Tantalum oxide thin films for electrochemical pH sensor

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Abstract

Present work demonstrates the fabrication and utilization of tantalum oxide (Ta2O5) thin films as prominent pH sensing electrode material. Ta2O5 film of 1 μm thickness was deposited on glass substrates using physical vapor deposition technique. Structural and morphological studies were performed on these thin films. Electrochemical studies were carried out on these films using amperometry, linear sweep voltammetry and cyclic voltammetry techniques. These Ta2O5 coated substrates were found to be sensitive to various assorted pH solutions and hence were used as pH sensing electrode. The performance of the electrode was studied in terms of stability, reusability and selectivity. Results reveal that the films were found to be suitable pH sensing material in 1.0–12.0 pH range. The sensing electrodes were found to be reliable and reusable with less than 5 s response time.

1. Introduction

pH sensing has been specifically shown to be of paramount importance in many areas such as environmental science, biological studies, sport, health care, as nature (acid or alkaline) of a solution is a marker of physiological state [1–3]. These are very useful in many applications, for instance; testing of water, blood samples, agricultural production, food processing, environmental monitoring etc [4–6]. Traditional methods for pH monitoring encountered with several disadvantages such as complex operating methods, expensive and need regular maintenance, which includes refilling of buffer solution. Pt-based pH sensors show good performance but proved to be expensive. Therefore, there is a need to develop a sensing platform, which can sustain in harsh chemical environment and has an extended electrode life. Metal oxides are found to be capable for the detection of hydrogen ions and hence can be used in determining pH value of the solution [7–9].

Metal oxides such as tantalum oxide (Ta2O5), aluminum oxide (Al2O3), ruthenium oxide (RuO2), titanium oxide (TiO2) etc show mechanical strength, stability, semiconducting nature in their bulk form [6–8]. These materials in their thin film form are found to be stable at high temperature. Reports reveal that these materials are also found to be prominent pH sensing material due to their high electronic conductivity as a result of defects produced such as high oxygen deficiency [9–15]. Metal oxides can be deposited on suitable substrates like glass, silicon etc using several techniques such as physical and chemical vapor deposition techniques [2, 10–16].

Among the metal oxides, Ta2O5, a transition metal oxide, exhibits thermal and chemical stability and excellent electrochemical reversibility [13, 14]. Ta2O5 is found to be more significant for the fabrication of ion sensitive field effect transistors (ISFETs) due to its low drift and high sensitivity [14]. The utilization of this material is reported as pH sensing electrode by several researchers using voltammetry and capacitance-voltage (CV) technique [17–20]. These reports do not explore the study in whole pH range and carried out the sensing on limited pH values. The response time, during these studies, was not discussed. Table 1 summarizes the work carried out by the other researchers on Ta2O5 based pH sensor.

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Table 1. Comparison of work carried out on Ta$_2$O$_5$ thin film for pH sensing using several techniques.

| S. No. | Coating technique Used | Response measurement technique used | Ta$_2$O$_5$ film Thickness (nm) | Response time (s) | pH range | Solvents pH values used | References |
|--------|------------------------|-------------------------------------|---------------------------------|-------------------|----------|-------------------------|------------|
| 1      | RF Magnetron Sputtering | Volt                                | —                               | 167               | 4.0–10.0 | 4.0, 7.0, 10.0          | [17]       |
| 2      | RF Sputtering           | Imp                                 | —                               | 155               | 1.0–10.0 | 1.0–7.0 & 10.0          | [18]       |
| 3      | MOCVD                   | ISFET                               | —                               | —                 | 3.0–11.0 |                        | [19]       |
| 4      | E-beam evaporation      | Pot                                 | —                               | —                 | 3.0–11.0 |                        | [20]       |
| 5      | E-beam evaporation      | cv                                  | LSV                             | 1000              | 1.0–12.0 | 1.0–12.0                | Present Work |
* Amp: Amperometric, Volt: voltammetric, Pot: Potentiometric, Imp: Impedimetric, Hyst: Hysteresis widths, CV: capacitance-voltage, LSV: Linear Sweep Voltammetry, cv: cyclic voltammetry.
Utilization of Ta₂O₅ as sensing surface needs to be explored to fabricate as pH sensor using electrochemical techniques such as amperometry and linear sweep voltammetry (LSV) as to the best of our knowledge, Ta₂O₅ based pH sensing has not been explored so far using these techniques. Keeping this in view, the present work reports the fabrication and utilization of Ta₂O₅ thin films as electrochemical pH sensing material. Thin films of Ta₂O₅ were prepared on glass substrates using E-beam coating technique due to its advantages such as good adhesion and chemical stability etc \[6, 21\]. These films were further characterized using XRD, CCI and SEM techniques for structural, roughness and surface morphology studies, respectively. These Ta₂O₅/glass substrates were further utilized to fabricate pH sensing electrodes and studied using electrochemical techniques. Steady and repeatable response of these electrodes was observed in 1.0 – 12.0 pH range. These received results reveal that Ta₂O₅ can be used as prominent electrode material for its use as pH sensing material.

