A novel route to ZnSnN₂ thin film growth

Andrew Oriani, Eric Blanton
Dept. of Physics, Case Western Reserve University, Cleveland, OH 44106

Introduction

II-IV-Nₓ materials have long been seen as cheap non-toxic alternatives to group II-V compounds commonly used in many semiconductor applications. ZnSnNₓ has been theorized to be a stable, easily tunable, direct band-gap material. Previous research however has given varying and contradictory thermodynamic and compositional results using techniques ranging from molecular beam epitaxy, to RF sputtering. This project sets to investigate a novel method of growing ZnSnNₓ via SnO₂ thin film annealing on an amorphous glass substrate. The following experiments were modelled after the successful growth of ZnSnP₂ by Sansegret, while also taking into account NH₃’s high stability, and substrate integrity at high temperatures. By varying substrate temperature and reactant composition, it is possible to identify the dominant competing thermodynamic mechanisms central to the proposed thin film annealing method.

Design

The substrate is a commercially available 1.5µm MOCVD SnO₂ thin film on borosilicate glass with an annealing point of 639°C. The growth chamber consists of a single zone silicon glass tube furnace with PID temperature control. The system is hermetically sealed to reduce the risk of oxide contamination. NH₃, H₂ and N₂ gases are passed into the chamber under constant vacuum and are controlled via a PID butterfly valve connected to a rotary vane pump. The relative concentrations of reactant gases are controlled via mass flow controllers. The substrate and zinc temperature are monitored by thermocouples (TC1 and TC2), while zinc temperature, and subsequently vapor pressure are controlled via relative position within the furnace.

Results

Growth 1: 550°C, 45 SCCM NH₃, 15 SCCM N₂, .043 SCCM Zn (511°C), 360 min, 715.5 Torr

Growth 2: 550°C, 70 SCCM NH₃, 5 SCCM H₂, .044 SCCM Zn (510°C), 360 min, 715.5 Torr

Growth 3: 600°C, 45 SCCM NH₃, 15 SCCM N₂, .049 SCCM Zn (512°C), 360 min, 715.5 Torr

Growth 4: 600°C, 60 SCCM N₂, .037 SCCM Zn (511°C), 360 min, 715.5 Torr

Discussion

The data indicates that at 550°C in an H₂ free environment there is no solid state conversion of SnO₂ to ZnSnNₓ. Likewise, in the presence of <7% H₂ the reduction of SnO₂ happens at a higher rate than the solid state formation of ZnSn nitrides. A high amount of SnO₂ reduction was also seen at 600°C in an H₂ free environment. However, at 600°C with no NH₃ the SnO₂ thin film did not noticeably reduce. This indicates that the partial pressure of hydrogen from the cracking of NH₃ is likely still high enough for SnO₂ reduction at 600°C.

Conclusion

- At 550°C NH₃ reactivity is too low for either solid state conversion or reduction of SnO₂
- SnO₂ reduction in the presence of H₂ at 550°C occurs at a higher rate than Sn/Zn nitride formation
- At 600°C NH₃ reactivity and subsequent H₂ partial pressures are high enough for SnO₂ reduction
- SnO₂ thin films are stable at 600°C in the presence of inert gases

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References