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Abstract.   In a recent paper Bowker *et al* (*J. Phys.: Condens. Matter* **10** 7713) attempt to explain the enhanced reactivity occurring at the ends of Cu(110)–(2×1)O structures by proposing that the Cu–O rows are unstable unless terminated by oxygen atoms. We present alternative views based upon scanning tunneling microscopy (STM) observations. We show that consecutive images of the (2×1)O structures show the ends of the rows constantly dissolving and reforming. Bowker *et al* also discuss the fates of Cu atoms released from the (2×1)O structures during reactions that produce adsorbed methoxy and formate. We discuss these interpretations with regard to reaction stoichiometries and models for methoxy structures as well as previous work on the formate system.

In a recent paper, Bowker *et al* [1] have addressed a number of significant issues regarding reactions occurring on Cu(110)–(2×1)O surfaces. Reactions on such surfaces have been quite extensively studied via STM, and some general trends have been uncovered. In particular, it has been shown in a number of systems that reactions occur at the ends of the Cu–O rows in the (2×1) structures [2–6]. Thus, a correct explanation of why the ends of the Cu–O rows are so reactive is extremely important. Bowker *et al* propose a model in which the Cu–O rows are unstable unless terminated by oxygen atoms. They also review reactions on Cu(110)–(2×1)O surfaces with methanol and formic acid to form adsorbed methoxy and formate, respectively, in particular discussing what happens during these reactions to the Cu atoms formerly incorporated in (2×1)O structures. In the case resulting in adsorbed methoxy, they propose that these Cu atoms are incorporated into a (5×2) methoxy structure, which represents a rare case of a molecularly-induced surface reconstruction involving added metal atoms. In the case of reactions which produce c(2×2) formate structures, they propose that Cu atoms liberated from (2×1)O structures migrate to step edges and are incorporated into a sawtooth restructuring of these step edges. In this Comment, we discuss observations from STM experiments which suggest alternative explanations to the model proposed by Bowker *et al* for the enhanced reactivity occurring at the ends of Cu–O rows. We discuss the incorporation of Cu atoms into (5×2) methoxy structures with regard to reaction stoichiometries; in particular, we argue that if models for the (5×2) methoxy structures are correct, then at most only half of the added Cu atoms needed for this structure are released from the (2×1)O reconstruction. We also discuss the rearrangements of Cu atoms during a formate-induced restructuring of step edges.

Reactions occurring at the ends of the Cu–O rows in Cu(110)–(2×1)O structures have been observed in a number of different systems [2–6]. Thus, a proper explanation of why the row ends are so reactive is important and may extend to systems where similar structures and effects are also observed [7]. The Cu(110)–(2×1)O structure has been shown to be an added

row reconstruction consisting of rows of alternating Cu and O atoms aligned along the $\langle 001 \rangle$ direction [8, 9]. Bowker *et al* [1] propose that these Cu–O rows are unstable unless terminated by oxygen atoms. In their model, when the end-most oxygen atom is removed by a chemical reaction, the adjacent Cu atom simply diffuses away, exposing another oxygen atom. If this model is correct it seems somewhat difficult for us to understand why the Cu–O rows should be inclined to form in the first place. Rather than discussing speculation, there is much to be gained by simply taking STM images of the ends of the Cu–O rows [6, 10, 11]. Previous work has shown that row ends often appear different: sometimes the outermost atom appears to be relaxed outward, or when two rows terminate at the same position one occasionally observes that the rows appear to bend back on themselves [10, 11]. These apparent relaxations and reconstructions that occur at the ends of the rows could also explain the enhanced reactivity that occurs there. Here, we show that consecutive images of $(2 \times 1)O$ structures (figure 1) also provide possible alternative explanations [12]. Comparisons between images show indications that the ends of the rows appear to be constantly breaking up and reforming. Segments of the rows also appear to break off and move laterally, as has been previously observed [10, 13].

We are also concerned about Bowker *et al* 's discussion of the fates of Cu atoms contained within the $(2 \times 1)O$ rows following reactions involving methanol and formic acid which result in the removal of oxygen from the surface. Bowker *et al* state that, in the case of resultant methoxy structures, these Cu atoms are incorporated into (5×2) methoxy structures, or, in the case resulting in $c(2 \times 2)$ formate surfaces into a sawtooth restructuring of step edges. We feel that this discussion is too simplistic and is inconsistent with prior work on these systems. For example, the overall reaction stoichiometry which produces methoxy on Cu(110) surfaces from oxygen and methanol is the following [14]:

$$2CH_3OH_{(g)} + O_{(a)} \rightarrow 2CH_3O_{(a)} + H_2O_{(g)}.$$
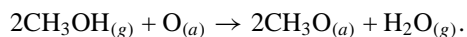
Proposed models for the (5×2) methoxy structure involve 0.4 monolayers (ML) of methoxy molecules and, depending on the specific model proposed, either 0.4 or 0.6 ML of added Cu atoms [3]. We note that Bowker *et al* have recently expressed a belief in a model involving 0.6 ML of Cu atoms [15]. If one wished, therefore, to produce a fully saturated (5×2) methoxy surface one would begin with an initial oxygen coverage of 0.2 ML and hence only 0.2 ML of added Cu atoms would be present in the corresponding islands of the $(2 \times 1)O$ structure. If any of the proposed models for the (5×2) structure are correct, then during the formation of a complete (5×2) methoxy surface an additional 0.2 or 0.4 ML of Cu atoms would have to be supplied by the substrate. We feel that by limiting themselves simply to a discussion of what happens to only those Cu atoms released from the $(2 \times 1)O$ structures Bowker *et al* [1] are not bringing sufficient attention to equally, if not greater, rearrangements of substrate atoms that must occur if any of the proposed models for the (5×2) methoxy structure are correct.

