Persistent optical phenomena in oxide semiconductors

Matthew D. McCluskey*[a,b], Christopher Pansegrau[a], Syeed E. Ahmed[a], Macarena Santillan[a], Jani Jesenovec[a,b], John S. McCloy[a,b]

[a]Department of Physics & Astronomy, Washington State University, Pullman, WA, USA 99164-2814; [b]Institute of Materials Research, Washington State University, Pullman, Washington, USA 99164-2711; *mattmcc@wsu.edu

ABSTRACT

The interaction of transparent oxide semiconductors with light is critically important for a range of applications. Persistent effects could be exploited for holographic memory or optically defined circuits. Conversely, they may also be detrimental to device operation. Large, room-temperature persistent photoconductivity (PPC) was discovered in strontium titanate ($SrTiO_3$, STO) after annealing in a hydrogen-containing atmosphere. Barium titanate ($BaTiO_3$, BTO), a ferroelectric material, was recently found to also exhibit PPC. Room-temperature photodarkening was observed in Cu-doped gallium oxide (β-Ga_2O_3) after exposure to sub-bandgap light. Hydrogen is believed to play a central role in these persistent phenomena. In the proposed model, a photon excites substitutional hydrogen (a proton inside an oxygen vacancy), making the defect unstable. The proton leaves and binds to a host oxygen atom, forming an O-H bond that is observed with infrared spectroscopy. An oxygen vacancy is left behind. Because oxygen vacancies in STO and BTO are shallow donors, this process results in PPC. In β-Ga_2O_3:Cu, however, the oxygen vacancy neighbors a Cu acceptor. In that case, photoexcitation results in the rare Cu^{3+} state, which absorbs visible light. The effect can be "erased" by annealing at 300-400°C.

Keywords: Gallium oxide, strontium titanate, photoconductivity, hydrogen, perovskites

1. INTRODUCTION

Semiconductors interact light through a variety of mechanisms, including intrinsic band-to-band transitions and extrinsic defect absorption [1]. Photoconductivity occurs when a photon excites an electron to the conduction band (or a hole to the valence band). Persistent photoconductivity (PPC) is a phenomenon wherein the enhanced electrical conductivity remains even after the light source is turned off. At room temperature, the conductivity versus time profile is typically modeled as a stretched exponential or similar function with a characteristic time of minutes or hours. Often this type of PPC is due to interface effects; for example, the contact resistance can be lowered by emptying traps at the metal-semiconductor junction.

In a bulk crystal, large PPC arises from deep-level defects [2] called *DX* centers. The prototypical example of this is Si in $Al_xGa_{1-x}As$ or GaAs under pressure. In its preferred *DX* configuration, Si resides in an interstitial site near the plane of three neighboring As atoms (Fig. 1) [3]. The substitutional site has a higher energy. Upon exposure to light, the Si atom moves from the *DX* to the substitutional site and becomes a shallow donor, which increases the free-electron density. Because there is a barrier to relax back to the *DX* ground state, Si remains in the shallow-donor configuration, at least at low temperatures. At room temperature, however, there is enough thermal energy to surmount the barrier. Therefore, PPC of *DX* centers in various compound semiconductors is only observed for temperatures below ~180 K [4].

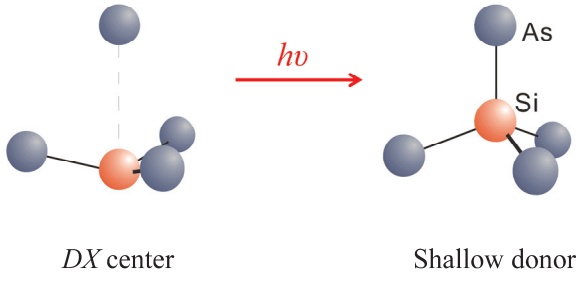


Figure 1. Ball-and-stick diagrams of Si in AlGaAs (or GaAs under pressure). The *DX* center is transformed to a shallow donor upon absorption of a photon with energy *hυ*.

The optoelectronic phenomena discussed in the following sections are notable because they persist at *room temperature*. Evidence from infrared (IR) spectroscopy suggests that hydrogen plays an essential role in this persistence.

