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# Observation of Gas-Solid and Gas-Liquid Reactions by In-situ Environmental Holder in TEM

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Recently an in-situ environmental holder which can be used in a conventional TEM without any major modification has been developed [1]. A gas injection nozzle was built in the specimen heating holder developed by Kamino and Saka [2]. The gas injection nozzle permits gas flow around the specimen sitting on the heating element made of a fine W filament. The pressure of the electron gun chamber could be kept in the range of $10^{-5}$Pa while the pressure at the specimen chamber was maintained at the range of $10^{-2}$Pa.

The microscope used in the study was a Hitachi H-9000 300kV high resolution TEM. The holder was used to observe gas-solid and gas-liquid reactions at near atomic level, which include oxidation and reduction of solid Fe and solid Si, and liquid Sn.

FIG1 shows processes of reduction of a natural oxide layer on Si and re-oxidation of Si. The Si particle observed was covered with a 10nm thick natural oxide layer and the EELS (inset) shows a peak from O(FIG1a). On heating at 723K at the vacuum of $2x10^{-5}$Pa, the oxide layer was reduced and the peak of O disappeared (FIG.1b). On introducing oxygen gas to $8x10^{-3}$Pa, the oxide layer grew again and the peak of O appeared in EELS (FIG.1c)

FIG.2 shows process of oxidation of Fe to $Fe_2O_3$ under oxygen. Fe particles were obtained by heating $Fe_2O_3$ in the vacuum of $2x10^{-5}$Pa at. 1173K. FIG.2a shows a particle of Fe and EELS (FIG.1-e) shows no peaks from O. FIG.2b shows a mapping of Fe. On heating the particle at 1173K under a pressure of $8x10^{-3}$Pa of $O_2$, the Fe particle was oxidized to $Fe_2O_3$ (FIG.2c-f). FIG2d shows mapping of O.

FIG.3 shows processes of oxidation of liquid Sn under a pressure of ~$10^{-4}$Pa in $O_2$. Initially, at a vacuum of $1x10^{-5}$Pa, the liquid droplet of Sn was perfectly spherical due to isotropic surface energy of the liquid Sn. On oxidation under oxygen atmosphere of (4-6)$x10^{-4}$Pa, the surface of liquid Sn was covered with an oxide layer, which grew layer by layer. The liquid droplet became facetted. In addition, the oxide layer penetrated into the interface between the substrate ($SiO_2$) and the liquid Sn. Thus, the liquid Sn was completely covered with an oxide layer. On decreasing the pressure to $10^{-5}$Pa, the oxide layer started to be reduced and eventually the system became completely free from the oxide layer.

References

[1] T. Kamino et al., *J.Electron Microscopy,* in printing
[2] T. Kamino and H. Saka. *Microsc. Microanal.Microstruct.* **4** (1993): 127-135