Likewise, we feel that there is no reason to assume that the sawtooth restructuring of step edges on Cu(110)–$c(2 \times 2)$ formate surfaces utilizes only those Cu atoms released from the $(2 \times 1)O$ islands. In the original paper [16] discussing the discovery of this formate-induced restructuring of step edges, the authors described instances of the formation of pits on the surface indicative of removal of Cu atoms from the substrate. They showed that prior to formic acid exposure their Cu(110) surface showed tightly bunched steps, which contained very little $(2 \times 1)O$ structures; afterwards these steps were reorganized into sawtooth shapes. They also observed a similar restructuring of Cu(110) step edges in the case of adsorbed benzoate in the absence of any pre-adsorbed oxygen. Subsequent experiments [17] also showed similar restructuring of step edges on clean Cu(110) surfaces following exposure to acetic acid. Hence, it is almost certainly the case that the $c(2 \times 2)$ formate-induced restructuring of step edges involves significant rearrangements of substrate Cu atoms as well as those Cu atoms formerly
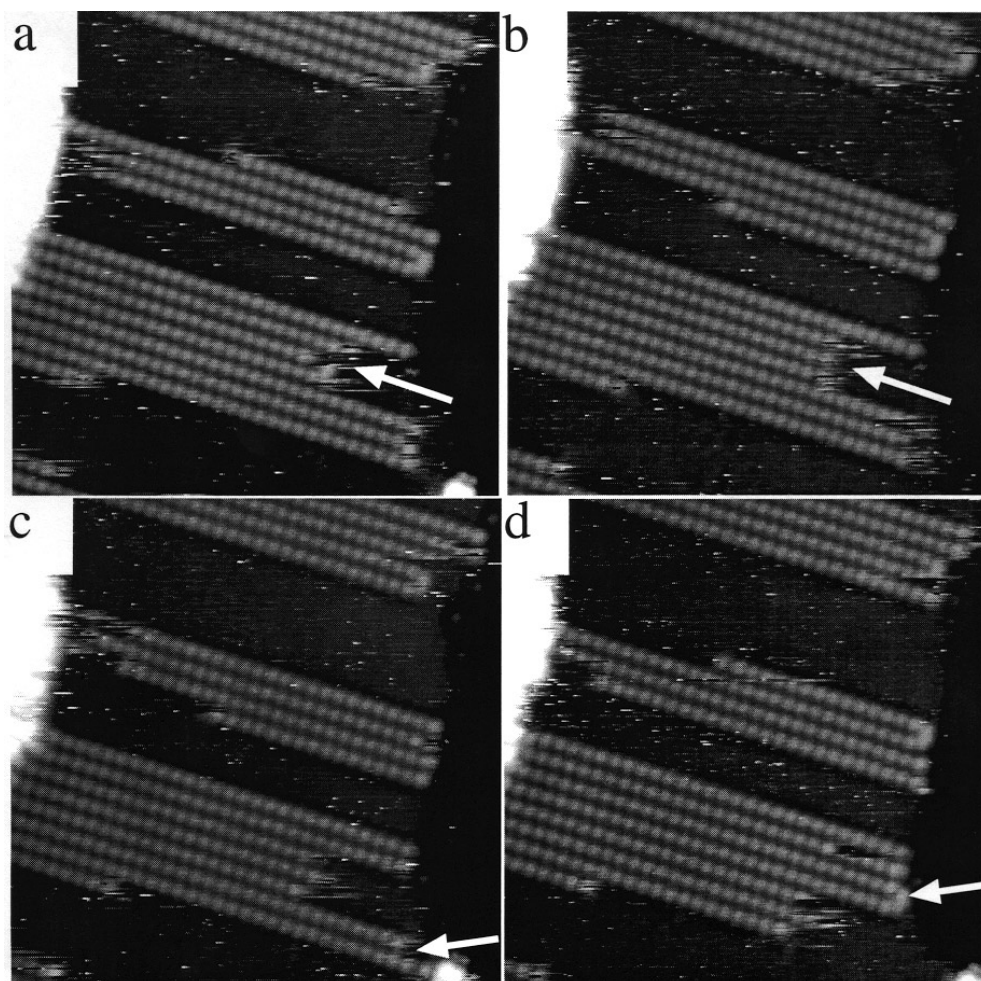
Figure 1. Four consecutive images of a 120 Å×120 Å area of a Cu(110) surface. These images were taken 45 seconds apart; one sees instances of the Cu–O rows appearing to bend back on themselves as reported in [3, 9, 10], but these images also show changes occurring at the ends of the rows. The arrows in (a) and (b) show instances of the ends of the rows appearing to dissolve and reform. The arrows in (c) and (d) show segments of the rows breaking off and moving laterally. Such instability of the row ends may contribute to the enhanced chemical reactivity occurring there and represent an alternative explanation to the one proposed by Bowker *et al* [1]. Sample bias and tunnelling currents are −2.0 V and 1.0 nA, respectively.

contained within (2×1)O islands.

In short, we present alternative explanations for the enhanced reactivity of the ends of the Cu–O rows in Cu(110)–(2×1)O structures. In the cases of reactions that produce methoxy and formate structures, we feel it important to point out that prior work suggests that these molecules may cause restructuring of the Cu(110) surfaces involving gross rearrangements of Cu atoms whose numbers may significantly exceed those released from (2×1)O islands during reactions with methanol and formic acid.

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