RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 31, NUMBER 8 15 APRIL 1985

Phonons in amorphous semiconductor superlattices

N. Maley and J. S. Lannin
Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802
(Received 28 December 1984)

Raman scattering measurements on amorphous *a*-Si:H/*a*-SiN$_x$:H and *a*-Si:H/*a*-SiO$_x$ superlattices indicate the first observation of heterostructure effects on the phonons of noncrystalline solids. With decreasing thickness the *a*-Si:H Raman spectra imply increased bond-angle disorder associated with interfacial induced modifications of network formation. The results suggest that interfacial bonding constraints in amorphous superlattices result in local disorder that qualitatively differs in character from that of crystalline systems.

It has recently been discovered that thin-film amorphous semiconductors can be prepared in heterostructure configurations with crystalline superlatticelike properties.[1] The electronic properties of *a*-Si:H/dielectric structures have exhibited, for example, quantum confinement effects and charge localization in these systems. The optical or Tauc gap of the *a*-Si:H layers has been found as a consequence to increase as its thickness decreases.[1,2] Electroabsorption studies[3] have implied highly localized charge transfer from *a*-Si:H to the dielectric layer. It has been suggested that this charge transfer is a consequence of crystal-like lattice defects at the interface.[3] Little is known, however, about the structure of these interfaces as well as the extent to which the structure of the layers is modified by their presence.

The formation of an layers of *a*-Si:H alloys with dielectric layers provides a means of modifying phonons by the production of a local strain field or by influencing film formation. Recent studies in *a*-Si:H alloys have demonstrated that Raman scattering is a sensitive means of observing quantitative changes in the microscopic structural order, particularly the bond-angle distribution width, $\Delta\theta$, as a function of deposition conditions.[4,5] In amorphous solids it is generally believed that phonons are highly localized excitations except at low frequencies. In addition, the absence of crystal momentum conservation in amorphous solids enables Raman scattering to study the changes in the full spectral density of vibrational states. It is thus of interest to determine if and in what manner the phonon spectra in amorphous superlattices have their behavior modified. The Raman scattering data presented below indicate that the interface results in increased structural disorder without a net microscopic strain effect similar to that at crystalline superlattice interfaces. This implies that the bond-angle distribution of the as-growing films of *a*-Si:H is modified due to local distortional effects at individual bonds in the network. The structural consequences of an interface in amorphous solids are thus different from those of crystalline solids. In the latter it has been observed in Raman scattering studies that local strain fields result in a shift of the $k \simeq 0$ phonons without appreciable broadening.[6]

The superlattice films reported here of *a*-Si:H/*a*-SiN$_x$:H were prepared at the University of Chicago by the group of Professor H. Fritzsche. Substrates at 250 °C were periodically exposed to alternating reactive gases of SiH_4 and 3.4:1 mixtures of NH_3 and SiH_4 without extinguishing the rf glow-discharge plasma. In addition, an *a*-Si:H/SiO$_x$ structure was prepared by oxidizing the *a*-Si:H film with an O plasma in a secondary chamber described earlier.[2] Film thickness was determined by x-ray diffraction, optical interference fringe and Talysurf measurements. Anode as well as cathode films with *a*-Si:H layers of thickness $d \simeq 20$–80 Å were prepared simultaneously for study. Previous infrared measurements[7] indicate some differences in H incorporation between anode and cathode films. Raman measurements on pure *a*-SiN$_x$:H films of thickness several times that employed for the superlattices indicate that this layer does not contribute to the spectra. Both depolarized (VH) and polarized (HH) Raman spectra were performed at 300 K using 5145-Å Ar laser excitation. A Spex third-monochromator system was employed for obtaining the inelastic spectra.

Figure 1 compares the VH Raman spectra of two superlattice films deposited on the anode surface and that of a single thick *a*-Si:H film. The spectra have been normalized for comparison to the same maximum TO-like peak intensity at 475 cm^{-1}. With decreasing thickness of the *a*-Si:H layer the spectra broaden in the high-frequency region, while maintaining essentially the same peak position. In addition, the lower- and intermediate-frequency spectral ranges are also modified as thickness decreases. Similar trends are also observed for the cathode films as well as in the HH Raman configuration. The $d = 12$ Å film in Fig. 1 indicates an additional low-frequency shoulder at ~ 50 cm^{-1} which is not observed, however, in the HH configuration. This indicates additional scattering which is not due to the glass substrate and whose origin is under further study in very thin layers.

