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Structure of unsupported bismuth nanoparticles

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Abstract. We present new results of electron diffraction experiments on unsupported nanometer-sized bismuth clusters. The high intensity cluster beam, necessary for electron diffraction, is provided by an inert-gas aggregation source. The cluster beam contains particles with average cluster sizes between 4.5 and 10 nm. When using Helium as a carrier gas we are able to observe a transition from crystalline clusters to a new structure, which we identify with that of amorphous or liquid clusters.

PACS. 36.40.-c Atomic and molecular clusters – 61.46.+w Nanoscale materials: cluster, nanoparticles, nanotubes, and nanocrystals – 61.14.-x Electron diffraction and scattering

1 Introduction

Electron diffraction applied to cluster beams allows the study of the structure of small particles, free of contamination and without interaction with a substrate. The exposure time of the clusters in the beam is very short limiting the possibility of altering the clusters by the electron beam. The structure of bismuth clusters has previously been studied mainly for supported clusters by high-resolution transmission electron microscopy (HRTEM) [1–4]. The structure of unsupported bismuth particles was first studied by Yokozeki and Stein [5], who reported rhombohedral structures for particles with sizes between 6 and 9.5 nm. Particles with a single-crystalline core (5-10 nm diameter, rhombohedral structure) surrounded by an amorphous or liquid shell and smaller non-crystalline particles on amorphous carbon films were described in Refs. [3,4]. Other investigations [1] have found a structural transition at a particle size of 8.4 nm. Particles larger than ~ 5 nm and smaller than 8.4 nm had the rhombohedral structure of the bulk material with the shape of a truncated rhombohedron, while larger particles had a complex structure containing lattice defects.

2 Experimental procedure

The bismuth clusters were produced in an inert-gas aggregation source using both Ar and He gases. The mixture of inert gas and small particles is extracted through two differential pumping stages and then probed by an electron beam (80 kV). The randomly oriented particles give rise to a Debye-Scherrer (powder) type diffraction pattern, which is detected by a pair of linear CCDs aligned along a diameter of the pattern. The apparatus is substantially the same as that used for previous studies of Cu and Ag [6–8]. The size and structure of the particles is controlled by the inert gas pressure P_G and by the temperature of the crucible T_C. The nucleation of the particles in the source chamber also depends on the geometry (flow pattern) and the cooling of the chamber. In later experiments a modified source chamber with an additional heat shield, that divides the source chamber into two separate halves, and therefore allows better cooling of the metal vapour has been used.

Before analysis of the data, the carrier gas contribution to the scattering intensity has been removed by subtracting experimental diffraction patterns from the pure gas. In this study, we determine the structure of the clusters by comparing the experimental diffraction patterns with calculated patterns from model structures. The model patterns used here were calculated in the framework of the kinematic theory of diffraction (Debye formula [12]) with a Debye-Waller factor set to one. The average size of the clusters is estimated from the width of the main diffraction peak using the Scherrer formula [12]. Further information on the cluster sizes is obtained from the comparison of the experimental pattern with calculated diffraction patterns.

3 Results

The results of experiments that use argon and helium as carrier gases are discussed separately below.

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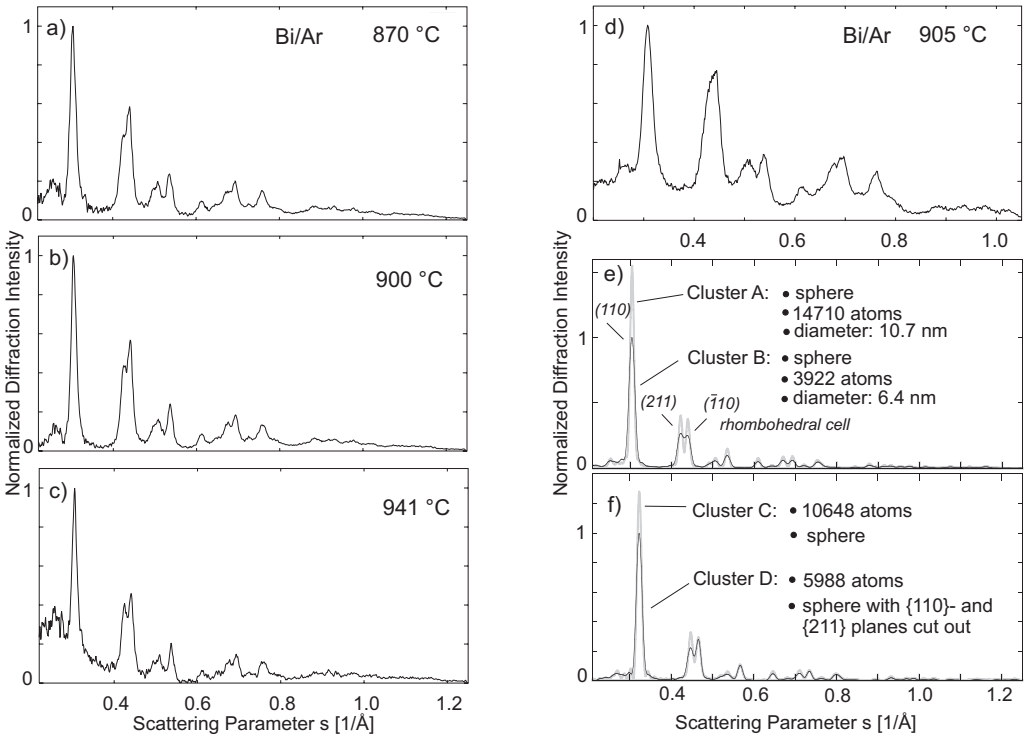

