Brief Reports

Near-surface Raman scattering in germanium clusters and ultrathin amorphous films

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Vibrational studies of Ge clusters and ultrathin amorphous semiconducting films have been performed *in situ* in ultrahigh vacuum. A combination of multichannel and interference-enhanced methods has allowed Raman scattering of a solid to be achieved at film thicknesses of less than an equivalent monolayer coverage. Substantial changes in the amorphouslike Raman spectral form with decreasing film thickness indicate the increasing role of near-surface dangling bonds and bond-angle disorder on the phonon density of states. This is confirmed by H chemisorption effects.

Recent studies have allowed information to be obtained about the vibrational states of crystalline surfaces as well as adsorbed molecules.[1] In contrast, it has not been possible to date to study the surface vibrational properties of noncrystalline solids or liquids. This is in part due to the absence of periodicity and the subsequent weak, broadband scattering from near-surface atoms. Difficulties also arise in applying surface-sensitive methods such as electron-energy-loss spectroscopy[1] or infrared absorption[2] as dipolar coupling is required, while He scattering[3] requires an atomically smooth surface. Studies of disordered systems with these methods and surface-enhanced Raman scattering[4] have thus been primarily restricted to date to the study of localized molecular modes of surfaces.

In this Brief Report we report on the use of Raman scattering methods to obtain information about the role of surface and near-surface atoms on the vibrational states of a noncrystalline solid. The Raman spectra obtained on amorphous (*a-*) Ge indicate the significant role of additional bond angle and coordination disorder in the near-surface region on the vibrational states. To achieve the necessary sensitivity of submonolayer detection capability, we have combined two Raman enhancement methods and *in situ* ultrahigh-vacuum measurements. Specifically, the method of interference-enhanced Raman scattering (IERS) (Refs. 5 and 6) has been utilized to enhance the field intensity near the surface of ultrathin films deposited on a trilayer structure, while multichannel Raman scattering (MCRS) has been employed to enhance collection efficiency. The combined use of these methods has allowed a means of studying the full spectral range of amorphous Ge films with a sensitivity that is approximately two orders of magnitude greater than conventional Raman scattering.

The *a-*Ge films reported here were deposited on disor-

dered C layers. As in the case of a number of crystalline metallic systems,[7-9] the Ge weakly interacts with C to form island structures, as noted below. These types of structures have been extensively studied, particularly in transition-metal systems, by electron microscopy and photoelectron and Auger spectroscopies. Valence-band photoemission spectra of transition metals have noted significant narrowing of the *d* bands with film coverage due to a reduction in the average coordination number in the near-surface regions of small islands.[8,9] The present work represents the first study of the vibrational properties of surface-supported semiconductor clusters. Previous studies of matrix isolated clusters have been restricted to very small molecular species with less than five atoms.[10] The Raman spectra demonstrate that in ultrathin films, near-surface structural variations modify the phonon density of states. The additional disorder in the neighborhood of the surface is attributed to the presence of increased bond-angle fluctuations and the presence of reduced coordination number. The latter is associated with dangling bonds on the surface of the amorphous semiconductor network or cluster.

Thin films of *a-*Ge were deposited on low-reflectance trilayer structures composed of Al, *a-*SiO$_2$, and a top layer of ~ 200 Å of C. These layers were prepared on polished Si substrates in conventional high vacuum systems and transferred to ultrahigh vacuum (2×10^{-10} Torr), where they were baked and Ar bombarded by a 200-eV Kaufmann ion source to remove surface contaminants. Films of *a-*Ge were deposited by dc magnetron sputtering at ~ 300 K at Ar pressures of 10^{-3} Torr. A weak Ar band obtained by He II ultraviolet photoemission spectroscopy (UPS) indicates a small incorporation of this gas. Given the high nucleation density of the disordered C substrates, the presence of Ar is not expected to significantly influence film growth. A quartz microbal-

ance calibrated for geometrical effects of flux variations was employed to determine the equivalent film thickness. Based on the surface density of atoms on (111) crystalline Ge, a single equivalent monolayer thickness corresponds to approximately 4 Å of deposited film. Both Auger electron and 16.85-eV Ne(I) ultraviolet photoelectron spectroscopies were utilized to monitor both film growth and the absence of contamination. Multichannel Raman scattering difference spectra were obtained at 5145-Å excitation wavelength using a Spex Industries Triplemate monochromator and an ITT Mepiscron microchannel plate device. The contribution of the C to the Raman scattering in the low-frequency a-Ge spectral range is featureless and thus conveniently subtractable. The high-frequency form of the Raman spectrum for the ~ 200 Å C film indicates a mixture of amorphous and microcrystalline structure.[10-12]

