[MS37-05] Role of Interfacial Energy and Crystallographic Orientation on the Mechanism of the ZnO + Al2O3 → ZnAl2O4 Solid-State Reaction. Serena C. Tarantin, a Paolo Ghigna,b Sonia Pin,c Girgio Spinolo,b Michele Zema,a

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A multi-technique experimental protocol have been recently suggested and used for exploring the initial steps of solid-state reactions. It essentially investigates 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 and compares the results obtained with films of different thicknesses and deposited onto different crystal orientations . In particular, the initial steps of the reaction between ZnO and Al2O3 have been investigated with 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 sapphire single crystals [1,2]. The reaction eventually yields the ZnAl2O4 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. Their number, composition, structure and kinetic role strongly depend on substrate orientation and film thickness. Once formed, the spinel grows four times faster on (001)sapphire than on (110) sapphire. In both cases the rate-determining step is the motion of the interface(s), and the growth of the spinel layer is linear with time, with rate constants k = 1.1(2) • 10−9 cm·s−1 and k = 4.8(1) • 10−9 cm·s−1 at 1000°C for (001) zincite □ (110)sapphire and (001)zincite □ (001)sapphire interfaces, respectively. At the (110) zincite □ (012)sapphire interface, the reaction shows dumped oscillations. Some information on the structure of the intermediate phases is given by EXAFS, for the films deposited onto the (001) and (012) sapphire faces. EXAFS data would indicate the presence of (Zn,Al)O solid solutions, with composition intermediate between those of zincite and spinel, essentially based on an hcp arrangement of oxide anions and a Zn-rich composition. A more detailed understanding of the reactivity can be inferred by the grazing incidence diffraction experiments of the films deposited on the (001)sapphire face reacted at 1000 °C for different lengths of time. Evidence is given of the fact that one of the side compounds has a crystal structure close to that of the Zn3In2O6 compound and that the spinel initially forms with a distribution of lattice parameters. The results are discussed by comparing different films thickness to clarify the role of interfacial free energy and crystallographic orientation.

[1] Pin, S., Suardelli, M., D'Acapito, F., Spinolo, G. Zema, M., Tarantino, S.C. & Ghigna, P. (2013). J. Phys. Chem. C 117, 6105-6112.
[2] Pin, S., Suardelli, M., D'Acapito, F., Spinolo, G. Zema, M., Tarantino, S.C., Barba, L. & Ghigna, P. (2013). J. Phys. Chem. C 117, 6113-6119.

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