High selectivity, enhanced sensitivity, short response times and long shelf-life are much sought-after features in solid-state chemical sensors for the detection and metering of gas(es) of interest. Because the sensing mechanism of semiconducting oxides is invariably surface dominated, benign microscopic features are desirable to realize a useful sensing material. In principle, such morphological features could be incorporated in a number of semiconducting oxides by employing a technique based on thermodynamic consideration of the metal/metal oxide coexistence. By dynamically modulating the equilibrium oxygen partial pressure across the metal/metal oxide proximity line, renewed formulation and growth of an oxide surface on an atomic/submolecular level with exotic morphological features under conditions of oxygen “deprivation” or “enrichment” has been achieved practically in a number of potential ceramic sensor systems. In the case of oxides that are not amenable to such classical oxygen partial pressure modulation, a novel high-temperature reductive etching process (HiTREP©) could be exploited to recreate the smart nanofeatures to impart the desired accentuation effect. This surface modification method was applied to a new commercially available aqueous plasma electro-deposited (PED) titania thick film, and the microscopic results of this strategy are presented.

Introduction

Work on sensor development is carried out worldwide in industry, academia, and government facilities. This is driven by the need for improved, fast, in situ and online detection and quantification of various gaseous pollutants in a host of industries including power generation, chemical, pharmaceutical, electronics, biomedical, health and environmental protection and preservation. High selectivity, enhanced sensitivity, and short response time are some of the key features
sought in these devices. Because the sensing mechanism and catalytic activity of ceramics are largely microstructure dominated, benign surface features such as small grain size, large surface area, and open/connected porosity are required to realize a useful sensor material.

A novel technique employed to impart such attributes by modifying the microstructural artifacts in a number of ceramic-based sensor materials (such as WO3 and MoO3 and MoO3–ZnMoO4) has recently been reported.1–3 The effect of the variation in the ambient oxygen partial pressure across the metal/metal oxide boundary on the microstructure and gas-sensing characteristics (viz., enhancement of sensitivity and shortening of response time) of potential oxides such as WO3 and MoO3 were also studied.4,5 The methodology adopted to bring about the desired morphological variations has been described in sufficient detail elsewhere3 and is stated briefly here.

At a given temperature and standard pressure (ambient; 1 atm), the oxidation of a metal to its oxide or the reduction of an oxide to its suboxide or the corresponding metal occurs at a well-defined oxygen partial pressure (pO2). At a given temperature, on either side of this unique pO2, one of the two coexisting phases must disappear. For a hypothetical metal oxidation reaction, M(s) + x/2O2(g) → MOx(s), the equilibrium pO2 for the M/MOx coexistence is given by

$$pO2(M/MOx) = \exp\left(\frac{2\Delta GR}{xRT}\right)$$

Equation (1) gives the thermodynamic equilibrium oxygen partial pressure for the coexistence of a metal with its adjacent oxide at a given temperature in terms of the standard Gibbs free energy change for the oxidation reaction, which in the present case also equals the standard Gibbs free energy of formation of the oxide, MOx. Consequently, a plot of pO2 or ln pO2 versus temperature gives the contour of the path of the M/MOx coexistence. It can then be visualized that at a pO2 lower than the “line of coexistence,” the metal oxide would experience reduction either to its suboxide or the corresponding metal. Similarly, at pO2 above the line, a metal (or its suboxide) would be oxidized to the corresponding stable oxide.