Experimental evidence for island growth of Ge is provided by a combination of Auger, Raman, UPS, and ellipsometry measurements. In Fig. 1, the variation of the Ge (47/52 eV) Auger derivative intensity is shown as a function of Ge coverage. Also shown is the theoretical Auger signal for layerlike growth with an electron escape depth of 6 Å.[13] The differences between the experimental and theoretical curve indicate that neither layerlike nor layer-plus island, Stranski-Krastanov,[14] growth occurs. The form of the Auger spectra is qualitatively in accord with an island (cluster) growth mode. This growth mode is confirmed by $in\ situ$ ellipsometry measurements[15] whose locus of the real versus imaginary parts of the pseudodielectric constants indicate an initial "loop" structure that is indicative of island growth.[16] Modeling studies are in progress to obtain information on the average particle size and spacing. A preliminary modeling of the Auger results for Ge suggests a hemispherical growth of islands separated by roughly 25 Å,[17] while ellipsometry studies suggest a somewhat smaller spacing.[15] These studies suggest partial coalescence for coverages of $\lesssim 6$ Å. Ultraviolet photoemission measurements (Ne I and He I), which exhibit changes in the Ge p band with decreasing coverage, indicate that beyond ~ 12 Å, quite
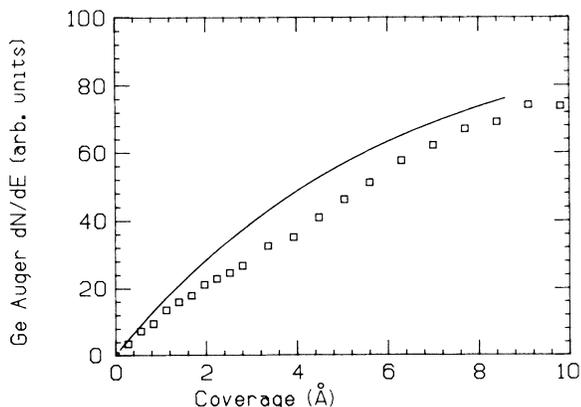
substantial coalescence has occurred.[17] The small size of the Ge clusters prepared here, their relatively low atomic number, and amorphouslike character have precluded to date their direct observation in very-high-resolution transmission electron microscopy studies utilizing 50-Å-thick C substrates.

Figure 2 indicates the variation of the difference Raman spectra, after substrate subtraction, for a range of equivalent thicknesses. The polarization unanalyzed, HU, spectra currently have a detection limit of ~ 0.4 equivalent monolayers. The Raman spectra exhibit changes in the width and relative intensity of the higher-frequency TO band that are qualitatively similar to that observed in thick a-Ge films with preparation or anneal conditions. The origin of these changes has been associated with variations in the distribution of bond angles in the amorphous structure.[18] The width changes in thick films primarily indicate changes in the phonon density of states, as the Raman coupling parameter changes are a weak function of short-range order.[19] The changes in the TO width in the present films are also somewhat analogous to those observed for amorphous multilayer structures of a-Si:H/a-SiN$_x$.[20,21] In these structures the changes in the TO width of the a-Si:H Raman spectra have been attributed to additional interfacial disorder within $\sim 2-3$ bond lengths of the interface. In contrast to thick film or multilayer spectra, the present results are distinguished by large shifts to lower frequencies of the TO peak with decreasing coverage. In addition, the widths of the TO peaks, determined from the high-

FIG. 1. Ge Auger dN/dE signal for 47/52 transition. The solid curve is the predicted intensity for layerlike growth with a 6 Å electron escape depth.
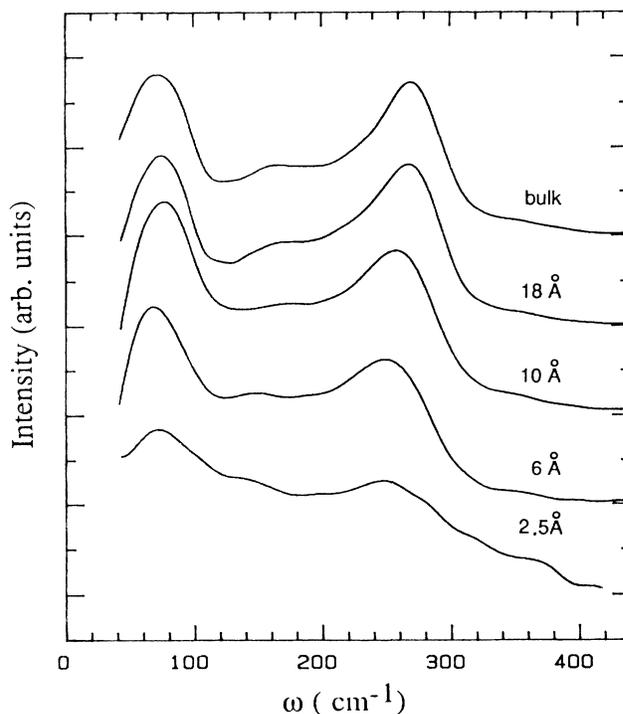
FIG. 2. Comparison of depolarized (VH) and 2.5 Å HU Raman spectra for five film thicknesses, approximately normalized to TO peak intensity. Note the change of TO position and width with coverage. Arrows indicate thick film values.

