



The effects of surface conditions of TiO₂ thin film on the UV assisted sensing response at room temperature



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ARTICLE INFO

Article history:

Received 15 May 2016

Received in revised form 28 June 2016

Accepted 11 July 2016

Available online 18 August 2016

Keywords:

XPS

AFM

Gas sensor

TiO₂ thin film

ABSTRACT

Thin film oxides have attracted attention in implementations of gas sensors, notably NO₂, 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 NO₂ sensing properties of TiO₂ thin film sensors. The TiO₂ 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 TiO₂ based sensor prolong the NO₂ 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, TiO₂ has been demonstrated extensively for the application of gas detection [1,9,10]. The unintentionally doped TiO₂ generally exhibits oxygen deficiency [9]. This nonstoichiometry of TiO₂ 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 TiO₂ sensor

to oxidizing gases, such as NO₂, increases the resistance. Ultraviolet (UV) illumination is widely used to induce the photoconductivity of TiO₂ and thereby to enhance the sensing performance of TiO₂ based sensors [1,10,11].

In this work, we investigated the role of surface conditions of a 10 nm thin TiO₂ film in the gas response towards NO₂ under UV illumination. This study aims to provide convincing explanations for the degradation of thin film oxide based sensors. The TiO₂ 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 TiO₂ thin films were prepared in a Denton Vacuum Discovery 550 sputtering system with a 99.9% TiO₂ target. The deposition process was maintained in a pure Ar environment. To prevail the catalytically

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active anatase phase of TiO₂ [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 TiO₂ 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 TiO₂ is around 10 nm. For the carbon contamination study, photolithography resist (PR) was firstly coated onto the annealed TiO₂ film and then cleaned with Acetone, IPA, and DI water. For the surface roughness study, the surface of TiO₂ films was coarsened by blasting the microwave plasma of O₂. The interdigitated metal contacts were e-beam evaporated onto the distinctively prepared films for electrical measurements.

The surface morphology and roughness of the prepared TiO₂ 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 μm 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 NO₂ 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 μW 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 TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ sample. This additional C, along with the conclusion that C lays on surface, suggests that

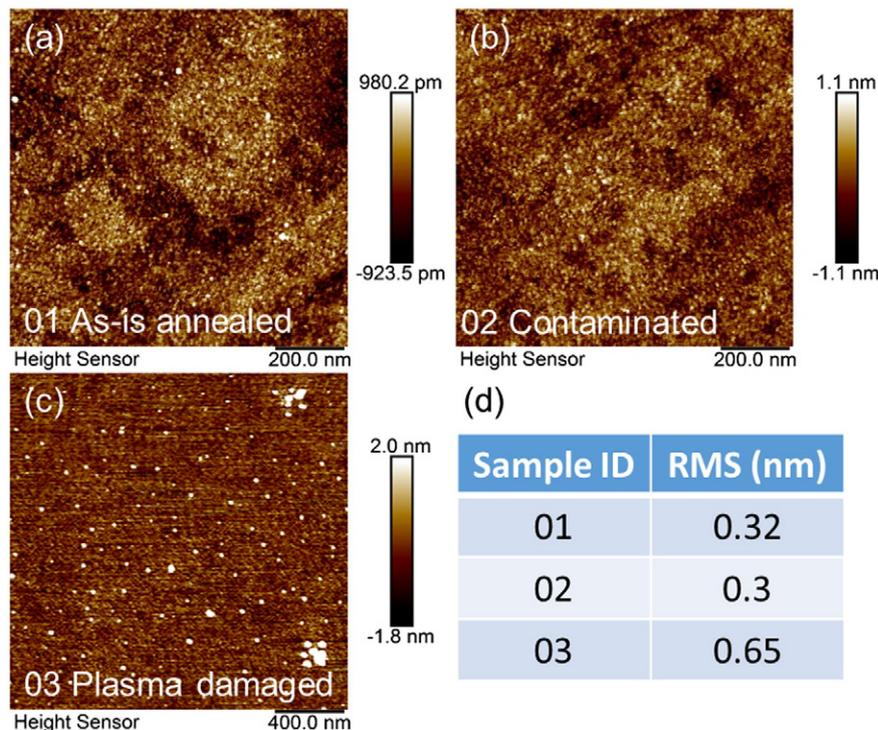


Fig. 1. AFM images of (a) as-is annealed TiO₂, (b) contaminated TiO₂, and (c) plasma damaged TiO₂. (d) Table of estimated rms roughness for each sample.

