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Raman coupling-parameter variation in amorphous silicon

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The Raman coupling-parameter variation of an *a*-Si film has been obtained from depolarized–Raman-scattering measurements by using inelastic–neutron-scattering results. The frequency variation is found to be quite similar to that of *a*-Ge with appropriate frequency scaling. The coupling parameter is utilized to calculate from the Raman spectra the approximate density of states of a maximally ordered, chemical-vapor-deposited *a*-Si film. The resulting density of states is shown to be in good agreement with the theoretical density of states of a Beeman model which is estimated to have a similar bond-angle deviation.

INTRODUCTION

Raman-scattering measurements in amorphous solids provide an important means of studying the dynamics of noncrystalline systems and yield information about variations in local structural order.[1-3] As the first-order Raman scattering is related in phenomenological models to a coupling-parameter–weighted density of states, it is important to determine the frequency variation of this parameter. Recent studies in two forms of *a*-Ge with large differences in short-range order (SRO) (Ref. 4) indicate that the density of states is the primary variable and that changes of the coupling parameter with such order appear to be relatively small. Given extensive interest in the vibrational properties of the related *a*-Si system, including its alloys with H, it is useful to determine the form of its frequency-dependent coupling parameter. In particular, it is of interest to know to what extent the frequency variation is similar to that of *a*-Ge when frequency scaling is employed. Previous coupling-parameter estimated for *a*-Si have compared neutron and Raman data on differently prepared films.[5] In the present study, similar films are employed to obtain the coupling-parameter variation.

Information about the coupling-parameter variation provides a means of utilizing high-resolution Raman spectra to obtain a useful estimate of the phonon density of states for thin films that are prohibitively difficult to obtain by neutron scattering experiments. Currently, inelastic neutron scattering requires rather large quantities of materials that may not be conveniently prepared. Of particular interest in this work is an estimate of the phonon density of states of *a*-Si prepared under conditions in which the SRO is maximized.

EXPERIMENT

Raman-scattering measurements were performed on *a*-Si films prepared at the Ames Laboratory at an argon rf sputtering pressure of 50 mTorr. These conditions[6] were also utilized for the preparation of samples for inelastic neutron scattering. Substrates of crystalline Si were employed for the Raman measurements, while Al was utilized for inelastic neutron samples. A Spex Industries third monochromator system was employed for room-temperature Raman measurements using 5145-Å excitation wavelength. The reduced TO width of the Raman spectrum (87 cm^{-1}) indicates that the order within the *a*-Si is relatively high in magnitude given the range of widths between most and least ordered samples of 78–120 cm^{-1}.[7] This is consistent with the high-pressure sputtering conditions.[8] In order to determine the stray-light background influence, which is related to film surface roughness, about 2000 Å of Al was deposited on the *a*-Si film by evaporation after Raman measurements. The form of the stray-light background was estimated from the Al-film spectrum.

RESULTS AND DISCUSSION

The depolarized, *VH* Raman spectrum of *a*-Si is shown in Fig. 1 along with the results of inelastic neutron scattering of Kamitakahara *et al.*[9] To obtain the first-order coupling parameter $\tilde{C}_\alpha(\omega)$ for component α, the relation[1]

$$I_\alpha^{(1)}(\omega)=\tilde{C}_\alpha(\omega)(n+1)\omega^{-1}G(\omega)$$

was utilized, where $n+1$ is the Stokes statistical factor and $G(\omega)$ the phonon density of states.[1] This neglects small contributions from second-order scattering that may enhance the high-frequency intensity and $\tilde{C}_\alpha(\omega)$. The resolution of the Raman-scattering measurements (4 cm^{-1}) is significantly greater than that of the neutron results, which depend on the phonon frequency ($\Delta\omega/\omega=7.6\%$). The latter was estimated by comparing the density of states of crystalline Si obtained from neutron scattering[9] and second-order Raman scattering.[10] The coupling parameter was calculated by broadening the Raman results to the same resolution as that of the neutron measurements. Previous studies in *a*-Ge, which estimated the effect of lower resolution, indicate that this procedure yields the general form of the coupling parameter reasonably well.[4]

The resulting coupling-parameter variation for the depolarized component ($\alpha = VH$) of *a*-Si and that of *a*-Ge are shown in Fig. 2. As *a*-Si and *a*-Ge give similar Ra-

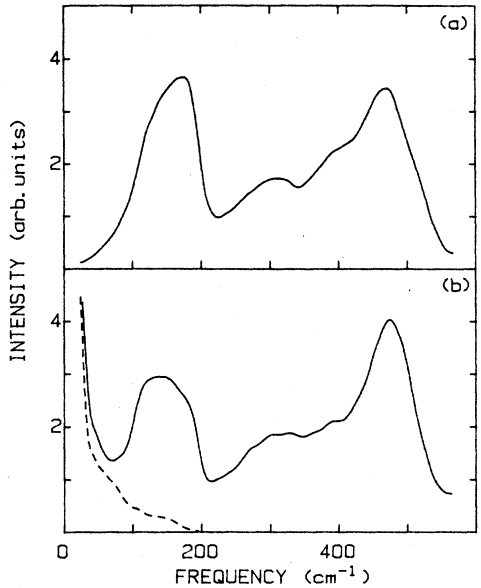

FIG. 1. (a) Neutron-determined phonon density of states (Ref. 9) and (b) *VH* Raman spectra of *a*-Si. The dashed line is the estimated Raman stray-light background.

