ_{VH}^{-1} (solid) and Δ_{HH}^{-1} (open) with the optical gap for sputtered (square) and CVD (circle) a-Si films.

lower frequencies. At low frequencies the trend of increasing TA-like peak intensity is complicated by an apparent increase in stray light background. While the spectra clearly indicate an enhancement of the low-frequency scattering in low T_p films, further studies are required to more accurately determine the ratio $I_{\rm TA}/I_{\rm TO}$. The high-frequency region is, however, less sensitive to the background, particularly the *VH* Raman component. It is useful to note that the present changes observed in the Raman spectra with T_p differ from earlier measurements on a-Si prepared under a variety of conditions and methods which suggested little change in the spectra with deposition conditions.[2] The present results in sputtered a-Si and CVD a-Si indicate, however, that substantial changes in the Raman spectra are possible, particularly for the deposition conditions employed here.

The optical-absorption spectra, $\alpha(\nu)$, of the sputtered films indicate a shift to higher frequencies with increasing substrate temperature with a qualitatively similar trend to that observed in evaporated and sputtered a-Ge.[1,8] In contrast, the CVD films, whose spectra are relatively independent of deposition temperature,[7] exhibit a somewhat more rapid variation of $\alpha(\nu)$ than the sputtered films. In Fig. 2 the inverse TO Raman widths, $1/\Delta_{VH}$ and $1/\Delta_{HH}$, are plotted as a function of the optical gap, E_0. The optical gap was obtained from Tauc plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$, while the Raman full widths at half maximum were obtained assuming a zero level to correspond to the intensity at 1200 cm^{-1}; at this frequency both first- and second-order scattering vanish. The *HH* width defined in this manner overlaps the lower-frequency LA-like band, so that the peak width is enhanced at low T_p. Represented in this fashion the data of Fig. 2 are conveniently independent of the precise substrate temperature. Figure 2 clearly indicates a direct correlation between quite different parameters that are a function of the phonon and electron states in the a-Si films. This correspondence between $1/\Delta_i$ and E_0, which both increase with deposition temperature, may be attributed to increasing network order. Also included in Fig. 2 are CVD a-Si film data. The CVD results are in accord with an extrapolation of the trend lines observed on the sputtered films. Figure 2 indicates for the present films a relatively direct proportionality between the optical gap and inverse Raman width. As the Raman spectra may be argued to be intrinsic in nature and dependent on network bonding and structure, this suggests that the optical gap and absorption spectra in this spectral range also have a predominant intrinsic network contribution. Additional evidence for this is provided by the E_0 values in CVD a-Si of variable T_s which are relatively constant, though the void fraction is known to vary substantially.[9] The origin of the changes in the Raman spectra and particularly Δ_i may be attributed primarily to variations in short-range order with T_s. Theoretical calculations[10] by Meek on models of a-Ge with different bond-angle distributions and ring statistics[11] have shown that small variations in short-range order may substantially increase the width of the high-frequency TO-like phonon band as well as decrease its relative intensity. In particular, a small increase in the bond-angle variation, $\Delta\theta_{\rm rms}$, results in large changes in the phonon density of states. While the Raman spectra of Fig. 1 do not directly yield the phonon densities of states, $\rho(\omega)$, their form, particularly within the higher-frequency spectral range for the *VH* component, may be regarded as a reasonable first approximation to the shapes of $\rho(\omega)$. This assumes for the high-frequency band that the coupling parameter variation is a smooth function of frequency in that interval and relatively constant higher-order phonon scattering contributions. This further assumes that changes in the *VH* component are not due to intermediate-range order. Thus, to a first approximation, the changes in $1/\Delta_{VH}$ primarily reflect relative variations in the TO-like width of the phonon density of states. Coupling parameter effects may be expected to modify more appreciably the low-frequency Raman spectra relative to the density of states. The somewhat different trend between Δ_{VH} and Δ_{HH} with E_0 is attributed to weak-coupling parameter effects, particularly for the *HH* component. The asymmetry and higher background level for the *HH* spectra also makes a determination of the TO width more difficult. The observation of increased relative TA intensity for both *VH* and *HH* components is attributed, in part, to modification of $\rho(\omega)$ with disorder which shifts phonon states to lower frequency.[5]

The correspondence between the Raman and optical spectra suggests that short-range order variations associated with changes in the bond-angle distributions, $P(\theta)$, may also directly modify the optical gap. Theoretical calculations[12,13] on structural models of *a*-Si have suggested such an effect. In contrast, it has also been suggested that the dihedal angle distribution, $P(\phi)$, may play an important role on the optical gap of *a*-Si.[14] Changes in $P(\theta)$ also generally result in modifications of $P(\phi)$ as has been noted in topologically varied models of *a*-Ge.[11] It is thus possible that some of the variation of E_0 with T_s may arise from changes in $P(\phi)$ *indirectly* via changes in $P(\theta)$. This possible effect of $P(\phi)$ would correspond to the influence of intermediate-range order on E_0, in contrast to the effect of short-range $P(\theta)$ variations. Changes in ring statistics with $P(\phi)$ and $P(\theta)$ have also been considered to influence the optical gap, though to a lesser degree.[13]

A comparison of the structural models[11] employed by Meek[10] indicate that the present changes in $\Delta\theta_{\rm rms}$ are not large. Radial-distribution-function studies[1] in sputtered *a*-Ge for $T_p = 150$ and 350 °C indicate an $\sim$7% decrease in $\Delta\theta_{\rm rms}$ from 10.8° to 10°. Thus small modifications of $\Delta\theta_{\rm rms} < 1-1.5°$ between the least- and most-ordered *a*-Si films appear to account for the changes in the Raman spectra observed here. Further study is required, however, to determine to what extent the results of Fig. 2 extend to other deposition conditions or methods of preparation. Preliminary results on *a*-Ge also indicate a correspondence between E_0 and Δ_i^{-1}.[5]

Changes in the optical gap with short-range order imply that band-tail states may also, in part, be a function of network structural disorder. Thus the often observed sharpening of the Urbach edge with increasing gap in both *a*-Ge, *a*-Si, and *a*-Si:H alloys suggests a decrease in band-tail states with increasing order.[1,8,15] This trend may also extend further into the midgap region, where transport and spin-resonance measurements have indicated in *a*-Si (Ref. 16) a decreasing density of states with T_s. Whether changes in the full range of gap states may be directly traced, in part, to short-range order modifications is an open question at this time. It is possible, e.g., that modifications of $P(\theta)$ may result in changes in both $P(\phi)$ and ring statistics that may in turn result in a distribution of defect states of variable range. It is useful to note that the sharper $P(\theta)$ form in many bulk pnictide and chalcogenide amorphous solids[3] may be the primary factor in yielding a narrower, qualitatively different distribution of defect and band-edge states relative to *a*-Si and *a*-Ge. Thus the present results in *a*-Si relating changes in the Raman spectra and optical gap provide a link between structural order variations and band-edge electronic states that may have broader implications for amorphous solids. The variability of *a*-Si to deposition conditions also emphasizes the need for structural models of changing order, rather than individual energy minimized configurations.

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