2. PERSISTENCE AT ROOM TEMPERATURE

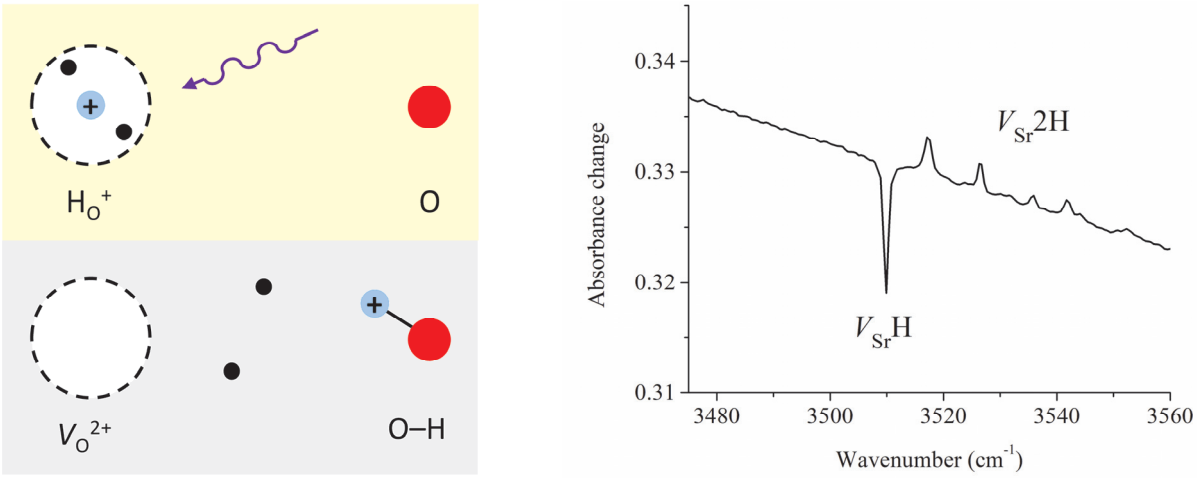
2.1 Strontium titanate

$SrTiO_3$ (STO) has the cubic perovskite crystal structure and a bandgap of 3.2 eV at room temperature. It does not show ferroelectricity even at low temperatures [5] unless perturbed by stress or doping (i.e., it is an "incipient ferroelectric"). Annealing in a hydrogen-containing atmosphere produces substitutional hydrogen (H_O^+) [6,7]. The H_O^+ defect is a neutral oxygen vacancy, which has two electrons, plus a proton. (Here, electric charge is expressed relative to the host.)

A photon with energy >2.9 eV can excite an electron into the conduction band, leaving hydrogen in an unstable H_O^{++} state [Fig. 2(a)]. The proton leaves the oxygen vacancy (V_O) and attaches to a host oxygen, forming an O–H bond. Because V_O is a shallow double donor, two electrons go into the conduction band, resulting in enhanced conductivity (Fig. 3) [8]. The O–H bond is metastable, lasting for *many years* at room temperature. Annealing the sample at 300°C breaks the bond and returns the system to its H_O^+ ground state.

The details of O–H bond formation depend on the defect population in the crystal. In the present case, the STO sample contained strontium vacancy – hydrogen complexes ($V_{Sr}H$). In these complexes, hydrogen attaches to an oxygen atom neighboring a strontium vacancy. After illumination, the liberated proton fully passivates $V_{Sr}H$, resulting in $V_{Sr}2H$, which has several O–H modes depending on the configuration of the two hydrogen atoms. Hence, the IR absorption shows a *decrease* in the $V_{Sr}H$ mode and an *increase* in $V_{Sr}2H$ modes [Fig. 2(b)].

This remarkable phenomenon was discovered accidentally. A sample was annealed at 1200°C in an evacuated ampoule with SrO powder. The SrO was intended to suppress Sr vacancies to determine whether specific hydrogen modes were $V_{Sr}H$ complexes. Unknown to the researchers, the SrO contained trace amounts of $Sr(OH)_2$ [6]. When annealed, the $Sr(OH)_2$ decomposed into H_2O and SrO. The H_2O vapor pressure was such that a high concentration of H_O defects was generated during the anneal. A sample in a transparent plastic container was illuminated by the overhead white fluorescent lights over the course of several weeks. When the IR transmission spectrum was measured, it showed strong free carrier absorption. A systematic series of experiments determined that the large increase in free-carrier density was due to PPC.



