



# The effects of surface conditions of TiO<sub>2</sub> thin film on the UV assisted sensing response at room temperature



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## ABSTRACT

Thin film oxides have attracted attention in implementations of gas sensors, notably NO<sub>2</sub>, owing to their unique physical, optical, and chemical properties. While the properties are presumed to be strongly dependent on the surface conditions of the thin films, it is not yet clear how surface properties of the thin film gas sensor affect its analyte sensing response. Here, we report the influence of surface carbon contamination and roughness on the NO<sub>2</sub> sensing properties of TiO<sub>2</sub> thin film sensors. The TiO<sub>2</sub> thin films were prepared by rf-sputtering. The surface of the films were intentionally contaminated and damaged with organic polymers (photolithography resist) and microwave plasma, respectively. The surface chemistry of the films was assessed by high resolution X-ray photoelectron spectroscopy, and atomic force microscopy was exploited to obtain the morphology of the fabricated sensors. The work aims to improve the long-term efficacy of gas sensors by studying the reasons for degradation in performance. Our results indicate that the carbon residue and surface roughness of the TiO<sub>2</sub> based sensor prolong the NO<sub>2</sub> response time by roughly threefold and fivefold, respectively. The recovery rate of the sensor is deteriorated by the poor surface conditions as well.

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## 1. Introduction

Solid-state semiconductor oxides have attracted sensor research community for the last decades as a facile solution to detect gas analytes [1–3]. The adsorption and desorption of gases on the surface of oxides change the electrical resistance of the sensors. Therefore, it is highly desirable to have a gas sensor scheme with high surface-to-volume ratios, such as thin films, to enhance the chemiresistive response. The implementation of thin film oxides into gas sensors and many other optoelectronic devices also depends on their intrinsic properties, including high optical transparency, thermal stability, and low impact to environment [4–8].

Among the various well-studied semiconductor oxides, TiO<sub>2</sub> has been demonstrated extensively for the application of gas detection [1,9,10]. The unintentionally doped TiO<sub>2</sub> generally exhibits oxygen deficiency [9]. This nonstoichiometry of TiO<sub>2</sub> results the generation of electrons in the oxygen vacancies and thus the n-type semiconductivity [2]. The gas sensing mechanism of the n-type oxide semiconductor is the depletion of surface electrons by the adsorbed oxygen anions. Therefore, the exposure of a TiO<sub>2</sub> sensor

to oxidizing gases, such as NO<sub>2</sub>, increases the resistance. Ultraviolet (UV) illumination is widely used to induce the photoconductivity of TiO<sub>2</sub> and thereby to enhance the sensing performance of TiO<sub>2</sub> based sensors [1,10,11].

In this work, we investigated the role of surface conditions of a 10 nm thin TiO<sub>2</sub> film in the gas response towards NO<sub>2</sub> under UV illumination. This study aims to provide convincing explanations for the degradation of thin film oxide based sensors. The TiO<sub>2</sub> films were examined carefully with X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) to elucidate the modifications of the film surface with various treatments. With the greatly enhanced surface-to-volume ratio in a thin film structure, the sensing properties mainly rely on the gas-oxide interactions on surface and thus are expected to be strongly affected by the microstructure and surface chemistry of the material. Our gas response results indicate that the carbon residue and surface roughness significantly degrade the response and recovery rates of the sensors.

### 1.1. Experimental details

The TiO<sub>2</sub> thin films were prepared in a Denton Vacuum Discovery 550 sputtering system with a 99.9% TiO<sub>2</sub> target. The deposition process was maintained in a pure Ar environment. To prevail the catalytically

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active anatase phase of  $\text{TiO}_2$  [12] and enhance the crystallinity of the films [13], the samples were prepared at a substrate growth temperature of 325 °C and a post-annealing temperature of 700 °C. These temperatures were chosen based on the factors that anatase phases dominate at deposition temperature <400 °C [14] and annealing temperature <900 °C [15]. Observed X-ray diffraction patterns confirmed the polycrystalline anatase nature of the prepared  $\text{TiO}_2$  films, as data presented in another work [1]. Based on the pre-calibrated deposition rate and ellipsometry (J. A. Woollam M2000) measurement, the thickness of deposited  $\text{TiO}_2$  is around 10 nm. For the carbon contamination study, photolithography resist (PR) was firstly coated onto the annealed  $\text{TiO}_2$  film and then cleaned with Acetone, IPA, and DI water. For the surface roughness study, the surface of  $\text{TiO}_2$  films was coarsened by blasting the microwave plasma of  $\text{O}_2$ . The interdigitated metal contacts were e-beam evaporated onto the distinctively prepared films for electrical measurements.

