

Microstructural Studies of Copper Sulfide Film Growth: Influence of Humidity

M. J. Campin,* J. C. Barbour,** J. W. Braithwaite** and J. G. Zhu*

*Dept. of Physics, New Mexico State Univ., Las Cruces, NM 88003

**Sandia National Laboratories, Albuquerque, NM 87185

Atmospheric sulfidation of copper is an important form of corrosion, producing multiple sulfide phases and complex morphologies. In this study, we have used focused ion beam (FIB) cross-sectioning, transmission electron microscopy (TEM), high-resolution TEM (HRTEM), x-ray diffraction (XRD), and ion beam analysis to characterize the product formed when thin films of Cu are exposed to a dilute (50-200 ppb) H₂S atmosphere at low (0.5%) to high (80%) relative humidity (RH).

First, our study showed that the thickness of the Cu₂S product layer is significantly higher when the sulfidation occurs over extended time at low RH compared with that at high RH. As shown in figure 1, the existence of the “parabolic” Stage-II at high RH implies that the mechanism of sulfide growth at high and low humidity differs (e.g. solid-state diffusion is rate controlling only at high humidity levels). We have also shown that for both low and high RH exposure during sulfidation, Cu and S react and form the low chalcocite phase (Cu₂S) as identified by x-ray and electron diffraction. In later stages of sulfidation, Cu diffuses through the Cu₂S layer leaving Kirkendall voids in the Cu near the Cu/Cu₂S interface; also other Cu and S phases, including sulfates and/or hydroxide hydrates, appear. The intent of this investigation is to examine possible structural differences in the sulfides grown at high and low humidity and correlate these differences to possible changes in sulfidation mechanisms.

Differences in grain sizes between low and high RH are found during the initial 150 nm of sulfide growth. Cross-section and plan-view TEM reveal that in the first 150 nm of Cu₂S growth, grains formed at low RH range in size between 30 nm and 50 nm whereas the grains formed at high RH range in size between 10 nm and 20 nm. Beyond the initial 150 nm of growth, similar grain size exists for both RH levels (figs. 2-3). TEM analysis reveals the high RH samples exhibit many bar or plate-like structures (25 x 75 nm), some of which span the entire Cu₂S layer and which tend to be more numerous at higher temperature. If the apparent solid-state diffusion of Cu depends on RH, then a correlation between the microstructure and differing diffusion pathways should exist, e.g., fast diffusion pathways along thick, defective grain boundaries. We have examined grain boundaries formed under different RH and found that all grains seem to have abrupt interfaces. Figure 4 shows a plan-view HRTEM image from the low RH sample. No evidence in support of a fast grain boundary diffusion pathway was found. Another possibility is that the low RH samples have grains that are oriented along crystallographic orientations that support fast diffusion. We see evidence for differences in dominant grain orientations between low and high RH samples using XRD. Local differences in grain orientations have been examined using HRTEM. The connection between Cu₂S grain morphology and the solid-state diffusivity of Cu will be discussed.

Acknowledgement:

This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy

General references:

1. T. E. Graedel et. al, Corrosion Science 23, 1141 (1983).
2. O. M. Magnussen and R. J. Behm, MRS Bulletin 24 (#7), 16 (1999).
3. S. Cassaignon, T. Pauporte, J. Guillemoles, and T. Vedel, Ionics 4 (#5-6), 364 (1998).
4. C. Leygraf and T. Graedel, Atmospheric Corrosion, Wiley-Interscience (2000).
5. J. C. Barbour et. al., Corrosion and Reliability of Electronic Materials and Devices, Electrochemical Society, 67 (1999).

