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Variations in atomic structure of liquid bismuth clusters

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A large number of elemental and compound semiconductors in bulk form become metallic upon melting due to changes in the local atomic structure occurring in the transition from the solid to the liquid state. We report studies of the vibrational properties of liquid Bi clusters that suggest that for the smaller sizes this atomic structure transition does not occur. Using interference enhanced Raman spectroscopy, *in situ* studies of bismuth ultrathin films, supported on weakly interacting carbon substrates, have been performed. Changes in the vibrational spectra with liquid cluster size have been correlated with *ex situ* transmission electron microscopy to estimate a critical size below which densification of the structure does not occur. For various models this yields clusters of diameter in the range of ~45–75 Å. [S0163-1829(98)00835-2]

I. INTRODUCTION

It is well known that upon melting many elemental systems, such as metals, maintain a high conductivity and a local liquid structure that is statistically related to that of the solid state. In contrast, semiconductors in elemental or compound form very often exhibit important structural and electronic property changes upon melting.[1] The loss of covalent bonding and the resulting metallic behavior in the liquid state occur for a majority of elemental and binary semiconductors, including the group-IV materials Si and Ge, as well as group-V semimetallic As, Sb, and Bi systems.[2] A basic question concerns the role of size on this behavior, particularly whether small liquid clusters formed from semiconducting solids will be metallic in character.

The properties of solids change in the cluster state due to the increased role of the surface atoms. In addition, small-scale systems may exhibit possible quantum-size effects that modify the electronic states of the small particles. While studies have been performed on molecular and atomic[3,4] clusters in the melting process and in the liquid state, little is known about finite-size effects in other systems such as metals, semimetals, and semiconductors. One exception is the study of the substantial depression of the melting point of metallic[5,6] clusters and of the liquid-solid phase coexistence in Ni_{1029} clusters.[7]

Information about the structure of liquid clusters is limited by the difficulty of performing diffraction measurements in the gas phase or of stable, isolated liquid clusters on substrates. However, structural information can be obtained indirectly by vibrational spectroscopy. For amorphous or liquid semiconductor systems it has been shown that Raman scattering reflects the form of the vibrational density of states.[8] As the peaks in the vibrational density of states are sensitive to changes in short-range order, including bond distances, the number of nearest neighbors, and bond angle distribution disorder, information about local order and bonding may be obtained. It has previously been observed[9] in Raman-scattering studies that clusters of solid Bi formed on a substrate at 110 K exhibit a transformation with decreasing size from nanocrystalline rhombohedral structures to smaller amorphous particles. Transmission-electron microscopy (TEM) images indicate that this transformation occurs in clusters with ~1300 atoms. In the present study of supported liquid Bi clusters it is shown that the liquid state of a cluster containing ~1000 atoms or less differs substantially from that of bulk Bi, with coordination not being modified in the melting process.

II. EXPERIMENT

The experiments were carried out in a multichamber UHV system with a base pressure of 2×10^{-10} Torr. Bismuth clusters were formed *in situ* by dc magnetron sputtering (5 mTorr of Ar, 3 W, 10 A/min) onto trilayer structures of $C/SiO_2/Al$ and subsequently melted by filament heating. For isolated amorphous or liquid clusters Raman scattering is quite weak, requiring methods that enhance the electric field. Therefore, the special $C/SiO_2/Al$ trilayer substrates were used to utilize interference-enhanced Raman scattering, which had been shown to provide a means for *in situ* studies of clusters on surfaces in ultrahigh vacuum.[10]

The Raman-scattering spectra were obtained with a Spex Triplemate spectrometer and a multichannel Mepsicron detector, using 6096 Å excitation from a Spectra Physics 375B dye laser pumped by a Spectra Physics 2020 Ar laser. The choice of the 6096 Å wavelength was determined by the resonance in the Raman cross section of Bi in the red and the maximum of the output power for an R6G dye used in the measurements. All liquid spectra were taken above the bulk melting point of 271 °C. At this temperature coexistence phase phenomena are precluded, as all clusters were in a molten state. Liquid count rates at the measuring temperature of 290 °C were quite low, having a maximum of ~0.13 counts/sec above background for the 6-Å spectrum (see Fig. 1). TEM studies were performed *ex situ* at 20 °C with a Phillips 420T instrument using bright field imaging. The structures of the C coating on the TEM grids and of the top C layer of the trilayers are alike. This allows for similar cluster growth conditions for the Raman and TEM studies.

