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Deposition and characterization of RF-sputtered-Ta_2O_5 thin films for O_2 reduction reaction in polymer electrolyte membrane fuel cells (PEMFC)

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ABSTRACT

Ta_2O_5 thin films, proposed as the replacement of the precious Pt-based electro-catalyst in fuel cells, were sputtered on laser textured silicon substrate at 200 °C and then air annealed at 350 °C, 400 °C and 450 °C with the aim to improve crystallinity and uniformity. Characterization such as FESEM, XRD, Hall effect and Cyclic Voltammetry were employed to investigate the morphological, structural, electrical and electrochemical properties of the as-sputtered as well as annealed samples. Initial results showed that the films obtained by increasing the substrate temperature during sputtering are smoother and have better adhesion to the etched silicon substrates. It has also been observed that the rate of deposition increases resulting in thicker films for longer deposition time at higher temperature. Upon annealing, Ta_2O_5 films achieved better crystallinity consisting of orthorhombic phases. The average thicknesses of the films are in the range of 400 nm–700 nm. The proposed catalyst also shows better enhancement for oxygen reduction reaction (ORR) in prolonged time of continuous potentiostatic electrolysis as to be used in fuel cells.

1. Introduction

Direct Methanol Fuel Cell (DMFC) and Proton Exchange Membrane Fuel Cell (PEMFC) are among the many types of fuel cell that possess impending potential application as portable power generation and electric drive system. Consequently, the general cost of a fuel cell and its performance must be optimized. However, the cost of Platinum (Pt) hampers the possibility of low cost fuel cell. Therefore, a non-precious metal catalyst material is desired. One of the common problems in polymer electrolyte membrane fuel cells (PEMFC) is the catalyst loading at the cathode due to the slow-moving oxygen reduction reaction (ORR). This reaction time is almost double compared to that of the anode. To increase the rate of ORR, PEMFC requires the use of highly active catalysts to promote both the fuel oxidation at the anode and ORR at the cathode [1]. The cathode demands a huge amount of potential (> 0.8 V) to hold a long period of operation. This is challenging because of the poor stability of Pt nanoparticles supported carbon (Pt/C) at the ORR catalyst

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[2]. Tantalum oxide (Ta_2O_5) based material is one of the favourable material to be used in a fuel cell because of its ability to sustain in acidic environments and act as an active electrocatalyst for ORR [3]. The ionization potential of Ta_2O_5, which tantalum with the highest oxidation state, is 7.8 eV [3]. The performance of Ta_2O_5 as a catalyst is comparable to platinum (Pt) even though Ta_2O_5 showed poor electrochemical activity due to limited electrical conductivity. The main focus of the catalyst structures is the pore size and its distribution because these two factors affect the interaction between the ionomer and the catalyst particles [4]. Therefore, a membrane-electrode assembly was developed from a structure consisting of high surface area, good electrical conductivity and porosity to improve the performance of a PEMFC. Another challenge here is to fabricate a non-precious metal nanocatalyst with a reliable method. To further improve the operating stability and performance, fuel cell electrodes with high surface area, good electrical conductivity, and suitable porosity must be developed. A study suggests to fabricate the electrode using macro porous silicon technology [5].

In this study, porous silicon structure is proposed as an alternative to the conventional carbon paper that is being used as catalyst support material [6]. The prospects of novel porous silicon based nanostructures being used as a catalysts support material for PEMFC synthesized by chemical etching methods will also be investigated [7]. Pichonat T. reported that by replacing carbon paper with porous silicon structure, the advantage of both Nafion® and silicon will promote proton conduction and mass production of a fuel cell. The physical parameter of interest is the catalyst support porosity. Porous support material such as porous silicon wafer was also reported to be utilized as a gas diffusion layer and as well as active area for electrocatalyst placement [8]. S. Aravamudhan et al. stated that fuel cell uses novel porous silicon electrodes that are fabricated by wet etching through macro-porous silicon technology. As the pores in porous silicon act both as structures and reservoir, it also helps reducing the size of the fuel cell. This will create a capillary action that will pump the fuel towards the cell's reaction sites. The porous silicon electrode thus eliminates the need for an active external fuel pump [9].

The reactive magnetron sputtering represents a good candidate to deposit optical and electrical structures on sensitive target material and substrates. By using RF sputtering, the prospect of controlling several deposition parameters such as pressure, gas flows, target material, and power is possible. It allows a wide range of film stoichiometry, thereby it permits to deposit layers with gradient of composition [9]. Bash E. et al. reported to have done a complete annealing study of Ta films after sputter deposition process. Their XRD results shows that samples that were annealed at 200 °C showed the strongest (002) peaks and disappears after annealing at 400 °C, but several oxides peaks appear at higher temperatures [10]. The synthesized new materials of nanostructured electrocatalyst will be evaluated in terms of cyclic voltammetry (CV). CV is the most useful technique in electrochemistry. It can quickly provide qualitative information about catalysts and electrochemical reactions. This can help to further improve the electrocatalyst layer or material structure. The development of electrodes for fuel cell can be clearly grouped into two, which are the catalyst support material and non-Pt electrocatalyst nanomaterials.

