Optical absorption and redox kinetics of $YBa_2Cu_3O_{7-\delta}$ thin films studied by optical in-situ spectroscopy

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ARTICLE INFO

ABSTRACT

Optical absorption and redox kinetics of $YBa_2Cu_3O_{7-\delta}$ thin films in oxidizing (O_2) and reducing (Ar/H_2) atmospheres were studied at temperatures from 200 °C to 500 °C by means of in situ UV–vis-NIR optical spectroscopy. The optical spectra in oxidizing atmospheres are characterized by optical absorption of oxygen holes, O^- (O_I'), e. g., at about 450 nm at 200 °C, whereas those in reducing atmospheres are dominated by a band at about 600 nm due to electron hopping between Cu-ions. The fast redox processes of oxygen incorporation into and oxygen release from YBCO thin films induced by sudden changes in the ambient atmosphere between O_2 and Ar/H_2 are found to be controlled by surface exchange reaction. The oxygen surface exchange coefficients, k^δ, determined from optical absorption relaxation experiments are about 4.96×10^{-7} m/s for the oxidation process and about 4.85×10^{-9} m/s for the reduction process at 500 °C. The temperature dependence of k^δ yields an activation energy of about 0.3 eV for both oxidation and reduction processes in the studied temperature range. In addition, the rapid oxidation processes can be explained in terms of a high concentration of electrons in the reduced state of YBCO thin films, facilitating electron-transfer steps at the surface of YBCO film for oxygen exchange.

1. Introduction

Since the discovery of superconductivity of copper-based complex oxides ($YBa_2Cu_3O_{7-\delta}$, YBCO) with a transition temperature above 77 K [1], YBCO and related materials are a well-studied class of oxides. Their crystal structure, chemical composition, and electrical conductivity were intensively investigated in order to understand superconductivity mechanisms and to find new superconductors, as well as to exploit technical applications [1–4]. The non-stoichiometry of oxygen in YBCO, i.e. $0 \leq \delta \leq 1$ not only plays an important role in superconductivity but also makes this material a good model system to study defect chemistry, redox kinetics and oxygen transport properties. Oxygen incorporation into and release from YBCO in the form of single crystals, ceramics and thin films were previously investigated by using electrical conductivity measurements, oxygen tracer diffusion, thermogravimetric analysis and ellipsometry [5–15]. In most of the previous work it was concluded that redox processes of YBCO are dominated by oxygen diffusion in the bulk, thus assuming fast equilibration of oxygen-surface exchange reaction. Several studies showed, however, that the surface exchange reaction contributes to the overall redox

kinetics of YBCO thin films [5,11–13]. Optical methods have recently drawn much attention in the solid state ionic community to investigate gas-solid reactions and ionic diffusion in oxides [16–19]. One of the advantages of optical methods is their non-contact nature during measurements, which can avoid any unknown effects or limitations due to electrode-sample interfaces in electrical measurements. In the present work, optical in situ spectroscopy in the UV–vis-NIR range has been used to study the optical absorption of YBCO thin films in oxidizing and reducing conditions, and to monitor redox kinetics upon sudden changes in the ambient atmosphere of YBCO thin films between O_2 and $Ar + 5\%H_2$ in the temperature range of 200 °C to 500 °C. It is found from the time-dependent optical absorption that redox processes of YBCO thin films are controlled by a surface exchange reaction step. The surface exchange coefficient, k^δ, and its temperature dependence were also determined.
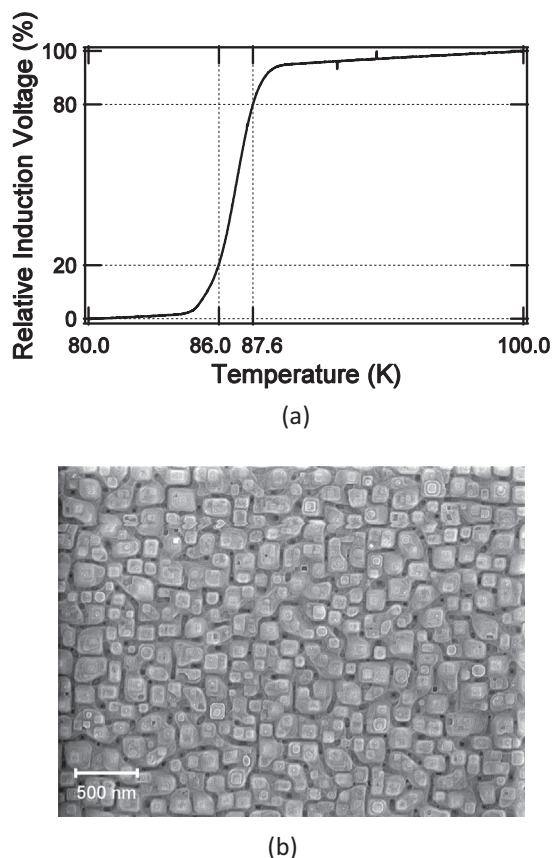
(a)

(b)

Fig. 1. (a) Measurement of the Meissner-Ochsenfeld effect of the YBCO thin film. Due to the shielding currents emerging beneath the critical temperature of the film, electromagnetic induction is prevented between two separated coils [22]. The drop of the normalized induction voltage in dependence of the temperature is a measure of the film quality and suggests a critical temperature of $T_C = (87 \pm 1)$ K. (b) Scanning electron micrograph of the surface morphology of the YBCO film indicating the typical c-axis epitaxial growth aligned to the a- and b-axis of a SrTiO$_3$ substrate.

