Ultrafast Carrier Trapping of a Metal-doped Titanium Dioxide Semiconductor Revealed by Femtosecond Transient Absorption Spectroscopy

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Abstract

We explored for the first time the ultrafast carrier trapping of a metal-doped titanium dioxide (TiO₂) semiconductor using broadband transient absorption (TA) spectroscopy with 120 femtosecond (fs) temporal resolution. The titanium dioxide was successfully doped layer-by-layer with two metals ions namely Tungsten (W) and Cobalt (Co). The time-resolved data demonstrate clearly that the carrier trapping time decreases progressively as the doping concentration increases. A global fitting procedure for the carrier trapping suggests the appearance of two time components: a fast one that is directly associated with carrier trapping to the defect state in the vicinity of the conduction band and a slow component that is attributed to carrier trapping to the deep level state from the conduction band. With a relatively long doping deposition time on order of 30 seconds, a carrier lifetime of about 1 picosecond is obtained. To confirm that the measured ultrafast carrier dynamics are associated with electron trapping by metal doping, we explored the carrier dynamics of the un-doped TiO₂. The findings reported here may be useful to the implementation of high-speed optoelectronic applications and fast switching devices.

Keywords: Ultrafast carrier trapping, titanium dioxide, transient absorption spectroscopy, metal-doped, deep level state.

Introduction

Semiconductor TiO_2 is a widely studied material¹⁻⁷ due to the chemical stability, nontoxic nature, inexpensive fabrication and abundance in nature.⁸ This highly versatile material has found many applications in a variety of research areas of significance, including electronics,⁹ photovoltaics,¹⁰ photocatalysis³ and photoelectrochemical conversion.¹¹⁻¹³ A prominent example is the use of the photocatalytic properties derived from TiO_2 ^{1,14} in the formation of photogenerated charge carriers (electron-hole pairs), which occur with the absorption of ultraviolet (UV) light. In addition, TiO_2 is classified as a unique photocatalyst under light doping in both the visible and UV regions.^{4,9,15} It is in fact true that the long carrier lifetimes of un-doped TiO_2 prevent its use in other potential applications, such as high-frequency switching devices and photo-detectors, which mainly rely on very fast carrier recombination as a recovery process to the initial state. In this regard, doping of TiO_2 using metal agents is quite beneficial as is evidenced in new localized electronic energy levels, defect levels and a deep-level trap state, induced in the band gap.^{6,16} Essentially, an electron is successfully excited from the valence band (VB) to the conduction band followed by trapping to the generated defect states. Accordingly, in this regime, it is well documented that deep-level states within the band gap can significantly reduce the carrier lifetime. Thus, efforts have been devoted to making these materials suitable for unique applications, including repetitive ultrafast electrical transients and high-speed electronics.^{17,18}

Gathering detailed information on intrinsic carrier recombination dynamics due to the metallic dopants in TiO_2 is important. Quantitative data on these carrier dynamics can be directly obtained through ultrafast pump-probe spectroscopy. As a consequence of the action of the pump pulse, electrons are successfully promoted to the conduction band (CB) and subsequently the decay process from the latter band to various defect levels can be directly probed in real time. To achieve this, transient absorption (TA) spectroscopy is a highly sensitive, broadband and powerful tool that allows the exploration of the ultrafast carrier dynamics in semiconductor materials and complex molecular systems.^{16,19-23} For instance, ultrafast carrier dynamics have been thoroughly investigated in numerous of semiconductor materials by implementation of this technique, including SrTiO_3 ,^{6,24} ZnO ,²⁵ ZrO_2 .²⁶ In this letter, we report results from unambiguous, time-

resolved experiments on carrier trapping in metal-doped TiO₂ as a function of the deposition time of two metals, Tungsten (W) and Cobalt (Co). We clearly show that the carrier recombination time decreases dramatically as the metal deposition time increases. Two time constants for the carrier trapping are observed, a fast component with a characteristic time constant of a few picoseconds associated with the trapped carriers near the conduction band and a slow component of a hundred picoseconds attributed to the trapped carriers in the deep-level state.

2. Experimental Section

In this section, we outline the experimental scheme, which includes the synthesis method of the materials and the ultrafast femtosecond transient absorption spectroscopy technique.

