

4.6 Heteroepitaxial Growth of Tri-Glycine Sulphate Crystals on Solid Substrates

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We successfully precipitated ferroelectric thin films and ferroelectric crystals of tri-glycine sulphate (TGS) to crystalline and solid substrate surfaces. A variety of substrates was tested including silicon, pyrex, and mica, which have already been used in a previous study by C.S. Fang and R. Roy, *J. Cryst. Growth* 60 (1982) 182. A saturated solution containing the glycine and sulphate ions was prepared by dissolving junk crystals from TGS in distilled water under permanent stirring of the solution. The substrates were then immersed in a small Petri-glass containing approximately 50 ml of the standard solution. Precipitation was initiated by two ways : (1) waiting at room temperature (23° C) until precipitation occurs and (2), by heating up the as-prepared Petri-glass (i.e. the solution and the sample) to 28°C for half an hour to obtain a supersaturated solution.

No precipitation was found for glass, pyrex, and silicon substrates which are covered by a amorphous oxide film of approximately 3 nm in thickness. Precipitation to cleaved mica substrates was observed for both the ambient (P1) and supersaturated method (P2). The P1-method, however, results in the simultaneous formation of several TGS crystals with the *b*-axis being oriented parallel to substrate surface but randomly distributed between neighbouring crystallites. Using the supersaturated solution resulted in the crystallization of one large TGS crystal growing to about 1 cm in diameter and 2 mm in thickness (*c*-axis) within 10 hours. This crystal firmly sticks to the mica surface most probably due to the ionic bonding between the TGS and the mica surface. Immersing this crystal in alcohol weakens the interfacial forces and dissolves the glycine molecules of TGS at the interface to the mica substrate.

Surprisingly, precipitation was also observed onto pre-treated silicon, mica or pyrex slides. Pre-treatment was achieved by chemically adsorbing an alkyl-silane monolayer to these hydrophilic surfaces. Although the orientation of the alkyl-chains suggests an amorphous ordering at the surface (as measured by scanning force microscopy) precipitation was successful. The pre-treated samples were further used to deposit a crystalline Langmuir-Blodgett (LB) bilayer resulting in a well ordered hydrophobic surface. Precipitation to such samples was again possible where the different domains of the LB film resulted in different orientations of the TGS crystals. The TGS crystals were found to weakly adhere to the hydrophobic sample surface. However, all these crystals were of a high brilliance and of an excellent quality having practically no defects.

An X-ray analysis revealed the as grown TGS crystals to have the same lattice parameters as the seed grown TGS. Furthermore, cutting the crystals perpendicular to the *b*-axis and observation in a polarization microscope by the liquid crystal decoration method showed the same lenticular domain structures to be present as are observed for bulk TGS crystals.

The method described above allows the growth of ferroelectric thin films and crystals in-situ with a scanning force microscope. This combination offers the advantage to control molecular growth processes on the molecular scale. Nevertheless, heteroepitaxial growth always resulted in TGS crystals having the *b*-axis parallel to the substrate. Furthermore,

growth was mainly initiated along the a - and b -axis, while the thickness of the crystals, the c -axis, was growing much slower.