

Liquid Phase Electro-Epitaxy of Memristive LiNbO₂ Crystals

*Jordan D. Greenlee, Joshua C. Shank, M. Brooks Tellekamp, Brendan P. Gunning, Chloe A. M. Fabien, W. Alan Doolittle**

Department of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta,
GA 30318 USA

S1. Materials and Methods

All reagents and materials were used as received unless otherwise specified. Lithium metaborate (LiBO₂) and niobium oxide (Nb₂O₅), both of 99.9% purity, were purchased from Aldrich Chemicals Company, Inc. (Milwaukee, WI). SiC substrates of type 6H with a surface roughness of <0.5 nm were purchased from Xiamen Powerway Advanced Material Co. Ltd. (Xiamen, China). Cylindrical graphite crucibles with dimensions of 2.285" OD x 1.415" ID x 3.05" deep were purchased from GraphiteStore.com, Inc. (Buffalo Grove, IL).

Trichloroethylene, acetone, and methanol (in order of first to last) were used to clean the Nb and SiC substrates in an ultrasonic bath at room temperature. The same solvents were used to clean graphite crucibles before use. Before loading powders, the graphite crucible was cleaned as detailed above and outgassed in a nitrogen atmosphere. The outgas included heating a furnace to 1050° C at a rate of 600° C/hour and holding at 1050° C for 30 minutes. After the hold was completed, the furnace was cooled to room temperature at 600° C/hour.

Once the furnace was cooled back to room temperature, 28.05 g of LiBO₂ and 5.02 g of Nb₂O₅ were mixed in a quartz beaker and loaded into the graphite crucible. The crucible was then loaded into

the furnace, and the temperature was ramped to 910° C at a rate of 600° C/hour. The temperature of the furnace was held at 910° C for 30 minutes before reducing the furnace temperature to 900° C at a rate of 100° C/hour. The crucible and $\text{LiBO}_2/\text{Nb}_2\text{O}_5$ mixture were allowed to equilibrate at 900° C for 30 minutes. After equilibration, the sample was lowered into the molten $\text{LiBO}_2/\text{Nb}_2\text{O}_5$ mixture, and voltage was applied between the Nb/SiC substrate and the graphite crucible. For Nb cathodes, 1.1 V was used for LiNbO_2 deposition while 1.8 V was required for the growth of LiNbO_2 on a SiC cathode.

After the deposition was complete, the furnace was cooled to room temperature at a rate of 600° C/hour. The crucible was removed from the furnace and separated mechanically from the previously molten mixture of LiBO_2 and Nb_2O_5 . The LiNbO_2 crystals were separated from the surrounding borates after a few days in an ultrasonic bath of deionized water.