TiO₂–M–TiO₂ (M = W and Co) Multilayer Film Synthesis: The procedure for the sample preparation was previously reported in detail.²⁷ We provide a brief description with the particular samples used in this work. TiO₂–M–TiO₂ (M = W and Co) multilayer films were deposited on glass substrates using radio frequency (RF) reactive magnetron sputtering. For each sample, four layers of TiO₂ and three layers of the selected metal were deposited. Alternately one layer of TiO₂ and one layer of the metal were deposited as this procedure was repeated three times. After the TiO₂/metal layers were deposited, an additional layer of TiO₂ was added as a cover. The total thickness of the TiO₂ layers was about 80 nm. The deposition rate of the W and Co layers was 10 and 5.3 nm/min, respectively, and two different deposition times of 10 and 30 s were selected. After deposition, all TiO₂–M–TiO₂ films were annealed at 500 °C in air for 2 hours.

Transmission electron microscope (TEM) cross-section specimens were prepared using the focused ion beam (FIB) technique on a FEI Helios 400S to identify the structure of the TiO₂ films and the concentration of the metal dopants. The TEM and scanning transmission electron microscopy (STEM) images were obtained using a FEI Titan 80-300 SuperTwin electron microscope, operated at 300 kV. To analyze the state of the dopant agents and clarify the distribution within the multilayer thin films, electron

energy-loss spectroscopy (EELS) was performed on a Gatan Imaging Filter (GIF) Tridiem.

Femtosecond Transient Absorption Spectroscopy: Ultrafast time-resolved transient absorption spectroscopy^{28,29} was used to study the carrier trapping. An Ultrafast Systems Helios UV-NIR (Ultraviolet-Near Infrared) system was used to explore the semiconductor samples in this study by employing the pump-probe technique (See Figure 3). The Helios is equipped with CMOS VIS (Visible) and fast InGaAs NIR spectrometers covering the wavelength range of 350-800 nm with 1.5 nm spectral resolution at 9500 spectra/s and a range of 800-1600 nm with 3.5 nm spectral resolution at 7900 spectra/s, respectively.

The output pulse from the laser system is split into two parts to generate the pump and probe pulses. A small portion ($\approx 60 \mu\text{J}$) of the Spitfire (Spectra-Physics Pro 35F-XP regenerative femtosecond amplifier) output is routed via a delay line, adjustable pinholes, a focusing lens and a variable neutral density filter to a crystal for white light continuum (WLC) generation and further to the sample via a focusing mirror. Three crystals are available to cover the UV-VIS and NIR spectrum. A computer-controlled delay line is used to vary the time delay between the pump and probe pulses that allows for transient absorption measurements within a 3.3 ns time window. For the UV-Vis white light continuum generation, we used CaF_2 crystal and sapphire plate for 340-700 nm and 440-830 nm spectral ranges, respectively. Another part (1mJ) of the Spitfire output is used to pump TOPAS-C (Spectra Physics) two-stage parametric amplifier equipped with frequency mixing stages and a non-collinear difference frequency generator that allows for tuning from 237 to 2700 nm. The TOPAS-C output beam is routed via the adjustable pinholes, a variable neutral density filter, a depolarizer, a chopper wheel and a focusing lens to excite the sample. The pump and probe beams are set to overlap spatially and temporally at the surface of the various thin films. The transmitted probe light from the samples is collected and focused on the broadband detector for recording the time-resolved excitation-induced difference spectrum (ΔA). During the measurements, the various thin films are constantly moved using a two-stage sample holder such that a fresh sample is

available for each laser shot as well as to prevent a potentially substantial laser-induced heating effect on the films. The experiments were conducted at the room temperature.

Results and Discussion

The fundamental features of the samples in terms of the classified diffusion of the metal ions and the respective oxides into the host TiO₂ layer were explored in detail. The core observation is that the dopant agents are mainly metal ions in the host ionic crystal of TiO₂. Here, we fully characterized the prepared Co-doped TiO₂ thin films by TEM and EELS; previously, they were investigated by x-ray diffraction (XRD) and Raman spectroscopy techniques.²⁷ The TEM image clearly confirms the preserved multilayer structures of the thin films even after the annealing process with four layers of TiO₂ and three layers of the respective metals well-defined and clearly distinguishable as presented in Figure 1A. The inset high-resolution TEM image shows that the TiO₂ layers are partially crystallized, agreeing well with previous XRD and Raman results.²⁷

In addition, we used EELS scans of the cross-section (Figure 1B) of the samples to investigate the actual diffused concentration of the metal ions into the TiO₂ layer. The obtained EELS spectra were acquired from the metal layer to the center of the TiO₂ layer as indicated in the figure by position P1 (the metal layer), P2 and P3 (both in the TiO₂ layer). In the Co/TiO₂ (ions and oxides) films, we found that the amount of Co ions diffused into the TiO₂ layer (P3) was relatively substantial. In addition, the significant relative difference in the elementary ratio of Co/(Co+Ti) between Co/TiO₂-10s and Co/TiO₂-30s is mainly apparent in the Co layer at 26.923% and 66.019%, respectively (Table 1). At positions P2 and P3, there is a remarkable decrease in these respective values compared with the case of the initial state (P1) but the actual percentages of diffused Co ions at P3 are 2.299% and 2.899%, confirming that Co was dispersed into TiO₂ layers. This is consistent with the transient absorption data (see below).

