

**Phase transitions at Cu(100)
in the presence of thiocyanate anions**

C. Safarowsky, A. Spaenig, P. Broekmann and K. Wandelt

Institut für Physikalische und Theoretische Chemie der
Universität Bonn, Wegelerstr. 12, 53115 Bonn,
Deutschland

In-situ EC-STM has been used to examine the potential dependent phase transition of an adsorbate covered Cu(100) electrode exposed to sulfuric acid electrolyte containing thiocyanate anions. In contact with the thiocyanate containing electrolyte a highly ordered adsorbate layer is formed at negative potentials revealing a regular striped pattern (fig. a, slightly distorted by drift). These chains of adsorbate particles are preferentially oriented parallel to the substrate $\langle 011 \rangle$ main symmetry axes. This smooth adsorbate structure could be described with a so-called $(2 \times \sqrt{10})$ unit cell. Another way to characterize this superstructure is to assume a rectangular $c(6 \times 2)$ unit-mesh (fig. a). The existing adsorbate coverage amounts to $\Theta = 0.33$ ML. Furthermore this adsorbate phase exhibits two rotational domains which are rotated by an angle of 90° with respect to the main symmetry axes of both domains.

By sweeping the electrode potential in positive direction an irreversible phase transition takes place which affects not only the atomic adsorbate structure but also the surface morphology. Several square and rectangular adsorbate covered copper islands arise on the surface and provoke a roughening of the copper substrate. Due to the kinetical hindrance it is possible to observe this phase transition by STM. A second process contributes to the roughening effect namely the formation of narrow and anisotropic ditches which grow preferentially along the $\langle 001 \rangle$ and $\langle 010 \rangle$ directions similar to the mentioned adsorbate covered copper islands (fig. b). The extent of this roughening caused by corrosion-like and deposition processes is promoted by shifting the potential to positive values. Finally, these two processes lead to an arrangement of islands and vacancy islands similar to a checkerboard pattern (fig. c). A plausible model for the appearance of this second adsorbate phase is based on a reconstruction of the topmost copper layer namely an expansion of the topmost copper layer. The adsorbate molecules reside in "pseudo fourfold hollow sites" of the isotropically expanded copper layer and arrange in a "pseudo $c(2 \times 2)$ " adsorbate structure. A decomposition of thiocyanate resulting in a semiconducting coppersulfide layer will be also discussed.