III. RESULTS AND DISCUSSION

The Raman spectra of Bi films of different phases and thicknesses are shown in Fig. 1. The spectra include nano-

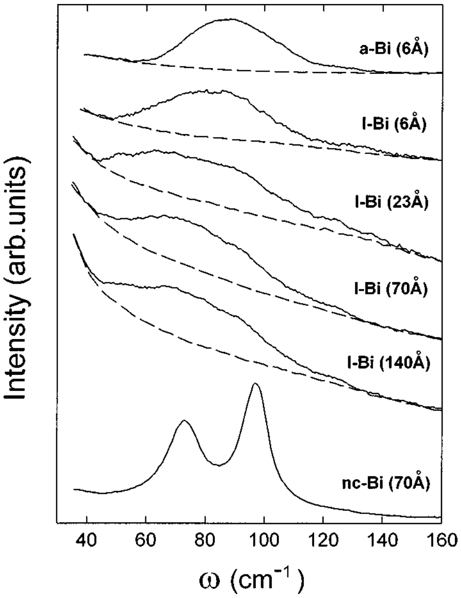

FIG. 1. Variations in Raman scattering for nanocrystalline (nc), liquid (1), and amorphous (a) cluster films for different thicknesses. The estimated stray light background is indicated by dashed lines.

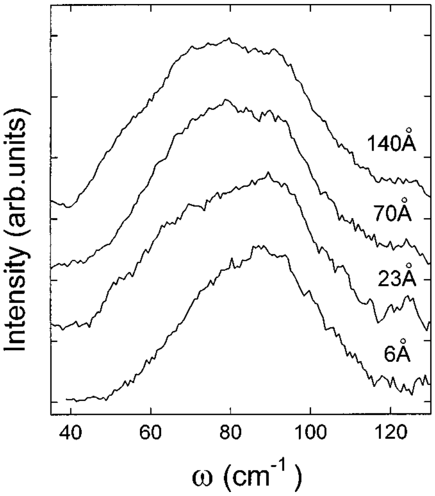

FIG. 2. Thermally reduced Raman spectra of liquid cluster films of different thicknesses.

crystalline (nc) clusters of a 70-Å-thick film, a 6-Å-thick amorphous (a) Bi low-temperature deposited cluster film and series of liquid (1) cluster films. Upon melting of nanocrystalline Bi clusters, the Raman spectrum of the 70-Å-thick film changes from two sharp peaks to a single, very weak broad peak superimposed on a smoothly declining background. Similar behavior is observed upon melting for other thicknesses. This is the first observation, to our knowledge, of Raman scattering from an atomic solid in the liquid state.

The change in the form of the spectra upon melting is due to the loss of periodicity. For nanocrystalline clusters the two peaks in the Raman spectra reflect the two allowed long-wavelength, A_g and E_g modes that are derived from that of bulk crystalline Bi.[9] For amorphous or liquid materials Raman scattering yields a phonon density of states weighted with a matrix coefficient. Therefore, the single broad peak exhibited by the liquid Bi films in Fig. 1 is associated with a maximum in the phonon density of states. The thermally reduced Raman spectra obtained after dividing the background subtracted spectra by the $n+1$ Bose factor yield the liquid cluster spectra shown in Fig. 2. For the films with average mass thickness of 70 and 140 Å the Raman spectra are similar, exhibiting a peak at $\sim 75\ \mathrm{cm}^{-1}$ after subtraction of the stray light background. For the 6- and 23-Å films the spectra show distinct changes in both form and in peak position. These substantial changes imply modification of the phonon density of states with the cluster size, i.e., the short-range order of the liquid clusters appears to be size dependent.