Apparently, the exact concentration of Co and W dopant atoms involved a large inaccuracy but, on the other hand, there was no clear signature to predict the possibility of the appearance of cobalt oxides and tungsten oxides in the actual layer of Co/TiO₂-10s and W/TiO₂-10s. The reason might be due to the relatively high amount of Ti effectively suppressing the crystallization of cobalt oxides especially in Co/TiO₂-10s. Direct evidence of the presence of cobalt oxides and tungsten oxides in Co/TiO₂-10s and W/TiO₂-10s was not observed in either the XRD and Raman spectroscopy experiments. However, we cannot exclude the possibility that the associated oxides were partially diffused into the layers Co/TiO₂-30s and W/TiO₂-30s due to the actual relatively high percentage of Cobalt and Tungsten in the respective metal layers. However, if we assumed that a small fraction of Co or W is present as metal oxides, this will not add appreciable uncertainty to the measured ultrafast carrier dynamics because these oxides will have their own band gap rather than creating electron trap states in the band gap of TiO₂, which is responsible for the quenching of the excited carrier.

The elementary ratio of Co/(Co+Ti) in the TiO₂ layer is approximately below 7% as indicated in Table 1, in good agreement with Griffin and Chambers et al.,^{30,31} who claimed that the maximum dopant concentration of Co ions associated with TiO₂ films can reach 10%. Nevertheless, more Co ions are contained in the TiO₂ configuration of Co/TiO₂-30s compared with the case of Co/TiO₂-10s. This observation was confirmed by our ultrafast spectroscopy results (see below).

The surface analysis demonstrated that Co ions and W ions indeed diffused into the TiO₂ layer and served as dopant agents and subsequently caused the modification of the electronic band structure. In addition, the respective oxides and O ions were incorporated alongside the atoms in the TiO₂ layer. It is appropriate to clarify that a small percent of the atoms were dispersed into the TiO₂ layer despite the fact the distribution was inhomogeneous as suggested by the TEM and EELS scans. Spatial compositional variations were clearly present and the deviations were pronounced but the atoms and the metal ions were both present in this regime. It is worth pointing out that the inhomogeneity of the metal distribution did not affect the measured dynamics because we

performed our transient absorption experiment in a transmission mode and the measured signal reflected the average dynamics of the excited area.

The obtained results from the steady-state and ultrafast transient absorption spectroscopy are discussed. It is appropriate to mention that the measurements were ensemble averages. In Figure 2, we present the steady-state absorption spectra of the un-doped TiO_2 (A) and the doped $\text{TiO}_2\text{-Co-TiO}_2$ (B) and $\text{TiO}_2\text{-W-TiO}_2$ (C) films with the wavelength ranging from 300 to 1500 nm. The absorption edges of the $\text{TiO}_2\text{-M-TiO}_2$ multi-layer thin films are red-shifted compared with the fundamental absorption edge, which is ascribed to the dopant metals that effectively cause a change in the band gap energy of the TiO_2 thin films. In other words, this observation indicates that the band structure of TiO_2 is modified significantly by metal doping. This red shift of the TiO_2 spectrum can be attributed to doping with ions of low electrical negativity since this mechanism is associated with the ability of an atom to attract the electron density towards itself.³² In addition, very often, a shift in the band gap transitions toward longer wavelengths is observed in the doped layers³³ in good agreement with our observation. It is worth mentioning that the band gap of TiO_2 polycrystalline thin film can be varied from 3.5-3.0 eV with tail down to visible spectrum range. This depends on post-deposition annealing, lattice constants, grain size, morphology, defects including oxygen ones, and annealing temperature.³⁴⁻³⁸