The surface morphology and roughness of the prepared  $\text{TiO}_2$  thin films were obtained with AFM using a Bruker Dimension FastScan system. The stoichiometry of chemical state of prepared films was measured by XPS. XPS measurement was conducted in a Kratos Axis-165 system with a monochromated Al source and a 30  $\mu\text{m}$  imaging spot. Survey scans were performed at 0° and 45° to the surface normal at a 1 eV step size. Additionally, high resolution scans with 0.1 eV step size were taken for Ti 2p, C 1s, and O 1s. XPS data analysis was performed using CasaXPS. The spectrum scale of the binding energy was calibrated towards the hydrocarbon peak at 284.8 eV.

The gas sensing behavior of the fabricated sensor was investigated at room-temperature in a custom-built apparatus. A gaseous mixture of  $\text{NO}_2$  and breathing air was introduced into the sensing apparatus. Mass flow controllers independently controlled the flow rate of each component, determining the composition of the mixed gas. The sensors were biased with a constant 5 V supply and currents were measured by a National Instrument PCI DAQ system. A 365 nm light emitting diode provided the UV illumination to the sensor. The output power of the UV source was maintained at 469  $\mu\text{W}$  with <0.5% variation, as verified with a Newport power meter.

## 2. Results and discussions

Fig. 1 shows the high resolution AFM images of the prepared samples. Gleaning from the first glance, the plasma damaged sample (Fig. 1.c) exhibits totally distinct morphology from the quite similar as-is annealed and carbon contaminated samples. Quantitatively, the root mean square (rms) surface roughness, listed in Fig. 1d, doubles for the plasma damaged sample from the other cases. The values are 0.32 nm, 0.3 nm and 0.65 nm for the as-is annealed, contaminated, and microwave plasma damaged samples, respectively. These results clearly indicate that the applied microwave plasma coarsens the surface of  $\text{TiO}_2$  film, while the morphology remains identical after the carbon contamination treatment.

Fig. 2a shows the collected XPS survey data of the O1 as-is annealed, O2 contaminated, and O3 plasma damaged  $\text{TiO}_2$  films, at the 0° incident angle to the normal of samples. All the detected peaks can be assigned to the prepared films (Ti and O), the expected adventitious contamination (C), and the sapphire substrates (Al). The escaping electrons which transverse through the thin  $\text{TiO}_2$  layer from the underlayer substrate attribute to the Al peaks. This collection of underlayer signal may be diminished with more surface sensitive analytic techniques, such as Auger electron spectroscopy [16]. Fig. 2b presents the ratios of the compositional concentration calculated from the XPS scan at 45° over 0°, for all the detected elements. Compared to the collection angle of 0°, the excited electrons travel a longer distance through the overlayer at the 45° and thus experience greater intensity attenuation. Therefore, those signals arising from elements beneath a super-surface layer will show a relative decrease (ratio < 1) with increased collection angle, as observed for O, Ti and Al. In contrast, the relative increase in atomic percentage of C in all samples at 45° indicates that C arises from the surface contamination. In general, the estimated atomic concentrations of the detected elements vary within a narrow range for the examined  $\text{TiO}_2$  films at 0° incident angle, as shown in Fig. 2b. The most notable difference is the increase of C from roughly 10% in the as-is annealed and plasma damages samples to 17% in the PR coated and removed  $\text{TiO}_2$  sample. This additional C, along with the conclusion that C lays on surface, suggests that