Ordinarily, an oxide can be reduced to a suboxide or the corresponding metal by H2 or CO. Heating the reduced species in air (static or dynamic; pO2 = 0.21 atm) leads to bulk oxidation, regenerating the parent phase whose morphological features may or may not be very different from the starting material. On the other hand, if the reduced surface is exposed to a well-defined pO2 that is only a few orders of magnitudes higher than the theoretical value for the M/MOx coexistence, interesting processes ensue. Under this condition, because the prevailing oxygen potential is only slightly above that established by virtue of thermodynamic equilibrium between M and MOx or between MOx and MOy, it allows the formation and growth of new oxide surface on an atomic/molecular level, under conditions of well-defined “oxygen enrichment” locally. Similarly, by exposing the oxide to a precisely controlled pO2 regime that is below the theoretical line of the metal oxide stability, one can modulate the extent of reduction of the said oxide either to a suboxide or ultimately to the metal under conditions of “oxygen deprivation” locally. In any event, it can be envisaged that such a pO2 manipulation will deplete/enrich oxygen in a manner so as to cause atomic- or submolecular-level chemical variations. Hence, upon exposure to an environment that is only slightly rich in oxygen, new material build-up takes place layer by layer, thereby creating whole new morphological features that are alien to the starting bulk oxide.

An oxygen potential in the vicinity of these equilibria could potentially be generated by manipulating the ratio of two gaseous species in a buffer mixture, such as CO2/CO or H2O/H2. For example, by controlling the ratio of the concentration of CO2 and CO, it is possible to control the partial pressure of oxygen. Mixing CO2 and CO in a ratio that ranges from 10−5 to 105 provides good buffered systems. In this range, the theoretical pO2 varies between 10−35 and 10−15 atm at 600°C and between 10−29 and 10−9 at 800°C. Similarly, by varying the H2O to H2 ratio in the range of 10−5 to 105, the corresponding equilibrium oxygen partial pressure at 600°C can be conveniently varied between 10−34 and 10−14 atm.

To put this in perspective, the equilibrium pO2 computed for the biphasic coexistence of several metal/metal oxide couples, using reliable Gibbs energy data, is shown in Table 1 as a function of temperature in the range 400–1100°C. The loci of log10 pO2 values of TiO and TiO2 are plotted in Fig. 1; also shown are the specific values at 450°C, 600°C and 800°C, generated by varying the CO2/CO ratio over 10 decades between 10−5 and 105.

Because the thermodynamic stability of titania is quite high (and the corresponding dissociation oxygen partial pressure in the Ti/TiO2 system is rather low),
thermodynamically it is impossible to cause reduction of TiO₂ to either TiO or Ti metal via the buffer gas technique. For example, the equilibrium \( p_\text{O}_2 \) in the Ti/TiO₂ coexisting mixture ranges from \( 2.7 \times 10^{-46} \text{ atm} \) at 600°C to \( 4.2 \times 10^{-29} \text{ atm} \) at 1000°C. In the case of Ti/TiO, the equilibrium \( p_\text{O}_2 \) values range from \( 1.2 \times 10^{-21} \text{ atm} \) at 600°C to \( 2.1 \times 10^{-33} \text{ atm} \) at 1000°C. No “practical” mixture of CO₂ and CO (Fig. 1) or even H₂O and H₂ is capable of establishing such low \( p_\text{O}_2 \) values. Hence, TiO₂ is not amenable to \( p_\text{O}_2 \) (and hence structural) modulation by the proposed scheme in this temperature regime. In this case, the desired morphological architecture could be developed by doing a high-temperature reductive etching (HiTREP) using a dilute H₂/N₂ mixture instead. Yoo \textit{et al.} \textsuperscript{6} and Carney \textit{et al.} \textsuperscript{7} have reported the development of single crystalline titania nanofibers in sintered pellets of TiO₂ and TiO₂–SnO₂, respectively. This communication reports the evolution of exotic microstructural artifacts in titania thick films deposited on commercial purity grade (cp) Ti substrates via electrolytic process, by systematic heat treatment in ambient air (\( p_\text{O}_2 = 0.21 \text{ atm} \)) followed by reduction in a 5% H₂/Ar mixture.

