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Electron beam induced small particle transformations: temperature

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Abstract

Real time high resolution microscopy of Au, Ag and Pb particles on C and SiO substrates was performed to determine the role of the electron beam on the morphology transformations. The data conclusively rule out high temperature excursions in the small particles due to the beam.

Keywords: Electron microscopy; Electron–solid interactions

The unique properties of small particles which have resulted in their application in areas such as catalytic materials and nanocrystals are often attributed to their structure. Frequently, these small particles exhibit a multiplicity of morphologies which can be observed by electron microscopy. Interestingly, in the presence of an electron beam the particles transform between morphologies [1–3], a phenomenon we refer to as quasimelting [4]. While there is general agreement on the experimental observations, the source and mechanism of these morphology fluctuations have been a topic of considerable debate. The primary focus of the controversy has been the role of the electron beam, with explanations ranging from charging [1], coulombic explosion [5], transient melting due to thermal spikes [6], electron beam heating [7], and softening of the potential energy surface [8].

One model [1] considers that charging is the source, following observations of enhanced fluctuations with decreasing conductivity of the substrate. In some not well-specified manner the coulombic forces due to temporary deviations from electrical neutrality of the particles or local areas within them drive the transformations. In a somewhat related concept, Howie [5] hypothesized a role for multiple ionization processes from the decay of inner shell excitation, with repulsions between the charges providing the driving force. A third mechanism [6] suggested that thermal spikes produced by decaying Auger electrons could be the source of a transient molten state. The fluctuations in a 2-nm cluster at a beam flux of 20 A/cm^2 were calculated to be 10–20 times per second. This seemed to be confirmed by the early experimental data, but the persistence of fluctuations at much lower beam fluxes [9] disagreed with this model, and also that of Howie. Theoretical results [4,8], confirmed by experimental observations [10], have shown that heating [7] can assist structural

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fluctuations by reducing the activation barriers between shapes. This model [4,8], where the energy barrier for the transformations is small, does not specify the exact fluctuation mechanism.

Although not explicit in any of the models in a qualitative form, the importance of the substrate adhesion term is known experimentally. A number of authors have mentioned that quasimelting occurs only when there appears to be relatively weak adhesion to the substrate [1,9,11,12]. There is also a variation in rate with different substrates [13].

To summarize the above, models assuming very large fluctuations and transient melting are not supported by the experimental data. Theoretical analyses support a softening of the potential energy surface and there are data supporting thermal heating as a source. However, while it is clear that thermal heating close to the melting point is sufficient to drive the fluctuation, it is not clear whether the particles must be thermally excited; is heating a necessary or just a sufficient condition?

The intent of this Letter is to report results of a study of small particles of Ag, Pb, and Au which provide incontrovertible evidence that small particles under the beam transform at temperatures well below the melting temperature, near to room temperature conditions.

Au and Ag particles were prepared by separate deposition onto carbon and SiO substrates by in-situ and ex-situ resistive evaporation. After ex-situ deposition the Au and Ag samples were observed in a 300 kV HREM Hitachi H-9000 microscope maintained at a vacuum of 1×10^{-6} Torr. Samples prepared by in-situ evaporation were observed in a UHV-HREM Hitachi H-9000 with a side chamber for specimen preparation. The base pressure in the microscope was 1×10^{-10} Torr. Pb was deposited ex-situ onto SiO grids and the sample was then transferred to the side chamber of the UHV-HREM Hitachi H-9000. Electron beam annealing was performed on the Pb samples to reduce the oxides to Pb before observations. All the observations were recorded onto a Sony video recorder at the rate of 30 frames per second using the TV cameras on the microscopes. The recorded images were processed later using SEMPER software.

The experiments on Pb and Ag severely constrain the possible temperature of the particles. Bulk Pb melts at 327.5 °C, while Ag sublimes above 600 °C; at small sizes both of these can be expected to be depressed further [14], but the above temperature values are strong upper bounds. In the experiments, Ag and Pb particles were subjected to the same beam fluxes that were imposed on Au particles.

Pb quasimelted on both C and SiO substrates and exhibited multiply twinned structures (MTPs), see for instance Fig. 1. No evidence was found for melting of the Pb particles. Ag quasimelted only under UHV conditions on the SiO substrate. More importantly, the particle sizes did not diminish throughout the experiments. Ag is known to quasimelt and an earlier study discusses a method of in-situ preparation of Ag from AgI [15]. However, AgI served as a source of Ag, so these results are not so conclusive.

The above experimental data demonstrate that the electron beam does not provide a temperature rise close to the melting point of the Au particles; the results for Pb indicate that the temperature rise is much less than 327°C. These observations therefore do not support any model requiring

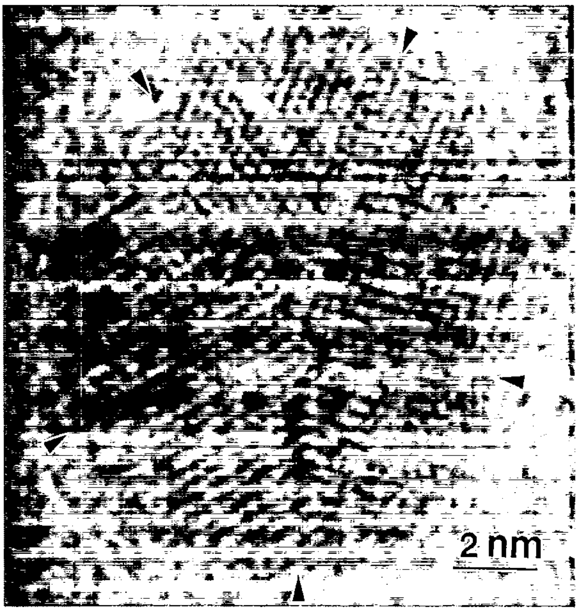

Fig. 1. A typical decahedral multiply twinned particle of Pb. The arrows indicate the location of the twins in the particle.

melting for periods longer than 1/30th of a second. Since, as mentioned earlier, transient melting due to localized thermal spikes can be ruled out [9], we can conclude that heating is a sufficient condition, but it is not a necessary one.

Finally, we note that although the electron beam does not appear to produce thermal fluctuations sufficient for Pb to undergo transient melting, it can produce smaller random fluctuations. In this regard, the electron energy loss results of Rez and Glaisher [16] also point to low temperature rises due to the electron beam and indicate that the energy provided by the beam is enough to surmount the barriers [8] between different structures. Borrowing from the literature on electron stimulated desorption [17,18], any excited electronic state must have a relatively long lifetime for conversion to displacements of atoms; the weaker the substrate coupling, the better the confinement of the excited states in the particle. This also correlates well with the observation that quasimelting appears to be quenched with conducting substrates [1].

In conclusion, the requirements for structural fluctuations are:

(1) At least one energy source to overcome the activation energy barriers between different structures. This can be thermal or valence/core excitations from an electron (or other) beam.

(2) A relatively low energy barrier between morphologies.

Both these requirements are satisfied for small particles in an electron beam without recourse to high temperature processes.

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