Understanding oxygen evolution reaction and charge transfer behavior at the electrode-electrolyte interface using pulsed laser-deposited ruthenium oxide thin films

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Ruthenium oxide (RuO_2), regarded as one of the benchmarks for oxygen evolution reaction electrocatalyst materials during water splitting, has been grown in epitaxial thin film form using a pulsed laser deposition method. The precision in the RuO_2 thin films structure, surface orientation, and oxygen stoichiometry have been investigated using high-resolution structural characterization techniques that include x-ray diffraction, x-ray reflectometry, Raman Spectroscopy, x-ray photoelectron spectroscopy, and transmission electron microscopy. Following the structural characterization, the films were subjected to four-probe resistivity and Hall measurements via the Vander Pauw method and electrochemical measurements via a three-electrode system. The control in the RuO_2 thin film surface orientation was realized using high-quality single crystal rutile Titanium oxide (TiO_2) substrates with (100), (101), and (110) orientations. Due to different atomic arrangements of Ru and O atoms and interatomic orbital positions in these planes, these films profoundly differ in electrical resistivity, charge carrier density, and dominance in the nature of charge carriers, hence, in the net electrochemical properties. For example, RuO_2 thin film grown on the TiO_2 substrates with (100), (101), and (110) orientations at 600 °C and 75 mTorr oxygen pressure using 4800 laser pulses and 2.5 J/cm^2 were found to possess electrical resistivity of 1.86×10^{-5}, 5.91×10^{-5}, and 2.09×10^{-5} $\Omega\cdot$cm, charge carrier density of 2.55×10^{23}, -3.63×10^{23}, and $2.03\times10^{23}/cm^3$, and Hall coefficient of 2.45×10^{-5}, -1.72×10^{-5}, and 3.08×10^{-5} cm^3/C, respectively. The electrochemical measurements and analysis carried out on the RuO_2 thin film with (101) orientation displays the highest electrochemical current density (1.25 mA/cm^2) and the lowest onset potential (1.49V vs. RHE) among the RuO_2 films with other orientations. The next part of our study has focused on understanding the role of oxygen defects in RuO_2 thin films in their electrochemical properties. For this purpose, RuO_2 thin films were on TiO_2 substrates with (110) orientation at substrate temperatures of 500, 600, and 700 °C. After the deposition was over, all the films were cooled to room temperature from the deposition temperature in two hours under the high vacuum conditions of $2\text{-}3\times10^{-6}$ Torr. The x-ray photoelectron spectroscopy results carried out on these films have shown that the binding energy center of the corresponding Ru3d doublet peaks, made of $Ru3d_{5/2}$ and $Ru3d_{3/2}$, for the 700 °C sample is 0.5 eV lower than for the 500 and 600 °C samples. These results indicate the formation of oxygen vacancies with the variation of Ru oxidation states near the top surface of the thin film. According to the electrochemical measurement, the 700 °C sample displays the lowest overpotential (500 mV) at the current density of 10 mA/cm^2 and also the lowest Tafel slope (101.6 mV/dec) than others. Additionally, the electrochemical double larger capacitance of the deposited thin films, measured by different

methods, indicates that the 700 °C has the highest value of 61.20 μF, compared with the 26.87 and 28.35 μF for 500 and 600 ° samples, respectively.