(a) (b)

Figure 2. (a) Schematic diagram of the PPC process. Substitutional hydrogen (H_O^+) absorbs a photon, which causes the proton to leave and form an O–H bond. Two electrons are liberated. (b) IR absorbance change of STO after illumination at a temperature of 125 K. The proton passivates a $V_{Sr}H$ defect, resulting in sidebands that correspond to O–H modes of $V_{Sr}2H$.

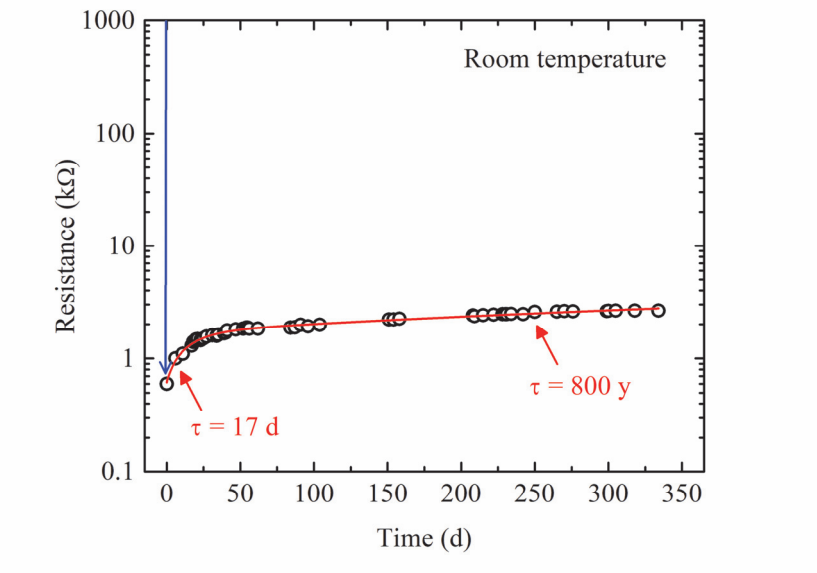


Figure 3. Resistance of an STO sample after illumination with 405 nm light. The resistance prior to light exposure was 1 MΩ. The data were fit by the sum of two decaying exponentials with time constants of 17 d and 800 y.

From experimental observations and first-principles calculations, a prepared sample should have the following properties for large PPC:

- A high concentration of H_O.
- V_O must be a shallow donor so that its electrons go to the conduction band.
- A low concentration of V_O, to ensure the sample is insulating before illumination.

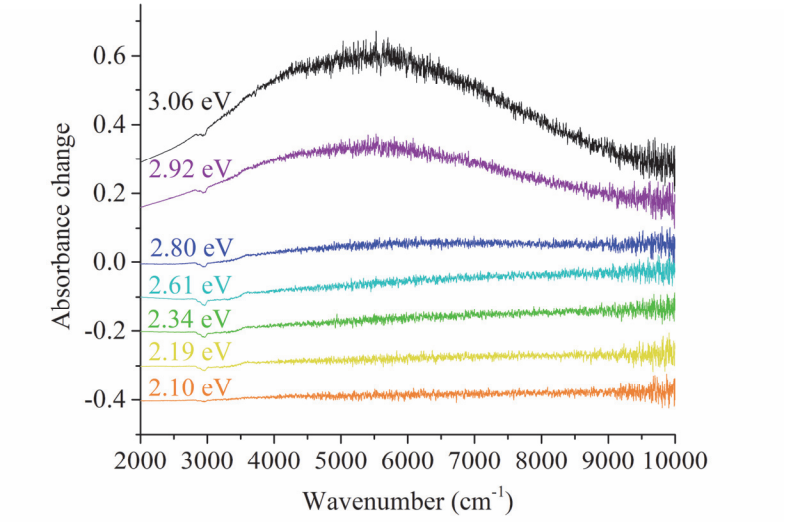


Figure 4. IR absorption change of BTO after exposure to LEDs with photon energies increasing from 2.10 to 3.06 eV. The appearance of a broad peak at ~5000 cm^{-1} is due to free-carrier absorption. The first four spectra are displaced downward for clarity. Measurements were taken at room temperature.