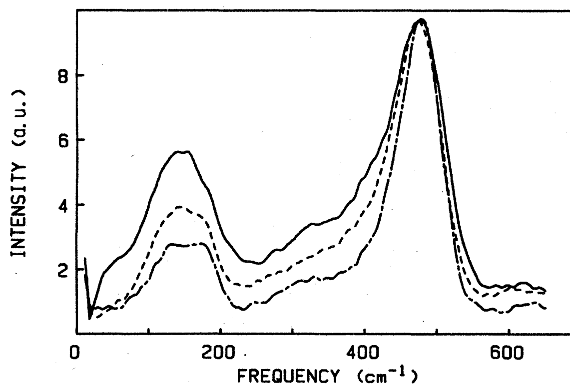

FIG. 1. Comparison of the VH Raman spectra of *a*-Si:H/*a*-SiN$_x$:H superlattice anode films of variable thickness of *a*-Si:H. $d = 12$ Å (solid), $d = 24$ Å (dashed), and individual thick *a*-Si:H film (broken). The peaks have been normalized to the same maximum TO intensities.

 ©1985 The American Physical Society

The results of Fig. 1 clearly contrast with crystalline c-$Ge_{1-x}Si_x$/c-Si superlattices in which the $k \simeq 0$ modes shift in frequency due to interfacial induced strain, but do not broaden.[6] The constancy of the peak position at that of bulk films also indicates that no appreciable net macroscopic stress is present in the a-Si:H layers as this has been shown to shift the TO peak to higher frequencies.[8] Figure 1 also indicates changes in the scattering intensity at 620 cm^{-1}. The increase of this scattering with the relative increase of the TA to TO peak ratios demonstrates that the changes are due to an increase in two-phonon combination processes with disorder.[4]

The increase of the TO bandwidth by a factor of 1.5 and of the increase in intensity of the low-frequency TA-like band with decreasing d are qualitatively similar to that observed in a-$Si_{1-x}H_x$ alloys as well as pure a-Si and a-Ge that arise from changes in structural order.[4,5] In these bulk films the changes in structural order are a consequence of modifications of $\Delta\theta$. The first-order VH Raman intensity for Stokes scattering varies as $I_{VH}^{(1)}(\omega) \sim \omega^{-1}(n+1) \times \overline{C}_{VH}(\omega)\rho(\omega)$, where $n+1$ is the phonon population factor, $\rho(\omega)$ the phonon density of states, and $\overline{C}_{VH}(\omega)$ an average coupling parameter. The latter is related in bond polarizability theory to a weighted sum of contributions from $({}_1D)^2$ and $({}_2D)^2$ polarizability modulation terms.[4] The changes observed in Fig. 1 are thus a consequence of variations of $\rho(\omega)$ or $\overline{C}_{VH}(\omega)$ or both with thickness. Theoretical studies indicate that changes in structural order within the first coordination sphere result in modifications of the phonon density of states[9] and ${}_2D$ Raman component[10] qualitatively similar to the trends observed experimentally in a-Si and a-Ge. As in thick a-Si films, changes in both the VH and HH Raman components imply changes in the phonon density of states with bond-angle distribution width. This suggests that the changes in the Raman spectra of superlattice films of Fig. 1 are also a consequence of modification of the a-Si:H network values of $\Delta\theta$.

Figure 2 indicates the variation with thickness of the full width at half maximum of the TO-like peak, Δ_i, for VH and HH components for a-Si:H in anode as well as cathode-deposited films. The horizontal lines at thicknesses above ~ 100 Å are the bulk a-Si:H values. Measurements on a single a-Si:H film of $d \simeq 100$ Å deposited on a-SiO_2 indicate the absence of changes in the spectra relative to bulk films of similar composition.[11] Figure 2 clearly indicates the systematic, similar variation of the TO full width at half maximum with thickness for the two different Raman components in anode and cathode films. This behavior qualitatively parallels changes in the Urbach slope in these superlattices.[1] This indicates an increase in the number of localized band-tail states in the thinner, more disordered a-Si:H layers. Although more extensive measurements are required to precisely determine the range of such interface effects, the data in Fig. 2 suggest that for $d \simeq 100$ Å, interfacial effects become rather small.

