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In-situ Heating Electron Microscopy on Cu/SnO_2 Bilayer Nanoribbons

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In-situ electron microscopy provides a means to directly visualize interfacial processes in real time and with high spatial resolution in real and in reciprocal spaces. However, the traditional preparation of electron-transparent samples from thin films often alters the interface(s) of interest. An innovative approach is to deposit a layer of a chosen material onto a miniature substrate that is already electron-transparent and mounted for TEM imaging. Cu/SnO_2 bilayer nanoribbons were made by coating about 10 nm-thick face centered cubic Cu layers on tetragonal single crystal SnO_2 nanobelts so to study as-made, extending hetero-structure interfaces. The SnO_2 ribbons typically have width and thickness ranging from 10 nm to 1 μm and width/thickness ratios as high as ten [1]. The thick and thin sides of a given ribbon can be either of the $SnO_2(\bar{1}01)$ or (010) surfaces.

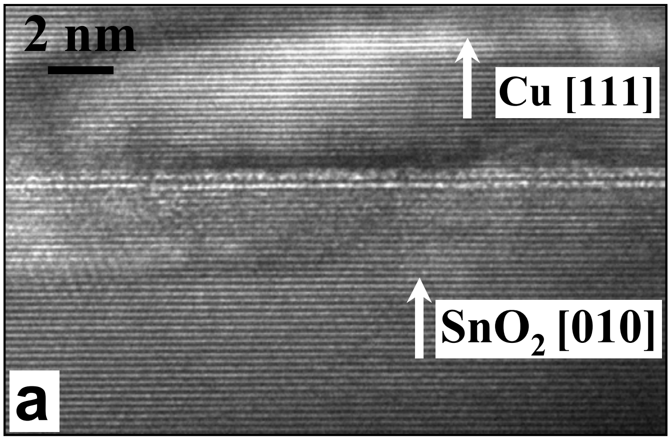
TEM observations of bilayers made at room temperature reveal the existence of distinct structural Cu types for growth on $SnO_2(\bar{1}01)$ and (010) surfaces, respectively. Cu on $SnO_2(010)$ always forms flat and epitaxial Cu(111) films, Fig.1a. In contrast, growth on $SnO_2(\bar{1}01)$ produces dense and continuous films of Cu grains with no preferred orientation relative to the substrate, Fig.1b. The response of the bilayers to in-situ TEM heating is studied using a 300kV JEOL 3010 transmission electron microscope equipped with a double-tilt heating stage. When subjected to repeated heating-cooling temperature cycles between 25 and 200°C, the epi-bilayers bent reversibly governed by the theory for macroscopic bimetallic strips, Fig.2. In contrast, the untextured bilayers always displayed a degree of plastic deformation.

The Cu layers became unstable when heated to above ~225ºC. Thermodynamic considerations indicate that Cu does not wet $SnO_2(010)$ or $(\bar{1}01)$ at equilibrium. Both the untextured and epitaxial Cu films irreversibly converted to thick, flat, pure Cu islands between 225 and 500ºC, Fig.3. The onset of island formation was followed by a rapid but brief increase in island number and then a sustained period of slow island thickening through surface diffusion of Cu.

Above 550ºC the Cu islands underwent a series of solid-state reactions with the SnO_2 substrate, leading to various phases and major changes in morphology. Sn was first diffused into many of the thickening Cu islands. On the $SnO_2(\bar{1}01)$ surface, these alloy islands began to etch rapidly into the ribbon substrate at about 600ºC, Fig.4, while the $SnO_2(010)$ surface proved to be more chemically resistant. As etching continued, many of the flat islands lost their faceting, became quasi-spherical in shape. By 725ºC the majority of these particles had transformed into Cu-Sn phases. Further heating fused the nanoribbons.

References

[1] Z.W. Pan et al., Science 291 (2001) 1947.
[2] This work was supported by LDRD Fund from Lawrence Berkeley National Laboratory.



