Thin Solid Films 519 (2011) 2103–2110

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Measurement method for carrier concentration in TiO_2 via the Mott–Schottky approach

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ARTICLE INFO

Article history:
Received 18 August 2010
Received in revised form 26 October 2010
Accepted 26 October 2010
Available online 4 November 2010

Keywords:
Atomic layer deposition
Anatase
Metal oxide semiconductor
Titanium oxide
Capacitance–voltage
Carrier concentration

ABSTRACT

In direct contrast to the way in which silicon is precisely doped for integrated circuit applications in order to optimize device performance, there is little nuanced understanding of the correlation between TiO_2 doping level, charge carrier concentration, and the operation of TiO_2-based photocatalysts, dye-sensitized solar cells, and sensors. The present work outlines a rigorous methodology for the determination of free carrier concentration for doped metal oxide semiconductors such as TiO_2 that are not amenable to standard metrology methods. Undoped, Cr-, Mn-, and Nb-doped polycrystalline anatase TiO_2 are synthesized via atomic layer deposition (ALD) using $Ti(OCH(CH_3)_2)_4$, H_2O, $Cr(C_5H_7O_2)_3$, $Mn(DPM)_3$ (DPM = 2,2,6,6-tetramethyl-3, 5-heptanedionato), and $Nb(OCH_2CH_3)_5$ as the source materials for Ti, O, Cr, Mn, and Nb, respectively. Chemical composition and crystallinity are investigated and a thorough "device-like" characterization of TiO_2 Schottky diodes is carried out to justify the subsequent extraction of carrier concentration values from capacitance–voltage (C–V) measurements using the Mott–Schottky approach. The influence of factors such as substrate type, contact metal type, and surface and interface preparation are examined. Measurements of donor carrier concentration are obtained for undoped, Cr-, Mn-, and Nb-doped TiO_2 synthesized by ALD. Possible causes for the obtained carrier concentrations are discussed.

1. Introduction

Many metal oxide semiconductors with wide band gaps (>3 eV) possess electronic properties that, in combination with chemical stability and modest cost, suit them well for important applications such as photocatalysis [1,2], dye-sensitized solar cells [3], and gas sensing of environmental pollutants [4], combustion products [5], and explosives [6]. Such applications would benefit greatly from the same precision in controlling charge carrier concentration via doping that is presently possible for conventional microelectronic devices based on silicon and III–V semiconductors. In photocatalysts and dye-sensitized solar cells, for example, such control would permit manipulation of near-surface or near-interface electric fields to optimize the flow of photogenerated charge carriers [7]. In gas sensors based on electrical conductivity such control would improve the sensitivity, which depends upon background charge carrier concentration [8].

Unfortunately, doping of metal oxides to achieve the requisite control is notoriously difficult due to the lack of readily available dopants providing shallow donor and acceptor levels [9]. Similarly troublesome is the accuracy of the available metrology tools for measuring carrier concentration. Commonly used methods such as four-point-probe or Hall effect measurements require ohmic contacts to the oxides, yet real contacts to wide-bandgap semiconductors usually create Schottky barriers that act like diodes. Both problems probably contribute to the wide variance of n-type carrier concentrations found in the literature in the case of anatase TiO_2, ranging from approximately 1×10^{16} cm^{-3} to 1×10^{20} cm^{-3} [10,11]. Such variations complicate attempts to perform defect engineering in TiO_2 [12].

This study focuses on metrology — in particular, the use of "Schottky diode" test structures for determining the carrier concentrations of anatase TiO_2 thin films synthesized via atomic layer deposition (ALD) based upon capacitance–voltage (C–V) measurements [13]. Related studies have been reported elsewhere for anatase TiO_2 deposited using alternative methods, as well as other metal oxides such as ZnO [14], but vital electrical characteristics of the diode structures are not always described or characterized adequately. In some instances, necessary current–voltage (I–V) data are not shown [15] or even collected [11,16]. Sometimes both I–V *and* C–V data are missing [17], which is problematic for such nontrivial measurements. Similar problems afflict literature for single crystal rutile TiO_2 [18,19].