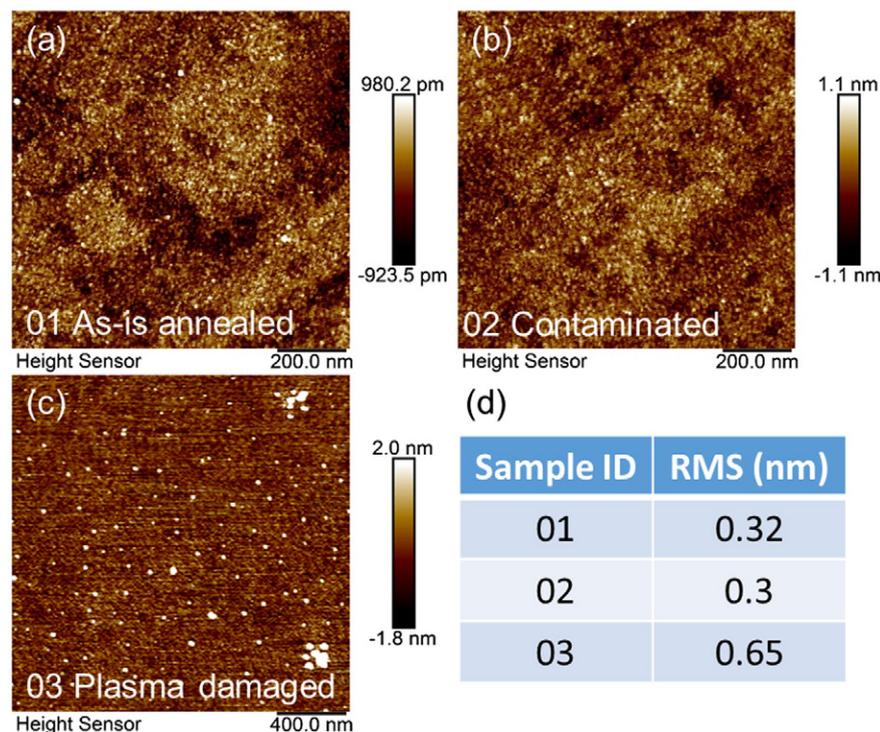
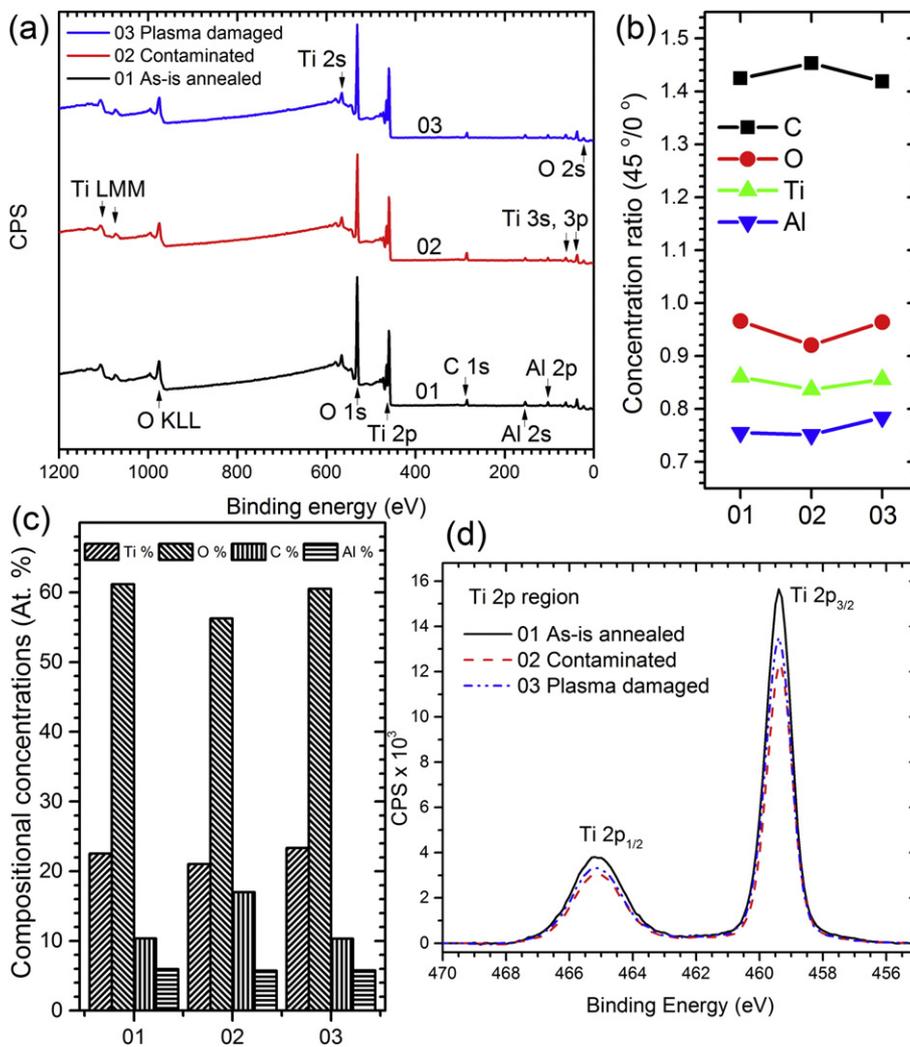


Fig. 1. AFM images of (a) as-is annealed  $\text{TiO}_2$ , (b) contaminated  $\text{TiO}_2$ , and (c) plasma damaged  $\text{TiO}_2$ . (d) Table of estimated rms roughness for each sample.



