

Supporting Information

Interaction of Molecular Oxygen with Hexagonally Reconstructed Au (001) Surface

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No Observed X-ray Effects:

During the experiments several attempts were performed to detect x-ray induced or catalyzed effects, but none were observed. On multiple occasions a surface phase transition would be started and the x-rays then removed for several minutes. Upon checking after this pause there would be no significant change in the resulting state when compared to the same transition conducted during constant x-ray exposure. An example of this is shown in Supplemental Figure 1. Furthermore, adjusting the x-ray beam intensity through the use of filters did not alter evolution rates. Because the observed kinetics could be adjusted comfortably to timescales of $10^2 - 10^3$ sec, through choices of pressure and temperature, and those rates were independent of x-ray exposure, it can be reasonably understood that x-ray effects do not provide a mechanism of catalyzing the surface processes observed at high temperatures.

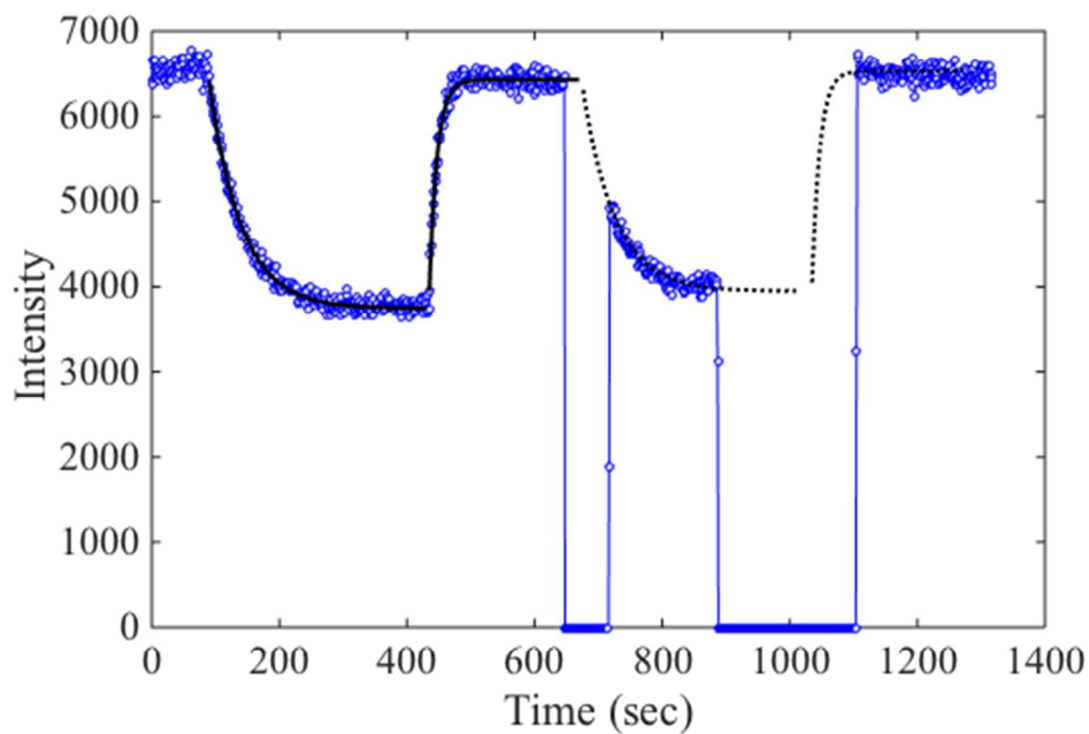
Phase Diagram:

For completeness, the values of the fitting returned for T_L from equation 1 are shown in Supplemental Figure 2. These are the temperatures where the “hex” reconstruction was observed to fully lift as they depend upon the oxygen content. The surface reconstruction is known to lift at about 1170 K in vacuum from earlier studies.^{23, 24, 25}

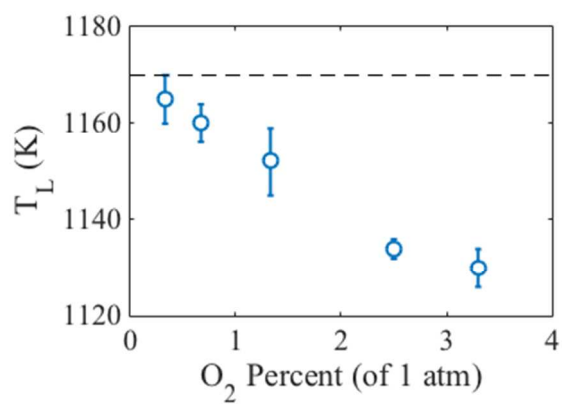
Additional Structural Information:

No ordered structure in the presence of oxygen was directly observed and the CTR measurements are consistent with a disordered bulk truncation for oxygen at high temperatures. Cuts through reciprocal space we made to look for any evidence of ordered surface structure. These include several radial cuts at fixed L and along angles of 0, 15, 30, 45, 60, 90 degrees from the HK plane. Circle scans were also conducted for radii at 0.1 increments, as well as multiples for $\sqrt{2}$, $\sqrt{3}$, and others. Likewise the shape of the “hex” peak did not appear to change during the kinetics measurements. Peak widths measured before, during and after a transition did not appear to change shape or size in a statistically meaningful fashion. Nor was any wide, diffuse signal observed in the presence of oxygen indicating only short-range ordering of “hex” phase.

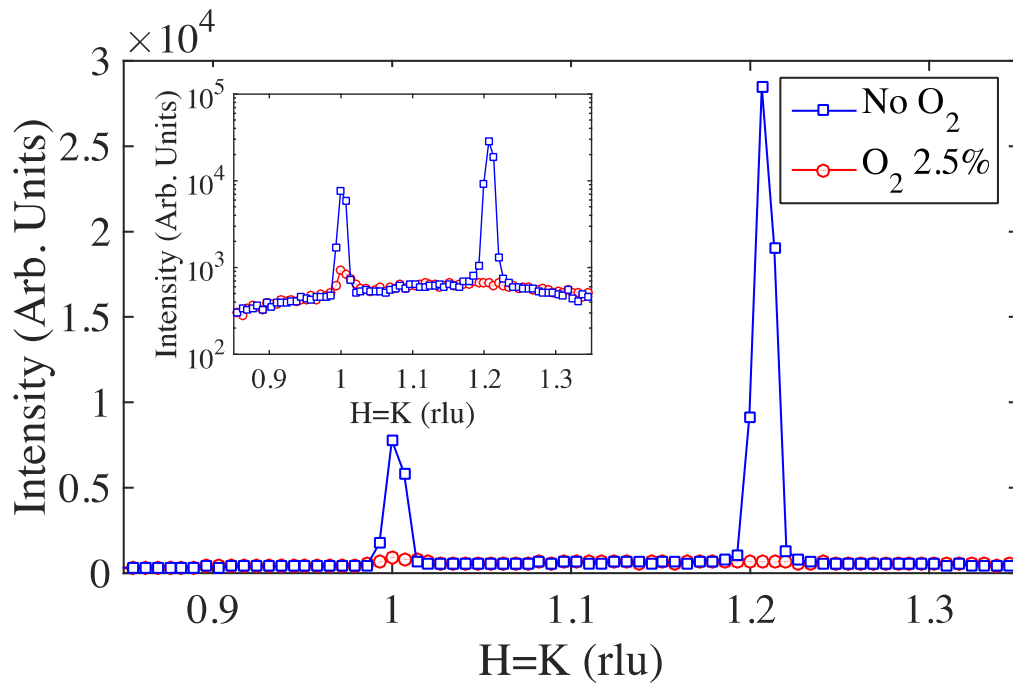
The intensity at the “hex” position itself would vanish entirely with sufficient oxygen and temperature, while the CTR signals themselves would still be visible, albeit at reduced intensity. An example of this is shown in Fig. S3 for the sample at 1130 K in the presence and absence of oxygen. This scan is along the H=K radial direction with L fixed at 0.4. The “hex” signal at H=K=1.2 vanishes, while the interception of the (1,1) rod shows a significant decrease in intensity. Narrow rocking scans fail to find any faint, sharp peaks. Wide rocking scans did not find any evidence of a faint increase over a large area.



Supplemental Figure 1. An example of the lifting and recovery of the surface “hex” being independent of x-rays. Oxygen is added and removed early first with the x-rays on, and then again with interruptions with the shutter being closed. It is possible to predict the behavior (dashed lines) based solely upon the previously measured fits (solid lines).



Supplemental Figure 2. Values of T_L , the temperature of lifting of the “hex” reconstruction, are plotted as a function of percent oxygen. The dashed line is 1170 K where the surface should lift in vacuum.



Supplemental Figure 3. Integrated intensity along the $(H,H,0.2)$ direction in reciprocal space in the absence and presence of oxygen at 1130 K. The surface reconstruction at $H=K=1.2$ has vanished entirely, while the scattering intercepted from the $(1,1,L)$ rod has dropped significantly. The inset shows the same data, but plotted on a log scale.