The evaluation of metal oxide carrier concentration in this manner is an attractive alternative to conventional four-point-probe or Hall effect measurements for several reasons. Given the 3.9 eV work function of TiO_2 [20], a characterization method that precludes forming an ohmic contact to the TiO_2 surface is preferable. Additionally, ohmic contact recipes that entail an annealing step (i.e. Al to n-type Si wherein the Al–Si eutectic region formed under the Al contact is critical) are out of the question, since high-temperature processing irreversibly alters the

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doi:10.1016/j.tsf.2010.10.071

stoichiometry and thus carrier concentration of metal oxides. Lastly, the C–V method circumvents the need to form multiple contacts to the semiconductor surface. The cloverleaf, square, or rectangular four contact geometries necessary for Hall effect measurements may be restrictive with respect to sample size or preparation method. Since these geometries assume a laterally homogeneous metal oxide film, it is also not possible to probe spatial variations in carrier concentration as a result of gradients in thickness or doping level.

The present work outlines a sound metrological method for the evaluation of TiO_2 charge carrier concentration using I–V and C–V measurements. In particular, detailed electrical characterization of TiO_2 Schottky diodes is performed. The influence of transition metal doping on TiO_2 donor carrier concentration is investigated using the Mott–Schottky approach.

2. Experiment

2.1. Preparation and characterization of polycrystalline TiO_2 films

Thin film polycrystalline anatase TiO_2 was synthesized via atomic layer deposition (ALD) and in some cases doped to ~2 at.% with transition metals such as Cr, Mn, and Nb. Deposition took place within an approximately 3 L stainless steel vacuum chamber evacuated with a mechanical pump to a base pressure of about 6.7 Pa. The substrates were mounted on a resistively heated chuck, whose temperature was maintained at 200 °C during deposition and monitored with a chromel–alumel (type K) thermocouple. Substrates of dimensions 2 cm × 2 cm were cut from commercial Si(100) wafers doped n-type in two different ways: Sb (0.013 Ω cm resistivity) and P (15 Ω cm). In almost all cases, Si substrates were etched with dilute aqueous HF immediately prior to insertion in the vacuum chamber to minimize native oxide formation at the TiO_2/Si interface. Gaseous precursors were introduced into the chamber through a delivery tube placed approximately 5 cm from the substrate. The precursors included $Ti(OCH(CH_3)_2)_4$ (TTIP, Strem Chemicals Inc., 98%) and H_2O (DI, no further purification), with N_2 (SJ Smith, 99.999%) serving as the carrier gas. The temperatures of the TTIP and H_2O bubbler sources were maintained at 65 °C and 23 °C, respectively, and the carrier gas flows were set to 60 sccm with mass flow controllers. A full ALD cycle consisted of a Ti $(OCH(CH_3)_2)_4$ pulse, N_2 purge, H_2O pulse, and another N_2 purge. A pulse time of 8 s and a purge time of 10 s yielded self-limiting growth. Total chamber pressure during growth was typically 53 Pa. Undoped TiO_2 was deposited with a total of 27 cycles in order to obtain 100 nm thick films for subsequent characterization. Following growth, thermal annealing at 550 °C was carried out under an ambient atmosphere for 24 h.

Dopants were introduced from the vapor phase during deposition as follows. $Cr(C_5H_7O_2)_3$ (Sigma Aldrich, 99.99%), $Mn(DPM)_3$ where (DPM) is 2,2,6,6-tetramethyl-3, 5-heptanedionato (Strem Chemicals Inc., 99%), and $Nb(OCH_2CH_3)_5$ (Sigma Aldrich, 99.95%) served as the source materials for Cr, Mn, and Nb, respectively. $Cr(C_5H_7O_2)_3$ and $Mn(DPM)_3$ are solids at room temperature, with respective melting points of 210 °C and 154 °C. These precursors were evaporated from a porous filter enclosure placed adjacent to the TTIP/H_2O delivery tube within the vacuum chamber. The enclosure resembles a refillable pouch; the inert pocket-like pouch, fabricated from thin, high porosity paper derived from Abaca fiber, was loaded with the solid precursor as necessary. The supply rate of the dopant source was controlled by changing the distance between the enclosure and the heated substrate chuck. $Nb(OCH_2CH_3)_5$, a liquid at room temperature, was placed in a quartz crucible with a vented lid, and the vapor pressure was also controlled by proximity to the heated chuck. Thirty to forty ALD cycles were typically necessary to deposit 100 nm thick Cr-, Mn-, and Nb-doped films. This increase in the number of cycles can be attributed to a change in the gas velocity profile when the porous filter enclosure is affixed to the delivery tube (Cr and Mn) and a reduction in the number of sites available for Ti, O precursor adsorption due to adsorption of dopant species (Cr, Mn, Nb).