**Fig. 2.** (a) XPS spectra of the prepared 01 as-is annealed, 02 contaminated, and 03 plasma damaged  $\text{TiO}_2$  thin films. (b) Ratios of concentrations calculated from the XPS  $45^\circ$  scan to  $0^\circ$  scan. (c) Atomic concentrations of the detected compositions in the examined  $\text{TiO}_2$  films at collection angle of  $0^\circ$ . (d) High-resolution XPS spectra of Ti 2p regions of the  $\text{TiO}_2$  films.

the implemented organic polymer cleaning process contaminates the surface with C residues. Fig. 2d shows the almost identical Ti 2p peaks, with only slight variations in the signal intensities, of the examined  $\text{TiO}_2$  films. These data are collected from high-resolution (0.1 eV) XPS scans at the incident angle of  $0^\circ$ . The binding energies and shapes of the Ti peaks are in good agreement with the reported  $\text{TiO}_2$  measurements [17].

The components of C in the  $\text{TiO}_2$  films are revealed by the high resolution XPS studies in the C 1s region. Fig. 3a, b, and c shows the obtained C 1s peaks from the 01 as-is annealed, 02 contaminated, and 03 plasma damaged  $\text{TiO}_2$  films, respectively. All the C 1s peaks are deconvoluted into C—C peaks at 284.8 eV and C—O peaks at 286.4 eV. While the carbon spectra of the as-is annealed and plasma damaged samples appear to be resembling, a much higher C—O peak is noticed from the contaminated film at the first glance. The concentrations of the C components in the  $\text{TiO}_2$  films are estimated by quantifying the areas of the fitted C—C and C—O curves, data shown in Fig. 3d. An additional 3% of C—C and 3.6% of C—O components appear on the surface of the contaminated  $\text{TiO}_2$  film, which increases the ratio of C—O to C—C in the film significantly to 50.8% as well.

Proper surface oxidation states of metal oxides are critical for high sensitivity as well as selectivity of the oxide-based gas sensors. O 1s regions of the  $\text{TiO}_2$  films are resolved in detail with high resolution XPS scans. Fig. 4a, b, and c shows the deconvoluted O 1s peaks, lattice oxide and hydroxide, of the 01 as-is annealed, 02 contaminated, and

03 plasma damaged  $\text{TiO}_2$  films, respectively. The main O 1s peaks at 529.6 eV are assigned to lattice oxygen from  $\text{TiO}_2$ , and the side peaks with higher binding energy are attributed to the hydroxylation of the films [11]. No notable difference is observed from the spectra of the O 1s regions, which means that the contaminated and plasma damaged films retain the oxidation information from the as-is annealed state. Fig. 4d shows the concentration of O components and ratios of lattice oxide to hydroxide in the investigated films. The concentrations of components are normalized to the percentage of Ti in the corresponding film to eliminate the influence due to the C variation in the examined  $\text{TiO}_2$  samples. Observed from the data, the normalized amounts of lattice O remain almost the same and the concentrations of hydroxide vary merely few percentages (within the error of the XPS tool) in the  $\text{TiO}_2$  films. Therefore, we believe that the studied  $\text{TiO}_2$  films share the same fingerprint of the oxidation states.

Having established the surface chemistry and morphology of the prepared  $\text{TiO}_2$  thin films, the films were further investigated by monitoring their chemiresistive responses to the  $\text{NO}_2$  analytes at room temperature. Fig. 5a shows the measured currents of the as-is annealed  $\text{TiO}_2$  film to 500 ppm  $\text{NO}_2$  under UV illumination and dark conditions. The film was repeatedly exposed to 500 ppm  $\text{NO}_2$  for 300 s followed by 300 s dry air under both UV and dark conditions. The increased baseline current under UV illumination is due to the generation of photon electron-hole pairs. Under UV illumination, the film exhibits reversible

