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We report an in situ thermochemical treatment that significantly increases the macroscopic electrical conductivity of insulating yttria-stabilized zirconia (YSZ) (001) single-crystalline substrates. We demonstrate the high-quality surface crystalline structure of the resulting “conductive” cYSZ (001) by low- and high-energy electron diffraction. Soft- and hard X-ray photoemission spectroscopy measurements reveal a sizable reduction of Zr cations to a metallic state and their homogeneous distribution within the cYSZ. We discuss the correlation between the microscopic chemical processes leading to the increased macroscopic metallicity. Finally, the heteroepitaxial growth of a functional magnetic oxide model system, ultrathin EuO on cYSZ (001), was demonstrated. cYSZ (001) whereby enables both high quality oxide heteroepitaxy and the advanced sample characterization by high electron-fluence characterization techniques. © 2014 AIP Publishing LLC.

The cubic oxide yttria-stabilized zirconia (YSZ) is an established model system for spintronics research, in particular, for the heteroepitaxial integration with the ferromagnetic oxide EuO. Ultrathin EuO has the unique property to filter electron currents according to their spin orientation by a highly effective spin-dependent tunneling process. Due to the perfect lattice match of the EuO/YSZ (001) model system or other YSZ (001)-based oxide heterostructures—with a significantly smaller resistivity q compared to pristine YSZ (001) substrates—we developed an in situ process consisting of successive annealing and electron bombardment steps. We start from commercial single-crystalline 10%-yttria-substituted ZrO₂ crystals (YSZ), which are cleaned by isopropanol, introduced into UHV and annealed at Tₐ = 600 °C. Next, those YSZ (001) substrates are bombarded by high-kinetic energy electrons emitted from a tungsten filament, which are accelerated by a voltage of U = 1000 V from 5 mm distance onto the YSZ substrate’s back side, as schematically depicted in Fig. 1(a). Two mechanisms may be considered for the generation of a macroscopic conductivity in YSZ at room temperature: (i) The creation of oxygen vacancies Vₒ/₂ from neutral oxide sites ZrO₂ (ZrO₂)_{ox vac} \rightarrow Vₒ/₂ + n \cdot Vₙ + n \cdot 2e⁻ and (ii) the substitution of Zr by Y ions in order to generate free electrons, Zr⁺/₂ \rightarrow Y₃⁺ + e⁻.

In this study, we present a thermochemical treatment that significantly increases the macroscopic electrical conductivity of otherwise insulating YSZ (001) by the creation of oxygen vacancies n \cdot Vₙ and demonstrate a sizeable metallic reduction of Zr cations. The surface crystalline structure of the resulting “conductive” YSZ (cYSZ) thereby remains basically unaffected, whereas the chemical reduction of Zr oxidation states was identified by soft- and hard X-ray photoemission spectroscopy (HAX-)PES). Moreover, ultrathin EuO magnetic oxide films were epitaxially integrated with cYSZ (001) and prove the single-crystalline quality by reflection high-energy electron diffraction (RHEED) intensity oscillations and low-energy electron diffraction (LEED). The employed characterization techniques are based on a high electron fluence and thus require a sizable sample conductivity, as is provided by thermochemically treated cYSZ (001).

In order to generate “conductive” cYSZ (001) substrates—with a significantly smaller resistivity ρ compared to pristine YSZ (001) substrates—we developed an in situ process consisting of successive annealing and electron bombardment steps. We start from commercial single-crystalline 10%-yttria-substituted ZrO₂ crystals (YSZ), which are cleaned by isopropanol, introduced into UHV and annealed at Tₐ = 600 °C. Next, those YSZ (001) substrates are bombarded by high-kinetic energy electrons emitted from a tungsten filament, which are accelerated by a voltage of U = 1000 V from 5 mm distance onto the YSZ substrate’s back side, as schematically depicted in Fig. 1(a).
electron emission current is regulated to not exceed ~20 mA. This hot electron bombardment is persistently applied for 2 h at an elevated substrate temperature of \( T_S = 400 \) °C. In a successive annealing step, the YSZ templates are kept at \( T_S = 700 \) °C under UHV without electron bombardment for 3 h. Structural investigations of the cYSZ (001) front side have been performed using \textit{in situ} RHEED, LEED and \textit{ex situ} X-ray reflection (XRR) techniques.