**Experimental Procedure**

The titania thick films used in this study were supplied by Henkel Corporation. The films were made by a patented aqueous plasma electro-deposition (PED) process in which the titanium (or aluminum) substrate is made the anode and titanium-based compounds in solution are deposited and cured \textit{in situ} by the glowing plasma at the surface. In contrast to the thin titania films created by the anodization of a titanium substrate,\textsuperscript{8,9} which is rather slow and quite time-consuming, the electro-deposition process is very rapid and results in films that are 5–100 times thicker than simple substrate oxidation. Wrought 3-mm-thick plates of cp titanium substrate were electrolytically coated for 3 min. 18 SWG (1024 μm diameter) wires made of cp titanium were also coated for 3 min. A pulsed DC voltage (240 V) was applied for 10 ms on and 30 ms off at a current density of approximately 1500 A/m². The films were about \( 10^7 \) μm thick. In the case of PED TiO₂-coated plates, 12 mm × 12 mm coupons were cut out. In anticipation of their subsequent use as sensors after subjecting to HiTREP,\textsuperscript{5} two tiny equispaced holes (1 mm ID) were drilled close to one of the four edges. These holes would be used to connect lead wires to complete the circuit and measure the film resistance in sensing experiments. In the second case, the PED titania-coated wire was wound tight around a metal rod. Cylindrical sections of the coil, about 1/2 in. long were cut out. The samples were placed in an alumina boat that was kept in the uniform temperature zone of a horizontal PID-controlled tubular Lindberg Blue (NC) furnace.

**Table I. Equilibrium \( p_\text{O}_2 \) Values for Some Representative Semiconducting Oxide Systems**

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>( p_\text{O}_2 ) / atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/MoO₃</td>
<td>W/WO₃</td>
</tr>
<tr>
<td>400</td>
<td>( 1.9 \times 10^{-30} )</td>
</tr>
<tr>
<td>600</td>
<td>( 1.2 \times 10^{-21} )</td>
</tr>
<tr>
<td>800</td>
<td>( 4.0 \times 10^{-16} )</td>
</tr>
<tr>
<td>1000</td>
<td></td>
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<td>1100</td>
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**Fig. 1.** Temperature dependence of the equilibrium oxygen partial pressure in Ti/TiO₂ and Ti/TiO. The variation in \( p_\text{O}_2 \) by changing the CO₂/CO ratio over 10 orders of magnitude in the range \( 10^{-5} - 10^{5} \) at 450°C, 600°C and 800°C is also shown (open triangles).
and calcined in static air at 700°C and 900°C for 4 h each, and at 1100°C for 2 h. Coupons and coiled wire samples in sets of four were used for heat treatment at each temperature. Two calcined samples from each batch were used for the reduction experiment in 5% H₂/Ar mixture (flow rate of 100 sccm) at 700°C for 6 h. In one case, reduction was carried out for 8 h. The phase evolution and morphological variation before and after each of these treatments was followed by systematic XRD and SEM analyses. The X-ray powder diffraction (XRD) signatures on the sample were collected on a Philips diffractometer (PW 3050/60 X’pert Pro, Philips, Westborough, MA) using monochromatic CuKα1 radiations (λ = 1.54056 Å) and a Ni filter. Scanning electron microscopy was carried out using Phillips XL30-FEG SEM (Phillips, Hillsboro, OR); gold coating was used to avoid charging.

Results and Discussion

As is evident from Fig. 2, the as-fabricated titanium dioxide thick films did not possess any well-defined microstructural features and hence were not attractive for the anticipated gas sensing applications. To make use of these simple geometries as potential gas sensor devices, the films were subjected to a series of heat treatments in a well-conceived temperature–time–environment profile. The samples were calcined in static air at 700°C or 900°C for 4 h each, or at 1100°C for 2 h. The calcined samples were then reduced in a 5% H₂/Ar mixture at 700°C for 6 h; in one case the reduction was carried out for 8 h.