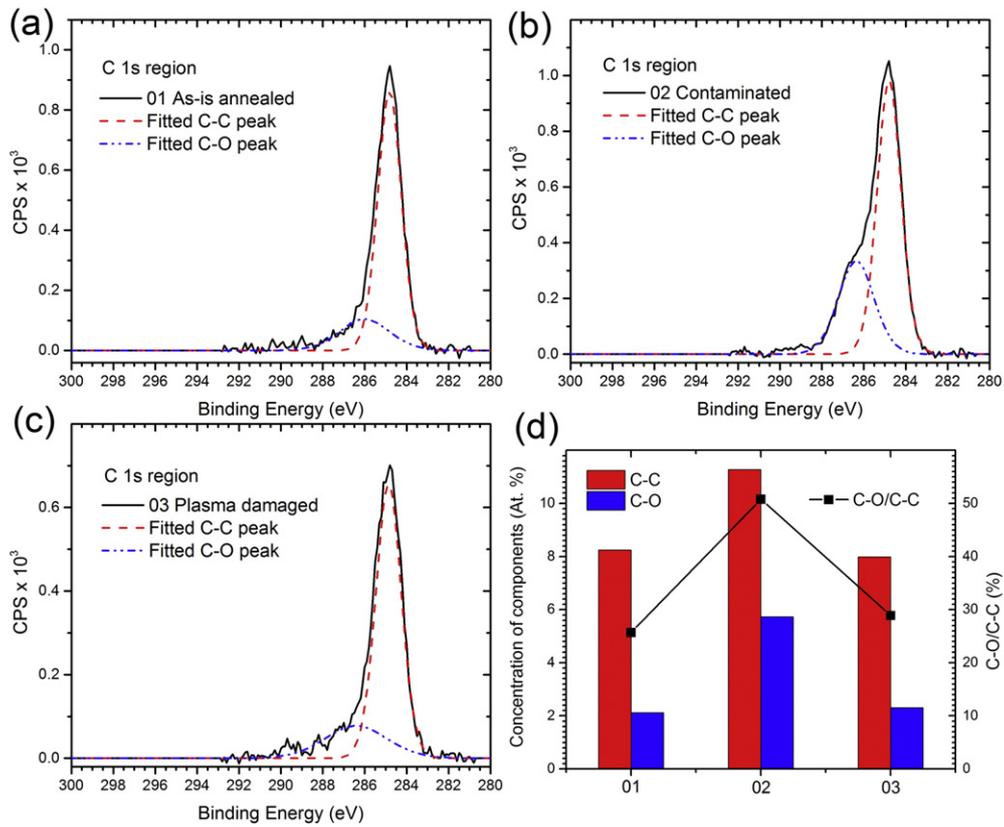


Fig. 3. XPS spectra of C 1s region of (a) 01 as-is annealed, (b) 02 contaminated, and (c) 03 plasma damaged  $\text{TiO}_2$  films. (d) Concentrations of the C–C, C–O components and the ratio of C–O to C–C in the  $\text{TiO}_2$  films.