Therefore, in this work, a membrane-electrode assembly was developed from a structure consisting of high surface area, good electrical conductivity and porosity to improve the performance of the catalyst. This study investigates the influence of different substrate temperatures during RF Sputtering growth of Ta_2O_5 thin films. Ta_2O_5 was sputtered onto silicon wafer via reactive sputtering and directly proceed to annealing process to achieve crystallinity of Ta_2O_5. The physical and electrical characterization of the samples such as X-ray diffraction, scanning electron microscopy and Hall measurement as well as the measurement of the ORR potential were performed. Lastly, the correlation between the physical and electrical properties of the samples with the resulting catalytic activity for the ORR was discussed.

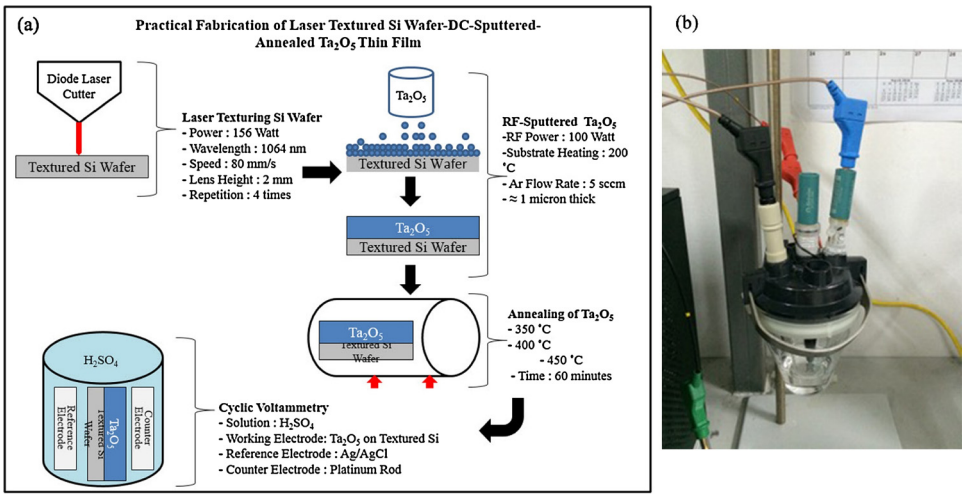

Fig. 1. (a) Schematic diagram of practical fabrication of laser textured Si wafer-DC-sputtered-annealed Ta_2O_5 thin film and (b) final CV measurement setup.

Table 1
Laser texturing parameters.

Parameter	Value
Power	156 Watt
Wavelength	1064 nm
Speed	80 mm/s
Lens Height	2 mm
Repetition	4 times

2. Experimental study

Fig. 1(a) shows the schematic diagram of practical fabrication of laser textured Si wafer-RF-sputtered-annealed. Deposition of Ta_2O_5 starts with laser textured silicon wafers. The parameter used to laser texture silicon wafers is shown in Table 1. Then RCA cleaning was conducted with sodium hydroxide and hydrophobic process with hydrofluoric acid followed by wet chemical etching. RCA cleaning or it is also known as standard silicon cleaning procedure is to remove organic residue and films from silicon wafers. This process is chosen because of its excellent repeatability in micro-fabrication and its low production cost [11]. These process is also to increase the surface area of the substrate which will promote ORR [12].

Ta_2O_5 thin films were then deposited using an RF magnetron sputtering system. A Ta_2O_5 disc (99.99% purity) was used as the sputtering target. Cleaned and textured wafers were then used as substrate. The flow rate of argon gas flowing into the chambers was 5 sccm, and the RF power supplied was 100 W. The wafers were subsequently heated during sputtering at 200 °C. The deposition time was maintained at 120 min. This was then followed by thermal annealing in oxygen ambient with temperature of 350 °C, 400 °C and 450 °C. C.Chaneliere et al. that when Ta_2O_5 is deposited at temperature below 650 °C, the film is amorphous [13]. It have been also reported that Ta_2O_5 films will change from amorphous to crystalline phase after a high annealing temperature which will also change the electrical characteristics of the films [14]. X-ray diffraction (XRD) was used to analyze the crystal orientation, phase identification, phase intensity and phase ratio. XRD was measured on a BRUKER aXS-D8 Advance Cu-Kα diffractometer at room temperature. XRD patterns were recorded in the 2θ range from 10° and 80° with a step size of 0.02° Cu-Ka radiation wavelength, λ = 1.5408 Å. Surface morphology and cross sectional view of the resulting Ta_2O_5 thin films were observed by using Carl-Zeiss Merlin field emission scanning electron microscope (FESEM) which was operated at 3 kV–15 kV. In order to investigate the electrochemical reaction rate of Ta_2O_5 thin films, which were sputtered and annealed at different temperatures, cyclic voltammetry (CV) (Autolab/PGSTAT 204) was conducted for 10 cycles. The cyclic voltammetry measurement setup is shown in Fig. 1(b). The catalytic activities of electrode toward methanol oxidation reaction were measured in N_2-saturated 1.0 M H_2SO_4 solution between −0.8 V and 1.0 V with a scan rate of 10 mVs^{-1}. The half-cell performance was evaluated with an active area of 0.5 cm^2. The electrical parameters such as carrier concentration, mobility, and resistivity were measured by Hall effect measurement system, HMS ECOPIA 3000 with a magnetic field of 0.57 T and probe current in the range of 30 nA to 10 mA for all samples. The data from Hall measurements were plotted with mean values from multiple measurements with standard deviation.

