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Persistent illumination-induced changes in polycrystalline TiO_2 majority carrier concentration

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ABSTRACT

In polycrystalline semiconductors for which grain boundaries mediate a persistent change in majority carrier concentration on super-bandgap photostimulation, the change generally involves an increase. Capacitance–voltage measurements on thin-film polycrystalline anatase TiO_2 demonstrate a photostimulated increase or decrease in majority carrier concentration, depending on film thickness. With the help of photoreflectance measurements, the results are interpreted in terms of deep-gap energy states that reside near grain boundaries, whose charge occupation is "frozen in," depending on synthesis history. Photostimulation provides the mechanism by which these states equilibrate with the band edges.

1. Introduction

Super-bandgap photostimulation of modest intensity is well known to influence semiconductor carrier concentration, typically via band-to-band excitation of equal numbers of electrons and holes. Such photoexcitation increases the concentrations of both types of charge carriers, leading to a rise in electrical conductivity. In polycrystalline semiconductors, grain boundaries can further affect photoconductivity through both carrier concentration [1] and mobility [2,3]—sometimes with a degree of controllability that has led to the concept of "grain boundary engineering", which finds use in dye-sensitized solar cells, photovoltaics, photocatalysts, gas sensors, and other devices. For example, experimental studies of polycrystalline ZnO [4], SnO_2 [5], and TiO_2 [6] suggest that surface states facilitate long-lived or permanent illumination-induced changes in majority carrier concentration and/or mobility.

In almost all such cases of strong persistence in polycrystalline material, however, the general effect of photostimulation is to increase both free carrier concentration as well as electrical conductivity, whether immediately on illumination or slowly over time [7]. It is much rarer for super-bandgap illumination by itself to prompt a decrease in majority carrier concentration and rarer still for that same illumination to cause either an increase or a decrease, depending on film thickness. The present work reports such an effect for thin-film polycrystalline anatase TiO_2. Capacitance–voltage (C–V) measurements are used to determine majority carrier concentrations, and optical photoreflectance (PR) is used to examine the qualitative behavior of electric fields that reside within the film. Results are interpreted in terms of deep-gap energy states that reside near grain boundaries, whose charge occupation is "frozen in", depending on synthesis history and film thickness. Photostimulation provides the mechanism by which these states equilibrate with the band edges.

2. Materials and methods

Thin-film polycrystalline anatase TiO_2 was synthesized on commercial n-type Si(100) (Sb, 0.013 Ω cm resistivity) by ALD, as described in Sellers and Seebauer [8]. In brief, the precursors were 65 °C $Ti(OCH(CH_3)_2)_4$ (TTIP, Strem Chemicals, Inc., 98%) and 23 °C H_2O (deionized, no further purification), with N_2 (S.J. Smith, 99.999%) carrier gas. The Si substrate was maintained at 200 °C during deposition, and film thickness was varied from 50 to 300 nm by number of ALD cycles (deposition rate = 3.7 nm/cycle). Following TiO_2 synthesis, thermal annealing at 550 °C was carried out in a Barnstead Thermolyne F79300 tube furnace under an ambient atmosphere for either 20 min (in studies of carrier concentration) or 24 h (in studies of PR).

For illumination studies, samples were cleaved in two and stored for a fixed period of time (i.e., one or two weeks) either in the dark or under a compact fluorescent lamp (Lights of America 9024B fluorescent linear quad bulb, 1800 lumens, 2.3 mW/cm^2). Because the lamp light was unfiltered, the incident light

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comprised ultraviolet as well as visible components. Light intensity was measured with a digital single-lens reflex (SLR) camera set to ISO 100, with an aperture of *f*/5.6 [9]. Illuminated samples were subjected to the incident light for 24 h/day.

Film thickness and morphology were characterized with a Rudolph Technologies AutoEL III ellipsometer and a Hitachi S4800 scanning electron microscope (SEM), respectively. X-ray diffraction (XRD) spectra were obtained 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. Carrier concentrations were determined using Schottky diode test structures comprising a 200-nm-thick sputtered Al (99.999%) contact to the TiO_2 surface and InGa eutectic contact to the Si substrate [8]. Current–voltage (*I*–*V*) and *C*–*V* measurements were acquired with an Agilent 4155C Semiconductor Parameter Analyzer and an Agilent 4284A LCR meter (1 MHz, applied bias voltage of −1.2 to 0.2 V). The Mott–Schottky relation was used to determine donor carrier concentration (N_d) for the subject n-type TiO_2, although it is worth noting that the relation is derived with the implicit assumption that the semiconductor is a uniform medium with randomly distributed donors. This assumption is not entirely valid for the polycrystalline semiconductor considered in this work, in which most of the donors that contribute to N_d reside at grain boundaries [10,11]. However, because the films considered here have thicknesses much greater than the grain size, a uniform-medium approximation is still satisfactory.

PR spectra were acquired as described in reference [12], with a variable-wavelength probe beam at a 45° angle of incidence. A mechanically chopped 375 nm wavelength light-emitting diode (Nichia Corporation, NSPU510CS) served as the pump beam. Wavelength was scanned at a rate of 0.15 nm/s for 425 to 325 nm. Four sequential spectra were acquired sequentially over the course of about one hour and averaged digitally. This procedure serves to average out transient spectral changes that involve charge exchange into the interface states responsible for generating the electric fields that lead to a nonzero PR signal.