Fig. 1. (a)-(c): Experimental diffraction patterns of bismuth clusters produced using Ar as an inert gas. The increase in the evaporation temperature of the bismuth leads to an increase in cluster size which is shown by the narrowing of the main diffraction peak and by the clearer splitting of the peaks at $s \sim 0.43$ Å^{-1}. These experiments were done with the modified source chamber (better cooling). (d) Smaller clusters were produced with the original source chamber. (e) Calculated diffraction patterns for two spherical model structures showing that the (211)/($\bar{1}$10) peak splitting becomes visible for clusters larger than approx. 6 nm. (f) Diffraction patterns of two model structures showing that the intensity ratio of the (211) and ($\bar{1}$10) peaks can be adjusted to the experimental pattern by removing some {211} planes from the spherical cluster.

3.1 Experiments using argon as the carrier gas

When using Ar as a carrier gas, we were able to obtain bismuth diffraction patterns for 770 °C $< T_C <$ 950 °C. The lower limit was due to low diffraction intensities, whereas at high temperatures the clogging of the nozzles stopped the experiment. The crucial parameter for the formation of a high cluster flux was P_G. The pressure for highest cluster intensities shifted from 12 mbar at 770 °C to 22 mbar at 893 °C.

The diffraction patterns are characteristic of relatively large clusters (Figs. 1 (a-d)), and display the rhombohedral structure of the bulk material. The average diameters determined by the Scherrer formula [12] were approximately 6.5 nm, 7.5 nm, 8.5 nm and 4.5 nm for the patterns of Figs. 1(a), (b), (c) and (d) respectively. The uncertainties in these estimates are ±1 nm. Relatively small clusters are produced with the original source chamber configuration (Fig. 1(d)), whereas larger clusters were produced in the modified source chamber with improved heat shielding (Figs. 1 (a-c)).

An additional method of determining the size of the clusters is by the comparison of the experimental diffraction patterns with calculated patterns of model structures. The splitting of the peak at $s \sim 0.43$ Å^{-1} is clearly visible in calculated patterns for spherical clusters that have a diameter greater than 6 nm (Fig. 1(e)). The intensity ratio of the (211) and ($\bar{1}$10) peak in the pattern of the spherical model structures (Figs. 1(e), (f)) does not agree with the experimental patterns. However, the intensity ratio can be adjusted to the experimental patterns by changing the shape of the model clusters *i.e.* by removing some of the {211} planes from the spherical clusters (Fig. 1(e)). Fig. 1(c) exhibits a residual diffraction background, which we believe is caused by an increased proportion of monatomic bismuth in the cluster beam at higher temperatures.

3.2 Experiments using He as the carrier gas

The production of bismuth clusters with helium as a carrier gas required very high gas pressures in the source chamber. Since our pressure gauge has limited sensitivity for He we know only that the pressure was higher than 12 mbar in these experiments. Diffraction patterns of crystalline bismuth clusters were obtained for $T_C >$ 846 °C (Fig. 2(a)). An additional feature in the diffraction pattern appears for $T_C >$ 915 °C (Fig. 2(b)), indicating the production of clusters with a significantly different structure. For $T_C >$ 930 °C only the new diffraction pattern could be detected (Fig. 2(c)). After the modification to the inert

