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X-Ray Photoelectron Spectroscopy Investigation of Direct Process Contact Masses: Reply to Gentle and Owen

Gentle and Owen's contention (*1*) that exposure to atmosphere of the contact mass may have given rise to the observed Cu^{2+} related Cu $2p$ satellite peaks in our X-ray photoelectron spectroscopy (XPS) examination is not tenable for the following reasons (*2*).

First, no surface oxidation of copper has been observed in the case of fresh contact mass which shows the presence of η-phase of copper silicide, Cu_3Si, and evidence of oxidation of silicon only. Sputter removal of ~30 Å shows no change.

Second, the partly spent contact mass shows weak Cu $2p$ signal which enhances significantly on sputter removal of ~30 Å and clearly shows the presence of Cu^{2+} as is evident by the significant presence of shake-up Cu $2p$ peaks.

Third, a sample of fresh contact mass on prolonged storage under ambient conditions was found to have developed only ~50 Å layer of cupric oxide as described earlier (*2*).

Fourth, the only surface oxidation attributable to short ambient exposure is that of silicon of the contact mass. This fact is amply supported by recent XPS studies of Cu_3Si (η-phase) (*3*).

Furthermore, there are other valid arguments which discount possible oxidation of copper due to ambient exposure. The contact mass used in our synthesis were grossly silicon-rich, although the surface showed the existence of the η-phase, Cu_3Si (*4*). Moreover, most silicides have been known to be highly sensitive to silicon oxidation (*5*); copper silicides are no exception (*3*).

The data presented by Gentle and Owen are incomplete in many aspects. One aspect relates to the nature of samples for XPS analysis. The state of contact mass at the time of withdrawal for analysis is controlled by the initial relative Si/Cu ratios and the extent to which the reaction has proceeded (*4*). For example, starting with Cu_3Si would lead to the presence of even elemental copper along with other phases of silicides, such as ε and γ, and XPS would detect elemental copper. No such details are provided in the paper (*1*). Complete XPS spectra of the contact mass are not given and the nature of silicon, which is an important ingredient of the contact mass, has not been examined.

It is not clear why ion-sputter removal of ~30 Å from the sample was done before XPS analysis, since under their experimental conditions with inert argon atmosphere, the unsputtered surface would be a better representative of the reactive surface conditions. They have neither given comparative XPS of sputtered and unsputtered samples, nor have commented upon this important aspect. In our investigation, comparative XPS of the as-received and sputtered samples were taken to pinpoint the effects of exposure to atmosphere also (*2*).

It should also be emphasized that observation of similar X-ray diffraction patterns of variously prepared contact masses as found by Voorhoeve (*4*) does not automatically lead to the existence of identical catalytically active sites. Catalytic processes mostly occur on the top few molecular layers which can only be characterized by techniques such as XPS. The observations of Frank *et al.* are noteworthy in this regard (*6*).

Undoubtedly, the approach of the au-

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thors in eliminating ambient exposure as possible variable in the study of this complex system is commendable. However, much more detailed study is required to explain their observations in contrast to our earlier conclusions and those of others (*2*, *7*, *8*).

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