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Anisotropy in the Electrical Conductivity of Rutile TiO_2 in the (110) Plane

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The bulk electrical conductivity of a TiO_2(110) single crystal has been measured in all azimuths parallel to the (110) plane using a four-point probe. A distinct anisotropy in the conductivity has been found, with the highest bulk conductivity direction being parallel to the ⟨001⟩ direction.

The electrical properties of TiO_2 are of importance due to its application in photochemistry, where electron−hole pairs are produced by absorption of a photon, causing oxidation−reduction processes on the surface of the semiconductor.[1] In addition, TiO_2 is the active material in the Graetzel photocell.[2] The TiO_2(110) single-crystal surface has been widely studied as a model surface both for photochemistry[3] and as a support surface for catalytically active metals.[4] We report here some measurements of the ratio of the electrical conductivity in various crystallographic azimuths parallel to the (110) plane. The result, showing the highest bulk conductivity along the ⟨001⟩ direction, confirms what has been known for some time from less modern measurement methods.

A four-point probe (FPP) was employed to measure the conductance of the crystal at 300 K in ambient air. The rutile single crystal (1 cm × 1 cm × 0.1 cm) was obtained from Princeton Scientific. The probe points were arranged in a square geometry with 1 mm spacing between the 0.1 mm diameter tungsten carbide tips, using a customized apparatus (Jandel). Each tip was spring loaded and was set to 100 g load. This caused the tips to visibly penetrate into the crystal, and the measurements reported here are therefore characteristic of the electrical conductivity of the bulk. The probe head was translated to the crystal surface until contact was achieved. Current was passed through two non-diagonal tips, and the potential drop was measured between the other two tips. Measurements at various azimuths were repeated at 5° increments for 360°. Prior to these measurements, the crystals were reduced in ultrahigh vacuum at 900 K to produce oxygen vacancy defect sites to impart electrical conductivity to the TiO_2.[5] The calculation of resistivity was carried out using the method of Yamashita,[6] taking into account the finite dimension and thickness of the TiO_2 crystal. The bulk electrical resistivity in the $\langle\bar{1}10\rangle$ direction was always 5−10 times greater than in the ⟨001⟩ direction. The results of the measurement are shown in Figure 1.

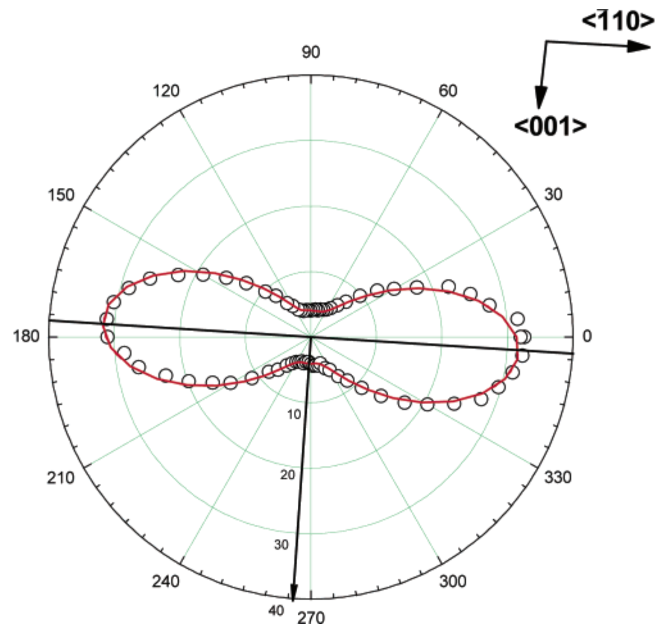

Figure 1. Bulk resistivity anisotropy of a TiO_2(110) crystal along various azimuths parallel to the surface. The curve is a fit of the data to the model of Yamashita[6] and the ratio of electrical resistivities in the $\langle\bar{1}10\rangle$ direction to that in the ⟨001⟩ direction is 8.

Reduced TiO_2 is an n-type semiconductor. At a high concentration of oxygen vacancies, electrical conduction in a TiO_2 crystal has been postulated to occur via the impurity banding mechanism.[6] According to this mechanism the TiO_2 crystal conductivity is caused by overlapping of electron wave functions associated with the oxygen vacancy sites, i.e., the greater the density of the oxygen vacancies the higher the sample conductivity. Since TiO_2 possesses tetragonal geometry, the resistivity in the ⟨001⟩ direction is lower than in either the ⟨100⟩ or ⟨010⟩ directions, as was reported earlier.[7,8] More recent studies[9] have indicated that instead of viewing the defects as oxygen vacancies, one should view them as Ti interstitials associated with oxygen vacancies and with a single paramagnetic electron.[9−11] At high defect concentrations, pairs of Ti interstitials form. It is not clear how these new insights connect to anisotropies in bulk electrical conductivity. A recent study[12] using THz time-domain spectroscopy reports significant anisotropy in the electron optical phonon scattering rate, resulting in an anisotropy in conductivity.

These measurements of the anisotropy of the bulk electrical conductivity of TiO_2 may correlate with recent investigations

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of the kinetics of the photodesorption of O_2 from a slightly defective TiO_2(110) single-crystal surface.[13] Here it was postulated that the transport of electrons between oxygen vacancy defect sites mediates the transport of photogenerated holes to adsorbed O_2 molecules present on surface defect sites. The rate-controlling step in the hole-induced O_2 photodesorption kinetics fits a one-dimensional fractal model. It was postulated that the fractal pathway involves empty surface oxygen vacancy defect sites which conduct electrons to holes, leading to recombination, and thereby reducing the rate constant for O_2 photodesorption as O_2 molecules photodesorb from vacancy defect sites on the surface. The anisotropy in the bulk conductivity of TiO_2, measured here, indicates that this one-dimensional electron conductivity channel is parallel to the $\langle 001 \rangle$ direction on the TiO_2(110) surface.

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