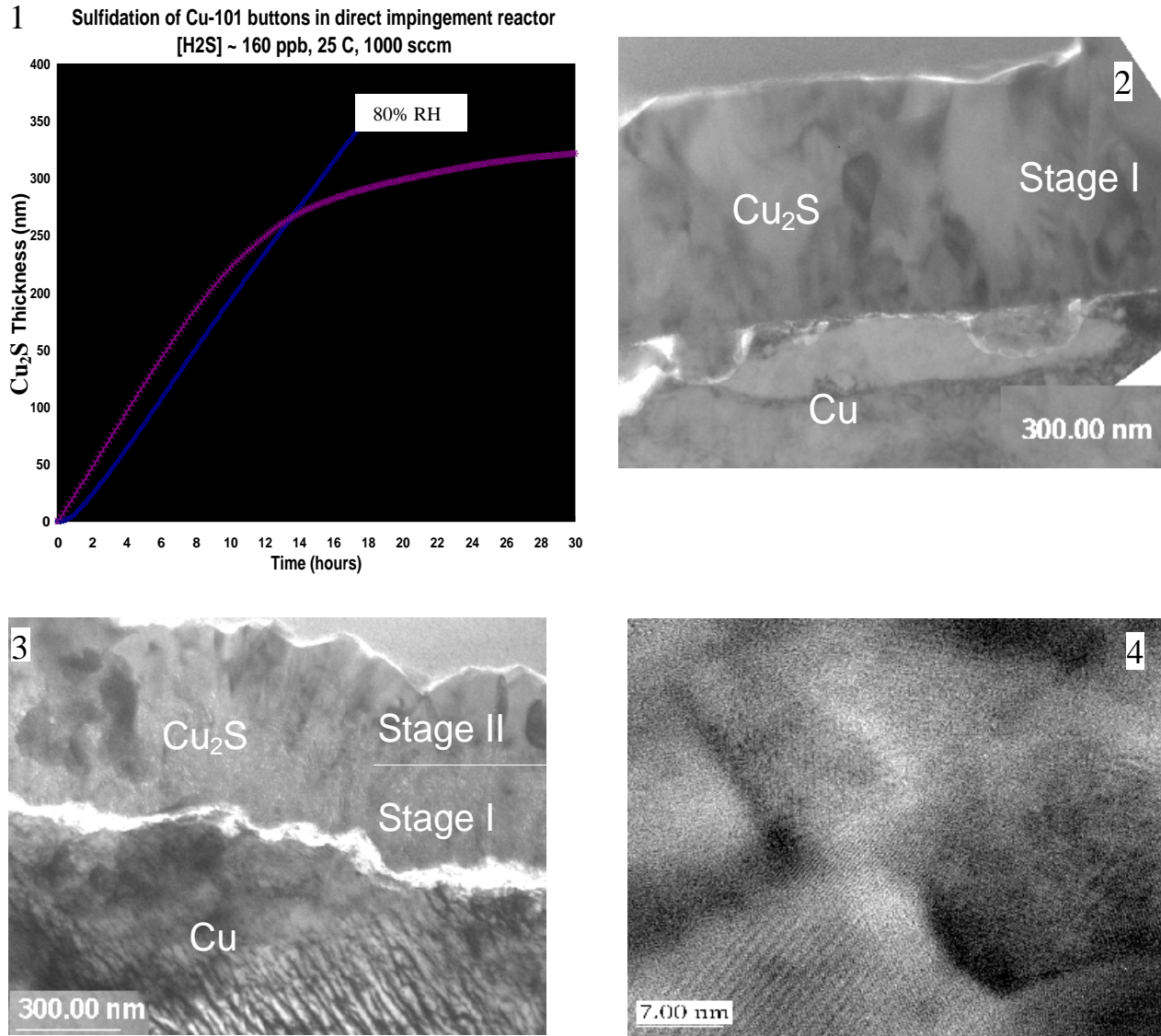


Figure 1: Plot of Cu₂S thickness vs. time.

Figure 2: Cross-sectional TEM image showing Cu₂S formed on Cu at 0.5% RH.

Figure 3: Cross-sectional TEM image showing Cu₂S formed on Cu at 70% RH.

Figure 4: Plan-view HRTEM image of a specimen from the low RH sample.