Persistent illumination-induced changes in polycrystalline TiO₂ majority carrier concentration

Meredith C. K. Sellers and Edmund G. Seebauer*

Department of Chemical & Biomolecular Engineering
University of Illinois at Urbana-Champaign
Urbana, IL 61801, USA

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 TiO₂ demonstrate a photostimulated increase or decrease in majority carrier concentration, depending on film thickness. With the help of photorefectance 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.

*Corresponding author: 600 S. Mathews Ave., Urbana, IL 61801, USA, Phone (217) 333-4402, Fax (217) 333-5052, E-mail eseebaue@illinois.edu.

Keywords

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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], SnO₂ [5], and TiO₂ [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 photorefectance (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 $\Omega\cdot\text{cm}$ resistivity) by ALD, as described in Sellers and Seebauer [8]. In brief, the precursors were 65°C $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ (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 minutes (in studies of carrier concentration) or 24 hours (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 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 hours/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 $\text{Cu K}\alpha 1$ 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 minutes 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 $\sim 1.2 \times 10^{17} \text{ cm}^{-3}$. 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.

Figure 3 shows PR spectra for 500 nm TiO_2 , collected one day and seven days after 24-hour annealing. This 500 nm thickness was chosen to suppress contributions to the PR signal from Si at the underlying TiO_2 -Si interface, which has been observed at 3.4 eV for thinner films prepared by the protocol employed here [12]. The waiting periods entailed exposure to low-level illumination from standard fluorescent laboratory lighting according to the usual rhythms of laboratory activity. At the one-day mark, a clear spectral feature corresponding to TiO_2 appears in the 3.05 to 3.10 eV range. The amplitude of this feature decreases noticeably after seven days to roughly one third its original value. A very similar effect was reported in reference [12] for nanopillared anatase deposited at 400°C , stored in an analogous way.

4. Discussion

Thermal annealing of amorphous TiO_2 prompts crystallization that normally originates from either the TiO_2 -substrate interface or the TiO_2 free surface. For both interface- and surface-nucleated grain clusters, outward and inward growth propels the voids in the direction of the crystallization front; some ultimately remain trapped within the film. For example, annealing of 200 nm TiO_2 on SiO_2 prepared by sol-gel processing results in the formation of microscopic voids ahead of the growth front within the film [15]. As discussed in references [10] and [11], the details of this void- and grain-formation process as a function of film thickness influence the overall concentration of electrically active defects. The reason is that grain boundaries annihilate or trap charge carriers [13]. Moreover, is energetically favorable for native donor defects such as oxygen vacancies and titanium interstitials to aggregate at grain boundaries [14] (although probably not at the interior surfaces of voids [11]). The details of grain boundary formation influence whatever energy state distribution the donors may have with respect to the band edges, and probably account for the thickness variation in the dark value of N_d observed in Fig. 2.

In a typical single-crystal semiconductor, changes in carrier concentration due to photostimulation often decay rapidly after illumination ends, either by direct band-to-band recombination, yielding photoluminescence, or thermal recombination mediated by energy states within the band gap. Subject to their positions with respect to electron and hole demarcation levels, such states may also serve as charge traps with potentially-lengthy trapping lifetimes that depend on the temperature-based kinetics of charge exchange with the conduction band (for trapped electrons) or valence band (for trapped holes). In single-crystal semiconductors with modest concentrations of such traps, room-temperature majority carrier concentration is usually minimally affected. In the present polycrystalline material, however, point defects located at or near grain boundaries often act as the primary donors.

We surmise that the thermal history of the polycrystalline material during synthesis leads to an energetically heterogeneous population of states whose energy distribution resides far from the valence or conduction bands, and whose charge occupation is “frozen in” from some higher temperature. Such states may be identifiable by the thermal excitation provided by metrological techniques such as deep-level transient spectroscopy. In the present case, however, photostimulation appears to provide the mechanism by which these “frozen in” states equilibrate with the band edges. Such equilibration would tend to drive the free carrier concentration observed in the C–V measurements toward a single value as observed here. Depending on the initial energy distribution and occupation of those “frozen in” states, the change in N_d could be either positive or negative.

In the case of the very thick films, the magnitude of the PR signal decreases on illumination. Such an effect was also observed for anatase TiO_2 grown by a different protocol involving ALD of nanopillared crystalline material at 400°C [12]. The microstructural [10, 16], magnetic [16, 17], and PR [12] behavior of that material differs in some respects from the

present material deposited amorphously at 200°C, followed by annealing at 550°C. Thus, certain analogies in behavior are possible but cannot be guaranteed. Previous PR measurements for polycrystalline anatase TiO₂ grown on HF-etched Si have indicated that negligible band bending exists at either the free TiO₂ surface or the TiO₂-Si interface, so it is not entirely clear where the electric field resides that gives rise to the PR signal. We speculate that the interface state that gives rise to the PR signal resides within the anatase grain boundaries rather than directly at the free surface or TiO₂-Si interface. To the extent that such states are located close to the TiO₂-Si optical discontinuity that causes reflection, they could contribute to the PR signal. The relevant electric field could then be that which exists within grains, which would depend on the interface potential (with respect to the intra-grain “bulk”). A decrease in PR signal probably indicates a decrease in the electric field at grain boundary interfaces and therefore a decrease in the interface potential.

The decrease in this potential suggests that carriers trapped at grain boundaries are released, which allows them to contribute to increases in the effective value of N_d observed in the C–V measurements. Alternatively, illumination could actually create grain boundary states that release free-roaming charge [18]. In other words, the effect of illumination for thick films is to free up charge trapped at grain boundaries. For very thin films, illumination serves to charge up the grain boundaries to the same value of interface potential, drawing charge from the uniform-medium reservoir, which decreases the effective uniform-medium value of N_d .

5. Conclusions

The thin-film polycrystalline anatase TiO₂ system is notably complex, in the sense that variations in deposition temperature and rate, as well as in annealing temperature and ramp rate, propagate into changes in the carrier concentration, crystallite size, and/or bulk density [11]. These surprising results probably stem from the existence of medium-range atomic order in the initial amorphous films, which allow for the occupation of deep electronic states to be “frozen in” in a way that can be reversed over time by super-bandgap illumination. Medium-range atomic order is also well known to exist in amorphous Si [19] and TiO₂ [20], although its existence in other metal oxides remains unknown. However, it seems possible that the mechanism observed here could generalize to other oxide semiconductors.

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Figures Captions

Figure 1 (a) Cross-sectional scanning electron micrograph of 500 nm TiO₂ on Si(100) deposited at 200°C with subsequent 24-hour, 550°C anneal, and (b) XRD data for the same film showing peaks consistent with polycrystalline anatase TiO₂. Data were fit to JCPDS card no. 21-1272 (tetragonal, $a = 3.7852$, $c = 9.5139$).

Figure 2 (a) N_d vs. film thickness measured at $t = 0$, one week, and two weeks for 20-minute 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.

Figure 3 PR spectra collected one day and seven days after deposition of 500 nm polycrystalline anatase TiO₂ on Si(100) (200°C deposition, 24-hour 550°C anneal). At the one-day mark, a clear spectral feature corresponding to TiO₂ appears in the 3.05 to 3.10 eV range.

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Figure 1

Figure 2

Figure 3