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Oxygen concentration as a combinatorial parameter: The effect of continuous oxygen vacancy variation on SnO_2 layer conductivity

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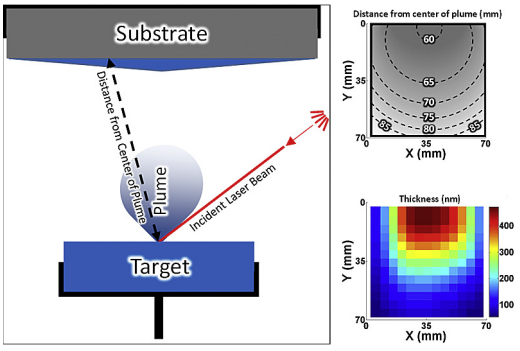
HIGHLIGHTS

- The first use of oxygen concentration as a combinatorial parameter.
- Pulsed laser deposited (PLD) SnO_2 film is used as a model system.
- The varying oxygen concentration strongly affects the material properties.
- Oxygen vacancies improved significantly the electrical conductivity.

GRAPHICAL ABSTRACT



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ABSTRACT

Combinatorial materials science is a powerful approach to discover new materials, especially by using the continuous compositional spread (CCS) method, which forms spatially varying stoichiometry across a sample. Though the chemical composition of the candidate materials is typically the primary parameter studied, in the case of metal oxides CCS the oxygen concentration is usually either neglected or studied in a discrete and non-combinatorial manner. The present work reports the use of oxygen concentration as a combinatorial parameter that varies continuously across a sample, using a pulsed laser deposited (PLD) SnO_2 film as a model system. As the oxygen concentration decreases, the SnO_2 crystal lattice expands, the number of defects is increased, and the electrical conductivity rises exponentially. A relatively low electrical resistivity of $8.16 \cdot 10^{-4}\,\Omega\,cm$ is achieved. The sample also showed superior infrared transparency, 67% at 2000 nm, compared to commercial F:SnO_2 (FTO) which is only 12% transparent at this wavelength. The improved transparency and conductivity were achieved within a single experiment, without any additional optimization steps, and with further improvement may allow reconsideration of SnO_2 as a transparent conductive oxide. Our findings serve as a demonstration for the importance of oxygen concentration as a combinatorial parameter.

1. Introduction

Combinatorial materials science, a powerful approach for the discovery of new materials, aims to accelerate materials science

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beyond the traditional trial-and-error processes [1]. The combinatorial approach involves rapid mapping and examination of a wide variety of compounds for desired physical or chemical properties, using high-throughput fabrication, characterization and analysis tools. From the synthetic point of view, the combinatorial materials science approach requires high-throughput fabrication techniques that will efficiently cover a wide range of combinations between materials (i.e. materials space) [2].

One of the main techniques for successful coverage of the materials space is the production of a continuous compositional spread (CCS) that forms a binary (or multi-component) phase diagram within a single experiment [3]. Using CCS, two or more materials are deposited on a single substrate, forming different ratios between the materials at different locations in the sample [4]. Ideally, one edge of the sample will be comprised of pure material A, for example, while the other edge will be comprised of pure material B, and the points between A and B will be comprised of A_xB_y with varying compositions [5]. The CCS method may be applied using several physical vapor deposition methods, such as pulsed laser deposition (PLD) [6], sputtering [7], and more [8]. The CCS concept can also be applied for additional parameters other than the chemical composition, such as the deposition temperature, by using intentional non-uniform heating of different parts of the sample [9,10]. One of the commonly used family of materials which can easily be fabricated as CCS is metal oxides [11,12].

In the case of metal oxide CCS, it is usually the metallic elemental content that is mapped, while the oxygen content is assumed to be constant [13–17]. However, if one would like to study the oxygen concentration in metal oxides, it is experimentally complicated, and therefore usually studied in an indirect way [18], using the oxygen partial pressure during deposition or the time of annealing in air as a measure for the oxygen content [19]. [10] Furthermore, when studying the oxygen concentration in a combinatorial metal oxide film, it is performed in a non-combinatorial manner, fabricating several samples with discrete oxygen concentrations [20,21]. In our previous work we have qualitatively analyzed different oxidation states in a combinatorial library, but a quantitative analysis has not been carried out [22].