3. Results

Fig. 1 shows the representative morphology and crystallinity of the TiO_2 specimens examined in this study. Fig. 1(a) reveals that 500 nm films have homogeneous texturing with no distinguishable cracks or voids at the subject spatial resolution. Fig. 1 (b) shows XRD peaks that correspond to the (101), (112), (200), and (211) anatase orientations. Analysis of the peak profile using a size-only fitting model yields an average crystallite size in the film growth direction of 53.4 ± 2.6 nm.

Fig. 2(a) displays values of N_d as a function of thickness for specimens annealed for 20 min and subsequently exposed to fluorescent light for one or two weeks. The uncertainties in the linear fits of the Mott–Schottky plots are not displayed, given that they lead to $< 2\%$ error in the determined carrier concentration. N_d varies significantly for some thicknesses, sometimes by as much as a factor of five. On illumination, N_d becomes relatively independent of film thickness and converges toward $\sim 1.2 \times 10^{17}$ cm^{-3}. To better illustrate the magnitude and direction of the carrier concentration change, Fig. 2(b) presents the changes in N_d referenced to the initial values. Depending on the magnitude of the initial value, illumination stimulates either an increase or a decrease in N_d. Large values of N_d decrease, and small ones increase. The net tendency is toward convergence, which takes place within one week for all films thicker than 100 nm, but remains incomplete even after two weeks for 60 nm films.

Fig. 3 shows PR spectra for 500 nm TiO_2, collected one day and seven days after 24-h annealing. This 500 nm thickness was

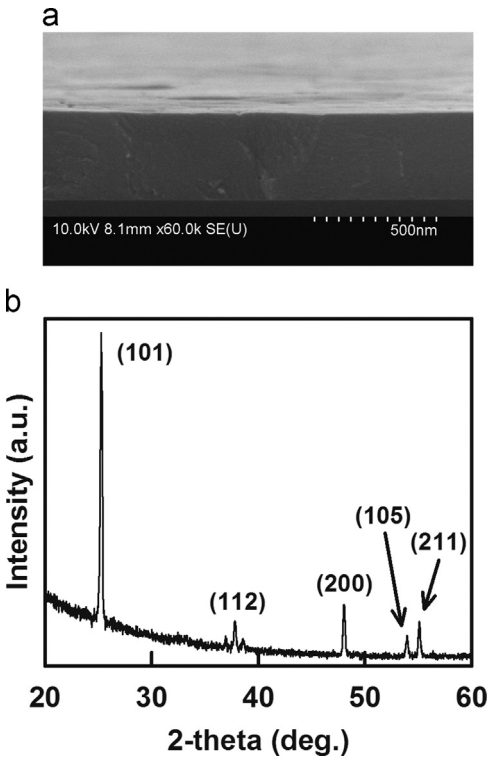

Fig. 1. (a) Cross-sectional scanning electron micrograph of 500 nm TiO_2 on Si(100) deposited at 200 °C with subsequent 24-h, 550 °C anneal, and (b) XRD data for the same film showing peaks consistent with polycrystalline anatase TiO_2. Data were fit to JCPDS card no. 21-1272 (tetragonal, $a = 3.7852$, $c = 9.5139$).

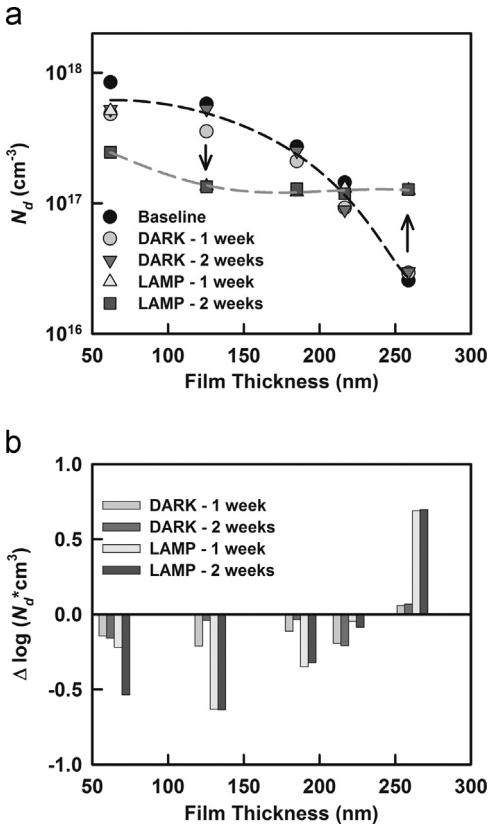

Fig. 2. (a) N_d vs. film thickness measured at $t = 0$, one week, and two weeks for 20-min anneal samples stored under fluorescent illumination, and (b) change in N_d from $t = 0$ plotted to better illustrate magnitude and direction of carrier concentration change. Full-range on the *y*-axis scale corresponds to two orders of magnitude (i.e., 10^{16} to 10^{18} cm^{-3}). Phenomenological curves are guides to the eye.