Film thickness was measured by a Rudolph Technologies AutoEL III single wavelength ellipsometer. The X-ray diffraction (XRD) and X-ray reflectivity (XRR) patterns were obtained at room temperature with a high-resolution Philips X'Pert diffractometer ($\lambda = 0.15406$ nm) operated at 45 kV and 40 mA with a Cu Kα1 primary X-ray beam from a hybrid monochromator and secondary optics consisting of a high-speed PIXcel line detector. X-ray photoelectron spectroscopy (XPS) spectra were obtained with a Kratos AXIS Ultra utilizing a pass energy of 40 eV; the excitation of the spectra was performed using monochromatized Al Kα radiation.

2.2. Preparation and characterization of TiO_2 Schottky diodes

A schematic of the TiO_2 Schottky diode designed to yield information about carrier type and concentration is shown in Fig. 1(a). 200 nm thick metal contacts of well-defined area (2.0×10^{-3} cm^2) were formed to the TiO_2 surface by photolithographic patterning followed by metal sputtering (Al) or evaporation (Au) and photoresist lift-off. High purity (99.999%) Al was sputtered in a Cooke Dual-Gun Sputter System with base pressure of 4×10^{-4} Pa, and Au contacts were formed using a CHA SEC-600 E-Beam Evaporator with base pressure of 7×10^{-5} Pa. Subsequently, the n-Si substrate was prepared for application of the ohmic contact by either manual abrasion with sandpaper or a two-step protocol involving a CF_4/O_2 capacitively coupled plasma and 49% HF wet etch (to prevent rapid removal of the entire TiO_2 film during wet etching). The contact to bare Si was then formed by the application of InGa metal eutectic using a metal 26 s-gauge needle affixed to a 10 μl syringe [21]. I–V and C–V measurements were performed using a probe station (Signatone SE-T tungsten probe tips) equipped with an Agilent 4155 C Semiconductor Parameter Analyzer and Agilent 4284A Precision LCR meter. The C–V measurements were done at a frequency of 1 MHz; the range of the applied bias voltage was −1.2 to 0.2 V.

3. Results and discussion

3.1. Structural and chemical characterization

XPS confirmed introduction of the metal dopants into the films and provided an estimate of surface elemental composition. Fig. 2 shows the XPS spectra for the Cr 2*p*, Mn 2*p*, and Nb 3*d* core-levels. The binding energy scale has been referenced to the C 1*s* peak at 285 eV.

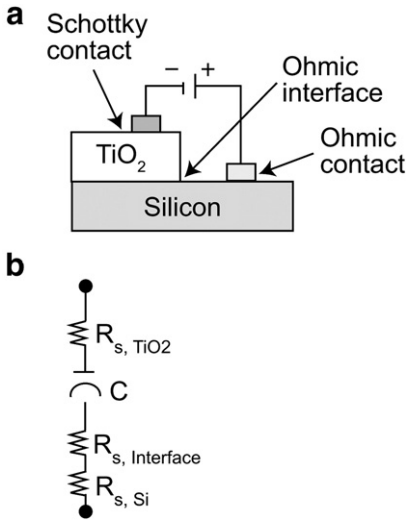

Fig. 1. Schematic of (a) TiO_2 Schottky diode structure with key features labeled and (b) equivalent lumped element circuit for TiO_2 Schottky diode.