Tin oxide (SnO_2) is a suitable material for combinatorial studies, since it is an abundant and easily-prepared material that was one of the first transparent conductive oxides (TCO) to be discovered. SnO_2 has been extensively investigated, yet because it suffers from relatively high resistivity for TCOs, other alternatives were developed, including doped SnO_2, ZnO [23], and In_2O_3 [24]. SnO_2 crystalizes in a tetragonal rutile structure [25], and has a bandgap of ~3.6 eV [26,27]. It is relatively more resistive than indium tin oxide (ITO), fluorine-doped tin oxide (FTO) and other commercial TCOs that contain tin oxide [20]. In addition, the number of oxygen vacancies, which are a possible cause for the changes in conductivity in SnO_2 [18,28], is quite unstable and hard to control [21]. For these reasons, undoped SnO_2 is not widely used as a commercial TCO [29].

In this study we demonstrate a CCS of oxygen concentration, in a broader context of combinatorial material science. Using PLD, we fabricate a model-system of a single material (SnO_2), in which the oxygen concentration varies continuously, due to the inherent PLD inhomogeneity [5]. Using the PLD, the oxygen content across the sample is varied, resulting in a change of several orders of magnitude in electrical resistivity. We correlate the oxygen concentration with the structural and electrical properties of the film. The use of oxygen content as a combinatorial parameter allowed us to achieve, in this case, SnO_2 with properties that better match TCO requirements.

2. Experimental section

A commercially available $72 \times 72 \times 2.2\,mm^3$, square glass (Hartford) was used as a substrate, onto which an SnO_2 layer was deposited by pulsed laser deposition (PLD, Neocera) consisting of a KrF excimer laser with a 248 nm emission wavelength (Coherent, CompexPro 102). The deposition was carried out at 525 °C onto a substrate that was preheated via a radiative heater, under an oxygen pressure of 7.5 mTorr. An SnO_2 target with a purity of 99.99% (Kurt J.Lesker co.) was used, with a target-to-substrate distance of 60 mm. Inside the vacuum chamber, a laser fluence of 70 mJ and a laser spot size of ~4 mm^2 were measured, corresponding to an energy density of ~1.8 J/cm^2. The SnO_2 target was ablated with 25,000 laser pulses, with a repetition rate of 5 Hz.

The electrical resistivity measurement and the first optical measurement were performed for a grid consisting of 13×13 points (169 points total), with a distance of 5 mm between adjacent points. The second optical measurement was performed for a single point.

Electrical resistivity measurements were performed using a home-built collinear four point probe resistance scanner system [30]. The system consists of a four point probe head (probes purchased from Ingun Prufmittelbau GmbH), sealed box for humidity control, Keithley 6517B and 2400 as a voltmeter and a current supply, respectively. The measurements were performed under a controlled atmosphere (<5% humidity). The resistivity (ρ) was calculated based on the measured resistance (R) and the calculated thickness profile.

Two separate optical measurements were performed. The first optical measurement was conducted using a home-built high-throughput optical transmission (total) and reflection (both specular and total) scanning system, with a spectral range of 320–1000 nm. The scanner is an optical fiber based system, consisting of two integrating spheres and three CCD array spectrometers (HR4000, OceanOptics) [22]. The results of the measurement were used for determining thickness, absorptance, and Urbach energy calculations. The second optical measurement was conducted using a commercial UV-Vis-NIR spectrometer (Varian Cary 500 Scan), and was used for evaluation of the visible light and infrared transparency of the film.

X-ray diffraction (XRD) measurements were performed with a Rigaku Smartlab work station, with a θ-2θ scan range of 20–90°. Since XRD measurements are considerably slower than the electrical and optical characterization, we performed this analysis only on 7 points in the central vertical line of the sample, overlapping with the grids of optical and electrical analyses.

The thickness of the SnO_2 layer was determined using a commercially available optical modeling software (CODE) [31], which fits simulated reflection and transmission spectra, to the measured ones. We used wavelengths ranging from 380 to 930 nm for the analysis. The simulation was based on the OJL inter-band transition model [32], and was validated on different samples using SEM images of focused ion beam (FIB) produced cross-sections of the films.

3. Results and discussion

Using the combinatorial material science approach, a sample with a CCS of SnO_2 was fabricated using PLD, and then measured in high-throughput scanners for optical, electrical and structural properties. The PLD chamber is described schematically in Fig. 1a. The incident laser beam strikes and ablates the target, generating a plasma plume comprised of high energy particles that are ejected away from the target, to be deposited on the substrate. The areas of the substrate that are directly in front of the center of plume (COP),