Our experimental setup to conduct highly sensitive transient absorption measurements executed by the pump-probe technique is displayed in Figure 3. The transient absorption spectra obtained by probing with white light in the UV-VIS range after 350 nm excitation are shown in Figure 4 for the case of un-doped TiO_2 and 30 s deposition time for W and Co doped TiO_2 . The probed data display clear excited states for decay times ranging from - 0.7 ps to 103 ps for the 30 s deposition time. The pronounced effect indicates that the transient spectra strongly depend on the doping deposition time. Consistency red shift as in the steady-state spectrum is clearly demonstrated throughout the displayed data. Utilizing a global fitting procedure, we report our major findings in terms of the characteristics of the trapped carrier states in Figure 5. Figure 5A shows the carrier recombination of the un-doped and Co doped TiO_2 films As can be clearly seen, the carrier dynamics of the un-doped TiO_2 is much slower

than the doped ones, indicating that the measured ultrafast carrier dynamics are associated with carrier trapping to the defect states created in the TiO₂ band gap by metal doping. Each decay curve has a fast component associated with a time constant of about 2-8 ps and a slow component with a time constant of 40-160 ps. More precisely, in the Co/TiO₂-10s system, two different time components are found with values of $\tau_1 = 4.2 \pm 0.40$ ps and $\tau_2 = 135 \pm 12.0$ ps. In the case of Co/TiO₂-30s, the time components are $\tau_1 = 1.8 \pm 0.35$ ps and $\tau_2 = 32 \pm 2.7$ ps. Analogously, the time components for W/TiO₂-10s are $\tau_1 = 7.5 \pm 0.85$ ps and $\tau_2 = 159.3 \pm 15.0$ ps and for W/TiO₂-30s they are $\tau_1 = 3.8 \pm 0.65$ ps and $\tau_2 = 77.9 \pm 7.6$ ps. It should be noted that the carrier trapping is estimated by fitting the kinetic data with a two-exponential decay function: $\Delta A = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where A_i and τ_i , $i=1$ and 2 are the time-independent coefficients and the time constants determined by the excitation fluence. As can be seen, the carrier trapping of W/TiO₂-30s is almost a factor of two slower compared with that for Co/TiO₂-30s. The determined time components are associated with fast and slow times, respectively. The former one is linked to the decay of the electron to the defect state located below the conduction band. Similarly, the second time component is attributed to electrons decaying to the deep-level trapping state allocated between the valence band and the conduction band, near the center of the band gap. These findings associated with the concentration gradient are consistent with the literature³⁹ as the generated defect states are shifted (closer to the conduction band edge) as the doping concentration is increased, eventually providing a faster trapping time.

A similar result was observed for other doped semiconductor materials.^{6,16,24-26,40}

In these cases, the slow component is also attributed to the carrier trapping in the deep-level energy states, which can attract electrons from the conduction band or holes from the valence band. Essentially, the time constants of both the fast and the slow component progressively decrease with increasing doping concentration. Similarities are obtained in with W-doped TiO₂ films (as shown in Figure 5B). Figure 5 further reveals that the values of the carrier lifetime in the doped TiO₂ films significantly depend on the dopant metals. Comparing the carrier lifetime of Co/TiO₂-10s in Figure 5A with that of W/TiO₂-10s in Figure 5B, we observe that the value of Co/TiO₂-10s is almost a factor of two

faster than that of W/TiO₂-10s. Similarities are also observed in the carrier lifetimes of Co/TiO₂-30s and W/TiO₂-30s. Similarly, the drift in the trapping carrier time caused by the dopant mass effect is explained by the creation of additional defect states or different distributions of the defect levels in the band gap.^{39,41}

Variations in the pump fluence and the concentration effects studied here suggest different behaviors. Whereas the former has no substantial effect on the carrier dynamics, the latter has a pronounced effect on the reduction of the carrier lifetime. Additionally, Co is a promising candidate as a dopant agent since it provides a relatively faster trapping time compared with W, which in turn has a larger mass. More specifically, Figure 6A shows the kinetics of Co/TiO₂-10s under low (5.3 mJ/cm²) and high (11.5 mJ/cm²) pump fluence conditions. As can be seen, the kinetics is relatively comparable in both cases and does not display any significant difference, suggesting that the observed dynamics reflect only carrier trapping and completely exclude any heat contribution to the measured signal. The contribution from lattice heating is considerable, but an increase in the fluence by a factor of two has no significant effect on the kinetics. The photo-generated carrier density is expressed by the following equation: $N = j_p \alpha$, where j_p is the pump fluence (photons/cm²) and α is the absorption coefficient of TiO₂ at the associated pump wavelength. The value of $\alpha = 0.23 \times 10^5 \text{ cm}^{-1}$ is determined from the measured absorbance (OD = 0.184) at the pump wavelength and the thickness ($l = 80 \text{ nm}$) of TiO₂ thin film sample. The spot size of the laser beam is 440 μm thus N is calculated to be $2.13 \times 10^{20} \text{ cm}^{-3}$. Figure 6B shows the kinetics of Co/TiO₂-30s under different excitation conditions at 350 nm and 475 nm. The lifetime of the trapped states of Co/TiO₂-30s at 350 nm excitation (Figure 6B) is slower than the one at 475 nm excitation. This can be associated with the mechanism whereby a higher excitation energy will inject electrons at an intrinsic energy level above the conduction band edge. Therefore, the electronic wavepacket undergoes intraband transitions in the conduction band, resulting in the fast component as the lifetime becomes slower and decays further to the defect level. In other words, the fast decay is slower at 350 nm excitation because the decay is convolved together with a growth due to intra-conduction band cooling.

