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## Greatly enhanced H<sub>2</sub>S sensitivity by defect-rich titanium oxide films

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Defect-rich titanium oxide films were prepared using laser ablation technique. The target pellet used for the ablation was rutile phase pure stoichiometric TiO<sub>2</sub>. X-ray photoelectron and synchrotron soft x-ray absorption spectroscopy measurements have revealed the chemical composition of the film. At 200 mJ of laser energy stoichiometric transfer of TiO<sub>2</sub> from target to the substrate has achieved. The films prepared at 500 mJ laser energy were observed to be highly defect-rich with composition of Ti/TiO<sub>x</sub>. The gas sensing characteristics of these films were tested. This unique defect-richness of the film favours the formation of excessive overlayers of chemisorbed oxygen on the surface of the film in large proportion as compare to lattice oxygen that made film rich in titanium forming Ti-Ti electronic bonds owing to great enhancement in the sensitivity of highly toxic H<sub>2</sub>S gas.

### Introduction

H<sub>2</sub>S is one of the common gases produced in various industry processes, which is highly toxic and corrosive in nature. It is colourless, low-lying and extremely flammable gas. Its leakage poses potential danger to the working environment. A human suffers by eye irritation, olfactory fatigue, and damage in lungs and nervous system. The threshold exposure limit value for H<sub>2</sub>S is 10 ppm. Inhalation of gas as low as 320 ppm concentrations may collapse heartbeats leading to sudden death [1-3] Thus, the critical monitoring and controlling of H<sub>2</sub>S is crucial in safety point of view in many laboratories and industrial areas. Moreover, real time detection of H<sub>2</sub>S gas produced by mammalian cells is also hot topic of research due to the proven role of H<sub>2</sub>S as a signaling molecule in many physiological functions and its abnormal generation causes human diseases.[4-5] Recently reports on oxide based H<sub>2</sub>S sensors are as CuO[6], ZnO[7], WO<sub>3</sub>[8], SnO<sub>2</sub>[9] etc. but very few are suitable for sensor technology unless modified or doped by another material. Specifically, tin oxide has been sensitive to many gases raising an issue of selectivity.[10] Thus, developing new materials with better selectivity and higher response is extremely important. So far, although a research to explore H<sub>2</sub>S sensors using TiO<sub>2</sub> [11,12]

is relatively new, nevertheless some efforts have been made which are as below.

E.D. Gaspera et al.[13] have reported Au-NPs dispersed in TiO<sub>2</sub>-NiO composite films for H<sub>2</sub>S sensing at operating temperature of 400°C with very poor response. Curry and co-workers [14] have fabricated single TiO<sub>2</sub> nanowire device and explored for H<sub>2</sub>S sensing between 10-80 ppm that seems less significant for large scale industrial use. Chaudhari et al.[15] proposed TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/Pd and TiO<sub>2</sub>/ZnO/CdO composite electrodes for H<sub>2</sub>S sensing with poor response at about 300°C operating temperature. Topalian et al. [16] detected low concentrations of H<sub>2</sub>S by noise spectroscopy when the TiO<sub>2</sub> gas sensor was irradiated by UV light with mere response of value ~ 10. In their report, no response was observed in the absence of UV. H<sub>2</sub>S detection by Pt-doped TiO<sub>2</sub> NCs based gas sensors showed the highest sensitivity about 70 quite low compare to our values towards 250 ppm H<sub>2</sub>S/Air at 500°C by 4.3 at.% Pt-doped sensors at operating temperature of 500°C.[17] Hydrothermally synthesized rice-grain shaped TiO<sub>2</sub> nanostructures are used for thick film preparation by screen printing technique and tested for H<sub>2</sub>S gas showed sensitivity (SR%) around 100 at 1000 ppm.[18] Upon critical review of the literature in the context of titanium oxide films and nanosystems as H<sub>2</sub>S sensors, none of the report was observed exclusively on undoped titanium oxide films that explores the promising capability of realization of commercial highly toxic H<sub>2</sub>S sensor technology with extra-ordinary response value.

TiO<sub>2</sub> is really very promising material due to its anti-corrosive, and chemically stable nature with band gap tailor-ability leading to electronic structure variations. It is mainly studied in the context of dye sensitized solar cells [19] and photo-catalysis.[20] Recently improved surface reactivity in TiO<sub>2</sub> systems have been reported wherein ultrathin nanotubes [21], nanohybrids [22] and sensitizers [23] have been used. Band gap of titanium oxide is engineered by

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doping metal/non-metal [24] elements that alters the electronic structure and enhances the surface-activity of TiO<sub>2</sub>. Although, role of bulk and surface defects in oxides have been studied in the context of magnetism [25] but such defect chemistry can play an important role in the surface-sensitive phenomena such as sensing and catalysis. Thereby, it is worth to investigate on engineering the surface defects in undoped titanium oxide films as it can lead to newer functionalities.

Herein, we report the explicitly prepared defect-rich undoped titanium oxide films by laser ablation technique for the gas sensing applications using set-up developed at our laboratory. Since the sensing is surface activated phenomenon, special emphasis has been given on engineering the surface defects of the films under identical preparative parameters except variation in laser energy used for ablation. The objective of the present study is to form defect-rich films by varying the laser ablation energy for highly toxic H<sub>2</sub>S sensing.