A quantitative estimate of the changes in $\Delta\theta$ with a-Si:H layer thickness may be obtained by comparison with results in a-Ge relating Δ_{VH} to $\Delta\theta$. Similar behavior of the Raman width parameter and optical gap as well as comparable estimates of $\Delta\theta$ in a-Si (Ref. 12) and a-Ge (Ref. 13) imply that a scaling between these systems is a reasonable first approximation. If a linear variation of the form $\delta\Delta_{VH}/\Delta_{VH}^0 = C(\delta\Delta\theta/\Delta\theta_0)$ is assumed for a-Ge and a-Si:H films, where C is a constant, then variations of $\Delta\theta$ may be obtained.

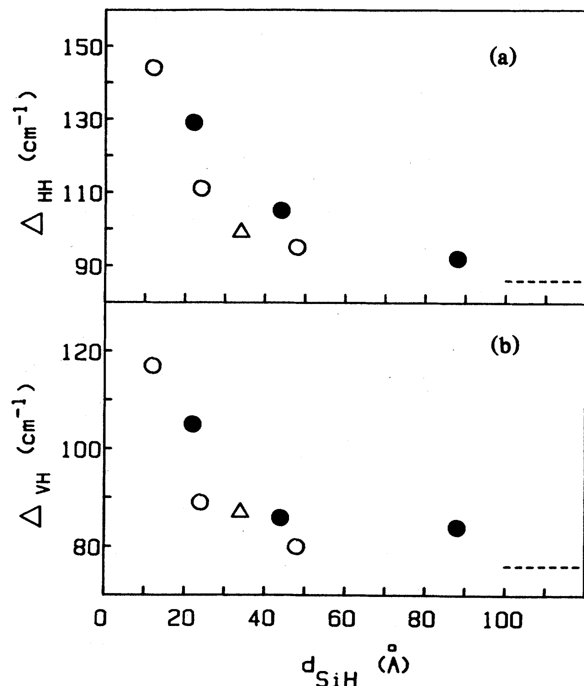

FIG. 2. Variation of the full width at half maximum of the TO peaks of a-Si:H/a-SiN_x:H films for the (a) HH Raman component and (b) VH Raman component. Open symbols represent anode films and solid symbols cathode films. The triangles correspond to an a-Si:H/a-SiO_x film. The dashed horizontal lines indicate the thick single-layer values.

Here $\Delta\theta_0$ and Δ_{VH}^0 correspond to the minimum values of the bond-angle distribution widths and Raman parameters,[4] respectively. In pure a-Ge this corresponds to anneal stable material where $\Delta\theta_0$ is estimated to be 9°.[4,14] For pure a-Si and a-Ge the experimental results yield $(\Delta_{VH}^0)_{Si} \simeq 1.5(\Delta_{VH}^0)_{Ge}$. Under these assumptions, the Raman width variations yield a change in $\Delta\theta$ between the 12- and 80-Å layers of $\sim 1.2°$. Thus, if the value of $\Delta\theta_0 \simeq 9°$ is assumed for bulk a-Si:H, bond-angle deviations of 10.2° and 9.1° are estimated for the 12- and 80-Å films, respectively.

In thick a-Si and a-Ge films the optical gap increases in an approximately linear manner with the inverse TO width for the VH and HH components.[4,5] This increase in electronic order as the phonon spectrum narrows is opposite to that observed in the superlattices studied here.[1,2] As the Raman spectra imply a decrease in a-Si:H bond-angle order with decreasing thickness, the interface induced changes in the optical gap of the superlattices are larger than those referenced to the thick, nonsuperlattice film. An extrapolation of the variation of the optical gap in a-$Si_{1-x}H_x$ films with Raman width[4] indicates from the 1.5 factor change in TO width that a corresponding *additional* increase in the gap of ~ 0.20–0.25 eV occurs in the 12 Å a-Si:H film due to carrier confinement.

The disorder within the a-Si:H layers need not in general be homogeneous. In particular, it is possible that bonding constraints on the first layer interface atoms of the growing film as well as on the second bonded neighbors result in greater angular distortion than in material further removed from the interface. Such localized, increased disorder could result in the behavior noted in Fig. 1 as well as result in part

in charge localization and local electric field effects that have been observed in these superlattices. Theoretical studies[15] have suggested that such bond-angle distortions can lead to charge transfer and fluctuation phenomena. It is thus possible that the observed local interfacial fields are a consequence of bond-angle distortions rather than the formation of structural defects analogous to crystalline misfit dislocations that have recently been suggested.[3] No evidence to date exists for the presence of such extended defects in amorphous solids.

