Solution-Based Deposition of Ultrathin Metal Oxide Films on Metal and Superconductor Surfaces

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Ultrathin metal oxide films (<10 nm) play an important role in catalysis,[1] corrosion prevention,[2] chemical sensing,[3] and microelectronics.[4] The most effective method available for fabricating uniform, pinhole free oxide films in this thickness range is by surface oxidation.[5] The goal of this work was to develop alternative techniques for depositing ultrathin metal oxide films from solution using molecular precursors. In particular, zirconia was deposited on $YBa_2Cu_3O_{7-\square}$ (YBCO) by condensation/hydrolysis chemistry, and molecular platinum-molybdenum oxide films were deposited by spontaneous adsorption of platinum containing polyoxometalates.

Superconductor-insulator-metal (S-I-M) tunnel junctions can be used to probe the density of states of superconducting materials.[6] The most commonly used method for fabricating ultrathin tunnel junctions on YBCO single crystals and thin films involves the evaporation of Pb.[7] Pb/YBCO devices are problematic because the formation of the Pb/PbO_x/YBCO junction results in the degradation of the YBCO surface; and the Pb density of states, as observed by differential conductivity measurements, masks the YBCO density of states at low temperatures.[8] In an attempt to avoid these problems, Covington et al.[9] used organic amine films as a tunnel junction, but as with the Pb based devices, the formation of the organic insulating layers also degraded the YBCO surface due to the oxidation of the amines by YBCO.[10,11]

Zirconia tunnel barriers were fabricated on the surface of (001) and (103)-oriented YBCO by alternating exposures to tetra-n-propyl zirconate, $Zr_4(OPr^n)_{16}$ (Figure 1.a), in

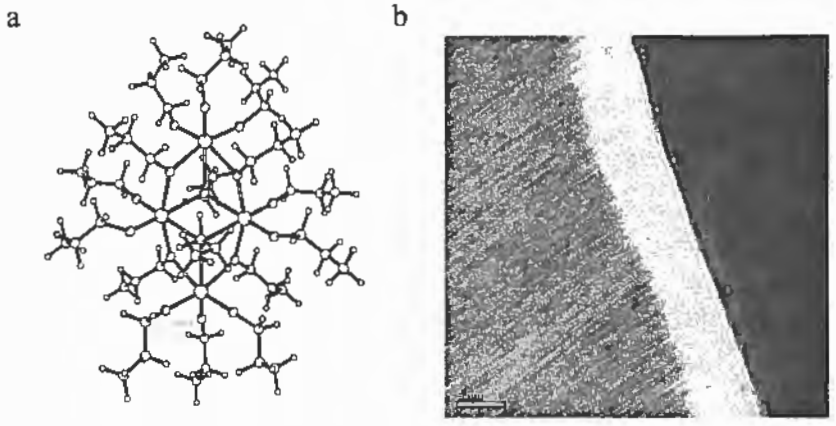

Figure 1.(a) Stucture of tetra-n-propyl zirconate, $Zr_4(OPr^n)_{16}$ and (b) a cross-section TEM image of ultrathin zirconia film deposited on YBCO from $Zr_4(OPr^n)_{16}$.

methylcyclohexane and water in n-propanol. After fourteen reaction cycles, the deposited zirconia films were highly conformal to the surface structures of (001) and (103)-oriented $YBa_2Cu_3O_{7-\square}$. Cross-section transmission electron microscopy images (Figure 1.b) show a zirconia film thickness less than 7 nm. Silver-zirconia-YBCO devices fabricated by this method display differential conductivity-voltage (G-V) curves with features as sharp, or sharper, than any reported to date for YBCO. A large percentage (30%) of fabricated junctions behave as high-quality tunnel junctions, and the remaining sample exhibited shorted or insulating behavior. These devices also display remarkable stability over time for a tunnel barrier on YBCO.[12]

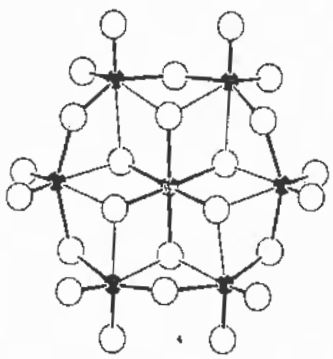

Figure 2. SCHAKAL drawing of hexamolybdoplatinate, $PtMo_6O_{24}^{8-}$, where the open circles are oxygen, the black circles are molybdenum, and the shaded circle is platinum.

Platinum-molybdenum oxide materials were deposited from solution by the spontaneous absorption of hexamolybdoplatinate, $PtMo_6O_{24}^{8-}$ (Figure 2). Using ^{195}Pt and ^{17}O NMR, $PtMo_6O_{24}^{8-}$ was observed to be stable in aqueous solution below pH 4. The anion was spontaneously adsorbed on Au, but was degraded upon adsorption on Ag. According to in situ scanning tunneling microscopy, the anion forms an amorphous phase upon adsorption on Au(111) with a coverage of 6 x 10 anions/cm^2. Strong adsorption of the anion was confirmed by cyclic voltammetry that also indicates a coverage of 8 x 10 anions/cm^2. The spontaneous adsorption and electrodepositon of hexamolybdoplatinate on Au electrodes yield electrodes with very different properties in terms of their composition, voltammetry, and reactivity. Methanol electrooxidation experiments showed that a near stoichiometric oxidation occurs with spontaneously adsorbed $PtMo_6O_{24}^{8-}$ on Au in methanolic solution, unlike the electrodeposited PtMo/Au electrode which displayed catalytic behavior similar to other PtMo methanol electrooxidation catalysts reported in the literature.

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