The coordination number of bulk liquid Bi was estimated by inelastic neutron scattering measurements[11] to be $\sim 7 \pm 1$. It is interesting to determine the coordination of atoms within liquid Bi clusters and to estimate the critical size below which the liquid short-range order changes. This change was suggested by the differences in the Raman spectra in Fig. 2. One way to obtain the coordination number is to compare the liquid cluster phonon density of states represented by the Raman spectra with that of other forms of Bi the coordination of which is known. For the 70- and 140-Å film spectra one finds that the peak frequency is considerably below that obtained for threefold-coordinated amorphous Bi clusters[9] (see Fig. 4) or that of the phonon density of states of nanocrystalline Bi, which is estimated from the second-order Raman scattering.[12] However, the peak for these thicker films is found to be near that observed in inelastic tunneling measurements[13] of higher coordinated, continuous thin amorphous superconducting films deposited and studied at low temperatures, <20 K. Structural studies by electron diffraction have indicated approximately sixfold coordination[14] for this latter form of amorphous Bi. These results suggest that the 70- and 140-Å films contain clusters the average coordination of which is similar to that of superconducting amorphous Bi, i.e., close to 6. The reduced phonon frequency for the optical modes is due to the weaker metallic bonding relative to that of amorphous or nanocrystalline, threefold-coordinated atoms. The high coordination for the liquid clusters is also supported by inelastic neutron scattering measurements of bulk liquid Bi. Although the latter spectra are not fully corrected for background, they also yield a peak in the correlation function $J_1(Q,E)$ near that of the 70- and 140-Å films for high Q momentum transfers. The more extensive high-frequency Raman scattering in both bulk and liquid Bi clusters relative to the low temperature amorphous films is attributed to thermal broadening and disorder effects. The fact that the 70- and 140-Å samples have higher-coordinated structure similar to that of bulk liquid Bi is supported by the relatively large size of the clusters noted in the TEM distributions of Fig. 3. The loss of the interference enhancement and the presence of high bulk liquid reflectivity preclude studying thicker films.

For the thinnest films studied, corresponding to 6 Å mean thickness, Raman spectra indicate a distinct peak at $\sim 85-90\ \mathrm{cm}^{-1}$. This peak is similar in position to that observed for a low-temperature deposited 6-Å-thick amorphous cluster film shown in Fig. 4. Previous Raman-scattering studies[9] have demonstrated that amorphous Bi clusters have threefold coordination. In addition, both the magnitude and shift of the main vibrational band of the clusters with de-

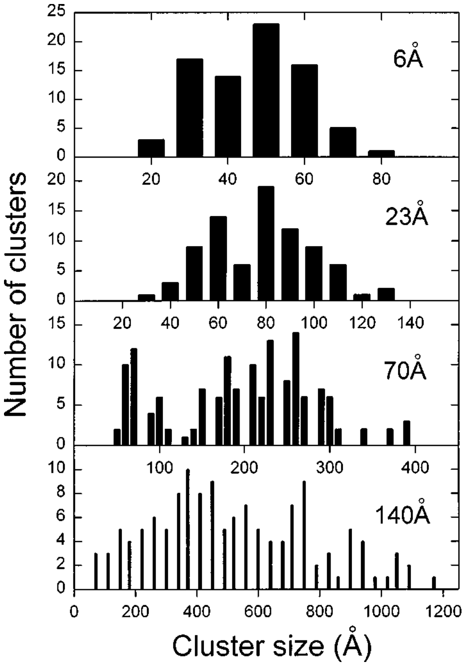

FIG. 3. Size distribution of the solidified liquid cluster films of Fig. 2 obtained from bright field TEM images.