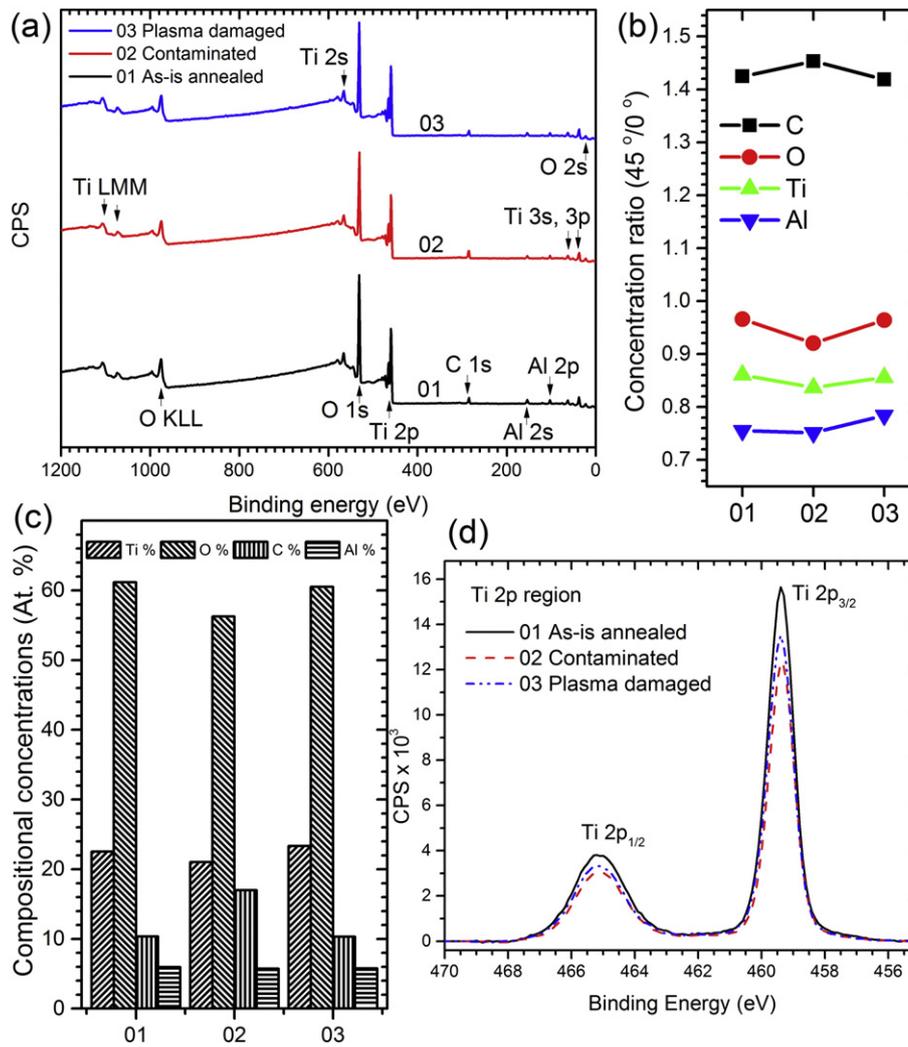


Fig. 2. (a) XPS spectra of the prepared 01 as-is annealed, 02 contaminated, and 03 plasma damaged TiO_2 thin films. (b) Ratios of concentrations calculated from the XPS 45° scan to 0° scan. (c) Atomic concentrations of the detected compositions in the examined TiO_2 films at collection angle of 0° . (d) High-resolution XPS spectra of Ti 2p regions of the 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 TiO_2 films. These data are collected from high-resolution (0.1 eV) XPS scans at the incident angle of 0° . The binding energies and shapes of the Ti peaks are in good agreement with the reported TiO_2 measurements [17].