## Experimental

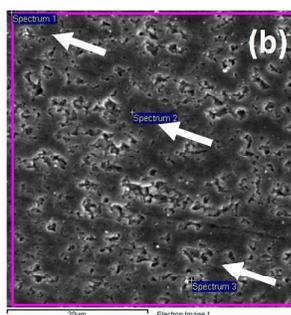
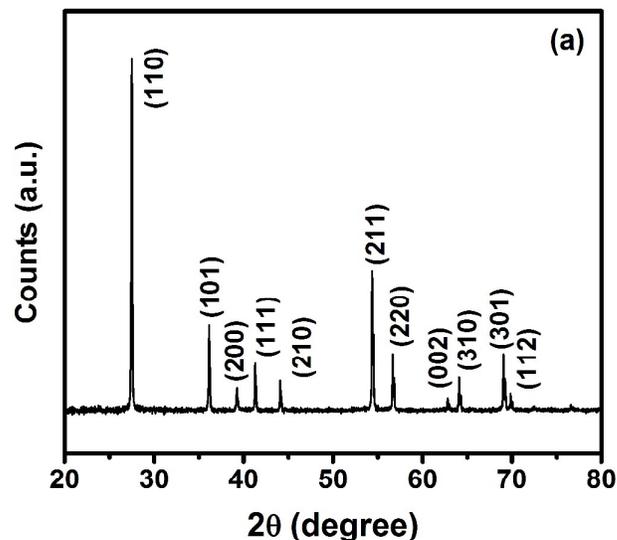
In a typical experiment, the TiO<sub>2</sub> target was pelletized using spark plasma sintering technique and was used for the laser ablation. The SEM and EDS measurements of the TiO<sub>2</sub> pellet were performed using TESCAN, Model: TS 5130MM, Oxford Instruments. KrF laser source (make: Lambda Physik) with wavelength of 248 nm was used to ablate TiO<sub>2</sub> pellet on (001) LaAlO<sub>3</sub> (LAO) substrate at 600°C in oxygen partial pressure of 1 X 10<sup>-5</sup> Torr for 10 min. The LAO substrates were chemically cleaned before the deposition. The laser pulse frequency and energy density at the target surface for the deposition were kept at 10 Hz and 2 J/cm<sup>2</sup> respectively. After the deposition, substrates were cooled down to room temperature in the same oxygen partial pressure as used during the deposition. The films were prepared at three different laser energies 200, 500 and 680 mJ. These films were characterized with X-ray photo-electron spectroscopy using Mg K $\alpha$  source (Make: RIBER system) and X-ray absorption spectroscopy (Synchrotron, INDUS-2 at Indore, India) to reveal the surface defects of the film and further investigated for H<sub>2</sub>S sensing at laboratory made set-up. H<sub>2</sub>S gas sensing measurements were performed on the films using actual gas sensing set-up as shown in supplementary information-I along-with its schematic at right. In brief, electrode contacts were defined by 120 nm thick Au layer (thermal evaporation) with 1 mm spacing. The sensor temperature was controlled using a controller circuit and two Pt-100's attached at the backside of the substrate (heater). The response curve (current as a function of time) is recorded upon exposure to different concentration of H<sub>2</sub>S using a personal computer (PC) equipped with Labview software. Required concentration of the test gas in the chamber is achieved by injecting the known amount of the gas using a syringe. Sensor response is calculated from the response curves using the formula:

$$SR\% = (I_g - I_a) / I_a \times 100\% \quad (i)$$

The response and recovery times of the films were calculated from the response curves. Response time was taken as a time to reach

90% of total change in current upon exposure to the test gas. Recovery time was taken as a time to return to 10% of its original baseline signal upon removal of the test gas.

## Results and Discussion



Spectrum	Ti (at. %)	O (at. %)
Spectrum-1	33.33	66.67
Spectrum-2	33.33	66.67
Spectrum-3	33.33	66.67
Mean	33.33	66.67
Std. Deviation	0.00	0.00

Figure 1: X-ray-diffraction data of TiO<sub>2</sub> pellet used for the pulsed laser ablation as a target is shown as fig. (a). Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) is shown in fig. (b); at right side of figure (b) shows table (i) of X-ray micro-analysis data

Figure 1(a) at upper panel shows XRD data of TiO<sub>2</sub> pellet used as a target for pulsed laser ablation. The pellet is sintered by spark plasma technique. Pellet is crystallized in pure rutile phase. Figure (b) at lower panel shows SEM and EDS measurement data of the pellet. It shows stoichiometric TiO<sub>2</sub> composition of pellet without defects. Table at left of lower panel shows Ti:O ratio as 1:2. This defect-free and stoichiometric TiO<sub>2</sub> pellet is used to prepare defect-rich non-stoichiometric as well as defect-free stoichiometric films of titanium oxide at different laser energies using pulsed laser technique.

Defect-rich titanium oxide thin films were prepared using critically optimised 500 mJ laser ablation energy and were tested for H<sub>2</sub>S sensing and resulting response kinetics are

shown in Figure [2a]. It exhibits an extra-ordinary sensor response equal to 102867% at 50ppm of H<sub>2</sub>S concentration which is conceivably the best response value for titania in the literature. It is remarkable to note the great enhancement in the sensing response of titanium oxide film processed at 500 mJ laser energy. The response increases in cumulative manner with successive addition of 5 ppm of H<sub>2</sub>S gas into the measurement chamber in regular steps. Additionally, the sensor film exhibited a highly selective response towards H<sub>2</sub>S with negligible or almost zero response towards other gases.

where a, b and c are constants and the value of exponent 'c' was found to be 0.54 in accordance with the Elovich adsorption model [26] which is usually used to explain chemical adsorption phenomena of gases on solid surfaces as shown in supplementary information [I1]. The exponential increase in sensor response at early is due to increase in surface coverage of the film by H<sub>2</sub>S at energetically heterogeneous active sites which later get saturated. It implies that the film was rich with the surface active defects.