Figure 3 shows representative SEM images of the samples fired in static air at 700°C and 900°C for 4 h each. Apparently, subsequent to the heat-treatment under these conditions, no noticeable morphological changes could be observed. However, dramatic morphological and microstructural changes ensued when the titania films were heated in air at 1100°C for 2 h. Arrayed platelets were found to grow from the deposited film surface, as seen in the SEM images shown in Fig. 4. As evident from the higher magnification SEM image, the platelets are clearly oriented along the...
c-axis (out-of-plane) and exhibit preferred texturing. Furthermore, the platelets appear to nucleate and grow individually rather than by the traditional global mechanism generally observed in ceramics; the plates are \( \sim 2-4 \) \( \mu \)m in width and \( \sim 500 \) nm in thickness.

To follow systematic phase evolution, the XRD signatures of variously heat-treated samples are compared in Fig. 5, which shows several interesting features. First, the anatase modification (ICDD# 21-1272) is retained in samples heated up to 900°C for 4 h, albeit with decreasing intensity as it is known to undergo irreversible transformation into the more stable rutile phase (ICDD# 21-1276), which increases in intensity gradually; there are no traces of anatase titania in samples fired beyond 900°C. Second, the peaks belonging to cp Ti substrate that were present in the film fired at 700°C disappear in those heated at higher temperatures. This could be due to the grain growth, good adhesion and protective nature of the titania film—all of which limit the access of oxygen to underlying metallic surface and mitigate its exposure. The bright gray surface belonging to cp Ti metal could be seen by scratching the top oxide layer, which reinforces the belief that the heat treatment employed in this work did not cause bulk oxidation of the underlying metallic titanium substrate. The third and most surprising observation is the fact

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**Fig. 4.** Microstructural evolution in the PED TiO\(_2\) thick films/cp Ti heated in air at 1100°C for 2 h that shows textured growth of plate-like structure.

**Fig. 5.** XRD patterns showing the systematic phase evolution in the PED-TiO\(_2\) thick films/cp Ti as a function of heat treatment in the range of 700–1100°C.
that the β-phase (ICDD# 35-0088) which was present in the as-fabricated thick film sample itself, is seen in those heated up to 1100°C for 2 h. Thus, structurally, the platelets seen in the SEM images in Fig. 4 are likely a mixture of titania in rutile and β (R+β) phases.

No noticeable morphological changes developed when the films fired at 700°C and 900°C for 4 h (Fig. 3) were subjected to reduction in 5% H₂/Ar environment at 700°C for 6 h, as seen from the SEM images shown in Fig. 6.

However, the morphological features underwent drastic change when films calcined at 1100°C/2 h were soaked at 700°C for 6 h in a 5% H₂/Ar mixture flowing at a rate of 100 sccm. The SEM images at different magnifications and locations of the same sample are shown in Fig. 7. The surface etching attended by the nucleation and growth of nanofibrils at the tip of the platelets is quite evident.

At this juncture, it is worth pointing out the similarities between the present results and those reported on TiO₂ dense pellets and on TiO₂–SnO₂ thin films by Yoo et al.6 and Carney et al.7, respectively. For example, based on the thermogravimetric experiments conducted on dense polycrystalline titania in the range 680–780°C in H₂/N₂ mixture, Yoo et al.10 speculated that the fiber formation was due to the anisotropic etching process. Furthermore, the results based on the mass spectrometry and the inductively coupled plasma spectroscopy data indicated that oxygen, and not titanium, was removed from the specimen surface during the reaction with hydrogen. The appreciable depletion of oxygen from the reaction zone without an appreciable change in the TiO ratio at such surfaces was found to be consistent with the solid-state diffusion of titanium cations from the surface into the bulk of the specimen. The migration of Ti⁴⁺ under the apparent concentration gradient created by the dynamic reductive etching leads to the creation of nanofibrillar structure along the path of migration. This mechanism is evident in the post-HiTREP microstructure shown in Fig. 8; the SEM image on the right shows continuously growing fibers 20–50 nm in diameter and length up to several micrometers.

