Nano-Microscale Structures in Chalcogenides via Sublimation-Condensation

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A wide range of nano-microscale microstructures have been achieved in a chalcogenide (arsenic trisulfide) (As_2S_3) system. The structures have been synthesized under near-equilibrium conditions via a sublimation-condensation process in an evacuated glass ampoule under a temperature gradient. The nanoscale droplets and wires deposit at the low-temperature region (77°–147°C), while thick continuous films and micron-scale wires and droplets form in a higher-temperature region (typically above 120°C). Nano-micro droplets coalesce to form continuous films. The as-synthesized nano-microscale structures are pure, stoichiometric, amorphous, and reproducible. The nanowires had diameters ranging from 40 to 840 nm and lengths ranging from few micrometers to a few millimeters. The distinct joints of the criss-crossing nanowires indicate potential for forming a structural network intrinsically. The nanostructures were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), Raman spectroscopy, and X-ray diffraction (XRD) to determine their structure, morphology, and chemical composition. Selected area diffraction (SAD) confirmed their amorphous nature. Stoichiometry of the nanostructures suggests an associative sublimation process. In a preliminary optimization study, the initial ampoule pressure was varied upon sealing (70 mTorr–70 Torr) and temperatures were recorded at 13 points along the temperature gradient of each sample. The dimensions and distribution of the resulting nano-microscale structures were measured using SEM. Based on these results, we have developed empirical equations that describe growth of the structures. The results have also been plotted on an area diagram (initial ampoule pressure versus temperature) that maps out the microstructures. We predict this approach can be applied to other chemistries with high vapor pressure at moderate temperature and pressures (i.e., halides, oxides, and other chalcogenides).