frequency portion of the peak, exceed that of thick a-Ge films deposited and studied *in situ* at 90 K.[22] The shift of $\sim 10 \pm 2 \%$ observed in Figs. 2 and 3 is appreciably larger than the maximum shift of $\sim 2.5\%$ noted in a-Ge and a-Si:H films prepared under diverse conditions.[23,24] The origin of the latter thin-film shift has been unclear.

In Fig. 3, a summary of the values of the half-widths and shifts is shown by open symbols; the widths were determined from the high-frequency side of the TO peak. The large shifts observed at low coverages suggest that structural changes occur in clusters and near-surface regions that are not present to the same degree in conventional thin films of thickness > 50–100 Å. We attribute the appreciable shift to the increased fraction of threefold-bonded atoms in such clusters and ultrathin films. Theoretical support for this is provided by calculations of Biswas *et al.*[25,26] of the local density of states of threefold-bonded atoms within models containing ~ 500 atoms. The local densities of states clearly indicate that threefold-bonded atoms have a reduction in the TO peak in the density of states assuming similar force constants to fourfold a-Ge. The larger shift observed in the experi-

FIG. 3. Variation of (a) higher-frequency portion of the TO peak half-width and (b) TO peak positions with coverage for both VH (open circles) and HH or HU (open triangles) Raman components. Solid symbols represent H chemisorption data. Error bars are shown at selected points for clarity.

mental results implies that the force constant is also reduced by the presence of a dangling-bond orbital. The contribution of threefold- and fourfold-bonded atoms to the density of states of clusters also implies that the TO width increase may be due to both bond angle and coordination disorder.

An experimental confirmation of the influence of dangling-bond orbitals on the phonon spectra is provided by Raman spectra obtained on clusters and films to which atomic H is chemisorbed. Use of a hot filament to dissociate H_2, which is nonreactive with a-Ge, allows H to bond to surface and near-surface dangling bonds. Auger spectra indicate essentially no change in the Ge and C signals upon the addition of H, demonstrating an unchanged microstructure. UPS difference spectra[27] indicate a shoulder at ~ 5-eV binding energy that is due to the formation of Ge—H bonds.[28] The influence of H on the widths and TO peak positions is shown in Fig. 3 by the solid symbols. Of importance is the observation that the TO peak is essentially shifted back to its thick-film value of 269 cm^{-1} independent of coverage. This is consistent with the essential independence of the TO peak of a-Ge:H and a-Si:H alloys to H concentration.[29] The observed effect of H on the Raman spectra thus demonstrates that the initial shift of the TO peak with decreasing coverage is due to the presence of primarily threefold-bonded atoms. This is also consistent with theoretical calculations which indicate that H bonded to threefold sites increases the TO peak frequency near to its fourfold value.[25] The experimental and theoretical results thus suggest that the predominant origin of the TO peak shift is due to the reduction in the restoring force on neighboring Ge atoms as coordination is lowered. This contrasts with the possible effect of increased bond charge in neighboring Ge sites of dangling bonds that would increase the TO peak frequency. Other changes in the lower-frequency TA spectral region, which are shown in Fig. 2 with decreasing coverage, also occur in a manner consistent with this conclusion. Such changes are also consistent with local density of states calculations which indicate a reduction of the TA peak frequency and an increase in the TA-to-TO intensity ratio for threefold bonded sites. The observed narrowing of the TO peak with H chemisorption is in accord with a substantial initial coordination disorder contribution to the width. Further detailed measurements are required to determine the extent to which H may also order neighboring, fourfold-bonded angles. Additional support for a reduction of average coordination of Ge atoms in the near-surface region of clusters and ultrathin films is provided by UPS spectral narrowing of the p band with decreasing coverage.[17]

In summary, the present work has demonstrated the capability of obtaining Raman spectra for amorphous and crystalline solids at monolayer coverages. The results on amorphous Ge clusters have demonstrated the important contribution of dangling-bond effects on the phonon density of states. This is confirmed by H chemisorption studies and theoretical calculations of the local densities of states.

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