We performed a depth-dependent chemical analysis using (HAX)PES by either Al K\( \alpha \) X-rays (\( h\nu = 1.5 \) keV) or hard X-ray synchrotron radiation (\( h\nu = 4 \) keV) at PETRA III (P09).\(^{17}\) Whereas the information depth of XPS is limited to the surface region of only few Å, the use of hard X-rays provides a bulk-like information depth of up to 20 nm.\(^{16}\) Photoelectrons were either collected in normal emission geometry \( \varphi = 0 \)° with a maximum escape depth \( \lambda' \propto \lambda \cos \varphi \), or under an off-normal emission angle \( \varphi = 45 \)° in order to enhance the surface-sensitivity. For a quantitative evaluation of the PES spectra, we subtracted Tougaard backgrounds and fitted by convoluted Gaussian–Lorenzian peak shapes.

In order to investigate e-beam treated cYSZ (001) as substrates for oxide heteroepitaxy, ultrathin films of the magnetic oxide EuO were grown by reactive MBE under UHV conditions. Stoichiometric EuO was synthesized by applying the Eu distillation condition at elevated substrate temperature.\(^{2,7,18}\) First, we start the Eu metal deposition immediately followed by a meticulous regulation of an oxygen supply in the \( 10^{-7} \) millibar regime. The samples are (finally) capped with 4 nm Si for air-protection.

In Fig. 1(b), we compare a YSZ (001) substrate before and after the \textit{in situ} conductivity treatment and observe its color changing from transparent (YSZ) to black (cYSZ). This effect is a clear indication for a modification of the material’s macroscopic electrical conductivity, with metallic donor states located in the optical band gap acting as multiple absorption channels for visible light. We probed the macroscopic electrical resistivity \( \rho \) of the substrates by two-terminal measurements and extracted averages of \( \rho_{YSZ} \geq 350 \) M\( \Omega \) m vs. \( \rho_{cYSZ} = 32.7 \pm 3 \) M\( \Omega \) m. Thus, we reduced the electrical resistivity of YSZ by ~90% by the \textit{in situ} electron bombardment under high voltage.

Next, we investigate the surface crystalline structure of the cYSZ (001) sample front side, which is a crucial parameter for its use as substrate for oxide heteroepitaxy. In Fig. 1(c), LEED and RHEED experiments on pristine YSZ (001) show large charging effects, which make a structural analysis impossible. Only by increasing the substrate temperature to \( T_S = 400 \) °C, the \textit{fcc} (001) lattice planes become qualitatively observable by RHEED. For the conductivity-treated cYSZ (001) substrates, in contrast, the surface crystalline structure can be easily monitored by both LEED and RHEED (Figs. 1(c) and 1(d)), even at room temperature. The experimental cYSZ (001) lattice parameter is determined as \( a_{cYSZ} = 5.14 \) Å in an \textit{fcc} structure, unchanged from the YSZ reference value. We can therefore conclude, that the surface crystalline quality of the cYSZ (001) front-side remains basically unaffected by our e-beam conductivity treatment.

In a further step, we aim at correlating the change of the YSZ macroscopic electrical conductivity with the microscopic electronic properties. Any induced metallicity will be directly reflected by a valence change in the cationic constituents of YSZ. Indeed, photoemission experiments (XPS and HAXPES) of pristine and “conductive” YSZ samples reveal a significant change in the oxidation state of Zr cations.

**FIG. 1.** (a) \textit{In situ} e-beam treatment from the back side generates “conductive” cYSZ while protecting the polished surface. (b) Pristine and cYSZ samples. (c) and (d) Characterization by LEED and RHEED. LEED (green) is only observable on cYSZ.

**FIG. 2.** Electronic structure analysis of the Zr 3d doublet in cYSZ by (a) soft X-ray PES and (b) HAXPES. In (b), depth-sensitive scans reveal a sizeable and homogeneous distribution of reduced, metallic Zr\(^{0} \) spectral weight.
homogeneous metallic conductivity in YSZ (001), as quantified by soft- and hard X-ray photoemission spectroscopy. At the same time, the surface crystalline structure remains basically unaffected, and ultrathin EuO films can be synthesized on cYSZ (100) with single crystalline quality as indicated by RHEED intensity oscillations. In that, the presented in situ conductivity treatment of YSZ (001) opens up a pathway for the application of various high electron-fluence characterization techniques, such as HAXPES, RHEED, and LEED, in any YSZ (001)-based functional oxide heterostructure.

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