Stable and Tunable Chalcogenide Perovskite Thin Films: Growth, Characterization, and Annealing Effects

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Computational studies suggest that chalcogenide perovskites, among which CaZrO3-xSx and $CaZr_{1-x}Ti_xS_3$ are promising materials for optoelectronic and photovoltaic applications due to their possible tunable band gaps, strong light absorption, and remarkable stability[1]. Indeed, CaZrS3 is a sustainable alternative to conventional materials due to its lower-toxicity than MAPI, and abundance of its elements[2,3], with a theory bandgap of 2.48 eV and 1.5 eV for Ti doped.[4,5] To date, no experimental film growth has been reported for these chalcogenide pervskites.

In this work, we investigate the direct growth of $CaZrO_{3-x}S_x$ and $CaZr_{1-x}Ti_xS_3$ films by pulsed laser deposition (PLD). Growth conditions were explored on various substrates, including $LaAlO_3$(100), $SrTiO_3$(100), $YAlO_3$(001), $SrTiO_3$:Nb(100), and Al_2O_3(1-102), over a temperature range from 600°C to 800°C. The resulting films were systematically characterized in terms of their structural, optical and electrical properties, as well as their semiconducting energy levels. For $CaZrO_{3-x}S_x$, optimal growth was obtained with LAO substrates at a growth temperature of 800 °C, resulting in a film with x = 2.7 and a reduced bandgap of 2.30 eV. These films exhibited strong absorption in the visible range and a high surface photovoltage (SPV) response, reaching 900 mV at 0.2 sun. Furthermore, by introducing Ti into the $CaZr_{1-x}Ti_xS_3$ lattice, we achieved further bandgap tuning down to 1.6 eV, enhancing the electrical properties and improving suitability for single junction or tandem photovoltaic architectures.

The films demonstrated excellent resistance to environmental conditions such as heat, illumination, and humidity, maintaining their crystalline structure and optical performance. They remained stable up to 350 °C and showed no detectable degradation under continuous illumination for up to 100 hours. With a tunable bandgap down to 1.6 eV, these materials highlight strong potential as stable, earth-abundant, and tunable candidates for next-generation photovoltaic technologies.

References:

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