2. Experimental details

2.1. Materials and methods

Ta₂O₅ granules were procured from Umicore, Liechtenstein. Sodium hydroxide (NaOH) pellets and hydrochloric acid (HCl, 35%) were procured from Merck, Germany. Glass substrates were procured from Nanoshel, USA. E-beam evaporation coating plant (Pfeiffer 570, Germany) was used for the evaporation of Ta₂O₅. Film thickness during deposition was measured in situ using quartz crystal monitor (Intellimatrics, UK). During the pH sensing studies, thickness of the deposited material was measured using a Reflectometer (F10-RT, Filmetrics, Germany). X-ray diffractometry (D8 Advance, Bruker, Germany) technique was used for structural analysis of the film. Surface morphology and roughness of the films were studied using FE-SEM (SU8010, Hitachi, Japan) and Coherence correlation interferometer (CCI 6000, Taylor Hobson, UK), respectively. The amperometric responses and linear sweep voltammetry were recorded using an electrochemical workstation (660C, CH Instruments, USA). Resistance measurements on Ta₂O₅ based electrodes were performed using a source meter (4200 Keithley, USA). A pre-calculated amount of HCl and NaOH was used to prepare various pH values solutions ranging from 1.0 to 14.0 with the help of a pH meter (pico+, Lab India, India). All solutions were prepared during double distilled water (18.2 MΩ) and the glassware used in this work was autoclaved every time before use.

2.2. Sensor fabrication

To fabricate the sensor, 100 glass substrates of 1.5 cm × 1.0 cm dimension were cleaned properly using isopropanol and acetone. For coating, molybdenum boat (Umicore) was filled with Ta₂O₅ granules for evaporation. Before coating, degassing of the material was allowed for about 15 min. Several coating parameters such as chamber pressure, substrate temperature, oxygen partial pressure etc were optimized after several trials and presented in table 2. Ta₂O₅ films of various thicknesses (0.5, 0.8, 1.0 1.5 and 2.0 μm) were prepared to achieve optimum thickness for further study. During the study, it was observed that the thickness above 1 μm did not have good adhesion and peeled-off in the form of flakes, when allowed to interact with alkaline pH solutions. Prior literature also confirms that higher thickness resulted into less sensitivity \[22\]. For thickness less than 1 μm, less film adhesion is observed during its interaction with the harsh solvents, which makes it unsuitable for sensing purpose. Ta₂O₅ film thickness of 1 μm was found to be suitable in whole pH range solution because of its stability. Hence, the glass substrates having 1 μm film of Ta₂O₅ were used as sensing electrodes during the pH sensing studies.