The moderate sensing response about (SR%)~1000 was observed for titanium oxide films prepared using 680 mJ laser energy as shown in figure 2[A]. This investigation is done to check the effect of further increase in laser energy on H<sub>2</sub>S response. The thickness of the films prepared using different laser energies are in the range of 55-100 nm (measured using ellipsometry technique). However, gas sensing is purely surface active phenomenon wherein the bulk contribution is often negligible. Thus, it is imperative to infer that thickness has no significant role to play in the H<sub>2</sub>S sensing response. [27, 28]

Another prominent fact to note from figure 3[A] is the initial increase in the current of the film which after 5 ppm H<sub>2</sub>S concentration tends towards almost saturation unlike film prepared at 500 mJ laser energy wherein saturation stage has started at later concentration. This implies the significant difference in the defective surface structure of the film prepared at 680 mJ as compare to film prepared at 500 mJ laser energy. Thus, the defect-rich unique composition of film prepared at 500mJ laser energy is solely responsible for the great enhancement in H<sub>2</sub>S sensitivity. The exactly similar composition of the film though rich in defects has not been achieved in case of 680 mJ laser energy.

Defect-free stoichiometric TiO<sub>2</sub> film has prepared using critically optimised 200mJ laser energy and have been tested for the H<sub>2</sub>S sensing. The data is shown in figure 3 [B]. It is observed that the sensing response increases with increase in the H<sub>2</sub>S gas concentration but the sensor response is of the order of (SR % ~) 100 even at 50 ppm of gas concentration. These films showed response and recovery time of 150 s and 2500 s respectively for 10 ppm of H<sub>2</sub>S. Figure [3C] shows sensor response of TiO<sub>2</sub> thin films prepared at laser energy 200 mJ at different temperatures with varying gas concentrations. It indicates that maximum sensor response is achieved at 100°C which confirms the optimum sensor operating temperature is 100°C which is relatively low. Figure [3D] supports the same with the similar trend in the SR% measured at different laser energies.

It is very important to note the faster and greatly enhanced response kinetics towards H<sub>2</sub>S by defect-rich titanium oxide films prepared using 500 mJ laser energy as compare to defect-free TiO<sub>2</sub> film made using 200 mJ laser energy. Another prominent feature of the film sensor was its extremely quick (< 5 min.) recovery on turning off the H<sub>2</sub>S showing a switch like behaviour. Relatively shorter response time was also noted. Interestingly, we further pursued sub-ppm level H<sub>2</sub>S-sensing that showed better response as given in inset of figure 2(a). Since the film was prepared at 600°C, it is very stable. This can certainly meet three requirements such as sensitivity, selectivity and stability for the realization of H<sub>2</sub>S sensor technology.

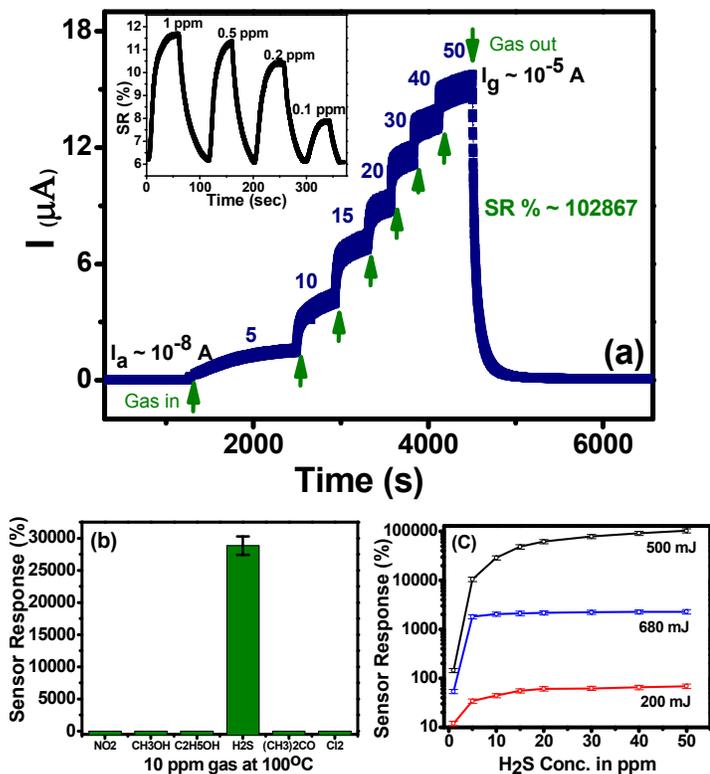
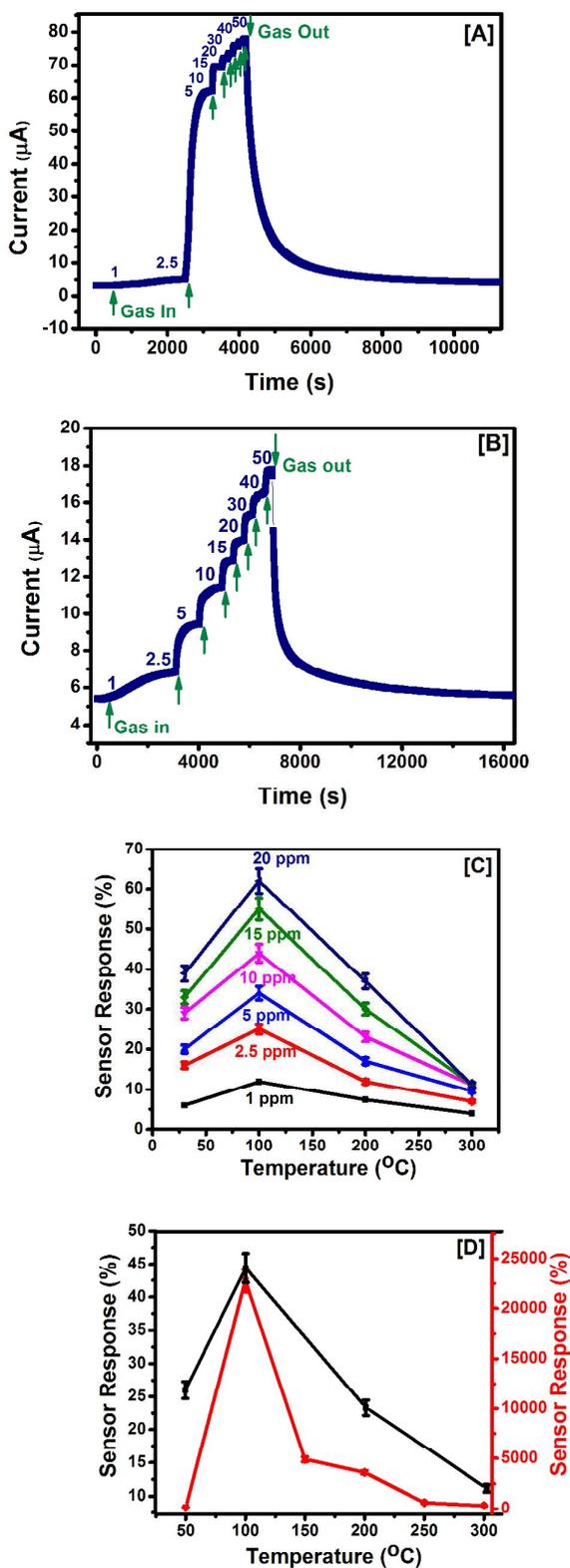


