Mechanisms of nucleation and post-nucleation of bismuth tri-iodide onto graphene substrates

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Crystalline nucleation results reported over the past two decades have shown several multistep nucleation processes, named as nonclassical nucleation, due to be different -at least in some extent- to the Classical Nucleation Theory (CNT) predictions. In this framework, nucleation and post-nucleation of bismuth tri-iodide onto graphene substrates is an interesting example for studying these processes in the case of growth from the vapor, while most of the reports correspond to cases of growth from solution.

BiI_3 (Aldrich 99,999%) nucleation and further growth was performed by physical vapor transport onto graphene covered TEM grids (single layer graphene film on a 2,5 μm holey silicon nitride film, Ted Pella) and onto 1 layer graphene film/200nm SiO_2 film on a 675 μm ultra-flat silicon substrates, 5x5 mm,Ted Pella, in an especially built equipment, varying initial pressure (10^{-6}–10^{-7} mBar), BiI_3 mass (6-80 mg), source (260.2 °C) and substrate (40±1 °C) temperature (and then supersaturation), and deposition time (10-120 s), with a source-substrate distance of 15.0±0.5 mm), under high purity Ar atmosphere. Particles were characterized by High Resolution Transmission Electron Microscopy (HR-TEM), Fast Fourier Transform (FFT), Energy Dispersive Spectroscopy (EDS), Scanning Electron Microscopy with Field Emission Gun (SEM-FEG) and Atomic Force Microscopy (AFM).

Entities less than 10 nm in size were observed for deposition times of about 10 s, crystalline and amorphous. They continue to be present even under the TEM beam and suffer rapid transformations between ordered and disordered structures, according their FFTs. As further growth of these entities shown they include about three layers of BiI_3, each entity can be assumed to be composed by about 7 unit cells and 42 formula units (a=b= 7.5 Å). These entities are an intermediate metastable state, and can be amorphous (different phase than the bulk crystal), results which disagree with Classical Nucleation Theory (CNT): the first critical nuclei (critical size) should be stable and crystalline, as the final layer is. Then, BiI_3 nucleation onto crystalline graphene by PVT follows a non-classical pathway, as was reported for other systems and materials. For longer times of about 120 s, oriented attachment and amorphous addition of these entities give larger ones of about 10-20 nm. Nanoparticles interact among them by these non-classical mechanisms giving stable and oriented crystalline structures, in agreement with the several pathways reported in non-classical nucleation investigations for post-nucleation growth. EDS of the entities show BiI_3 as particle composition. All these results are similar to the ones reported for non-classical nucleation in solution and chemical vapor deposition (CVD) systems.

BiI_3 presents two phases at PTN, R-3 rhombohedral and P-31m hexagonal. Statistical results show that nucleation proceeds in the rhombohedral phase R-3 for the established conditions of nucleation. Due to its anisotropy, BiI_3 might nucleate with different orientation. Statistical results show that it nucleates mainly oriented with *c* axis perpendicular to the substrate.

Results obtained contribute to the investigation on the mechanisms of nucleation and the post nucleation growth, and to the development of models for multistep nucleation processes.