MS15.O05

The role of point defects in multinary chalcogenide compound semiconductors

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The electronic properties of multinary chalcogenide compound semiconductors, like chalcopyrite type ternary Cu(In,Ga)Se2 and quaternary kesterite type Cu2ZnSnSe4, depend strongly on their intrinsic point defects. For instance it is generally believed that in CuInSe2 the copper vacancies (VCu) cause p-type conductivity, whereas copper on interstitial positions (Cui) or InCu anti-sites act as donors and promote a n-type character. These defects are resulting from deviations from the stoichiometric composition. In order to keep the charge balance in the non-stoichiometric compounds, only a number of cation substitution reactions are possible: for example the transition to Cu-poor CuInSe2 goes via the defect pair 2VCu+InCu, whereas the transition to Cu-poor and Zn-rich Cu2ZnSnSe4 goes via the substitution 2Cu+->ZnCu + VCu. The presentation will give a comparison of the role of cationic point defects in chalcopyrite and kesterite type compound semiconductors concerning the following features: (i) Phase stability: the chalcopyrite type structure is very flexible to hold defects and can adapt itself to substitutions. Beyond a given copper vacancy rate, a vacancy compound (for instance CuIn3Se5) is formed, thus avoiding the occurrence of binary secondary phases (like copper selenides). For kesterite type Cu2ZnSnSe4 the situation is different: due to the lower flexibility of the kesterite type structure and the absence of vacancy compounds, secondary phases, like ZnSe, occur when the compound becomes Cu-poor. (ii) Atomic disorder: The cationic point defects cause an atomic disorder on the short range level which also influences the electronic properties (for instance the bandgap energy). For instance in Cu(In,Ga)Se2 defects such as antisites or interstitials lead to variations in the local atomic arrangements and thus broaden the bond distance distribution due to static disorder. The discussion will be underlined by the experimental results of neutron diffraction [1], anomalous scattering of synchrotron X-rays [2] as well as X-ray absorption spectroscopy [3].

[1] *S. Schorr, Sol. En. Mat. Sol. Cells, 2011, 95, 1482-1488,* ***[2]*** *C. Stephan, S. Schorr, H.-W. Schock, M. Tovar, Appl. Phys. Lett., 2011, 98, 091906,* ***[3]*** *C. Schnohr, H. Kämmer, C. Stephan, S. Schorr, T. Steinbach, J. Rensberg, Phys. Rev. B, 2012, 85, 245204*

Keywords: compound semiconductors, intrinsic point defects