Fundamentals of competing phase formation at reacting interfaces

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Sequence of phase formation in thin-film reactions still presents a significant scientific challenge in material science. Up to date, no general consensus exist on a unified model description to describe phase competition at interfaces in low-dimensional systems. Various approaches to this problem have been suggested by U. Goesele and K.N. Tu, F. d'Heurle, J. Philibert, P. Gas, P. Desre and A. Yavari, Ya. Geguzin, A. Gusak and C. Gurov, F. Hodaj, D. Beke and Z. Erdelyi, K. Barmak and others. Different phase formation sequences may arise during reactive diffusion at the interface between two solid or liquid phases. Temporary or full suppression of competing metastable and/or stable intermediate reaction phases can have either a thermodynamic or a kinetic origin, as dependent on the delicate interplay between the evolving compositional gradients at the interface, interface motion, spatial confinement and nucleation.

The theory of nucleation in sharp concentration gradients was first suggested in 1990 simultaneously by Desre, Yavari and Gusak. The critical concentration gradient concept is reconsidering the thermodynamics of nucleation in a concentration gradient by including a principally new size dependence of the Gibbs free energy. In addition to the well-known energy contributions due to the bulk (i.e. the bulk energy gain, negative third-order term) and the interface (i.e. energy penalty, positive second-order term), an additional term is introduced, which is proportional to the fifth (or in special cases to the fourth) power of size and the square of the concentration gradient between the parent and product phase. According to this advanced model description of the nucleation process, even without diffusive competition, phase nucleation can be suppressed at the very initial stages of the reaction due to spatial constraints for the phase transformation, especially if the evolving concentration gradients between parent and nucleating phases are initially very sharp.

Kinetic suppression of product phases during the first stage of interface reaction was first suggested by Tu and Goesele, Geguzin, Gurov and Gusak around 1980. The theoretical description was recently combined with the Fokker-Planck approach to allow model descriptions of phase nucleation in open systems. The advanced modeling approach predicts suppression criteria for the nucleation of competing product phases in dependence of the evolving concentration gradients at the interfaces between the parent and competing product phases. The approach successfully rationalizes phase competition in recently discovered point-contact reactions between oxidized Si nanowires and metalic nanowires or nanoparticles.

The current talk addresses the basic concept of the critical concentration gradient approach in describing the thermodynamics and kinetics of competing phase formation at reacting interfaces. Models predictions on the sequence of phase formation are compared with experimental observations for phase formation in multilayers and thin-film couples of e.g. Cu-Sn, Ni-Al, metal-silicon and Ni-Zr.