Even though the physical make-up of the system in the present case (thick film on cp Ti substrate) is different from that employed by Yoo et al.6,10 (sintered pellet), identical processes appear to be operative in both the cases. Interestingly, in the present case as well, the gross composition of the thick film surface remained intact, despite the dynamic nature of HiTREP in a dilute mixture of non-combustible gases (H₂:Ar = 5:95). This is strengthened by the fact that no new phase (i.e., titanium oxide with a different TiO ratio and hence a different crystal structure) was detected in the diffraction pattern of the film subsequent to high-temperature etching. The XRD patterns collected on the films after calcination (1100°C/2 h in static air) and HiTREP (700°C/6 h in 5% H₂/Ar stream) are compared in Fig. 9.

As can be easily discerned, the two diffraction patterns are identical except for the intensity of some peaks; both could be indexed as rutile TiO₂ with some peaks still belonging to monoclinic β-TiO₂. Therefore, the reductive etching did not cause variation in phase structure, nor did it lead to the formation of any new chemical species. When soak time was increased from 6 to 8 h keeping all other parameters of reduction identical, no discernable morphological changes were recorded. However, the XRD pattern of the titania films subjected to 1100°C/2 h (air calcination) + 700°C/8 h (5% H₂/
Ar reduction) showed preferential texturing along the \(\langle 211 \rangle\) plane; in all the other samples, \(\langle 110 \rangle\) is the most intense reflection. More importantly, \(\beta\)-TiO\(_2\) phase eventually disappeared. This is shown in Fig. 10.

Not much literature is available on \(\beta\)-phase and we speculate that its formation in our experiments is an artifact of the deposition technique. Moreover, there is no reported evidence on the gas-sensing behavior of...
β-TiO$_2$ in the published literature and, therefore, evaluation of sensing characteristics of textured rutile phase obtained after reduction for 8 h at 700°C in a 5% H$_2$/Ar stream appears to be a more adequate protocol, so that the uncertainty arising due to the role of the former can be ruled out.

Figure 11 shows the morphological features evolved in TiO$_2$ thick films coated on 18 SWG cp Ti wire when calcined in static air at 1100°C/2 h.

The formation of unique 3D prismatic solid structure in this case as opposed to the 2D platelets in the case of films deposited on cp Ti plates under conditions of identical heat treatment is likely an interplay of the structural stability of the film and the interfacial Gibbs free energy per unit surface area. For example, in both cases, thermodynamically stable rutile titania is formed on cp Ti. Therefore, the macroscopic bulk Gibbs free energy is identical in both the cases. Furthermore, the Pilling–Bedworth ratio for titania film (1.77) lies almost midway between those for magnesia (1.28) and silica (2.14)—two well-known stable oxides$^{11,12}$—corroborating the visual and microstructural observation that stable titania films were formed on both the platforms. Therefore, the growth of the polycrystalline titania films in different morphological motifs could be explained as arising from the difference in the interfacial Gibbs free energy in the two cases.

If $\Gamma$ denotes the interfacial Gibbs energy, then

$$\Gamma = \frac{\Delta G^2 \text{kJ/mol}}{\text{area}}$$

for 12 mm × 12 mm coupons, and,

\[\text{Fig. 9. Comparative XRD patterns of PED TiO}_2\text{ thick films/cp Ti samples before and after HiTREP}}, \text{ both the diffraction plots conform to the rutile phase of TiO}_2\text{. HiTREP, High-Temperature Reductive Etching Process.}\]

\[\text{Fig. 10. XRD of the titania thick film on cp Ti reduced at 700°C/8 h in 5% H}_2\text{/Ar stream.}\]