The components of C in the 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 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 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 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 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 TiO_2 films, respectively. The main O 1s peaks at 529.6 eV are assigned to lattice oxygen from 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 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 TiO_2 films. Therefore, we believe that the studied TiO_2 films share the same fingerprint of the oxidation states.

Having established the surface chemistry and morphology of the prepared TiO_2 thin films, the films were further investigated by monitoring their chemiresistive responses to the NO_2 analytes at room temperature. Fig. 5a shows the measured currents of the as-is annealed TiO_2 film to 500 ppm NO_2 under UV illumination and dark conditions. The film was repeatedly exposed to 500 ppm 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

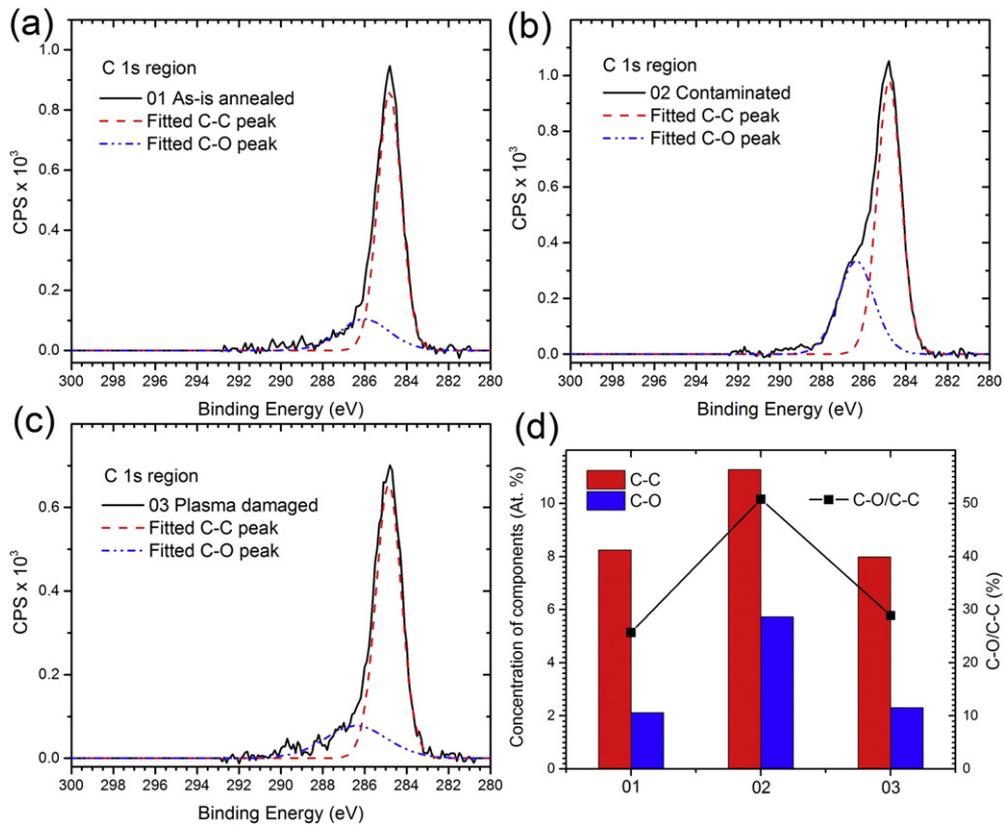


Fig. 3. XPS spectra of C 1s region of (a) 01 as-is annealed, (b) 02 contaminated, and (c) 03 plasma damaged TiO₂ films. (d) Concentrations of the C–C, C–O components and the ratio of C–O to C–C in the TiO₂ films.