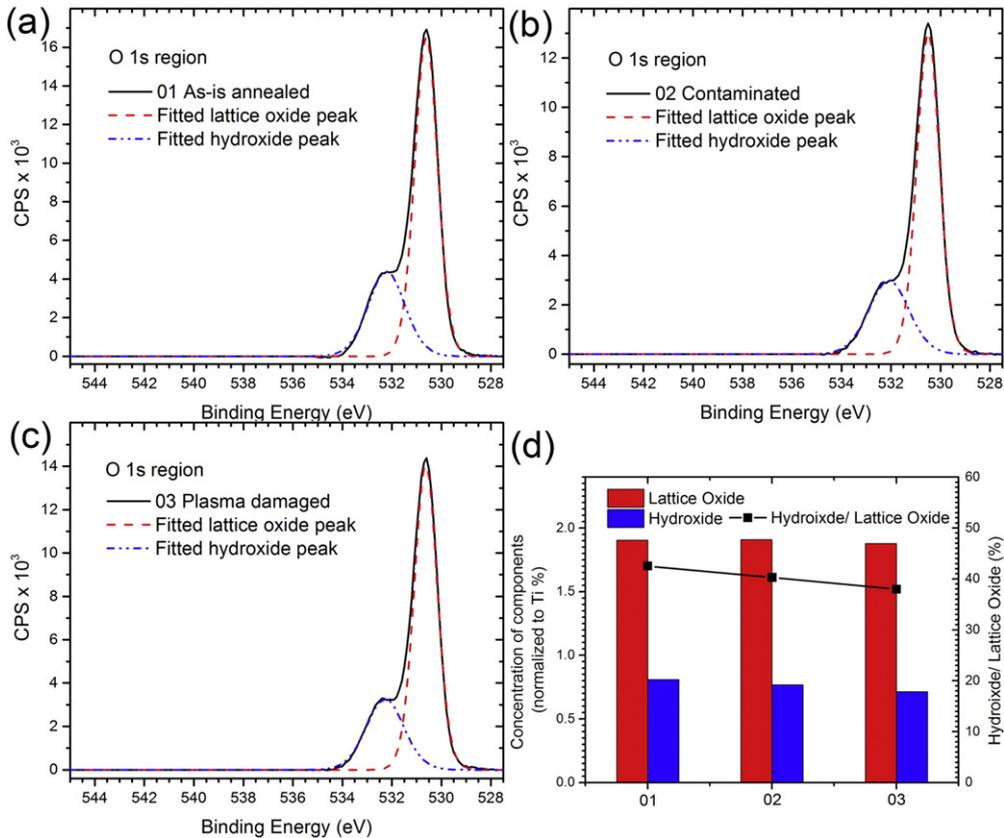
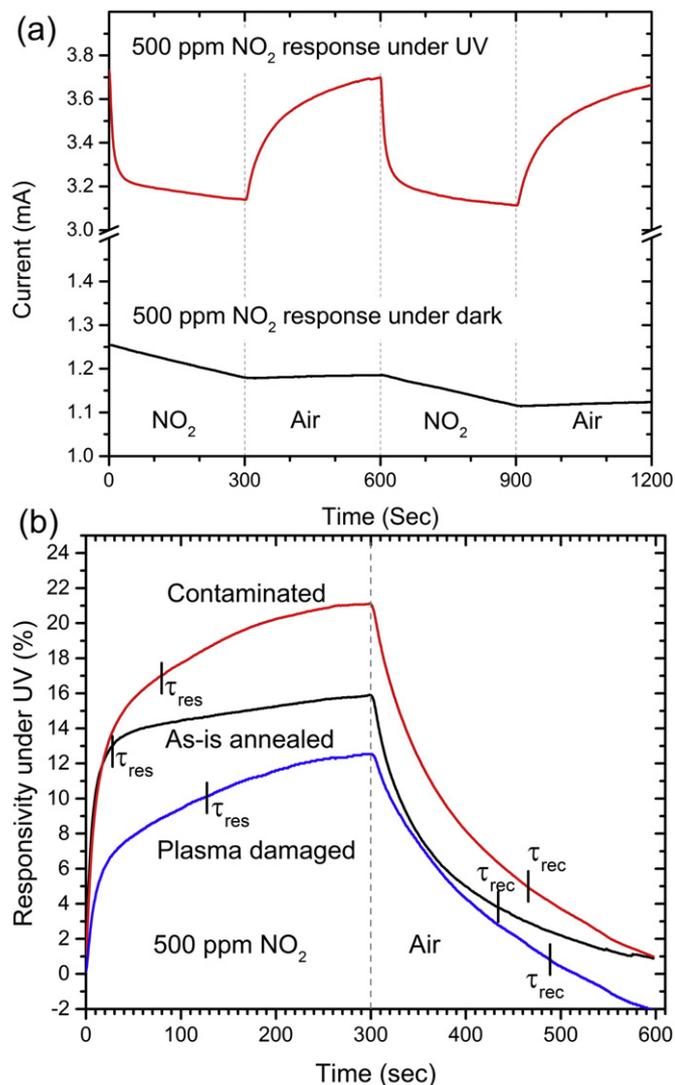
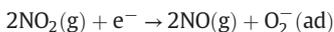


Fig. 4. XPS spectra of O 1s region of (a) 01 as-is annealed, (b) 02 contaminated, and (c) 03 plasma damaged  $\text{TiO}_2$  films. (d) Concentrations of the lattice oxide and hydroxide normalized to the concentrations of Ti in the films, and ratios of hydroxide to lattice oxide.



