

In situ High Resolution Electron Microscopy of Material Reactions, at the Atomic Level

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This paper gives an overview of how our group has applied in situ observations, under controlled experimental conditions, in a transmission electron microscope (TEM), to understand the mechanism of material reactions, at the atomic scale [1].

Firstly, because of the thin nature of the samples required for high resolution imaging, it must be established that reproducible data can be obtained by this experimental approach. We have provided guidelines to ensure this [2], including, most sensitively, comparison of reaction activation energies determined in situ with those obtained from parallel bulk material. It cannot be emphasized enough how important this is, as in situ observations at the necessary magnifications almost always reveal changes never seen before.

The reactions studied include surface and defect re-arrangements in semiconductors, crystallization of amorphous materials, solid-state amorphization reactions in multilayers and at interfaces, metal-mediated crystallization of amorphous carbon, silicon and germanium, and several others (e.g., [1]) Arguably one of the most interesting of all concerns both solid-state amorphization and metal-mediated phase transformation in Cu-Ta multilayers [3], which are purportedly immiscible elements. This turns out to be important for the use of tantalum as a diffusion barrier metal for copper in current transistor technology. Extension to environmental TEM observations will also be discussed (e.g., [4])

[1] R. Sinclair, In Situ High-Resolution Transmission Electron Microscopy of Materials Reactions, *Mats. Res. Soc. Bull.* 38 (2013) 1065-71

[2] R. Sinclair, T. Yamashita, M. A. Parker, K. B. Kim, K. Holloway and A. F. Schwartzman, The Development of In Situ High Resolution Electron Microscopy, *Acta Crystallogr. Sec. A* 44 (1988) 965-75.

[3] H. J. Lee, , K. W. Kwon, C. Ryu, and R. Sinclair. "Thermal Stability of a Cu/Ta Multilayer: an Intriguing Interfacial Reaction." *Acta Mater.* 47, (1999): 3965-75.

[4] A. L. Koh, E. Gidcumb, O. Zhou and R. Sinclair, Observations of Carbon Nanotube Oxidation in an Aberration-Corrected, Environmental Transmission Electron Microscope, *ACS Nano* 7(3) (2013) 2566-72.

[5] The contributions of many group members over many years are deeply appreciated.