Table 2. Process parameters for the coating of Ta₂O₅ thin films.

| S. no. | Deposition parameters | Values          |
|--------|-----------------------|-----------------|
| 1      | Base Pressure         | 1.0 × 10⁻⁶ mbar |
| 2      | Oxygen Partial Pressure | 2 × 10⁻⁴ mbar  |
| 3      | Substrate Temperature | 200 °C          |
| 4      | Substrate Rotation    | 20 RPM          |
| 5      | Deposition rate       | 0.307 nm s⁻¹    |
3. Results and discussion

3.1. Structural analysis

XRD technique was used for electrode material stability studies. For this, Ta2O5/glass electrode was dipped in solution of pH 1.0 for different span of time i.e. 3, 6, 9, 12 and 15 min. The electrodes were then dried under vacuum at 70 °C before recording XRD data. For bare Ta2O5, the characteristic 2θ peaks of Ta2O5 were found at 30, 38, 52 and 60 in the XRD pattern (figure 1), which are in accordance with earlier reports [23, 24]. In the XRD pattern of other Ta2O5/glass substrates (figure 1), after dipping for different duration, 2θ peaks appears at similar position as appeared in the case of bare substrate. This confirms that harsh environment (pH 1.0), did not affect Ta2O5 structure.

3.2. Thickness measurement

Thickness of Ta2O5 was also confirmed using a Reflectometer before and after their use in pH sensing studies. It was found that thickness of Ta2O5 films remain 1 μm before and after their use in sensing studies in solutions of

![Figure 1. XRD data of bare Ta2O5 thin films and after exposing them to harsh solvent (HCl) for different time.](image-url)
different pH. This confirms that the material did not dissolve in the solution during the study. Even the thickness of the Ta$_2$O$_5$ film, which was dipped in pH 1.0 solution for 15 min shows the similar thickness as before its use.

Based on XRD pattern and thickness measurement data, it can be stated that the material retains its structure during the experiments in low pH solutions, which confirm its stability.

### 3.3. Roughness studies

Roughness of Ta$_2$O$_5$ thin films was measured using CCI technique and found to be 0.3 nm (figure 2), which shows better film quality.

### 3.4. Morphological studies

Figures 3(a) and (b) presents the cross-sectional and 2D surface morphology of the electrode material before sensing studies. Whereas, figures 3(c) and (d) presents the cross-sectional and 2D surface morphology of electrode material after dipping it in 1.0 pH solution for 15 min. Figure 3(a) shows the globular like structure of Ta$_2$O$_5$ films, which is suitable for sensing applications. Figure 3(c) confirms that the material retained its globular structure after its treatment with harsh solutions. Film thickness of the electrode material was also estimated using cross-sectional surface micrographs (figures 3(c) and (d)) and found to be approximately similar as 1 μm, which again confirm that the electrode material did not dissolve in the solution during the study and remains stable.

### 3.5. Sensing mechanism

The fundamentals of liquid media and electrochemistry are hard to perceive. Similarly, in the case of the Ta$_2$O$_5$ thin film surface, relocation of potential and charge would occur during the interaction of two dissimilar surfaces i.e. solid and liquid. Therefore, the same theory can be used to study the electrochemical properties. Charging of metal oxide in several electrolyte solutions is based on the site binding theory, which is driven by the potential of hydrogen and hydroxide ion. The interaction of Ta$_2$O$_5$ with aqueous solutions, leads to the formation of tantalum hydroxide groups as shown in following equations:

$$\text{TaOH}_2^+ \leftrightarrow \text{TaOH} + H^+$$  \hspace{1cm} (1)
During the above reversible reactions, the material will either accept or donate the protons. Accordingly, the sensing process is governed by the above two mechanisms and the change in hydronic ion concentration in the solution results in the resistance. Before applying the voltage, thin-film surface would have zero charges or point of zero charges (pHzc). When the pH of electrolyte exceeds pHzc, the Ta2O5 surface becomes negative because of more negative ion (O−) formation. Therefore, it will favor acidic nature. A vice versa phenomena can be explained when the pH of electrolyte is lesser than pHzc. Whereas, when the OH− ions present in the solution will be equal to pHzc, the solution will be recognized as neutral [18].

3.6. Measurement techniques

Amperometric and Linear sweep voltammetry (LSV) detection techniques were used to study the electrode material sensitivity in various pH solutions. In these studies, current was measured as a function of potential and time, respectively. The study was performed using three-electrode configurations. During the studies, Ta2O5 coated glass substrate, Pt electrode and Ag/AgCl electrode were used as working, counter and reference electrodes, respectively. The solutions of various pH (1.0–14.0) were used as electrolyte. The results obtained are discussed below:

3.6.1. Amperometric detection

In this study, response of the electrodes was observed in the solutions of 1.0–14.0 pH range by applying constant bias voltage of 0.5 V for 120 s. The current was measured as a function of time and the data is presented in figure 4. It was observed that the coating on the substrates peeled out after dipping it in 13.0 and 14.0 pH solutions (highly alkaline) due to high corrosion rate under these conditions [25].