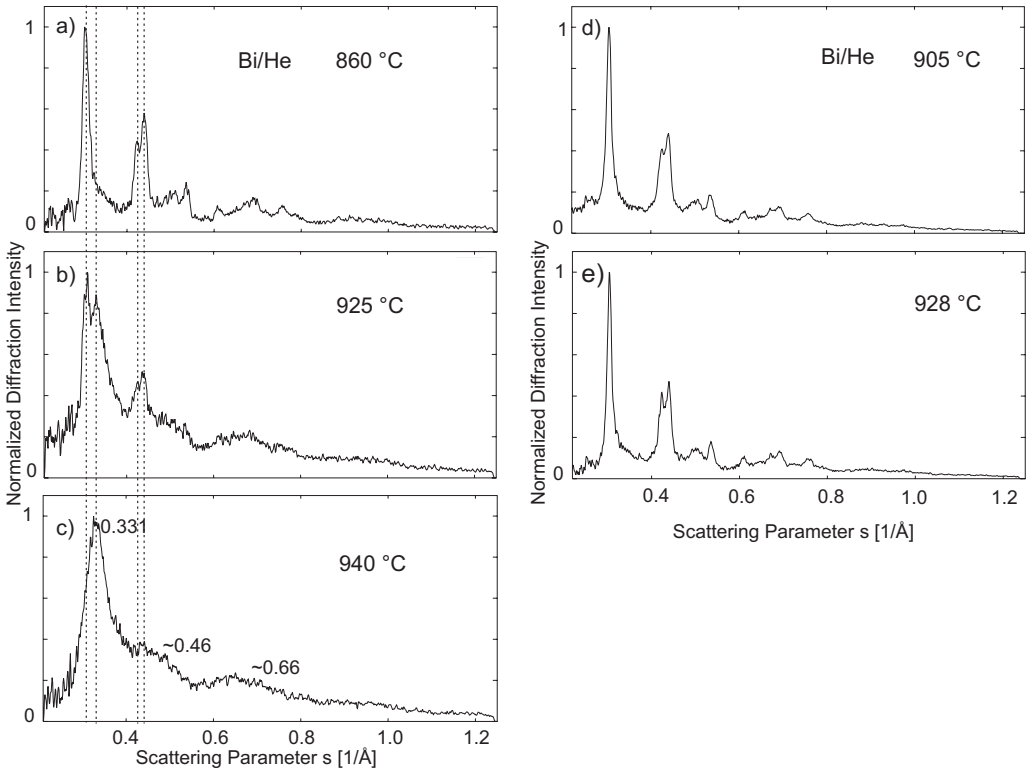

Fig. 2. (a)-(c): Experimental diffraction patterns for clusters produced with helium at various evaporation temperatures. The diffraction pattern at 860 °C is clearly from crystalline clusters. At 925 °C additional features appear in the diffraction pattern. The new structure dominates the diffraction pattern at 940 °C. (d)-(e): A modified source chamber (better cooling) produces only crystalline clusters in the whole accessible temperature range.

gas aggregation source, which lead to an improved cooling of the metal vapour, only diffraction patterns from crystalline clusters could be observed (Figs. 2(d), (e)). The diffraction patterns in Figs. 2((a), (d), (e)) are for particles with the rhombohedral structure, with the lattice parameters of the bulk material. The average diameter of the clusters, determined with the Scherrer formula, were 6.5 nm, 8.5 nm and 9.5 nm for Figs. 2 (a), (d) and (e), respectively.

4 Discussion

In our experiments we were able to obtain diffraction patterns for crystalline bismuth clusters with an average size covering the range from 4.5 to 10 nm. For equivalent source temperatures, the clusters were slightly larger when using helium instead of argon. The following trends concerning the cluster size can be observed for our inert gas-aggregation source. Firstly, an increase in the temperature of the bismuth in the crucible T_C leads to an increase in cluster size. Secondly, the clusters become larger when cooling by the carrier gas is enhanced.

With He as the carrier gas and with the original source chamber configuration it was possible to observe evidence for a new structure in the diffraction pattern for $T_C > 925$ °C. The pattern from the new structure became stronger with increasing T_C. The broad features in the diffraction pattern suggest the presence of amorphous or liquid clusters. The experimental diffraction patterns are very similar to diffraction patterns obtained with electron and X-ray diffraction from liquid bismuth [9,10] and so we identify the new structure with that of liquid clusters. The fact that is was not possible to observe liquid patterns with argon as a carrier gas is attributed to the more efficient cooling of the argon. All the other experimental diffraction patterns are from crystalline clusters with the rhombohedral structure of the bulk material.

The low intensity of the (211) peak indicates a non-spherical shape for the clusters, suggesting that the clusters have the same structure as reported in Ref. [1] (truncated rhombohedron) for bismuth clusters with a diameter smaller than 8.4 nm. No evidence has been obtained to support the claim [1] that larger clusters undergo a transition to a new cubic-like structure.

The transition from solid to liquid clusters is a subject of substantial current interest [11]. Further experiments are underway with the objective of probing the structure of free clusters close to the melting transition.

5 Conclusions

Bismuth clusters produced with an inert-gas aggregation source using He and Ar gases were investigated by electron

diffraction. The cluster beams contained clusters with an average size between 4.5 and 10 nm. Experiments with He as a carrier gas showed a transition from crystalline to non-crystalline particles with increasing crucible temperature. The non-crystalline particles have been identified with liquid clusters since the diffraction patterns are very similar to electron and X-ray scattering data from liquid bismuth.

All the other diffraction patterns appear to originate from crystalline bismuth clusters with the rhombohedral structure and lattice parameters of the bulk material. The comparison of the crystalline diffraction patterns with calculations indicates a non-spherical shape for the crystalline clusters.

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