MS103.O04

Early stages of solid state reactions: insights from micro-XRD and XAS

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The mechanism of a solid state reaction in its early stages can be explored by investigating the time evolution of a model reactive system made of a thin layer of one reagent deposited onto a single crystal slab of the other reagent. Insights can be retrieved by comparing results at both local and long length scales obtained with films of different thicknesses and deposited onto different crystal orientations. In particular, reaction between ZnO and Al_2O_3 has been chosen, as the spinel-forming reactions have been and still remain a model experimental system for investigating solid state reactions and because in the ZnO/Al_2O_3 phase diagram, spinel is the only stable compound. The reaction initial steps have been investigated by using synchrotron X-ray diffraction, atomic force microscopy and X-ray absorption spectroscopy at the Zn-K edge starting from zincite films deposited onto (110)-, (012)-, (001)-oriented corundum single crystals [1,2]. The reaction eventually yields $ZnAl_2O_4$ spinel but via a complex mechanism involving side and intermediate non-equilibrium compounds that do not appear in the equilibrium phase diagram of the pseudo-binary system. Spinel, when occurs, is polycrystalline at the end but initially forms with a few preferred orientations. Intermediate phases form before and in parallel with the growth of the spinel. Their number, composition, structure and kinetic role strongly depend on substrate orientation and film thickness. A more detailed understanding of the reactivity can be inferred by comparing EXAFS results to those of grazing incidence diffraction experiments of the films deposited on the (001) face of Al_2O_3 and heat-treated at 1000 °C for different lengths of time. Information on the structure of the intermediate phases is given and results are discussed by comparing different films thickness to clarify the role of interfacial free energy and crystallographic orientation.

[1] *S. Pin, M. Suardelli, F. D'Acapito, et al., J. Phys. Chem. C, 2013, 117, 6105-6112,* ***[2]*** *S. Pin, M. Suardelli, F. D'Acapito, et al., J. Phys. Chem. C, 2013, 117, 6113-6119*

Keywords: solid-state reactions, X-ray diffraction, XAS