\[\text{Fig. 11. Microstructural evolution in the EPD-TiO}_2\text{ thick films coated on 18 SWG diameter cp Ti wire and fired at in static air at 1100°C for 2 h.}\]
\[ \Gamma_{\text{TiO}_2(\text{wire})} = \frac{\Delta G^\circ_f(\text{TiO}_2)}{\gamma(0.001024)^2} \text{ J/mol} \cdot \text{m}^2, \] for 18 SWG cylindrical wire. This gives,

\[ \Gamma_{\text{TiO}_2(\text{plate})} = 6944.44 \times \Delta G^\circ_f(\text{TiO}_2) \text{ J/mol} \cdot \text{m}^2 \]

and,

\[ \Gamma_{\text{TiO}_2(\text{wire})} = 1.21 \times 10^6 \Delta G^\circ_f(\text{TiO}_2) \text{ J/mol} \cdot \text{m}^2 \]

Therefore, \( \Gamma_{\text{TiO}_2(\text{wire})}/\Gamma_{\text{TiO}_2(\text{plate})} = 174.24 \).

We believe that in order to accommodate about a 174-fold difference in interfacial Gibbs free energy, the titania–cp Ti interface on the wire platform undergoes systematic self-reconstitution and re-organization on the microscopic level. This is manifested in the form of tightly packed growth consisting of stacked layers of consecutive triangular prismatic ridges, signifying the microstructural adjustment at each stage to satisfy the above-mentioned interfacial Gibbs free energy criterion. The near-identical cone-shaped termination in sharp tips seen in Fig. 11 typifies the end of the growth process under this condition. These features can be seen more clearly in the SEM images presented in Fig. 12.

In order to substantiate the mechanism proposed above, the heat-treatment schedule was slightly modified. In this case, the titania films on the cp Ti wire were soaked for 2 h at 1100°C at ambient pressure (1 atm) in an environment of \( p_{\text{O}_2} = 3.8 \times 10^{-21} \text{ atm} \). This was realized by using a CO/CO\textsubscript{2} gas buffer containing 100 ppm of CO\textsubscript{2}; at 1100°C, thermodynamic calculations as per
Eq. (1) gives an equilibrium $p_{O_2}$ value of $2.26 \times 10^{-26}$ atm for the Ti/TiO$_2$ couple (Table I). Thus, a $p_{O_2}$ ~ 5 orders of magnitude higher than the theoretical value for the Ti/TiO$_2$ coexistence ensures that oxidizing conditions prevail and no reduction of the TiO$_2$ film either to TiO or to Ti is likely. The microstructural features evolved under such an acute lack of oxygen are shown in Fig. 13. Three-dimensional prismatic growth via stacked-layer ridge formation is quite evident.

Phase identification by XRD analysis (pattern not shown here to avoid redundancy) indicated the film structure to be rutile. The surface morphology showing the onset of nanofiber formation and growth as a result of reductive etching of these samples with 5% H$_2$/Ar is presented in Fig. 14.

Fig. 14. SEM images of the TiO$_2$ films on cp Ti wire subjected to heat-treatment in CO$_2$/CO ($p_{O_2} = 3.8 \times 10^{-21}$ atm) at 1100°C/2h followed by HiTREP at 700°C/6h. HiTREP, High-Temperature Reductive Etching Process.

Conclusions

Titania thick films deposited on cp Ti (plates and/or wires) as ready-to-use sensor modules were subjected to a suite of heat treatment in a variety of environment–temperature–time matrices to accentuate their morphological attributes. It was found that novel microstructural features could be incorporated in a semiconducting oxide such as titania via precise oxygen potential modulation. The formation and growth of new oxide surface on an atomic or submolecular level, under conditions of oxygen deprivation or enrichment, appears to be the most likely pathway. A combination of oxidative treatment in CO$_2$/CO (100 ppm CO$_2$–rest CO) buffer followed by reductive etching in a 5% H$_2$/Ar mixture led to the formation of 3D prismatic stacked-layer structure on which nanofibers nucleated and grew; this combination could be benign in accentuating the sensing behavior of titania thick films. These aspects are under investigation now.

References