3. Results and discussion

X-ray diffraction (XRD) was performed on the samples to identify the phases and investigate crystallinity of the Ta_2O_5 films. Fig. 2 shows the XRD patterns of as-sputtered and annealed Ta_2O_5 thin films on textured silicon wafer. It was observed at a lower annealing temperature of 350 °C the XRD readings did not show clear distinct peaks. Kukli K. et al. and C. Chaneliere et. al. earlier confirmed that the films deposited at low temperature were amorphous [13,15].

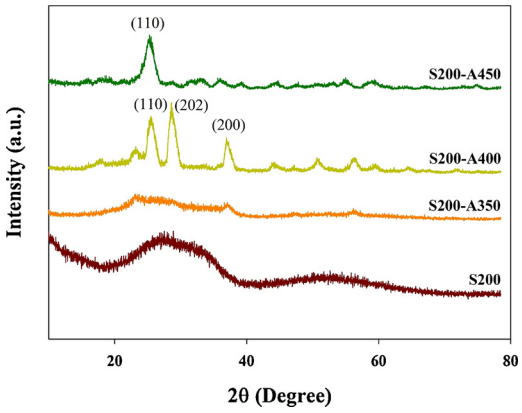

Fig. 2. XRD patterns of as-sputtered and annealed Ta_2O_5.

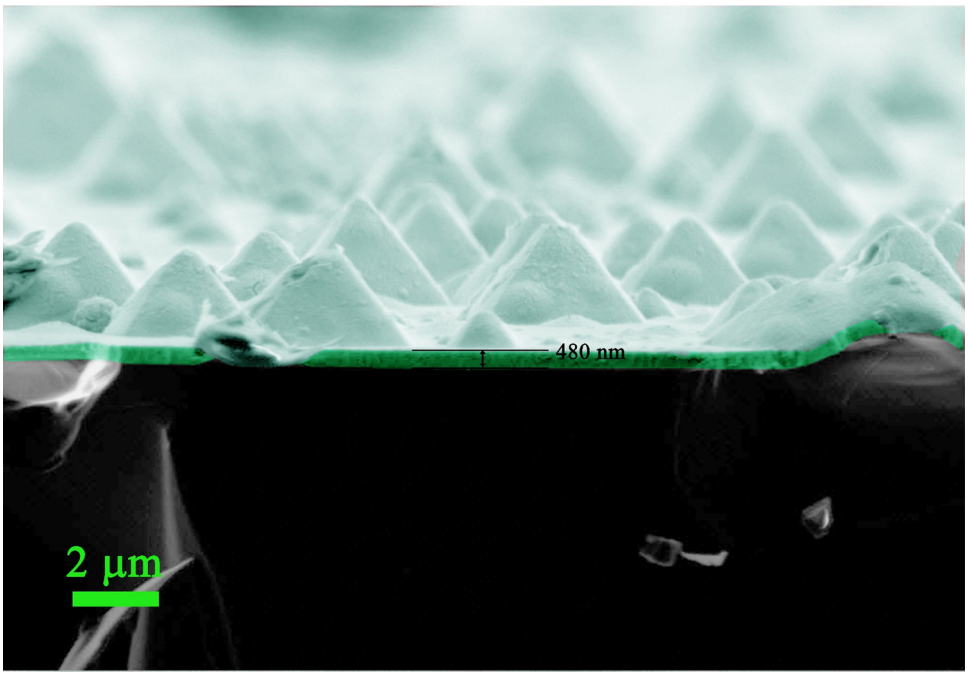

Fig. 3. Cross-sectional image of Ta_2O_5 film sputtered at 200 °C (colour contrast was applied to distinguish the Ta_2O_5 film from the underlying Si substrate).

However, as the annealing temperature is increased to 400 °C, several distinct peaks are observed. Although F.X. Jiang et. al found that at Ta_2O_5 exhibits orthorhombic phase after a film being annealed at above 700 °C [16], it was found that at 450 °C one distinct peak was centered at 25.00°, corresponding to body-centered orthorhombic phase crystals with (110) plane. This distinct peak seems to dominate other peaks such as (200), (202), (300) and (310) which existed at 400 °C. The lack of crystalline peaks for the samples annealed at 350 °C confirms the amorphous nature of the films. Several peaks observed for 400 °C indicated the shift of the film's amorphous nature to polycrystalline. At 450 °C the film showed evidence of crystallinity when (110) plane dominated other phases. The increase in crystallinity was also depicted in the increase in peak intensity of (110) plane from 400 °C to 450 °C in the XRD patterns. All the films showed a relative right peak shift from the reference peak (PDF 01-073-0005) suggesting presence of compressive stress within the film. The observed displacement of the diffraction peaks indicates a lattice contraction towards a formation of solid solution [17]. The stress gradually decreased for higher annealing temperature indicating stress relieve at higher energy. This also shows in the growth of (110) peak and replacing the (200) and (202) peak in sample annealed at 450 °C.