creasing cluster size suggested the formation of a semiconducting state. The similarity of the 6-Å liquid spectrum to that of the amorphous phase indicates that a substantial number of atoms in this sample are threefold coordinated. These results imply a structural transformation from predominantly high- to low-coordination clusters with decreasing film thickness. However, the liquid Raman spectrum for the 6-Å-thick film exhibits a substantial asymmetry toward low frequency relative to the amorphous clusters. This result for the 6-Å film and the broad flat form of the spectrum of the 23-Å film in Fig. 2 suggest that a mixture of high- and low-coordination clusters occurs within their particle distributions.

The next step is to estimate the critical size below which the transition from high to low coordination occurs. In order to do this, TEM studies should be employed. As Bi weakly interacts with carbon, thin liquid films have an island structure. Upon solidification the dimensions of the clusters are not substantially modified, so that TEM of solidified clusters yields the approximate liquid cluster size distributions. The *ex situ* TEM determined distributions are shown in Fig. 3. A crude estimate of the critical size can be done in the following way. For the 70- and 140-Å-thick films that consist mostly of high coordination clusters, a small number of clusters have sizes below $\sim$70–80 Å. In contrast, the 6-Å film contains both low- and high-coordination clusters and has few clusters with size above 70–80 Å. This places an upper limit of $\sim$75 Å for the liquid cluster transition from high to low coordination. In order to obtain a lower limit, the cluster size distribution for the 23-Å film has to be considered. The 23-Å film contains a small yet detectable fraction of clusters with low coordination. The TEM studies for this film indicate very few clusters with sizes below 45 Å. At the same time, clusters with sizes up to 45 Å constitute a significant fraction in the cluster size distribution for the 6-Å film that is consistent with the Raman-scattering observations. This places a lower limit of $\sim$45 Å for the transition.

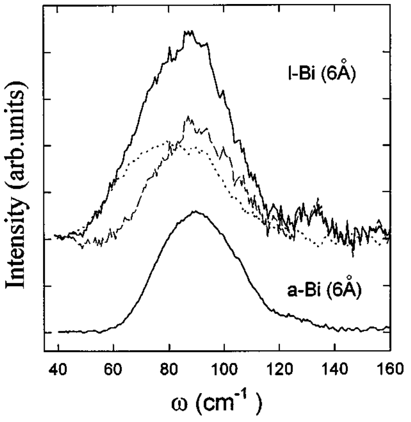

FIG. 4. Comparison of the thermally reduced Raman spectra of 6-Å-thick, amorphous and liquid cluster films. The liquid spectrum is decomposed into a contribution similar to the 70-A-thick film of Fig. 2 (····) and a difference peak (----).

A more detailed estimate of the transition size may be obtained by considering the Raman spectra to be due to a linear combination of clusters with higher and lower coordination. For the 6- and 23-Å spectra it is reasonable to decompose these spectra into two contributions with one being similar to the 70-Å spectrum. This yields for the 6-Å film the decomposition shown in Fig. 4 in which two peaks of comparable areas are obtained. The high-frequency difference peak is found to have both a very similar peak position and half-width as the 6-Å as-deposited amorphous Bi film. This is consistent with the presence of smaller clusters of threefold bonded atoms in the distribution of particles for the 6-Å film. For the 23-Å film, this procedure yields a smaller fraction of $\sim$10–20 % of the scattering having a higher-frequency contribution. The intensity of Raman scattering is proportional to both the volume of the material studied and to the Raman cross section of this material. Therefore, it is possible to estimate the critical size by considering the relative Raman cross section for the two bonding configurations and the volumes of threefold and sixfold bonded clusters within one particle distribution necessary to yield the high- and low-frequency portions of the Raman spectra obtained with the decomposition procedure (see Fig. 4). TEM studies of Bi particles suggest approximate hemispherical shapes,[15,16] implying that the scattering volume for each particle varies as the cube of its radius. Thus, partial volumes occupied by low- and high-coordination clusters and consequently the critical size can be readily calculated from the TEM size distributions (see Fig. 3) and the decomposed Raman spectra (see Fig. 4). Unfortunately, the relative bond polarizability scattering cross section for the proposed lower- and higher-coordinated atoms is not known. If a cross section ratio of one is assumed this yields from Fig. 3 and the Raman-spectra decomposition procedure a transition diameter of $\sim$55 Å for the 6-Å-thick film and $\sim$63–67 Å for the 23-Å film. Increasing the ratio of the lower- to higher-coordination scattering to a value of 2–3 reduces the difference between the transition sizes, yielding a value of 48 ± 5 Å.