Figure 2: Sensing response curves for the titanium oxide film prepared at 600°C using laser energy 500mJ. In lower panel, left graph shows H<sub>2</sub>S selectivity of the same film & right graph shows variation of SR% with H<sub>2</sub>S concentration at different laser energies. Error bars with 5% standard deviation are added to Fig. (b) & (c).

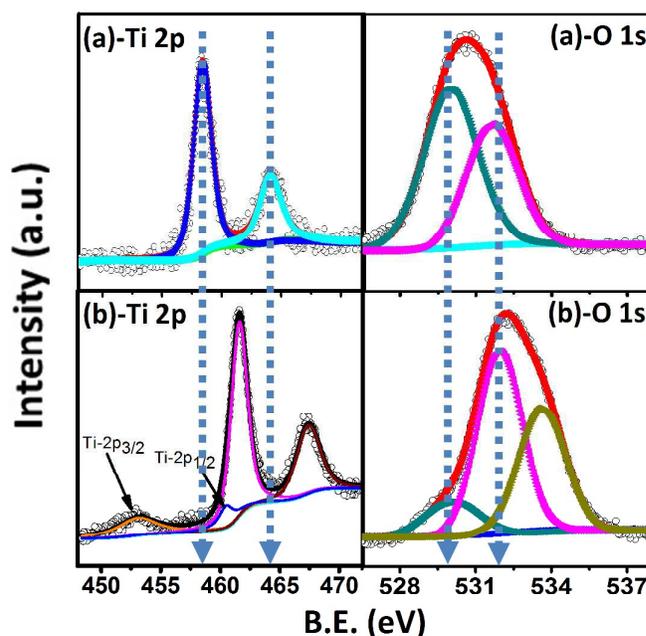
Figure [2B] shows the variation of sensor response with respect to different gases which cleared that the films are exclusively sensitive to H<sub>2</sub>S only with almost no response to other gases. The initial increase in sensor response with respect to gas concentration and its eventual equilibrium is shown in the figure [2C]. The green curve for sample prepared at 500 mJ laser energy fits well with equation (i), given as;

$$y = a + bx^c \quad (ii)$$



**Figure [3]:** [A] and [B] gave real-time H<sub>2</sub>S gas sensing data of titanium oxide film prepared using 680mJ and 200 mJ laser energy. Figure [C] & [D] informed about optimized sensor operating temperature i.e. 100°C

Figure (4) summarizes the XPS results of the titanium oxide films prepared at 200 mJ and 500 mJ laser energies. The Ti 2p<sub>3/2</sub> & 2p<sub>1/2</sub> core levels for titanium oxide prepared at laser energy 200 mJ were seen to appear at 458.3 eV and 464 eV, respectively with the peak separation of 5.7 eV. Also, both Ti core-levels are symmetric in nature ruling out the possibility of reduced species like Ti<sup>2+</sup> or Ti<sup>3+</sup>. It proves the formation of stoichiometric titanium oxide. However for the films prepared at 500 mJ and 680 mJ, the Ti2p<sub>3/2</sub> core levels showed considerable shift to higher binding energies as 461.5 eV and 460.8 eV and also similar in case of 2p<sub>1/2</sub>, as 467.4 eV and 466.5 eV was noted. Please see supplementary information (III) for XPS spectra of films prepared using 680 mJ laser energy. The difference in energies of the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> core-levels is almost same in all i.e. 5.7 eV. It shows the formation of oxidized titanium. The slight shift in peaks towards lower BE was observed in case of 680mJ film as compare to 500 mJ indicating more stoichiometric TiO<sub>x</sub> formation. Additionally a small contribution can be noted around 453 eV and 460 eV in data for 500 mJ & 680 mJ samples. These can be attributed to the presence of 2p<sub>3/2</sub> and 2p<sub>1/2</sub> core-levels for Ti<sup>0</sup> i.e. metallic titanium in trace amounts. This invites discussion.