Keeping this in view, for further studies, the solutions of 1.0 to 12.0 pH solutions were used. The experiments were performed three times with fresh 1.0–12.0 pH solutions as well as fresh coated substrates. The response time of electrodes was found to be less than 5 s in most of the pH solutions. However, in case of pH 7, the response time was found to be little bit higher i.e. about 7 s. For other pH values, the amperometric data was recorded and presented as supplementary data is available online at stacks.iop.org/MRX/7/036405/mmedia of

\[ TaOH \leftrightarrow TaO^- + H^+ \] (2)
this manuscript. Almost repeatable results were obtained in these studies, which show the consistency in the behavior of Ta$_2$O$_5$.

3.6.2. Linear sweep voltammetry (LSV)

The LSV studies were performed in $-0.5$ to $0.5$ V potential ranges at a constant scan rate of 10 mV/s using solutions of 1.0 to 12.0 pH. The response in terms of resistance was measured as a function of current and the obtained results are shown in figure 5. A sudden decrease in current was observed with increase of potential and found to be saturated at higher potential. These electrochemical studies results determine the presence of electroactive species in the solution. For other pH values, the LSV data was also recorded and presented as supplementary data of this manuscript.
3.6.3. Cyclic voltammetry studies

Cyclic voltammetry (CV) experiments were also performed using three-electrode configurations as used for earlier studies. The solutions of various pH (1.0–12.0) were used as electrolyte at a scan rate of 10 mV/s. The data received for all the pH values was received. The data for lower and higher pH (2.0 and 11.0) is presented in figure 6. For other pH values, the CV data was recorded and presented as supplementary data of this manuscript. The repeatable CV curves represents the stability of the thin films and as a result shows the better electro catalytic activity.

4. Application

During these experiments, Ta2O5/glass substrates were used as pH sensing electrodes. The response of electrodes was recorded in terms of resistance in various pH solutions and the data is presented in figure 7.

Figure 7 shows that the resistance of the electrode was found to be decreased in the solutions of 1.0–7.0 pH range. On the other hand, in case of high pH (8.0–12.0), the response of the electrode was found to be increased with the pH values. A steady but slow increase was found in the resistance in 9.0–14.0 pH solutions. The experiments were repeated 5 times with fresh electrode and pH solutions and a similar response was observed. The data is presented in supplementary data.

5. Reliability of sensors with Tap Water

Reliability of the fabricated sensors was checked with ordinary water samples also using the similar techniques used earlier for a range of controlled pH solutions and the received data is presented in figures 8(a)–(c).
comparing these results with the results received earlier for various pH solutions, it can be stated that the presence of other ions does not affect the performance of the Ta2O5 based sensor.

Five water samples collected from different sources were taken and their pH was measured using Ta2O5/glass electrode fabricated in this study and standard pH measuring system. The values were compared and presented in table 3. Results reveal that less than 2% error was found, which shows the reliability of the sensing material.

6. Conclusion

In this work, tantalum oxide (Ta2O5) was evaporated in the form of thin films on glass substrates using E-beam evaporation technique. Thickness of the films was kept 1 μm using in situ thickness monitor. These Ta2O5 thin films were characterized using XRD, CCI and FE-SEM techniques for its structural, roughness and surface morphology, respectively. These thin films were found to be sensitive with a range of pH solutions and hence an amperometric pH sensor has been fabricated using these films. Repeatable response of the electrode was observed in 1.0–12.0 pH range solutions, which suggests the possible use of Ta2O5 as prominent electrode material for pH sensing in this pH range. The reliability of the fabricated sensors was also checked with tap water and on the basis of results received, it can be stated that the presence of other ions in solution, does not affect the performance of the sensor.

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