**Fig. 5.** Dynamic responses of (a) as-is annealed TiO<sub>2</sub> film to 500 ppm NO<sub>2</sub> under UV illumination and dark at room temperature. (b) Comparison of the sensitivity of the as-is annealed, contaminated and plasma damaged TiO<sub>2</sub> films to 500 ppm NO<sub>2</sub>. The time for 80% response and recovery was labeled.

and much intense NO<sub>2</sub> response over the dark condition. Moreover, the response current to NO<sub>2</sub> in the two cycles remains constant under UV illumination, unlike the linear shifting of the current observed during the dark operation. These remarkable differences in the chemiresistive responses clearly indicate that UV light enhances the NO<sub>2</sub> sensing of the TiO<sub>2</sub> films drastically. As discussed in another work [1], the NO<sub>2</sub> chemiresistive change of the TiO<sub>2</sub> films results from the surface adsorption and desorption of oxygen anions, and consequently the modulation of the conduction path in the *n*-type semiconducting films. The anions are introduced onto oxide surface during the exposure to NO<sub>2</sub> with the following chemical equation,



The landing NO<sub>2</sub> gas takes the free electrons on TiO<sub>2</sub> surface and loads adsorbed oxygen anions on the surface. The absorbed oxygen anions then deplete the surface mobile carriers and thus lower the conductivity of the film. Under UV illumination, the interaction between NO<sub>2</sub> and oxide is greatly enhanced with the abundant photogenerated free electrons in the TiO<sub>2</sub>. Thereby the measured NO<sub>2</sub> response and response rate are significantly improved under UV. Similarly, UV

illumination facilitates desorption of oxygen anions into neutral gaseous oxygen by providing photogenerated holes during the recovering period.

Fig. 5b shows the measured responses to 500 ppm NO<sub>2</sub> under UV illumination of the as-is annealed, contaminated, and plasma damaged TiO<sub>2</sub> films. The response is defined as the relative change in resistance in the presence of NO<sub>2</sub>,

$$S = \frac{R_g - R_0}{R_0}$$

where  $R_g$  and  $R_0$  are measured resistances of the film in NO<sub>2</sub> and air flow, respectively. The maximum sensitivity is observed at the end of the NO<sub>2</sub> exposure with the values 15.9%, 21.1% and 12.5% for the as-is annealed, contaminated, and plasma damaged TiO<sub>2</sub> films, respectively. Therefore, the TiO<sub>2</sub> films are chemiresistively sensitive to the NO<sub>2</sub>, regardless of the distinct surface conditions. The important figures of merits for the gas sensors, namely the response time ( $\tau_{\text{res}}$ ) and the recovery time ( $\tau_{\text{rec}}$ ) are defined as the time taken by the measured current to reach 80% of total current change in the presence of NO<sub>2</sub> ( $\tau_{\text{res}}$ ) and air ( $\tau_{\text{rec}}$ ), respectively. For the as-is annealed, contaminated, and plasma damaged TiO<sub>2</sub> films, the observed response time are 26 s, 78.6 s, and 125.4 s and the recovery time ( $\tau_{\text{rec}}$ ) are 132 s, 166 s, and 189 s, respectively. Therefore, both the surface carbon contamination and roughness of the TiO<sub>2</sub> film suppress the response rate and recovery rate significantly. The drastic reduction of the gas adsorption rate in the C contaminated sample agrees with results observed from the C contamination Pt [18]. In this case, the contamination on the surface increase the diffusion length of the gas to the oxide as NO<sub>2</sub> chemisorbs on carbon sites as well [19,20]. This affects the number of NO<sub>2</sub> molecules interacting with the oxide and thereby slows the temporal response of the thin film. The reduced response rate of the plasma damaged sample may be attributed to the decreased self-diffusivity due to the increased surface roughness, as predicted by theoretical analysis [21]. Overall, the transient responses of the sensors suggest that the adsorption and desorption rates of the gas analyte depend strongly on the surface conditions of the oxide thin films.

### 3. Conclusion

In this work, we have demonstrated that surface conditions affect the NO<sub>2</sub> sensing performance of the TiO<sub>2</sub> films, under UV illumination at room temperature. The high sensitivity of the TiO<sub>2</sub> films makes them suitable for NO<sub>2</sub> detecting applications. XPS and AFM measurements of the contaminated film show detectable trace of carbon residues and resembling surface morphology to the as-is annealed TiO<sub>2</sub> films, respectively. High resolution AFM data manifests the damaged surface of the blasted film to the as-is state, whereas XPS data reveals the close stoichiometry and chemical states of the two films. The measured NO<sub>2</sub> response attribute to the elongated response and recovery time to both the surface carbon contamination and roughness.

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