**Figure 4:** XPS spectra (Ti2p, O1s) of titanium oxide films prepared using (a) 200 mJ, (above panel) and (b) 500 mJ, (lower panel) laser energy.

Literature survey shows very rare reports on XPS results of such a type of uncommon titanium oxide systems. Most relevant reference reported in 1987 by Ocal & co-workers [29] wherein they have characterized with XPS thin films of titanium oxide grown by oxidizing Ti (0001) surface. They studied evolution of the Ti 2p XPS spectrum during the oxidation of a Ti surface and consequent thermal treatment. At plus 5 mTorr of O<sub>2</sub> at 400 K, a completely oxidized surface was obtained. Basically it stated that the oxide film had grown since the electronic equilibrium among the gas-oxide and metal-oxide interfaces established an electric field in the oxide

that had driven oxygen anions through it from the gas-oxide to the metal-oxide interface. The basic idea was to realize that oxygen anions may diffuse across the oxide since its electron affinity energy was larger than the work function of the Ti-metal. Subsequently the existence of anionic overlayers that were stable at or below room temperature had also been reported. Cut to short, this report showed the formation of Ti/TiO<sub>x</sub> composition of the grown film having excessive oxygen over-layers evidenced by XPS results and those data are matching exactly with our XPS results. Another recent report wherein existence of Ti-Ti electronic bonding gave quite similar XPS findings with enhanced catalytic activity.[30]

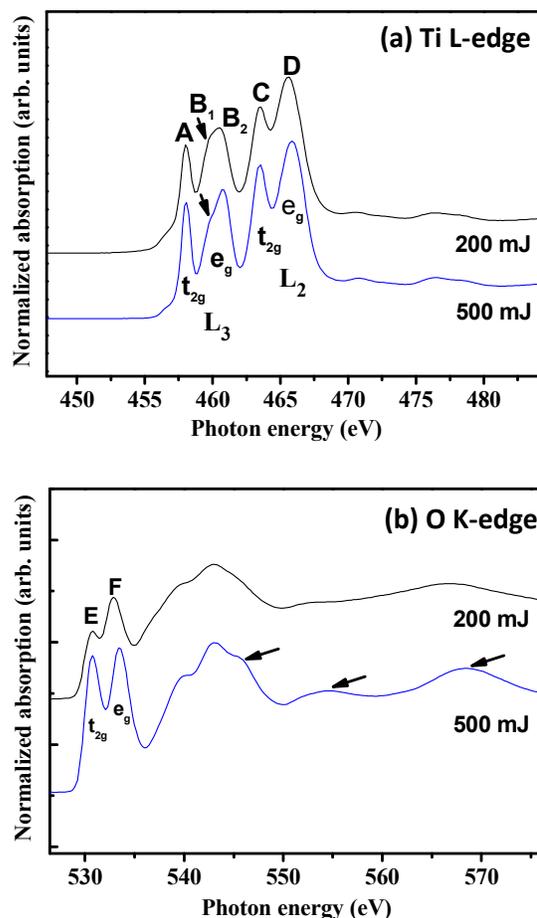
Quantitative estimates of the ratio of O<sub>lattice</sub>/O<sub>chemi-sorbed</sub> species were also calculated from XPS data (see the Table I below). In case of the films made at 500 mJ, this ratio comes out to be nearly ~ 54% whereas for 200 mJ it is just 67% and for 680 mJ samples it is considerable i.e. ~ 330% reflecting clearly on H<sub>2</sub>S sensitivity. So, the main contributing factor for the enhancement in H<sub>2</sub>S sensitivity is the excessive chemically adsorbed oxygen on the defect-rich films made at 500mJ laser energy. Such a defect-rich off-stoichiometric titanium oxide film has better sensitivity than stoichiometric film.

Defect-free TiO <sub>2</sub> film prepared at 200 mJ laser energy		
	Area under curve	Relative proportion in the film
<b>Metallic Ti</b>	----	----
<b>Oxidised Ti</b>	2P <sub>1/2</sub> :2127, 2P <sub>3/2</sub> :4288	
<b>O<sub>lattice</sub></b>	O1s:14952	60 %
<b>O<sub>adsorbed</sub></b>	O1s:10162	40 %
Defect-rich titanium oxide film prepared at 500 mJ laser energy		
	Area under curve	Relative proportion in the film
<b>Metallic Ti</b>	2P <sub>1/2</sub> :1450, 2P <sub>3/2</sub> :2888	
<b>Oxidised Ti</b>	2P <sub>1/2</sub> :5626, 2P <sub>3/2</sub> :11135	
<b>O<sub>lattice</sub></b>	O1s:3010	10 %
<b>O<sub>adsorbed</sub></b>	O1s:13979, O1s:9125 (-OH)	<b>O<sub>chemi-sorbed</sub> : 54 %</b> and 36 % oxygen bonded with carbon and -OH
Defect-rich titanium oxide film prepared at 680 mJ laser energy		
	Area under curve	Relative proportion in the film
<b>Metallic Ti</b>	2P <sub>1/2</sub> :2008, 2P <sub>3/2</sub> :4000	
<b>Oxidised Ti</b>	2P <sub>1/2</sub> :7684, 2P <sub>3/2</sub> :15668	
<b>O<sub>lattice</sub></b>	O1s: 3174	10 %
<b>O<sub>adsorbed</sub></b>	O1s: 11728, O1s:19743 (-OH)	<b>O<sub>chemi-sorbed</sub>: 33 %</b> and 57 % oxygen bonded with carbon and -OH