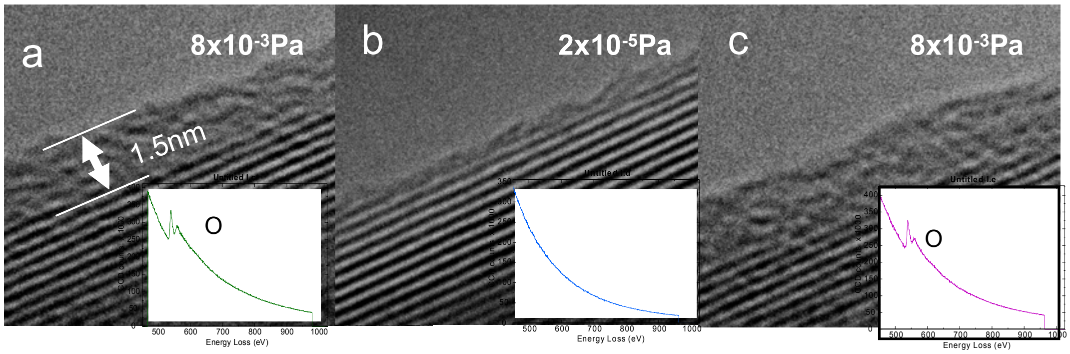


FIG. 1 Reduction of natural oxide on Si and re-oxidation of Si. Insets are EELS

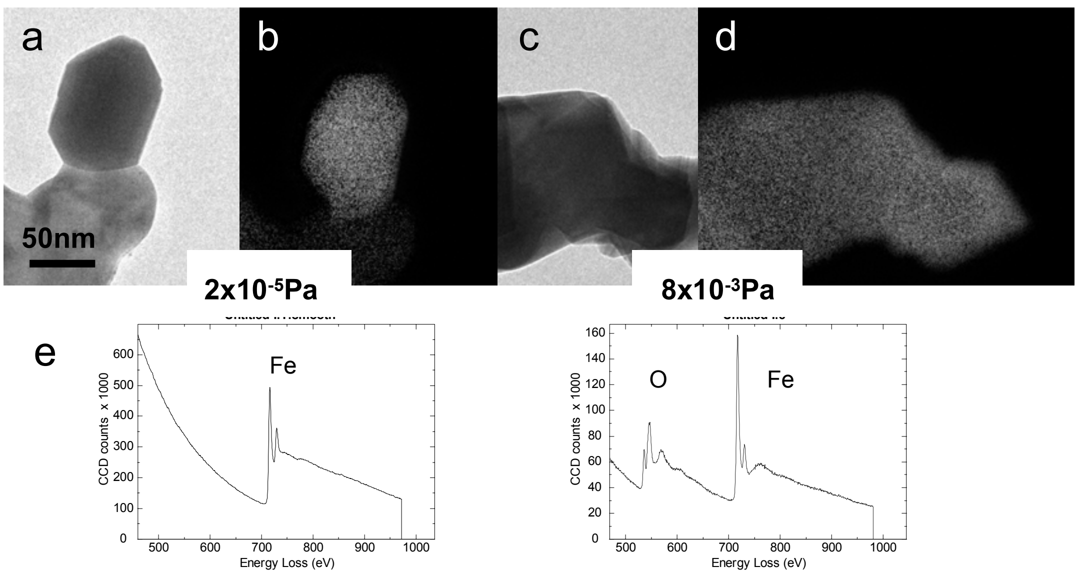


FIG. 2 Oxidation of Fe. a,b,e are before oxidation and c,d,f are after oxidation. b and d are mapping of Fe and O, respectively. e and f are EELS spectra

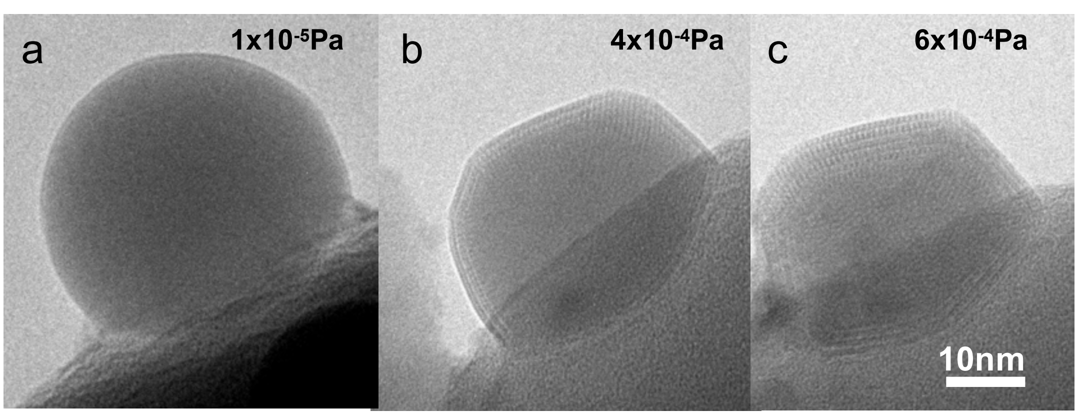


FIG. 3 Oxidation of liquid droplet of Sn on a $SiO_2$ substrate.

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