The transition size obtained above assumes a simplified model in which clusters beyond a critical size have a change in the coordination of all the atoms of the cluster. However, more sophisticated analysis should take surface effects into account. A 48-Å hemispherical cluster with a density approximately that of crystalline Bi contains ~1000 atoms. A substantial fraction of the atoms in such a cluster is on or near the surface, where the electronic states of atoms are modified. For higher-coordination clusters with size somewhat larger than the 48-Å transition estimate, a substantial fraction of surface atoms might have lower coordinations. This implies that the origin of the higher-frequency scattering may be partially associated with the presence of such atoms. If, for example, it is assumed that the surface coordination of the clusters is threefold then it would reduce the transition size since the surface of large, high-coordination clusters would contribute additional low-coordinated atoms. Assuming similar Raman cross sections for all atoms, within a continuum approximation, for a thin shell of surface atoms, this shifts the transition to 50 and 55 Å, for the 6- and 23-Å films correspondingly. More complex models with thicker shells are also feasible. The assumption of substantial scattering from low-coordinated surface atoms, as well as the unknown relative Raman-scattering cross section for atoms with different bonding, places significant constraints on more accurate microscopic cluster modeling.

It also has to be mentioned that a possibility of a continuous transition from threefold to sixfold coordination exists. The transition can be continuous by simply decreasing the difference between the three shorter and three longer interatomic distances for Bi atoms. Simple quantitative analysis is unfeasible in this case. It would only be safe to conclude that this effect would appear in liquid Bi clusters with size below ~75 Å. Similar to the previous discussion, this statement follows explicitly from the TEM cluster size distributions in Fig. 3.

In addition to the effects described above, modification of longer-range interactions may yield quantum-size effects that influence the electronic states and modify the bonding within clusters. It has been suggested that the structure of liquid Bi is determined by an interatomic potential with a repulsive core and attractive interactions having longer-range Friedel oscillations.[17] It is possible that quantum-size effects modify these longer-range oscillations, allowing for enhanced covalent interactions in Bi clusters. In addition exchange-correlation effects, known to be important in Bi, might be modified by finite-size effects.

IV. CONCLUSIONS

In conclusion, Raman-scattering studies of liquid Bi clusters on weakly interacting C support have been performed. The results suggest that structural phase transition occurs for the clusters of ~45–75 Å in diameter. The observation of this size-dependent transition from higher to lower coordination with decreasing size in the Raman spectra also suggests that the smaller clusters may be nonmetallic in character. Either semiconducting or semimetallic behavior is possible. Other techniques, such as, for example, high-resolution electron energy loss spectroscopy (HREELS), that are sensitive to greater electronic screening in the metallic state as compared to that of the semimetallic or semiconducting states should be employed to differentiate between the three possibilities. The size effect noted in Bi clusters suggests that similar effects may also occur in other semiconducting systems in which large coordination changes occur upon melting. For group-IV and -V systems, such as Ge, Si, and Sb, the increase in density and metallic character of the bulk liquid may, for example, be replaced in clusters by lower coordination, semiconducting, or semimetallic structures similar to that of bulk crystalline and amorphous phases.

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