2.2 Barium titanate

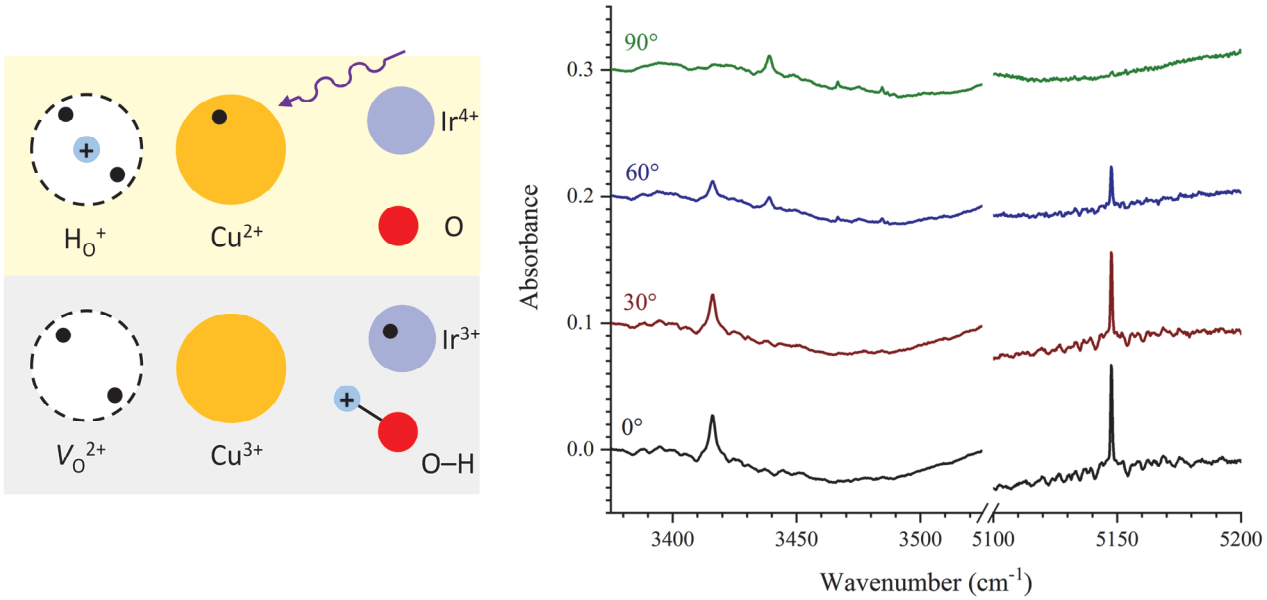
Motivated by first-principles calculations [9], Pansegrau and McCluskey [10] attempted to produce PPC in barium titanate ($BaTiO_3$, or BTO), a ferroelectric perovskite semiconductor. As with STO, samples were annealed at 1200°C. The annealing atmosphere was controlled by mixing flowing argon-hydrogen gas with water vapor. Free-carrier absorption measurements (Fig. 4) showed PPC with an optical threshold of 2.9 eV, similar to that of STO. However, the conductivity increase was only a factor of two, as opposed to the order-of-magnitude effect seen in STO. This is due to the conductivity prior to illumination, presumably due to V_O defects. Similar results were obtained for $Ba_xCa_{1-x}TiO_3$ (BCTO) crystals grown at Washington State University [11]. These studies suggest that PPC is a phenomenon that could occur in many different materials. Combining PPC with ferroelectricity could form the basis for novel optoelectronic devices where the electric field is "turned off" by photo-excited free carriers.