**Table (ii):** Quantitative estimates of the O<sub>lattice</sub>, O<sub>chemi-sorbed</sub> Ti-cations done using by XPS data

To confirm the findings of XPS, these films were further pursued for x-ray absorption spectroscopy (XAS) to understand the surface electronic structure. The soft X-ray absorption near edge structure (XANES) experiment was carried using Indus-2 beamline-1 (BL-1) at the RRCAT, Indore, India. Spectra at the Ti L-edge (~458 eV) were acquired at room temperature using a Si (111) monochromator by TEY method. The XANES spectra were processed to obtain

normalized absorbance. Further the spectra have been analyzed using the “fingerprint” method by comparing sample’s spectra with those taken for reference bulk compounds. The complete data is shown in supplementary information IV.

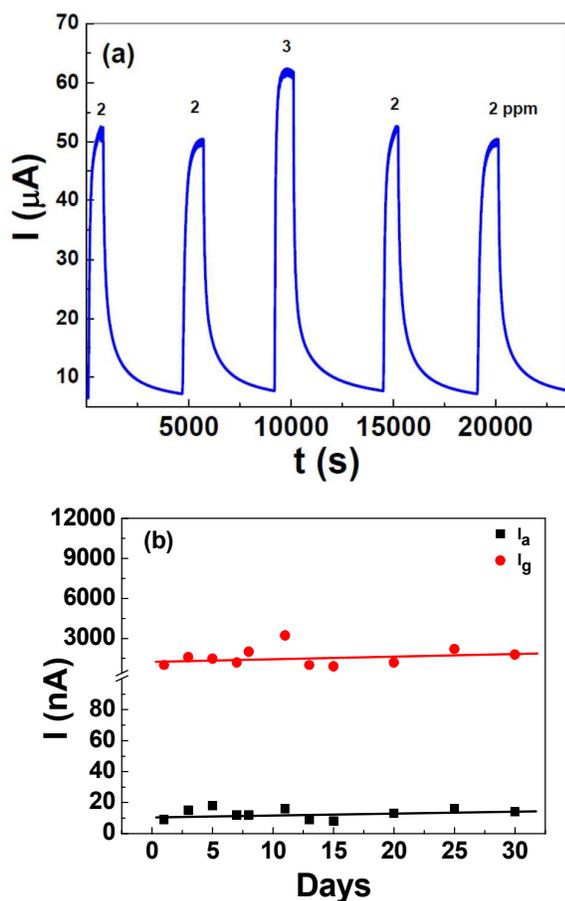


**Figure 5:** XANES spectra of titanium oxide films at (a) Ti L<sub>3,2</sub>-edge and (b) O K-edge for films made at energy 200 mJ and 500 mJ. Data for 680 mJ energy with bulk reference are shown in SI-VI.

Ti L<sub>3,2</sub>-edge spectra as shown in Fig. [5a] demonstrate four different features at 458.1 eV, 460.7 eV, 463.5 eV and 465.8 eV, namely A, B (B<sub>1</sub>/B<sub>2</sub>), C, and D, respectively. These four main peaks are the L<sub>3</sub> and L<sub>2</sub> absorption peaks wherein each peak split-up into doublets i.e. e<sub>g</sub> and t<sub>2g</sub> (L<sub>3</sub>:457–462 eV and L<sub>2</sub>:462–468 eV) due to crystal field and spin-orbit interaction of Ti-core levels.[31] Features of L<sub>3</sub>- and L<sub>2</sub>-edge are related to the transitions from 2p<sup>3/2</sup> to 3d<sup>5/2</sup> and 2p<sup>1/2</sup> to 3d<sup>3/2</sup> states respectively. The absorption edge of all the samples is almost same i.e. around 458 eV indicating maximum of Ti species in single oxidation state i.e. Ti<sup>4+</sup> that corroborates with XPS findings where absence of Ti<sup>2+</sup>/Ti<sup>3+</sup> species was observed. Nonetheless, the Ti metallic species shows similar features without splitting.[32] Its clear indication is not visible in the spectra for the films prepared using 500 and 680 mJ laser energy due to overlapping features with oxidised titanium and the relatively less proportion of Ti<sup>0</sup> in the films. Since e<sub>g</sub>B<sub>1</sub> feature is more related to defect-rich phase, its pronounced appearance in the film prepared

using 500 mJ laser energy supports the defect-richness in the film.[32]

Fig. [5b] presents the features of O K-edge XANES spectra of the samples. There are four major peaks present in the O K-edge spectra of film at 530.7 eV, 532.8 eV, 539.8 eV and 543.1 eV. These features can be distinguished in two different energy ranges viz. first below 535 eV owing to transitions from O 1s to unoccupied 2p states and second above 535 eV attributing to existence of complex wide band relating to transitions to the antibonding O 2p and Ti 4sp states. The presence of some extra black arrowed absorption peaks indicate the existence of chemisorbed oxygen overlayers on the films.[32] The broadening of peaks at higher energy side is not only due to disorder but reflect an important surface chemical changes.[33] The appearance of all such interesting features are intriguing and requires further investigations that are underway using techniques like synchrotron EXAFS, SPM and DFT calculations to reveal the detailed surface electronic structure of defect rich titanium oxide films. Thus, XPS and XANES investigation reveals overlayers of chemisorbed oxygen in case of defect rich titanium oxide film.

