# Natural Superlattice Structures of Bi-Chalcogenide Topological Insulators grown by MBE and Controlled by Stoichiometry

**S. Wimmer[1*], J. Stangl[1], H. Groiss[2], M. Albu[3], F. Hofer[4], V. Holý[5], D. Kriegner[5], O. Caha[6], G. Bauer[1] and G. Springholz[1*]**

[1] *Institute of Semiconductor Physics, Johannes Kepler Universität, A-4040 Linz, Austria*
[2] *Center of Surface and Nanoanalytics, Johannes Kepler Universität, A-4040 Linz, Austria*
[3] *Center of Electron Microscopy (ZFE), Steyrergasse 17-3, A-8010 Graz, Austria*
[4] *Institute for Electron Microscopy and Nanoanalytics, TU Graz, Steyrergasse 17, A-8010 Graz, Austria*
[5] *Department of Condensed Matter Physics, Charles University, 121 16 Prague 2, Czech Republic*
[6] *Department of Condensed Matter Physics, Masaryk University, 61137 Brno, Czech Republic*

Bismuth chalcogenide compounds are outstanding materials because of their unique topological properties of their electronic band structure, making them an outstanding representative of topological insulators that exhibit a Dirac-like surface state that is spin polarized and topologically protected by time-reversal symmetry [1]. Moreover they are the best thermoelectric materials for power conversion applications. The bismuth chalcogenides $Bi_2Se_3$ and $Bi_2Te_3$ and their various alloys exhibit a complicated hexagonal crystal structure, which basically consists of X-Bi-X-Bi-X (X=Se, Te) quintuple layers (QL) van der Waal bonded to each other. Deviation from the 2:3 stoichiometry, however, results in a wide range of homologous superlattice structures, where the QL stacking is interrupted by insertion of Bi-Bi double layers (DL) or even septuple layers.

In this work, we present a systematic study on epitaxial growth and structural properties of various binary and ternary Bi-chalcogenide layers grown by molecular beam epitaxy on $BaF_2$ (111) substrates. This includes $Bi_2Se_{3-\delta}$ and $Bi_2Te_{3-\delta}$ with different stoichiometric composition, as well as of ternary alloys were Bi is replaced by magnetic (Mn) or non-magnetic (In, Sn) dopants. The crystal structure was investigated by high-resolution x-ray diffraction, scanning transmission electron microscopy and EXAFS measurements.

For MBE growth under low excess Se or Te conditions, we observed random incorporation of Bi double layers, leading to a strong modification of the surface morphology (see Fig. 1 (a-d)) as well as crystal structure (e). Incorporation of more than 3% Mn induces the formation of X-Bi-X-Mn-X-Bi-X (X=Se, Te) septuple layers whereas for In incorporation the usual quintuple layer stacking remains. From our data a general structure model is derived that explains the peculiar structure of the epilayers and the consequences on the electronic properties are discussed.

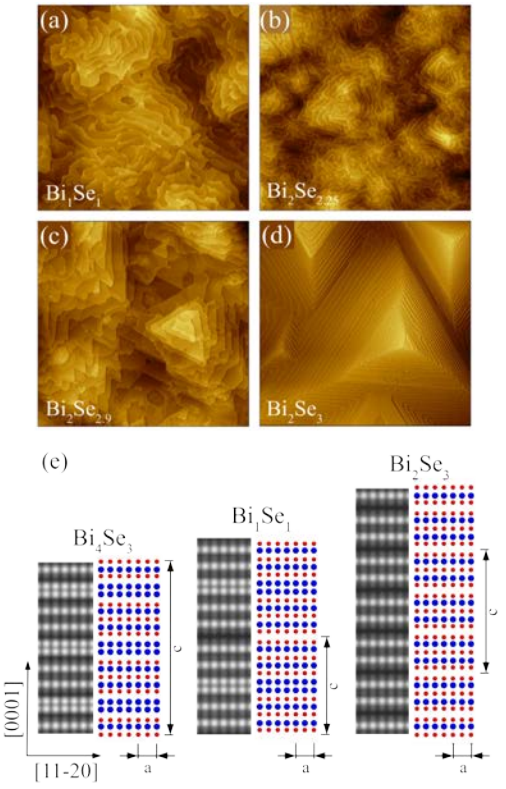


Figure1: (a-d) AFM images of 500 nm $Bi_2Se_{3-\delta}$ layers with the Se excess value δ determined by XRD. (e) STEM simulations and crystal structure of various $Bi_mSe_n$ phases in the $(\bar{1}100)$ plane.

[1] X. L. Qi, S. C. Zhang, *Rev. Mod. Phys.*, **83**, 1057 (2011).

*Contact: stefan.wimmer@jku.at