2. Materials and methods

2.1. Preparation of YBCO thin films

The YBCO thin films were deposited on a (100) SrTiO$_3$ single crystal substrate ($10 \times 10 \times 0.5$mm^3) by means of pulsed laser deposition (PLD). The target was fabricated from stoichiometrically mixed Y$_2$O$_3$, BaCO$_3$ and CuO powders and sintered in an oxygen atmosphere. For the deposition, a KrF excimer laser (wavelength 248 nm) and optimized parameters from Refs. [21,22] were used. An energy density of 2.0 J/cm^2 and pulse frequency of 3 Hz for 12 min resulted in a film thickness of around 200 nm. The oxygen partial pressure of 12 Pa and deposition temperature of 840 °C used are near the CuO-Cu$_2$O-O$_2$ equilibrium line for optimal in situ film growth of the tetragonal phase with $\delta \cong 1$. After post-deposition annealing in O$_2$ at 400 °C, the superconducting orthorhombic phase ($\delta < 0.1$) was obtained [2]. The critical temperature T$_c$ of the YBCO film is (87 ± 1) K determined by using the Meissner-Ochsenfeld effect as shown in Fig. 1a [23]. SEM investigations confirm the expected epitaxial c-axis growth of YBCO films on the SrTiO$_3$ substrate, Fig. 1b, as previously observed using XRD for YBCO thin films [22].

2.2. Optical in-situ spectroscopy

Optical absorption spectra of YBCO thin films in O$_2$ and Ar + 5%H$_2$ at high temperatures were measured in the range from 300 nm to 850 nm using an experimental setup consisting of a UV–vis-NIR high-

precision optical spectrometer (Perkin Elmer, Lambda 900), a home-made high-temperature furnace and an atmosphere control unit [17,18]. Optical absorption relaxation experiments were performed at a fixed wavelength of 625 nm by switching the atmosphere between O$_2$ and Ar + 5%H$_2$ at a given temperature, in order to monitor redox processes of YBCO films. The time-dependent change in optical absorption was fitted to kinetic models involving a surface exchange reaction coefficient k^δ and/or a chemical diffusion coefficient D^δ of oxygen. It turned out that the kinetic processes are dominated by the surface exchange reaction step, thus were fitted with an exponential function, Eq. (1).

$$\frac{A_t - A_\infty}{A_0 - A_\infty} \propto \frac{c_t - c_\infty}{c_0 - c_\infty} = \exp\left[-\frac{k^\delta}{d} \times t \right] \tag{1}$$

In case of very short re-equilibration times, Eq. (1) simplifies to a linear function,

$$\frac{A_t - A_\infty}{A_0 - A_\infty} \propto \frac{c_t - c_\infty}{c_0 - c_\infty} = 1 - \frac{k^\delta}{d} \times t \tag{2}$$

Here, A_t and c_t denote the optical absorbance and the concentration of absorption species in the YBCO thin film with the thickness of d, respectively, at time t. k^δ is the surface exchange coefficient of oxygen. A_0, A_∞, c_0 and c_∞ are absorbance and concentration at $t = 0$ and $t = \infty$, respectively.

3. Results and discussion

3.1. Optical absorption spectra and point defects in oxidized and reduced states

Representative optical absorption spectra of YBCO thin films in O$_2$ and in Ar + 5%H$_2$ at 200 °C and 500 °C are shown in Fig. 2. Two distinct features in the optical spectra can be seen. One is the red-shift of the optical absorption edge due to the temperature effect. The shift amounts to about 40 nm for a temperature change from 200 °C to 500 °C for both the oxidized and reduced states. Another feature is the appearance of an optical absorption band at about 600 nm in the spectra of YBCO thin film in reducing atmospheres. The intensity of the absorption band increases with increasing temperature. This absorption band is attributed to the electronic transition of Cu-ions, particularly, to electron hopping between Cu-ions (Cu^{2+} or/and Cu^{3+}) due to chemical reduction. It is also noted that a weekly absorption band at about 450 nm found in the spectrum at 200 °C in O$_2$ can be assigned to the optical absorption of holes trapped at oxide ions, like in other oxides [20], i.e., O$^-$ or O$_I^{'}$ in the Kröger-Vink notation of point defects, see below. However, this band is not resolved at higher temperatures,
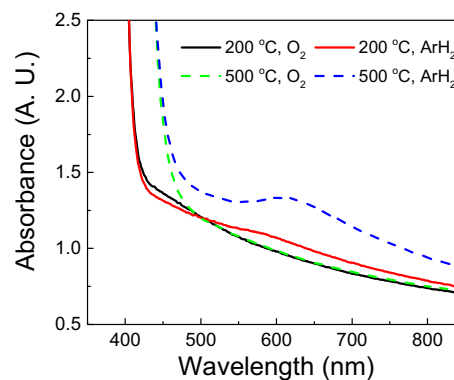

Fig. 2. Optical absorption spectra of YBCO thin films in oxidizing and reducing atmospheres at high temperatures: black and red solid curves represent spectra at 200 °C in O$_2$ and in Ar + 5%H$_2$, green and blue dash lines show spectra at 500 °C in O$_2$ and in Ar + 5%H$_2$, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)