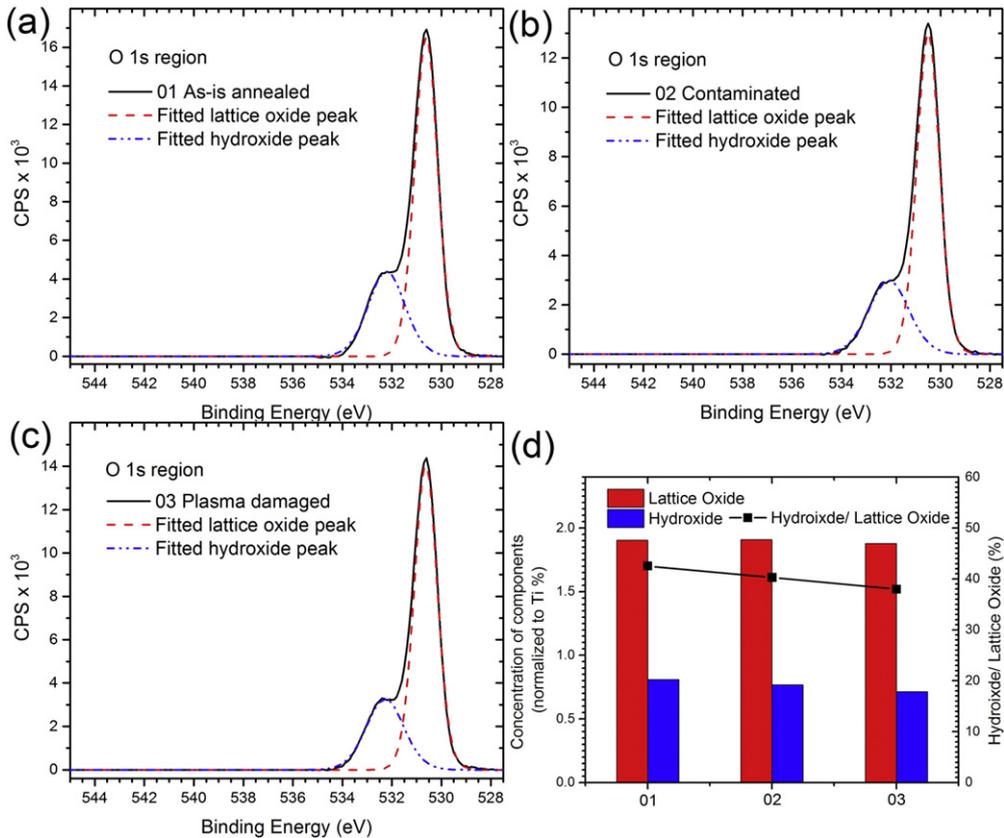


Fig. 4. XPS spectra of O 1s region of (a) 01 as-is annealed, (b) 02 contaminated, and (c) 03 plasma damaged TiO₂ films. (d) Concentrations of the lattice oxide and hydroxide normalized to the concentrations of Ti in the films, and ratios of hydroxide to lattice oxide.

