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$SrTiO_3$ (001) ($\sqrt{13}$ x $\sqrt{13}$)R33.7º Surface Reconstruction

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$SrTiO_3$ is a member of the perovskite family with a cubic structure (a=b=c=3.905Å, α=β=γ=90º) having a wide range of applications including catalysis and thin film growth. In both of these cases, the surface structure of $SrTiO_3$ is very important. For the (001) orientation of $SrTiO_3$, many surface reconstructions have been observed including the ($\sqrt{13}$ x $\sqrt{13}$)R33.7º reconstruction[1-3]. In particular, the ($\sqrt{13}$ x $\sqrt{13}$)R33.7º reconstruction has previously been observed under oxidizing and UHV annealing conditions with temperatures ranging from 1073-1373K. Computational analysis of the arrangement of atoms on the surface for the ($\sqrt{13}$ x $\sqrt{13}$) R33.7º reconstruction has yet to be attempted.

We have observed the ($\sqrt{13}$ x $\sqrt{13}$)R33.7º reconstruction reproducibly on the $SrTiO_3$ (001) surface by treating the sample with an HF etch for 45 seconds followed by a 5 hour oxygen flow anneal at 1323K. The reconstruction was observed by way of transmission electron diffraction (TED) shown in Figure 1A. By use of Direct Methods, a set of possible 2D surface scattering potential maps have been obtained directly from our TED data. One such pattern map exhibiting better measures of fitness, with a symmetry of p4, is shown in Figure 1B where areas of high scattering potential represent the strong-scattering atoms strontium or titanium. In this case, titanium atoms refine better than strontium, allowing us to extract the cation positions for this surface. The number of oxygen atoms at the surface was determined by the amount that would be make the surface valence neutral. The oxygen atoms were initially placed around the titanium atoms (in plane) in bulk-like positions and then allowed to relax to their lowest energy configuration using density functional theory. This structure is shown in Figure 2.

Preliminary x-ray photoelectron data from a sample exhibiting the ($\sqrt{13}$ x $\sqrt{13}$)R33.7º reconstruction indicates the presence of hydroxyl or water at the surface in the form of a higher binding energy shoulder on the O-1s peak (Figure 3). However, if there is indeed water at the surface, it is unknown if it is physisorbed or chemisorbed. In the latter case, it is possible that water and/or hydroxyl molecules are incorporated into the surface structure. Furthermore, it is unknown if water is needed at the surface for this reconstruction to take place.

These results will be presented along with further x-ray photoelectron analysis to determine the role that water molecules play in the $SrTiO_3$ ($\sqrt{13}$ x $\sqrt{13}$)R33.7º reconstruction.

References

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[4] This work was supported by the National Science Foundation under grant number DMR0455371/001.

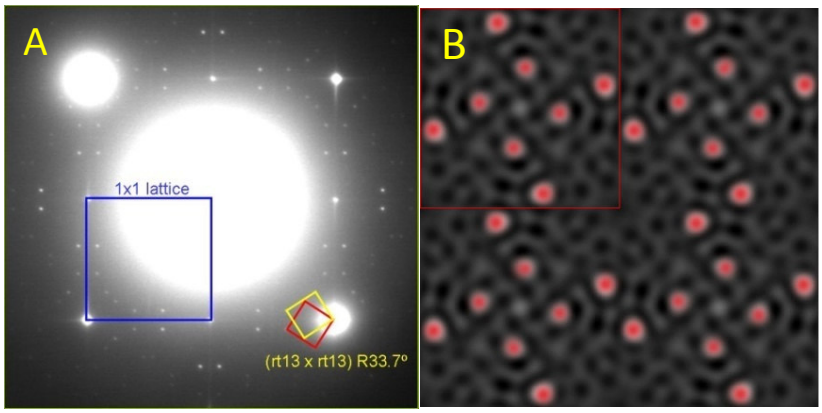

Figure 1. (A) Off-zone TEM diffraction pattern of the 2 domains of the ($\sqrt{13}$ x $\sqrt{13}$) R33.7º reconstruction outlined in red and yellow. (B) 2D scattering potential map generated from TEM surface diffraction data. Pink color added to areas of high scattering potential i.e. titanium atoms. Surface cell outlined in red.

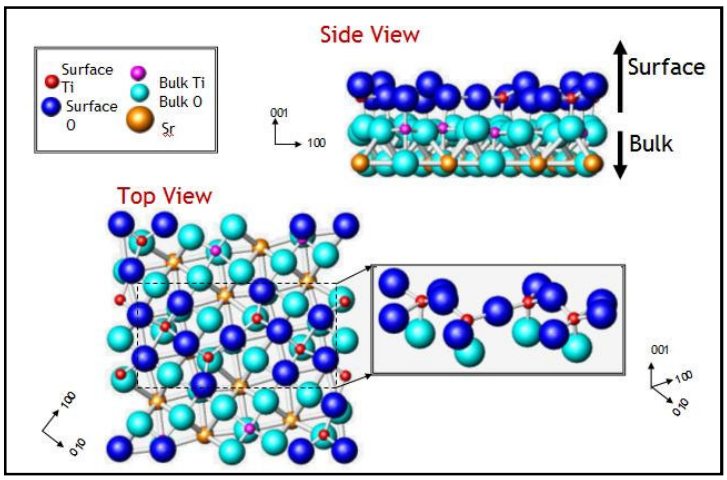

Figure 2. Model of the $SrTiO_3$ ($\sqrt{13}$ x $\sqrt{13}$) R33.7º reconstruction after being geometrically minimized to its lowest energy configuration with DFT. Close-up box shows the orientation of a row of two 5-coordinated Ti and two 4-coordinated Ti.

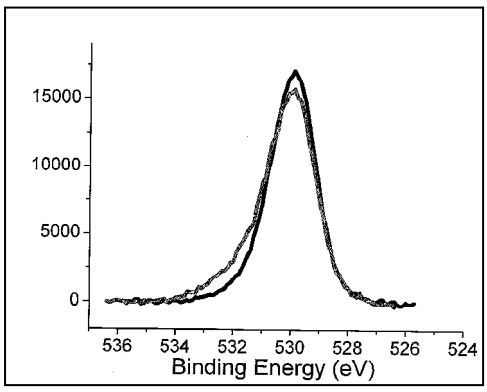

Figure 3. XPS spectrum of the Oxygen 1s peak showing normal detection angle (black) and grazing detection angle (grey). The grazing detection angle is more surface sensitive and exhibits a higher binding energy shoulder on the peak.

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