

The structural features of dimorphite thin films grown by thermal evaporation and cathodic magnetron sputtering

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Abstract: Dimorphite (As_4S_3) is a rare arsenic sulfide compound of growing interest for optoelectronic applications. The present work reports the structural characterization of two types of dimorphite thin films prepared by thermal evaporation of As_4S_3 powder and RF magnetron sputtering from a pressed As_4S_3 powder target. The films obtained via thermal evaporation in vacuum $\sim 10^{-5}$ Torr have been grown onto quartz or titanium (*Ti*) substrates using a quartz crucible, heated by a tungsten coil. The velocity of film growth was controlled varying the temperature of the crucible from 120 to 180 °C, which allowed to vary the deposition rates in the range of 0.2–8 $\mu\text{m}/\text{h}$. The set-up allowed us to grow dimorphite layers with different thickness (0.1–10 μm) without breaking the vacuum. It was established that As_4S_3 sublimates at a pressure of 10^{-5} Torr and temperature around 120 °C. Shown by scanning electron microscopy (SEM), the films obtained via sublimation are fibrillar with a high porosity. The fibrils are randomly distributed and are around 1–2 μm in length. At advanced crucible temperatures dimorphite evaporates and the grown films are dispersive and homogeneous. The X-ray diffraction (XRD) analysis showed that either thin films grown by sublimation or evaporation contain both α and β phases of dimorphite as in the raw material, serving as a source. However, it was pointed out that the ratio β/α concentration strongly depends on the rate of growth, as well as on material and temperature of substrate. Thus, it was found that As_4S_3 thin films obtained via either sublimation or evaporation onto *Ti* substrates contain β -dimorphite in much larger quantities than α -dimorphite, and the ratio β/α tends to increase with increasing evaporation temperature. Sputtered films were deposited at room temperature on quartz and silicon substrates in Ar atmosphere at applied powers of 7 W and 10 W, corresponding to low deposition rates ($\sim 0.1\div 0.2$ $\mu\text{m}/\text{h}$). Films in the thickness range of 60 to 320 nm were obtained, as determined by X-ray reflectometry and spectroscopic ellipsometry. Energy-dispersive X-ray spectroscopy (EDX) indicates near-realgar stoichiometry (As:S $\approx$ 49:51 at.%), close to realgar (As_4S_4) stoichiometry. Grazing incidence X-ray diffraction (GIXRD) analysis of as-deposited films reveals their polycrystalline structure, cubic As_2O_3 (arsenolite) accompanied by an unknown isostructural cubic phase, its lattice parameter $a \approx 10.936$ Å being smaller (-1.4%) than that of arsenolite ($a = 11.088$ Å). Post-deposition annealing at 130°C for 120 min in a sulfur atmosphere eliminates the oxide and the unknown cubic phase, as GIXRD analysis reveals. The sulfurized films seem to be composed of a single polycrystalline phase, monoclinic $\text{As}_2\text{S}_{2.11}$, and a minority amorphous phase. GIXRD diagram of the sputtered target surface shows that it is composed by a balanced mixture of polycrystalline phases, β - As_4S_3 (β -dimorphite) and β - As_4S_4 , and a minority amorphous phase. SEM shows smooth films with scattered surface crystallites in as-deposited layers, which are eliminated after sulfurization, consistent with removal of the oxide phases. These results establish the structural baseline for dimorphite thin films prepared by two complementary deposition routes, thermal evaporation and RF magnetron sputtering, and demonstrate that phase composition is governed by deposition rate and substrate properties in evaporated films, while surface oxidation control is the key requirement for phase-pure sputtered films.

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