FESEM in Fig. 3 shows pyramid shaped surface morphology for all the annealing temperatures, which suggests the increase of the surface area. Hence the overall area for electrochemical reaction to take place is increased. The pyramid shaped surface morphology was a result of the RCA cleaning that involves the use of liquid etchants in the removal of exposed areas of the wafer. Isotropic or anisotropic profiles can be achieved, depending on the crystalline orientation of the silicon wafer and the etchants used in the process [18]. Thin films with higher substrate temperature during sputtering exhibit smoother and better adhesion to the etched silicon substrates. Earlier experiments show Ta_2O_5 sample with lower substrate temperature of RT peels off, whereas sample deposited at higher substrate temperature of 200 °C shows no peeling off.

Fig. 4 shows SEM of the samples that were annealed at 350 °C, 400 °C, and 450 °C. The appearance of sample in Fig. 4(a) shows a rough and porous surface which was observed for the thin film annealed at 350 °C. As the annealing temperature increased to 400 °C, as shown in Fig. 4(b), the Ta_2O_5 appeared to be rough and peeling off from the pyramid structure on the silicon substrate. This shows that the annealing temperature is not sufficient for the deposited Ta_2O_5 to adhere on to the pyramid structures. Fig. 4(c) displays the SEM image of Ta_2O_5 that was annealed at 450 °C. In this sample, the size of pyramids appears smaller and more compact than sample annealed at lower temperatures. The film shows that the pyramid structure throughout the silicon substrate was homogenous. There was still some peeling off observed but lesser than previous samples.

Cyclic voltammetry measurements were carried out in a typical three-electrode cell. Fig. 5 shows the CV results of Ta_2O_5 that was annealed at 350 °C, 400 °C, and 450 °C and the combination of all CV results. CV results of sample annealed at 350 °C appears to have a complete cyclic activity with considerable amount of noise resulting in very less electrochemical surface area (ECSA). CV results of sample annealed at 400 °C, shown in (b) exhibited substantial leve of noise. It appears to be cyclic but the ECSA is indeterminate because the high amount of noise. CV results of sample annealed at 450 °C the most promising cyclic activity with lesser noise and the ECSA seems higher than that of sample annealed at 350 °C but is still not significant enough to result in an effective ORR. Noise in these results indicates less or no cyclic activities in the samples possibly as a result of very low signal to noise ratio (SNR). The recorded noise seems to reduce or at least SNR seemed to increase with the increase of temperature, which was accompanied by

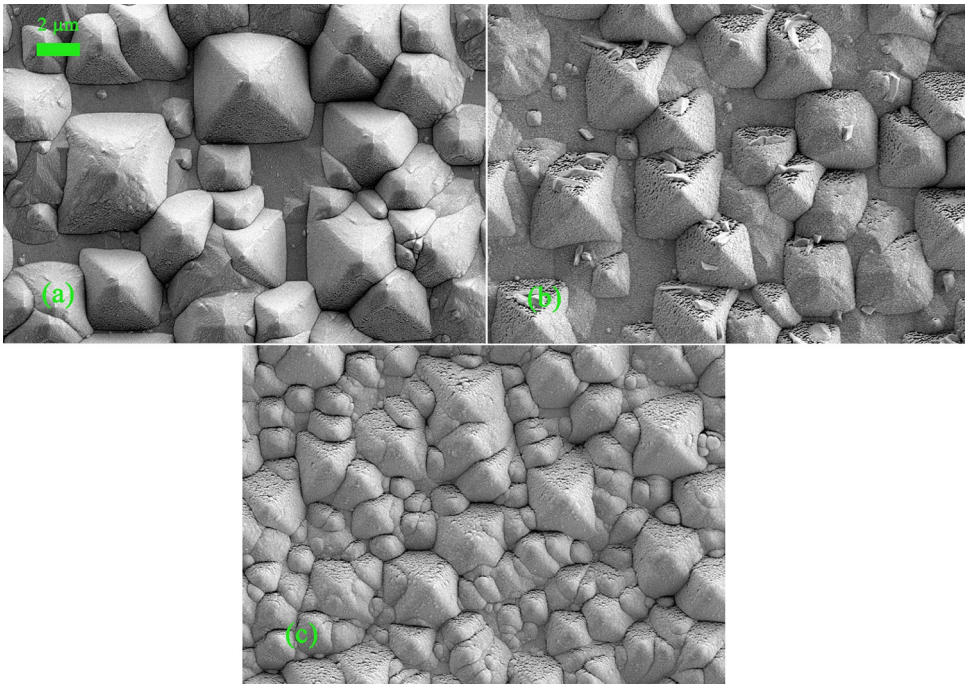

Fig. 4. SEM image of Ta_2O_5 films annealed at (a) 350 °C, (b) 400 °C, and (c) 450 °C.