It is also possible that finite thickness or boundary effects perpendicular to the film plane influence the vibrational states or Raman coupling parameters. The extended range of thickness, noted in Fig. 2, for which this effect is observed, suggests that the disorder is the more probable origin of the observed spectral changes. In particular, the phonon eigenvectors are expected to be highly localized in amorphous solids at high frequencies[16] and as such relatively insensitive to finite boundary effects. It is useful to note that variations in H content that might perhaps arise in the *a*-Si:H layers with d are not expected to significantly modify the present results as the Raman widths are relatively independent of H in homogeneous CVD and glow-discharge films.[17]

In summary, the present Raman spectra indicate the first reported influence of interfaces on the phonons of noncrystalline solids. The *a*-Si:H/SiN_x:H and *a*-Si:H/SiO_x superlattice spectra indicate a decrease in *a*-Si:H structural order with thickness due to interface-induced bond-angle disorder. In contrast to crystalline superlattices, wherein either dislocations are produced or the lattice constants are modified by interfacial-induced strain, the amorphous network is modified by local bond-angle variations. The increase in the mean bond-angle distortion with interface-induced disorder results in an increased local strain and free energy. The disordered noncrystalline network thus allows, via its inherent structural flexibility, interfacial effects to be incorporated in a manner qualitatively different from that of periodic systems. It is not clear at this time whether or not this effect is solely dictated by growth effects in Si:H due to bond-angle constraints at the dielectric interface. It is also possible that the next dielectric layer may subsequently lead to some lattice relaxation via changes in the bond-angle distribution of the previously grown layer.

We wish to gratefully thank Professor Hellmut Fritzsche and his group at the University of Chicago for providing superlattice samples. This work was supported by the National Science Foundation under Grant No. DMR84-1909033.

[1]B. Abeles and T. Tiedje, Phys. Rev. Lett. **51**, 2003 (1983).

[2]J. Kakalios, H. Fritzsche, N. Ibaraki, and S. Ovshinsky, J. Non-Cryst. Solids **66**, 339 (1984).

[3]C. B. Roxlo, B. Abeles, and T. Tiedje, Phys. Rev. Lett. **52**, 1994 (1984).

[4]J. S. Lannin, in *Semiconductors and Semimetals,* edited by J. Pankove (Academic, New York, 1984), Vol. 21B, p. 159; note on p. 182 a linear variation of Δ_{VH} with $\Delta\theta$ should be indicated rather than Δ_{VH}^{-1}.

[5]J. S. Lannin, L. J. Pilione, S. T. Kshirsagar, R. Messier, and R. C. Ross, Phys. Rev. B **26**, 3506 (1982).

[6]F. Cerdeira, A. Pinczuk, J. C. Bean, B. Batlogg, and B. A. Wilson, Appl. Phys. Lett. **45**, 1138 (1984).

[7]C. C. Tsai and H. Fritzsche, Sol. Energy Mater. **1**, 29 (1979).

[8]T. Ishidate, K. Inoue, K. Tsuji, and S. Minomura, Solid State Commun. **42**, 197 (1982).

[9]P. E. Meek, in *The Physics of Noncrystalline Solids,* edited by G. H. Frischat (Trans Tech SA, Aedermansdorf, Switzerland, 1977), p. 586.

[10]D. Beeman, R. Tsu, and M. F. Thorpe (unpublished).

[11]C. C. Tsai and R. J. Nemanich, J. Non-Cryst. Solids **35&36**, 1203 (1980).

[12]S. C. Moss and J. F. Graczyk, in *Proceedings of the 10th International Conference on Physics of Semiconductors,* edited by S. P. Keller, J. C. Hensel, and F. Stern (U.S. DOE, Washington, DC, 1970), p. 658.

[13]W. Paul, G. A. N. Connell, and R. J. Temkin, Adv. Phys. **22**, 529 (1983).

[14]J. S. Lannin, N. Maley, and S. T. Kshirsagar, Solid State Commun. **53**, 939 (1985).

[15]L. Gutmann, W. Y. Ching, and J. Rath, Phys. Rev. Lett. **44**, 1513 (1980).

[16]R. J. Bell, Rep. Prog. Phys. **35**, 1315 (1972).

[17]N. Maley, J. S. Lannin, and B. A. Scott, J. Non-Cryst. Solids **59&60**, 201 (1983).