Conclusion

In summary, the ultrafast carrier dynamics has been examined for the first time for W/TiO₂ (10s and 30s) and Co/TiO₂ (10s and 30s) using broadband transient absorption spectroscopy with 120 femtosecond (fs) temporal resolution. The observation of a fast and slow time component was reported for each sample. These time components were attributed to the associated decay of the electronic wavepacket to the defect state near the conduction band and the deep-level trapping state, respectively. The obtained values for the time components are typically on the order of 2-8 ps for the fast one and analogously around 40-160 ps for the slow one, demonstrating the pronounced vital impact of the doping deposition time on the carrier trapping. In addition, our steady-state spectroscopy and imaging and fs transient absorption data demonstrate clearly that Co and W are present in the TiO₂ layer as metal ions rather than oxides. Our results may have implications for applications in electronic devices requiring high-frequency obtained through trapped states, providing fast carrier recombination. We further anticipate that our findings might serve as motivation for further investigation of the ultrafast carrier trapping dynamics in other semiconductor materials.

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Notes

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Table caption

Table 1: Co/(Co+Ti) elementary ratios in Co/TiO₂-10s and Co/TiO₂-30s thin films.

sample	Co/(Co+Ti) ratio		
	P1	P2	P3
Co/TiO ₂ -10s	26.923%	5.000%	2.299%
Co/TiO ₂ -30s	66.019%	6.154%	2.899%

Figure captions

Figure 1: A high-resolution TEM image of a Co/TiO₂-30s film (A). A STEM image of a Co/TiO₂-30s film (B). P1 refers to the position in the metal layer, P2 and P3 refer to the positions at the edge and the center of TiO₂ layer, respectively. EELS spectra were taken at positions P1, P2, and P3 for analyzing the distribution of Co in the multilayer thin films.

Figure 2: The steady-state absorption spectra of a TiO₂ film (A), Co/TiO₂-10s and Co/TiO₂-30s films (B) and W/TiO₂-10s and W/TiO₂-30s films (C). TiO₂-M-TiO₂ multilayer thin films are red-shifted compared with the non-doped TiO₂ films, indicating that the band structure of the semiconductor oxide is modified significantly by metal doping.

Figure 3: The experimental setup of femtosecond transient absorption spectroscopy showing the integration of the ultrafast Helios UV-NIR spectrometers (Ultrafast systems, FL, USA) with both a Spitfire Pro 35F-XP regenerative amplifier (Spectra physics) and a TOPAS-C two-stage parametric amplifier.

Figure 4: Average transient absorption spectra of a TiO₂ film (A), W/TiO₂-30s film (B) and Co/TiO₂-30s film (C) at different time delays and an excitation of 350 nm.

Figure 5: Comparison of the different doping concentration effects on the kinetics: (A) TiO₂, Co/TiO₂-10s and Co/TiO₂-30s films. (B) W/TiO₂-10s and W/TiO₂-30s films. A global fitting procedure for the carrier trapping indicates that a significant effect of the doping concentration.

Figure 6: (A) The kinetics of a Co/TiO₂-10s film under different pump fluences, clearly indicating that the observed dynamics reflect only carrier trapping and completely exclude any contribution of heat to the measured signal. (B) The kinetics of a Co/TiO₂-30s film under different excitation conditions.

Figure 1:

Figure 2:

Figure 3:

Figure 4:

Figure 5:

Figure 6:

TOC Graphic

Femtosecond transient absorption results demonstrate that there are two time components for carrier trapping in metal-doped titanium dioxide (TiO_2) thin films: a fast one that is directly associated with carrier trapping to the defect state in the vicinity of the conduction band and a slow one that is attributed to the carrier trapping at the deep-level state from the conduction band.