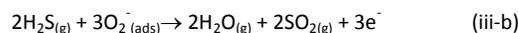
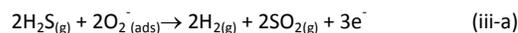


**Figure 6:** (a) Sensor response curves recorded upon repetitive exposure of 2 and 3 ppm of H<sub>2</sub>S and (b) long term stability measurements performed over a period of 1 month upon repetitive exposure towards 5 ppm of H<sub>2</sub>S.

Further, figure 6 (a) shows the response curves recorded upon repetitive exposure to 2 and 3 ppm of H<sub>2</sub>S. The sensor films exhibited similar response values with identical response kinetics indicating its high repeatability. Moreover, the long term stability measurements as shown in figure 6 (b) indicated that the sensors response is highly stable over the measurement period of 30 days. No significant variations in the response values were observed indicating its highly stable behaviour of film based sensors.

Furthermore, the higher electrical resistivity of defect-rich film as compare to defect-free films was observed from the H<sub>2</sub>S sensing data taken in cumulative method as shown in figure 2(a) and 3(B). This is due to this excessive chemisorbed oxygen preventing inter-grain charge transport. Titanium oxide films prepared using 200 mJ energy were showing initial current about 10 (μA) and films prepared at 500 mJ energy were showing initial current about 10 nA at same temperature revealing that films prepared using 500 mJ energy were highly resistive in nature. This increase in resistivity is attributed to the excessive overlayers of chemisorbed oxygen on the film surface.

These chemisorbed oxygen species play crucial role in enhancing H<sub>2</sub>S gas sensitivity as explained by the schematic figure 6 given below. These chemically adsorbed oxygen species due to higher oxidation potential accept electrons from oxide surface thereby creating electron-deficient layers. The H<sub>2</sub>S reacts with these oxygen species and get dissociated after releasing trapped electrons via either of the speculated reactions given below;

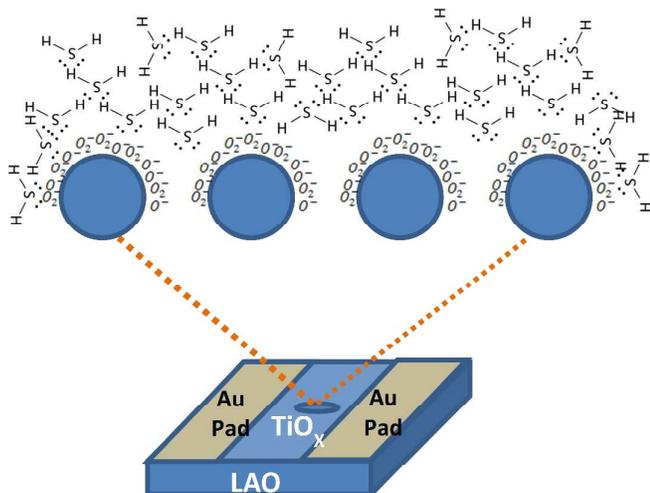


This release of large number of trapped electrons decreases thickness of electron depletion layer that facilitates access for charge carriers into the conduction band of the film which was evident as a sharp increase in the conductivity of the film. The process was recovered if H<sub>2</sub>S was removed and the film was exposed to ambient conditions. In other words, the adsorbed oxygen on the surface causes the oxidation of H<sub>2</sub>S and during recovery the adsorption of ambient oxygen species easily refreshes the sensor surface.

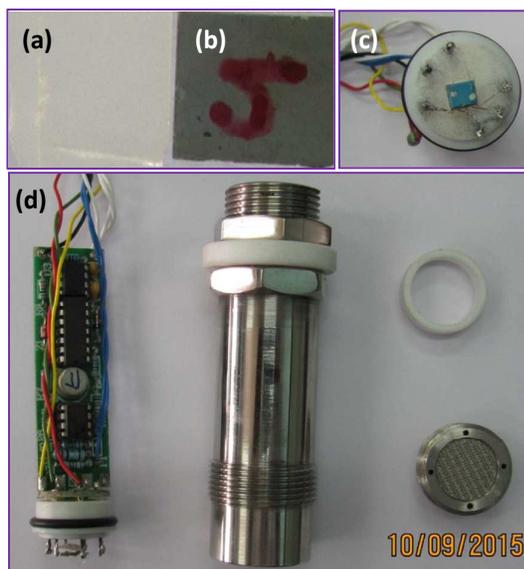
Thereby herein, the interaction with the H<sub>2</sub>S gas is primarily governed by the nature of adsorbed oxygen species. The surface active defects facilitate the chemical adsorption of oxygen which oxidizes the target gas. The exposed H<sub>2</sub>S gets dissociated on donating electrons to the sensor via chemisorbed oxygen thereby lowering the resistance thus such type of sensors are often categorized as chemi-resistive sensors. The unique strength of our defect-rich titanium oxide films is availability of enormous amounts of surface states that facilitates chemical adsorption of ambient oxygen in significant amount which greatly enhances H<sub>2</sub>S sensitivity.

The photograph of the LAO substrate and the defect-rich TiOx film with an attempt to show its optical transparency has been shown as figure 8(a) and (b). The actual sensor film mounted on Teflon head with temperature control circuit and SS housing used for sensor packaging are shown in the figure 8(c) and (d). It clearly

demonstrates the high potential of defect-rich TiO<sub>x</sub> films towards realisation of H<sub>2</sub>S sensor technology.