man spectra, the frequency scale of *a*-Ge has been enlarged by multiplying the ratio of *a*-Si to *a*-Ge high-frequency TO peaks. The two curves are area normalized. As Fig. 2. illustrates, the behavior of the coupling-parameter–frequency variation is very similar for both tetrahedral amorphous semiconductors when scaling is employed. This result is physically plausible given the forms of the Raman- and inelastic-neutron-scattering spectra.[1,4,9] Both Si and Ge coupling parameters indicate small variations about a monotonically increasing behavior. These variations may be due, in part, to both limitations of the neutron-scattering analysis employed to obtain $G(\omega)$ or to nonmonotonic behavior in the coupling parameter. For *a*-Si, the amplitudes of small features are comparable to the experimental uncertainty in both intermediate-frequency $[\Delta C(\omega)/C(\omega)\simeq 10\%]$ and high-frequency $[\Delta C(\omega)/C(\omega)\simeq 5\%]$ regions. In addition, small second-order contributions which are expected to be broad in form for the Raman spectra may modify the higher-frequency coupling parameter to a small degree. At low frequencies, previous experimental and theoretical studies[11] indicate that for the regime of Debye-like modes, $\tilde{C}(\omega)$ is approximately quadratic in frequency. For *a*-Si the range for this behavior is estimated to be similar to that of *c*-Si, i.e., for $\omega < 64$ cm^{-1}.

As implied in Ref. 4, the coupling parameter may be combined with depolarized Raman spectra to obtain the approximate phonon density of states. Figure 3 indicates the calculated density of states of the anneal-stable form of *a*-Si prepared by the conventional chemical-vapor-deposition (CVD) process. This material, with $[H] < 0.2\%$, exhibits a minimum value of the *VH* width.[12] The addition of *H* at higher concentration results in an $\sim 5\%$ further narrowing for homogeneous CVD films.[13,14] Also exhibited in Fig. 3 as a dashed curve is the theoretical density of states of *a*-Si obtained for model *B* of Beeman.[7] The later represents the average of the $G(\omega)$ calculated for 500- and 519-atom models. The lattice dynamics was determined by a two-parameter model with a ratio of the Born parameters β/α of 0.143.

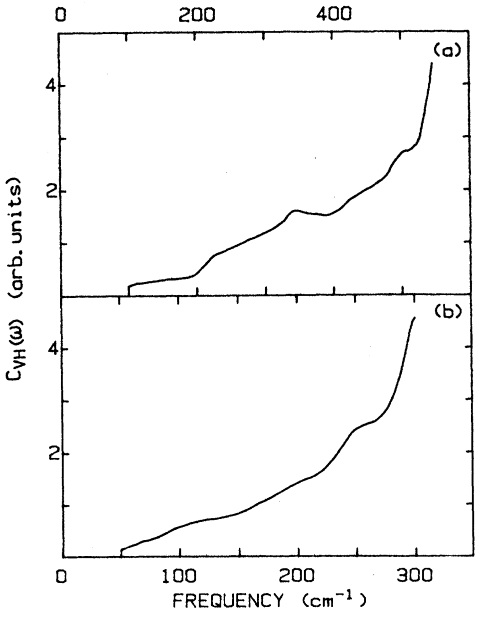

FIG. 2. Coupling parameters for the *VH* Raman component for (a) *a*-Si (the background has been subtracted) and (b) *a*-Ge (Ref. 4). The frequency scaling has been normalized to the TO Raman peak positions. The curves are area normalized.

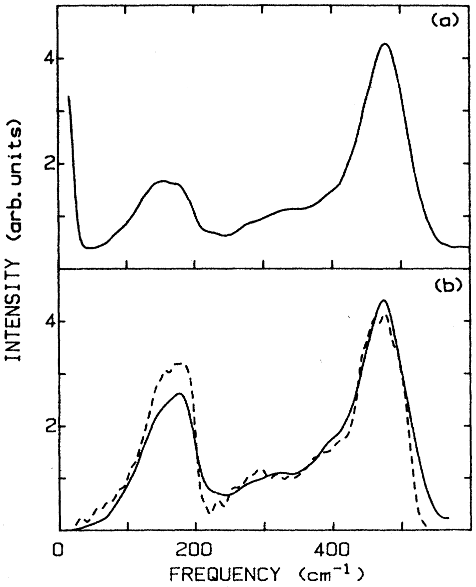

FIG. 3. (a) *VH* Raman spectrum of CVD *a*-Si and (b) comparison of calculated (solid line) and theoretical (dashed line) phonon density of states. The curves in (b) are area normalized and for the calculated one the low-frequency region has been modified by considering the background influence.

The average bond-angle deviation of these models, which is the dominate SRO parameter, is approximately 9.4°.[7] This value is comparable to that estimated for the structural order in anneal-stable, CVD a-Si based on recent radial-distribution-function studies.[15] As shown in Fig. 3, the comparison is excellent between theory and experiment for both peak positions and relative intensities. Small differences in the area-normalized intensities for the low-energy TA peak may be a consequence of small variations of $\widetilde{C}_{VH}(\omega)$ with structural order noted in a-Ge.[4] The results in Fig. 3 support the structural and lattice-dynamical models and their sensitivity to SRO. Similar estimates of the density of states for other forms of a-Si may be obtained from depolarized Raman spectra and the present coupling-parameter frequency dependence.

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