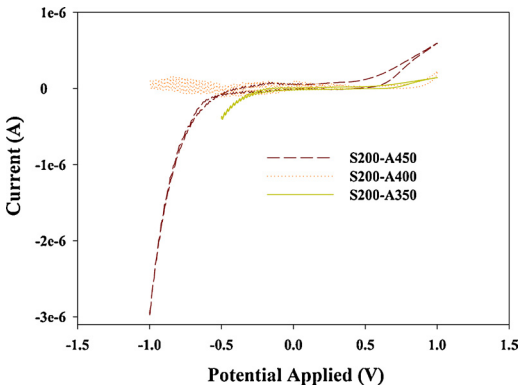

Fig. 5. CV of Ta_2O_5 films annealed at different temperatures of (a) 350 °C, (b) 400 °C, and (c) 450 °C.

improved crystallinity. This is supported by the previous XRD results which show samples with higher substrate temperature during sputtering obtained smoother and better adhesion to the etched silicon substrates.

It was evident from the structural, morphological and electrochemical analysis of the films, that higher temperature of 450 °C yielded better performance towards achieving an effective catalyst. But to further improve the ORR, the substrate temperature was increased to 400 °C keeping the annealing temperature fixed at 450 °C. The resulting films clearly showed better cyclic activity shown in the Fig. 6. In the first cycle, the curve is not in a general shape as it is speculated that this anomaly is due to a "formation" effect associated with the development of the electrode during the first discharge [19]. After the first cycle until its third cycle, the scan shows repeating and stable shape, as presented in Fig. 6. At the point before the peak corresponding to the reduction, a small amount of Ta_2O_5 has been consumed at the electrode surface [20]. At 1.0 mV the maximum reduction current in the voltammetric wave is evident and the diffusion layer is suspected to increase in thickness [20]. After this significant point, current is decreasing with the increasing potential and the concentration of Ta_2O_5 at the electrode surface approaches to close to zero, rendering this part of the CV curve in diffusion mode. After the voltammetric scan is reversed at 0.2 mV, the electrode potential is insufficient to reduce or oxidize Ta_2O_5. At 0.1 mV shows the peak in the reverse scan, this will also show the build-up or depletion of catalyst [20]. Higher substrate temperature of 400 °C with annealing temperature of 450 °C yielded clear cyclic activity with a significant noise reduction and ECSA improvement. It shows the activity of Ta_2O_5 as a catalyst towards H_2O reduction. The slight reduction peak is found at 0.8 V. The peak size and peak position depend on the composition of the catalyst as discussed by Wu.T et.al. [21]. This is also supported by Alexander I. et. al which indicates that Ta_2O_5 demonstrated chemical sensitivity toward catalysts at high temperatures at above

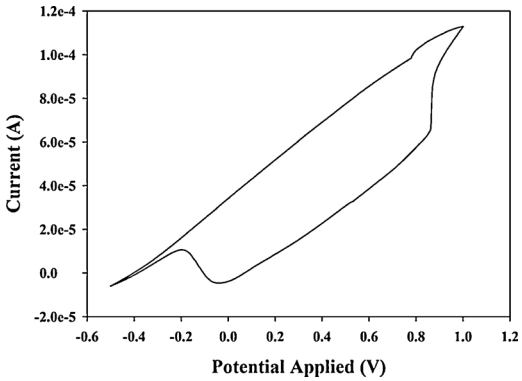

Fig. 6. Cyclic voltammetry of sputtered Ta_2O_5 thin film at 400 °C and annealed at 450 °C.

400 °C [22]. This is also confirmed by Jha N. et. al., that catalytic activity improves with the increase in reactive surface which can be attainable with higher thermal energy and improved support material [23]. Fig. 7(a) shows the SEM image of the surface morphology and cross section of the sample that was annealed at 450 °C with a new T_{sub} of 400 °C. The pyramid size appears to be smaller and more compact with significant reduction of peeling off. It can be seen in Fig. 7(b), that the Ta_2O_5 deposits homogenously on the textured silicon substrate with a film thickness of 700 nm. The lack of homogeneity in the lower T_{sub} and lower annealing temperature was also confirmed by the inability to acquire cross section images as uniform as found in Fig. 7(b). The XRD results of this new sample also supported the results from CV and SEM. It can be seen from the Fig. 8, that the peak (110) intensity increased significantly by raising the T_{sub} from 200 °C to 400 °C suggesting further improvement in crystallinity of the film. The FWHM value also decreased from 1.54° to 1.22° indicating grain growth.