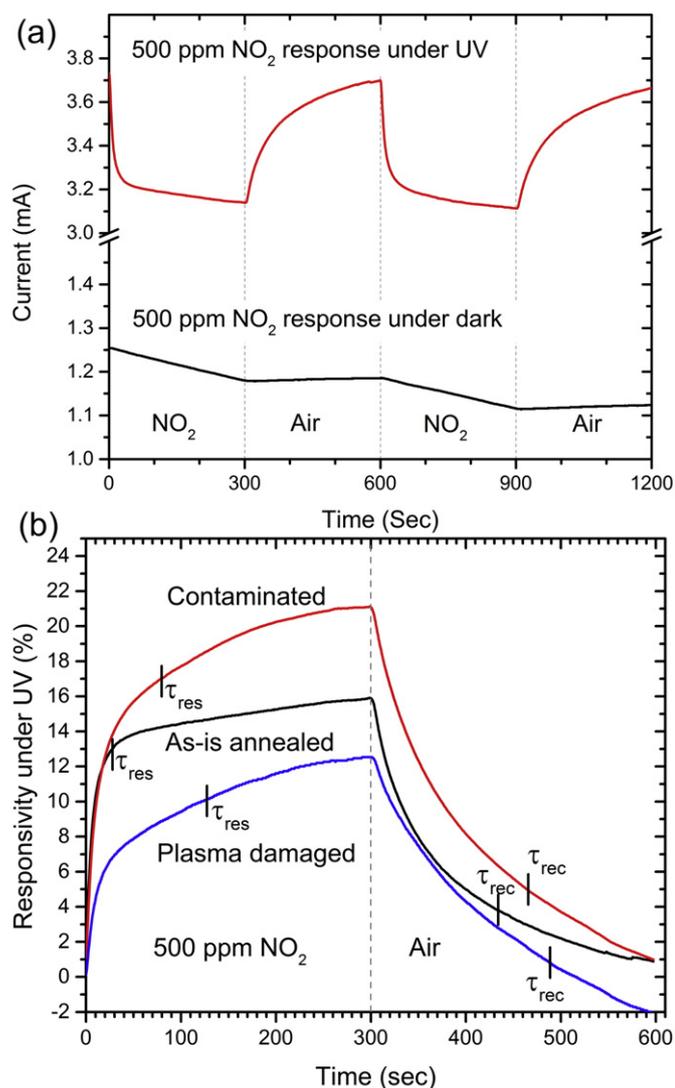
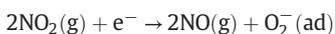


Fig. 5. Dynamic responses of (a) as-is annealed TiO₂ film to 500 ppm NO₂ under UV illumination and dark at room temperature. (b) Comparison of the sensitivity of the as-is annealed, contaminated and plasma damaged TiO₂ films to 500 ppm NO₂. The time for 80% response and recovery was labeled.

and much intense NO₂ response over the dark condition. Moreover, the response current to NO₂ 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 NO₂ sensing of the TiO₂ films drastically. As discussed in another work [1], the NO₂ chemiresistive change of the TiO₂ 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 NO₂ with the following chemical equation,



The landing NO₂ gas takes the free electrons on TiO₂ 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 NO₂ and oxide is greatly enhanced with the abundant photogenerated free electrons in the TiO₂. Thereby the measured NO₂ 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 NO₂ under UV illumination of the as-is annealed, contaminated, and plasma damaged TiO₂ films. The response is defined as the relative change in resistance in the presence of NO₂,

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

where R_g and R_0 are measured resistances of the film in NO₂ and air flow, respectively. The maximum sensitivity is observed at the end of the NO₂ exposure with the values 15.9%, 21.1% and 12.5% for the as-is annealed, contaminated, and plasma damaged TiO₂ films, respectively. Therefore, the TiO₂ films are chemiresistively sensitive to the NO₂, regardless of the distinct surface conditions. The important figures of merits for the gas sensors, namely the response time (τ_{res}) and the recovery time (τ_{rec}) are defined as the time taken by the measured current to reach 80% of total current change in the presence of NO₂ (τ_{res}) and air (τ_{rec}), respectively. For the as-is annealed, contaminated, and plasma damaged TiO₂ films, the observed response time are 26 s, 78.6 s, and 125.4 s and the recovery time (τ_{rec}) are 132 s, 166 s, and 189 s, respectively. Therefore, both the surface carbon contamination and roughness of the TiO₂ 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 NO₂ chemisorbs on carbon sites as well [19,20]. This affects the number of NO₂ 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 NO₂ sensing performance of the TiO₂ films, under UV illumination at room temperature. The high sensitivity of the TiO₂ films makes them suitable for NO₂ 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 TiO₂ 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 NO₂ response attribute to the elongated response and recovery time to both the surface carbon contamination and roughness.

Acknowledgements

This work was sponsored through N5 Sensors, Inc. and the Maryland Industrial Partnerships (MIPS, #5418). The TiO₂ based NO₂ gas sensing devices were fabricated in the Nanofab of the NIST Center for Nanoscale Science and Technology. Gas sensing measurements were conducted at N5 Sensors, Inc.

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