2.3 Gallium oxide

Monoclinic gallium oxide (β-Ga_2O_3) is an ultra-wide bandgap semiconductor with potential applications in power electronics [12]. Semi-insulating substrates can be produced by doping with acceptors such as Fe, Mg, and Zn. A Cu-doped crystal was grown to determine if Cu could also serve as a viable acceptor dopant. Unexpectedly, the β-Ga_2O_3:Cu samples showed *persistent photodarkening* [13]. First-principles calculations indicate that a Cu-H_O pair is responsible. When a photon is absorbed by this defect, the Cu oxidation state goes from Cu^{2+} to Cu^{3+}, which absorbs visible light due to an internal transition. O–H modes are also observed following illumination.

The process is similar to that in STO (Sec. 2.1). However, rather than an isolated oxygen vacancy, the defect after illumination is a copper-vacancy pair (Cu-V_O). As shown in Fig. 5(a), upon photoexcitation, hydrogen leaves the oxygen vacancy and forms a metastable O–H bond. The liberated electron is captured by an iridium donor, changing its oxidation from Ir^{4+} to Ir^{3+}. Because no electron is placed into the conduction band, this does not result in PPC. As with the prior examples, the effect can be erased by annealing in air at 300-400°C.

The O–H modes that appear after illumination are in the 3400-3500 cm^{-1} range [Fig. 5(b)]. The Ir^{4+} peak near 5150 cm^{-1} is also shown. The polarization of the IR light is indicated, where 0° is along the **b** axis and 90° is the **c** axis. The Ir^{4+} peak is maximized for **b**-polarized light. Interestingly, the strongest O–H peak also has its maximum along the **b** axis, in contrast to nearly all other hydrogen modes in β-Ga_2O_3.



(a) (b)

Figure 5. (a) Schematic diagram of photodarkening in β-Ga_2O_3. A Cu-H_O pair absorbs a photon, which causes the proton to leave and form an O–H bond. An electron is captured by an Ir donor. Oxidation states of Cu and Ir are indicated. (b) Polarized IR spectra (10 K) after illumination, where 0° = **b** axis and 90° = **c** axis.

2.4 Potassium tantalate

Current efforts are focusing on potassium tantalate ($KTaO_3$, or KTO), a cubic perovskite semiconductor with a bandgap of 3.6 eV [14]. Single crystals can be grown by hydrothermal, top-seeded solution, or Czochralski methods. Like STO, its dielectric constant increases with lower temperature but it does not become ferroelectric. Unlike STO, it does not undergo a structural phase transition at low temperature, but rather remains cubic. This cubic symmetry is desirable for Czochralski crystal growth and simplifies spectroscopic studies.

To create H_O defects, KTO samples were sealed in a silica ampoule that had been evacuated and backfilled with ~0.5 atm hydrogen gas. A piece of Ta wire was included in the ampoule to create an oxygen-poor environment and thus encourage oxygen vacancy formation [15]. Two-point resistance measurements were performed with a Keithley multimeter. Preliminary results (Table 1) show that electrical resistance for annealed samples decreased by a factor of 10-100 after illumination with 340 nm light from an LED. This resistance decrease persisted for several weeks. Future experiments will include Hall effect and free-carrier absorption measurements, as well as determine the photon energy onset for PPC.

Table 1. Two-point resistance measurements of annealed samples, before and after exposure to 340 nm light.

Sample	Before light	After light
KTO-G	230 kΩ	4.5 kΩ
KTO-M	118 kΩ	0.6 kΩ
KTO-N	28.6 kΩ	0.5 kΩ

3. CONCLUSIONS

Room-temperature PPC has been observed in the perovskite semiconductors STO, BTO, BCTO, and tentatively KTO, while persistent photodarkening was seen in β-Ga_2O_3. Experimental and theoretical studies suggest that hydrogen plays a central role in these phenomena. Specifically, a photon can excite substitutional hydrogen, causing the proton to leave and form a metastable bond with a host oxygen atom. Potential applications of PPC include holographic memory storage, selective electroplating, and optically defined circuits [16].

Proton diffusion is an important process in solid oxide hydrogen fuel cells. It is conceivable that light could enhance diffusivity by liberating hydrogen from oxygen vacancy traps. More generally, hydrogen-related defects influence properties in a wide range of oxide materials. The role of hydrogen should always be considered when studying defect reactions and optoelectronic phenomena.

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