All of the above analysis suggest that the improvement of this outcome is due to the sufficient thermal energy provided by the higher deposition temperature of 400 °C followed by higher annealing temperature of 450 °C. It is assumed that higher thermal energy is required to obtain the desired crystallinity. C. Chaneliere explained that annealing in oxygen ambient at a temperature above 650 °C will reduce the oxygen deficiency observed in as-deposited Ta_2O_5 and achieve crystallinity [13]. This is supported by A. S. Arico et. al., that stated the crystallographic structure plays a significant role being the oxygen reduction catalyst with a structure sensitive process [24]. Improved crystalline structure is needed in order for Ta_2O_5 to acquire effective electrochemical catalyst properties. It can be seen from the Fig. 9, the relative peak intensity of Ta_2O_5 (110) with respect to the other two competing peaks

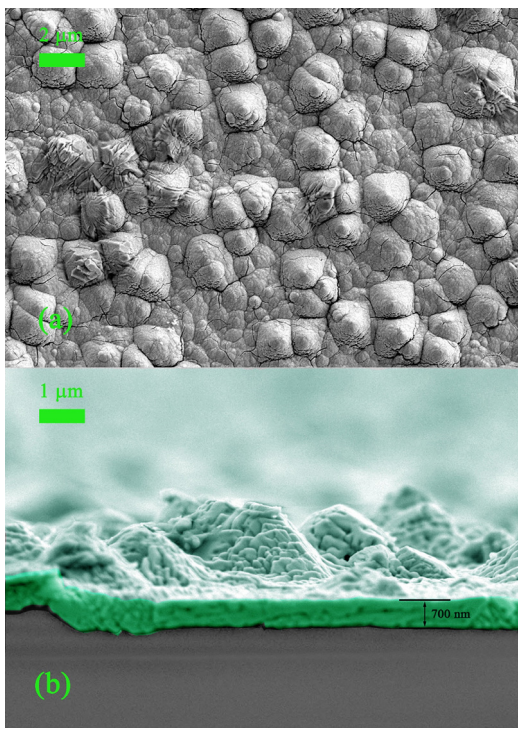

Fig. 7. SEM images of Ta_2O_5 thin film sputtered at 400 °C and annealed at 450 °C (a) surface morphology (b) cross section.

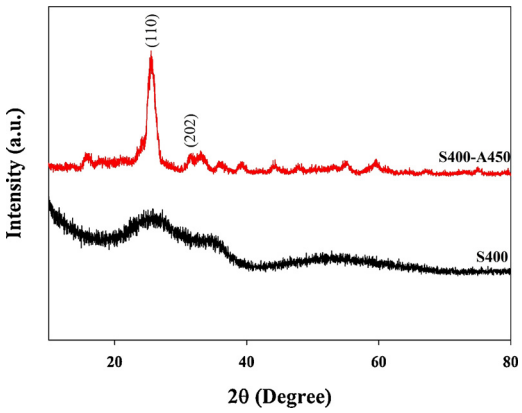

Fig. 8. XRD spectra of as-sputtered (S400) and annealed (S400-A450) Ta_2O_5 thin film.

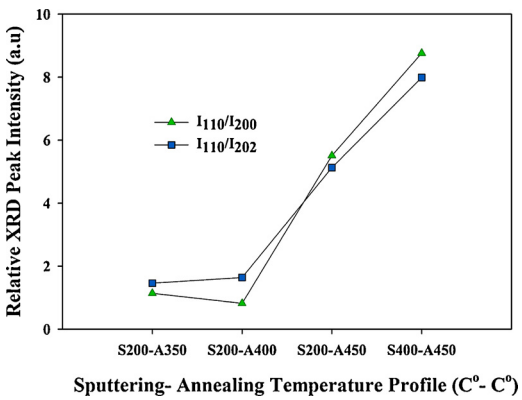

Fig. 9. Relative XRD peak intensities of $I_{(110/200)}$ and $I_{(110/202)}$ of Ta_2O_5 thin films at various sputtering temperature (S) and annealing (A) conditions.

(200) and (202) grew larger with increase in both sputter deposition temperature and post deposition annealing temperature suggesting increase in crystallinity. The analysis of electrical properties of Ta_2O_5 is not extensively performed in existing literature as a potential catalyst. It is noteworthy to mention that, improvement of crystallinity and electrochemical performance of Ta_2O_5 was

