

In-Situ Atomic-Scale Observation of Intermediate States of Melting and Crystallization of Supported Bi Nanoparticles in the TEM

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Melting and crystallization are first-order phase transitions which have great importance in diverse areas including condensed-matter physics,¹ material science² and climate change.³ However a detailed understanding of their relevant kinetic pathways is still evolving. Recently, Samanta et al. conducted large-scale atomistic calculation of a phase transformation process of a metal from solid to liquid and predicted that the process takes place via multiple competing pathways involving the formation and migration of point defects or dislocations.⁴

In the present work, we observe in-situ atomic-scale dynamic behavior of melting and crystallization in supported Bismuth nanoparticles under heating or cooling within an aberration-corrected TEM. We provide direct evidence that pre-nucleation in either melting or crystallization takes places via multiple intermediate state pathways involving the formation and migration of domain boundaries, dislocations and the ordering of interface and surface at the atomic scale. The pre-melting of the nanoparticles initiates at a grain boundary and expands to interfaces and dislocations and finally undergoes a catastrophic transformation from a solid-liquid structure to a liquid droplet as a whole in a rather short time when their size exceeds a threshold value. When the size is smaller than the threshold value, the melting of nanocrystals takes place via two barrier-crossing pathways, i.e. pre-melting at grain boundary and a rapid solid-liquid transformation. Interestingly, pre-crystallization in a droplet occurs first at a solid-liquid interface and subsequently at the liquid surface, and eventually the droplet undergoes a fast complete transformation to a solid nanocrystal when undercooled. These experimental findings highlight the importance of nonlocal behaviors.⁵

References

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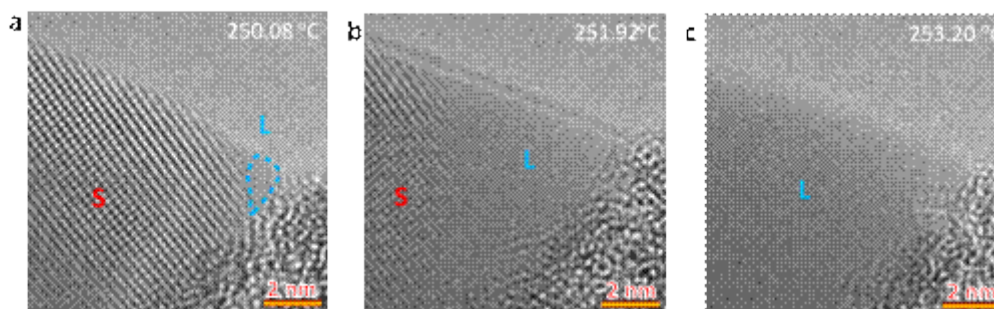


Figure 1. Sequential HRTEM images showing pre-melting at heterointerface of supported Bi nanocrystal.

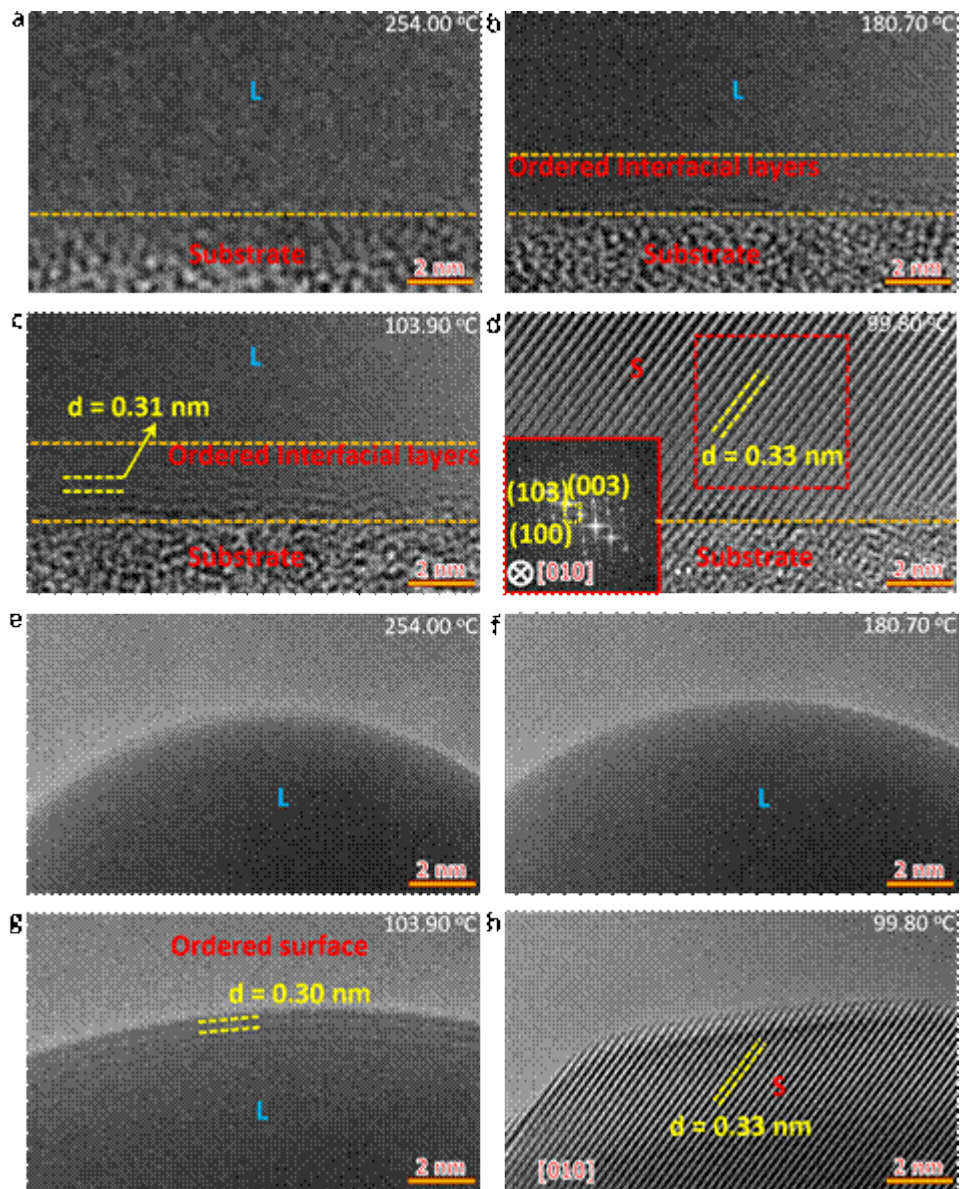


Figure 2. Sequential HRTEM images showing multiple intermediate states in the crystallization pathway of a supported droplet driven by undercooling.