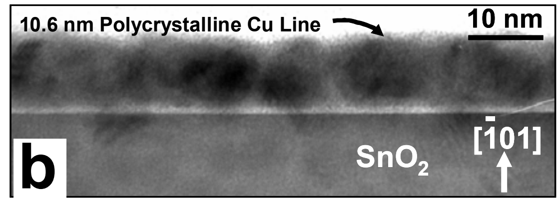
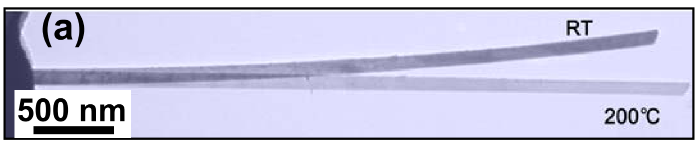


Fig. 1. (a) Epitaxial Cu layer formed on the (010) surface of a SnO_2 nanoribbon. (b) 10.6 nm thick untextured Cu film coated on the ($\bar{1}$01) surface of a SnO_2 nanoribbon.



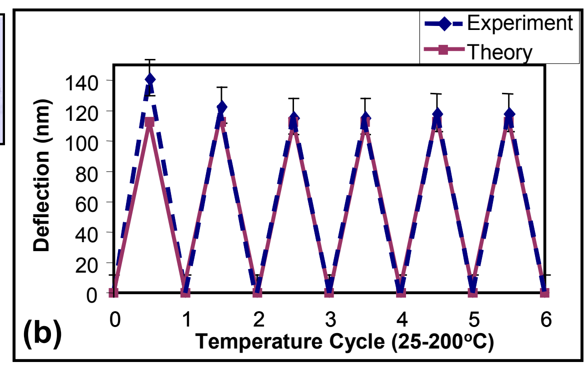


Fig. 2. (a) Superimposed TEM images for an epitaxial Cu/SnO_2 bilayer nanoribbon (Cu on the top side) at room temperature and 200°C, respectively. Note the tip displacement. (b) The corresponding plot of tip displacement versus temperature illustrates that bending is linear with temperature and reversible through multiple heating-cooling cycles.

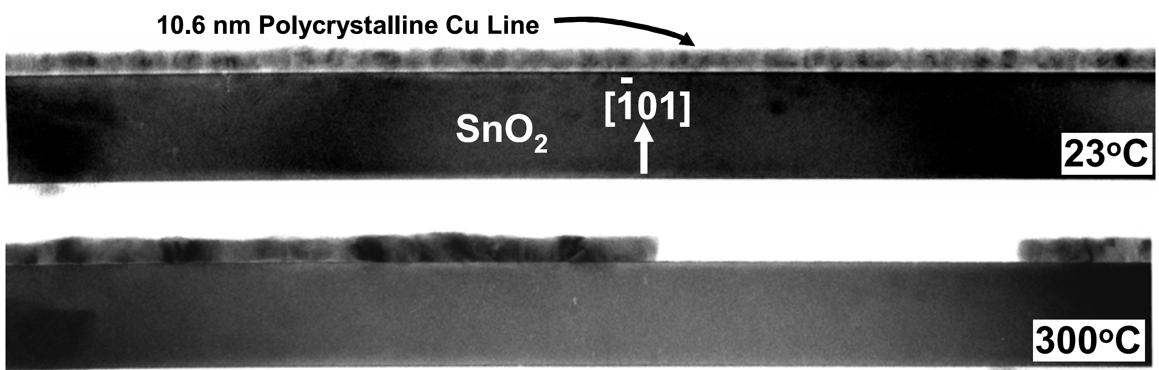


Fig. 3. An untextured, 10.6 nm-thick Cu layer on the SnO_2($\bar{1}$01) surface is seen at room temperature. Dewetting of the Cu layer is seen at 300°C, and diffusion of Cu from the gap area thickened the Cu islands.

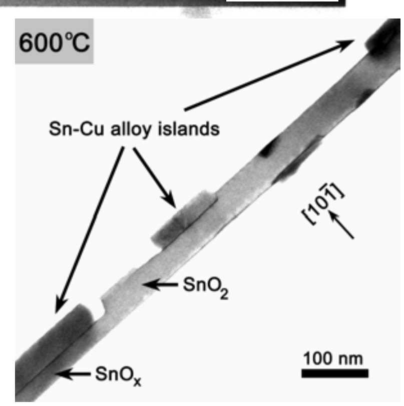


Fig. 4. Cu-Sn alloy islands are formed at about 600°C, and etched into SnO_2 nanoribbon substrate.

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