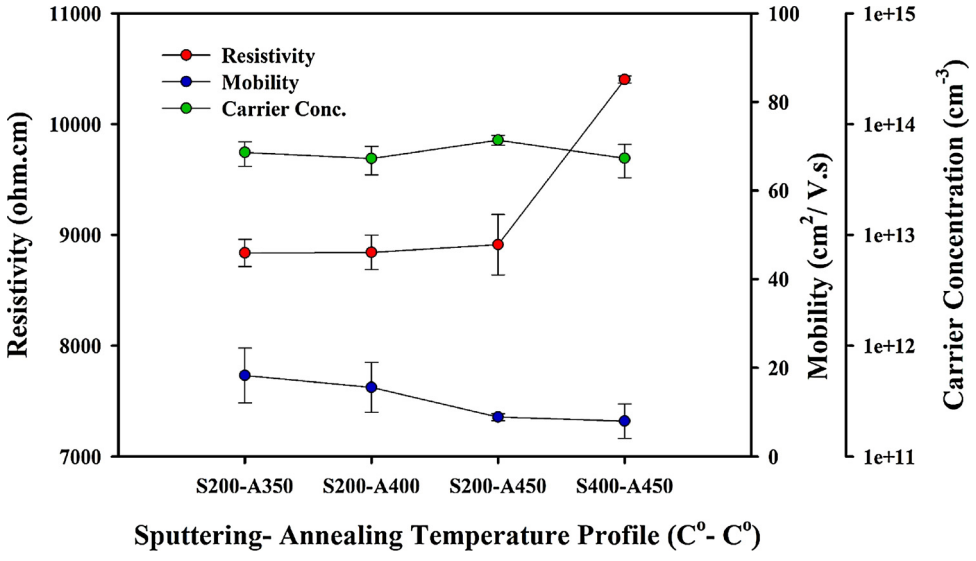

Fig. 10. Electrical properties of Ta_2O_5 thin films at various sputtering (S) and annealing (A) temperatures.

accompanied by a slow but steady increase in film resistivity obtained from Hall effect measurement shown in Fig. 10. The decline in resistivity was accompanied by a drop in mobility values while carrier concentration remained somewhat insignificantly affected. The insulating nature of Ta_2O_5 film is well known [25] and also supported by the resistivity value of 10^4-10^5 ohm.cm observed from the Hall effect measurement. Fig. 10 also shows significant increase in Ta_2O_5 resistivity with increase in sputtering and annealing temperature which can be correlated with the improvement in catalytic activity shown by Ta_2O_5 in the same range of deposition and annealing temperature. All the films exhibited carrier concentration and electrical mobility in the range of 10^{13}–10^{14} cm^{-3} and 5–20 cm^2/(V-s) respectively. We suggest that the improvement of its insulating properties linked to the increasing of catalytic activity. From our electrical charge point of view, a higher degree of insulation prohibits external electrical interference to the intended chemical redox.

4. Conclusions

Ta_2O_5 thin film can be a promising replacement for Pt as a catalyst in aim of favoring the O_2 reduction reaction in catalytic activity. This study investigated the performance dependence of the film to various deposition and post deposition temperature treatment. It was found that a higher deposition temperature i.e. 400 °C together with subsequent annealing temperature of 450 °C result in a Ta_2O_5 film that has improved structural, morphological and electrochemical property needed for an effective catalyst in fuel cells. Upon annealing, Ta_2O_5 films achieved better crystallinity consisting of orthorhombic phases. From the results shown, it can be proven that the higher degree of insulating nature of Ta_2O_5 is conducive to its catalytic activity. The proposed catalyst shows better enhancement for oxygen reduction reaction (ORR) in prolonged time of continuous potentiostatic electrolysis as to be used in fuel cells.