**Figure 7:** Upper figure shows schematic demonstrating the H<sub>2</sub>S sensing mechanism by defect-rich titanium oxide film and lower photograph shows the actual photograph of the defect-rich TiO<sub>x</sub> film at left and LAO substrate at right



**Figure 8.** Photograph of (a) LAO substrate and (b) defect rich TiO<sub>x</sub> film deposited on the LAO substrate. (c) Teflon head on which the sensor film is mounted. (d) temperature control circuit and the stainless steel housing used for the sensor packaging.

Ultimately it is necessary to project the possible causes of formation of highly defect-rich Ti/TiO<sub>x</sub> film at 500 mJ of laser energy only with relatively less defective and pure TiO<sub>2</sub> film formation at laser energies of 680mJ and 200 mJ respectively. PLD is popular for the stoichiometric transfer of material from target to

substrate. Nevertheless, it is well-known that such favourable results do not occur in all experimental conditions. By controlling the experimental parameters like gas pressure, laser energy, etc. target material composition can be harmoniously transferred to the growing film. In case of all the films under investigation, the growing conditions were same except laser energy. So, it is quite straightforward that the changes in stoichiometry of the films occurred in the plume rather than at the target or substrate. It is further inferred that the non-harmonious transfer is due to differential scattering in the plume itself. This can be due to difference in the mass of the species or differences in the charge states of the species, or due to the rapid expansion of ionic species of the plume in or near to vacuum ( $\sim 10^{-5}$  torr) conditions. The time lag between the ablation of the target materials and particulate formation on the substrate is the crucial factor. Higher the time lag meaning slower the movement of species leading to negligible scattering events.[34] Thus, 200mJ of laser energy yields lower ablation rate, slower transfer to substrate so is optimised to form stoichiometric TiO<sub>2</sub> however latter cases of higher laser energy yields higher ablation rate, thus species could not get enough time to go well together due to difference in their masses and charge states, encountering many scattering events thereby getting disparately accumulated on substrates. Thus, defect-rich TiO<sub>x</sub> film formation is attributed to the non-harmonious transfer of the ablated species leading to the differential scattering in the plume. Moreover, such defect-rich films are perfectly reproducible so PLD has also the potential of non-congruent transfer of materials to substrate with greater accuracy and reproducibility which finds the extreme usability for certain surface activated applications such as sensors or catalysis.

## Conclusions

In conclusion, we have successfully demonstrated the explicit preparation of defect-rich titanium oxide film of composition Ti/TiO<sub>x</sub> exhibiting an extra-ordinary H<sub>2</sub>S response (SR%>100000). This remarkable and exclusive sensing response towards H<sub>2</sub>S is conceivably the best in the literature. Moreover, this unique film composition was highly reproducible by pulsed laser deposition. The enhanced response characteristic is attributed to the enormous surface defects arising from the lattice oxygen-deficiency and Ti-Ti electronic bonding that facilitate formation of over-layers of chemisorbed oxygen species. Further these films exhibited quicker recovery and better stability thereby emphasising its suitability for realization of sensor technology. In addition, these defect rich films may find usefulness in visible light catalysis or solar cells due to its Ti-Ti electronic interaction that helps to narrow the band gap.

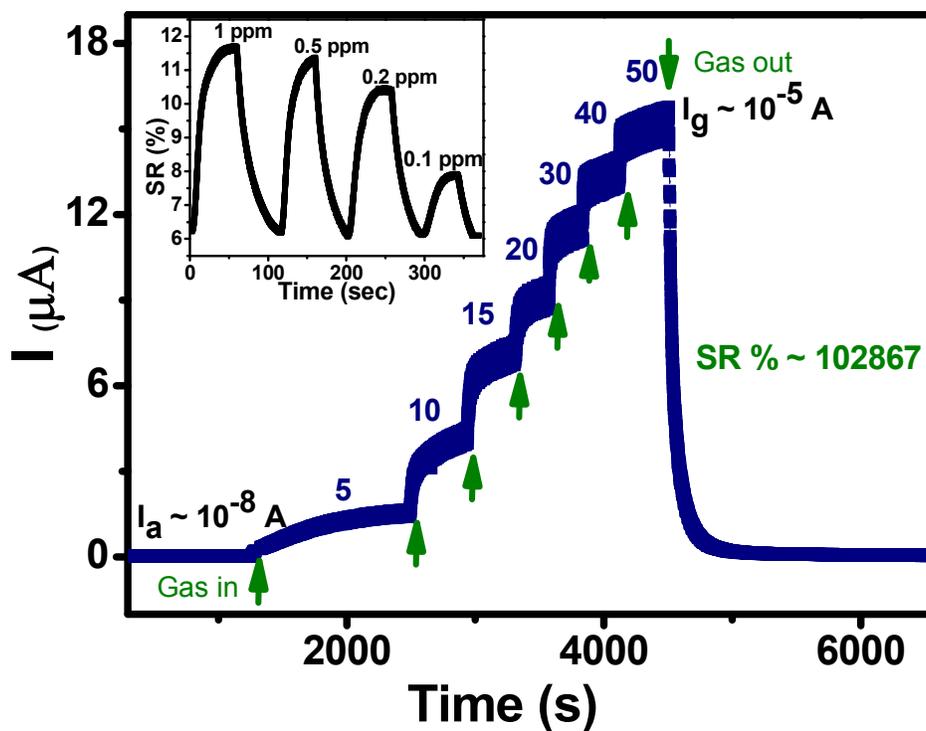
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## Graphical Abstract



Defect-rich titanium oxide films revealed with overlayers of chemisorbed oxygen in large proportion compare to lattice oxygen owing to significant enhancement in the sensitivity of highly toxic  $\text{H}_2\text{S}$  gas, with greater stability, better selectivity and quicker recovery.