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References

[1] R. Othman, A.L. Dicks, Z. Zhu, Non precious metal catalysts for the PEM fuel cell cathode, Int. J. Hydrogen Energy 37 (2012) 357–372, http://dx.doi.org/10.1016/j.ijhydene.2011.08.095.
[2] Z. Awaludin, T. Okajima, T. Ohsaka, Preparation of reduced tantalum pentoxide by electrochemical technique for oxygen reduction reaction, J. Power Sources 268 (2014) 728–732, http://dx.doi.org/10.1016/j.jpowsour.2014.06.102.
[3] A. Ishihara, S. Doi, S. Mitsushima, K. Ota, ichiro, Tantalum (oxy)nitrides prepared using reactive sputtering for new nonplatinum cathodes of polymer electrolyte fuel cell, Electrochim. Acta 53 (2008) 5442–5450, http://dx.doi.org/10.1016/j.electacta.2008.02.092.
[4] J. Lobato, H. Zamora, P. Canizares, J. Plaza, M.A. Rodrigo, Microporous layer based on SiC for high temperature proton exchange membrane fuel cells, J. Power Sources 288 (2015) 288–295, http://dx.doi.org/10.1016/j.jpowsour.2015.04.102.
[5] S. Aravamudhan, A.R.A. Rahman, S. Bhansali, Porous silicon based orientation independent, self-priming micro direct ethanol fuel cell, Sens. Actuators A Phys. 123–124 (2005) 497–504, http://dx.doi.org/10.1016/j.sna.2005.03.069.
[6] T. Pichonat, B. Gauthier-Manuel, D. Hauden, A new proton-conducting porous silicon membrane for small fuel cells, Chem. Eng. J. 101 (2004) 107–111, http://dx.doi.org/10.1016/j.cej.2004.01.019.
[7] M. Jaouadi, W. Dimassi, M. Gaidi, R. Chtourou, H. Ezzaouia, Nanoporous silicon membrane for fuel cells realized by electrochemical etching, Appl. Surf. Sci. 258 (2012) 5654–5658, http://dx.doi.org/10.1016/j.apsusc.2012.02.050.
[8] S. Sharma, B.G. Pollet, Support materials for PEMFC and DMFC electrocatalysts—A review, J. Power Sources 208 (2012) 96–119, http://dx.doi.org/10.1016/j.jpowsour.2012.02.011.
[9] F. Zoubian, E. Tomasella, A. Bousquet, Potential of TaO X N Y thin films deposited by reactive sputtering as antireflective coatings: composition and optical properties, Adv. Mater. Res. 324 (2011) 73, http://dx.doi.org/10.4028/www.scientific.net/AMR.324.73.
[10] E. Bash, Synthesis and characterization of TaO based nanowire heterostuctures for photocatalysis, PhD Proposal 1 (2015), http://dx.doi.org/10.1017/CBO9781107415324.004.
[11] H.S.I. Park, Optimization of KOH Wet Etching Process in Silicon Nanofabrication, (2001), pp. 3–7.
[12] L.-Y. Cao, B.-H. Zhang, L.-H. Lu, Fabrication of large-area platinum-coated silicon nanowire arrays and its application to enhanced electrocatalytic activity for methanol oxidation, Chin. J. Anal. Chem. 39 (2011) 994–997, http://dx.doi.org/10.1016/S1872-2040(10)60455-0.
[13] C. Chaneliere, J. Autran, R.A. Devine, B. Balland, Reports: a review, J. Mater. Sci. Eng. 22 (1998) 269–322.
[14] J.S. Lee, S.J. Chang, J.F. Chen, S.C. Sun, C.H. Liu, U.H. Liaw, Effects of O_2 thermal annealing on the properties of CVD Ta_2O_5 thin films, Mater. Chem. Phys. 77 (2002) 242–247.
[15] K. Kukli, J. Aarik, A. Aidla, O. Kohan, T. Uustare, V. Sammelselg, Properties of tantalum oxide thin films grown by atomic layer deposition, Thin Solid Films 260 (1995) 135–142, http://dx.doi.org/10.1016/0040-6090(94)06388-5.
[16] Jian F-XJF-X, S.K. Kurinec, Tantalum oxide thin films for microelectronic applications, Proc. Eleventh Bienn. Univ. Ind. Microelectron. Symp. (1995) 101–104, http://dx.doi.org/10.1109/UGIM.1995.514124.
[17] I. Radev, G. Topalov, E. Lefterova, G. Ganske, U. Schnakenberg, G. Tsotridis, et al., Optimization of platinum/iridium ratio in thin sputtered films for PEMFC cathodes, Int. J. Hydrogen Energy 37 (2012) 7730–7735, http://dx.doi.org/10.1016/j.ijhydene.2012.02.015.
[18] T.S. Monteiro, P. Kastytis, L.M. Gonçalves, G. Minas, S. Oh, S. Oh, Dynamic wet etching of silicon through isopropanol alcohol evaporation, Micromachines (2015) 1534–1545, http://dx.doi.org/10.3390/mi6101437.
[19] M. Green, E. Fielder, B. Scrosati, M. Wachtler, J.S. Moreno, E.S. Lett, et al., Structured silicon anodes for lithium battery applications, Electrochem. Solid State Lett. 6 (2003) 1–6, http://dx.doi.org/10.1149/1.1563094.
[20] D.A.C. Brownson, Banks CE. Interpreting Electrochemistry, (2014), http://dx.doi.org/10.1007/978-1-4471-6428-9.
[21] S.J.C. Cleghorn, D.K. Mayfield, D.A. Moore, J.C. Moore, G. Rusch, T.W. Sherman, et al., A polymer electrolyte fuel cell life test : 3 years of continuous operation, J. Power Sources 158 (2006) 446–454, http://dx.doi.org/10.1016/j.jpowsour.2005.09.062.
[22] A. Imbault, Y. Wang, P. Kruse, E. Strelcov, E. Comini, G. Sberveglieri, et al., Ultrathin gas permeable oxide membranes for chemical sensing : nanoporous Ta_2O_5 test study, Materials (Basel) (2015) 6677–6684, http://dx.doi.org/10.3390/ma8105333.
[23] N. Jha, R.I. Jafri, N. Rajalakshmi, S. Ramaprabhu, Graphene-multi walled carbon nanotube hybrid electrocatalyst support material for direct methanol fuel cell, Int. J. Hydrogen Energy 36 (2011) 7284–7290, http://dx.doi.org/10.1016/j.ijhydene.2011.03.008.

[24] a.S. Aricò, a. Stassi, E. Modica, R. Ornelas, I. Gatto, E. Passalacqua, et al., Performance and degradation of high temperature polymer electrolyte fuel cell catalysts, J. Power Sources 178 (2008) 525–536, http://dx.doi.org/10.1016/j.jpowsour.2007.10.005.
[25] R. Baca, J.A. Andraca, M.G. Arellano, GRP and RPS. Development of ZnO/Ta2O5 heterojunction using low-temperature technological processes, Mater. Res. Soc. 33 (2006) 1001–1006, http://dx.doi.org/10.1557/opl.2011.