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A. Abduvalov*, Zh. Taubaldiyeva, K. Baigarin
Nazarbayev University, Astana, Kazakhstan
*e-mail: alshyn.abduvalov@nu.edu.kz

INFLUENCE OF DEPOSITION PARAMETERS ON THE SURFACE MORPHOLOGY AND PHOTOCATALYTIC PROPERTIES OF WO_3 THIN FILMS SYNTHESIZED BY MAGNETRON SPUTTERING AT A GLANCING ANGLE DEPOSITION

The growing need for sustainable energy has intensified research on photoelectrochemical (PEC) water splitting for hydrogen production. Tungsten trioxide (WO_3) is a promising photoanode due to its stability, suitable bandgap (~2.4–2.8 eV), and strong visible-light absorption. However, performance limitations arise from short hole diffusion length and high recombination rates. This study examines the effect of substrate rotation during magnetron sputtering on WO_3 thin films' morphology and PEC performance, employing the glancing angle deposition technique to achieve nanostructured films that enhance light trapping.

SEM analysis reveals that films deposited without rotation exhibit greater porosity, improving light absorption and charge transport. As a result, these films demonstrate higher photocurrent density and enhanced electrochemical impedance properties. These findings highlight the significance of deposition dynamics in optimizing WO_3 for PEC applications. This study provides insights into controlling thin film morphology to improve PEC efficiency, contributing to the development of more effective water-splitting devices.

Keywords: tungsten trioxide, PEC water splitting, magnetron sputtering, glancing angle deposition, thin film deposition, nanostructured photoanodes.

А. Абдувалов*, Ж. Таубалдиева, Қ. Байғарин
Назарбаев Университет, Астана, Қазақстан
*e-mail: alshyn.abduvalov@nu.edu.kz

Магнетронды шаңдату арқылы сүйір бұрышпен синтезделген WO_3 жұқа пленкалардың беттік морфологиясы мен фотокаталитикалық қасиеттеріне синтез параметрлерінің әсері

Тұрақты энергия көздеріне деген өсіп келе жатқан қажеттілік сутегі өндіруге арналған фотоэлектрохимиялық (ФЭХ) су ыдырауын зерттеуді жандандыруда. Вольфрам триоксиді (WO_3) химиялық тұрақтылығы, қолайлы тыйым салынған аймағының ені (~2,4–2,8 эВ) және көрінетін жарықты тиімді сіңіру қабілеті арқасында перспективалы фотоанодтық материал болып саналады. Алайда, оның тиімділігі тасымалдау ұзындығының қысқалығымен және фотогенерацияланған заряд тасымалдаушылардың жоғары рекомбинация жылдамдығымен шектеледі. Осы зерттеуде магнитрондық шашырату процесінде субстраттың айналу жылдамдығының WO_3 жұқа қабықтарының морфологиясы мен ФЭХ қасиеттеріне әсері зерттелді. Наноқұрылымды қабықтардың жарықты тиімді ұстап қалуын қамтамасыз ету үшін қиғаш бұрышпен шөктіру (glancing angle deposition) әдісі қолданылды.

Сканерлеуші электрондық микроскопия (СЭМ) нәтижелері субстрат айналымынсыз алынған қабықтардың жоғары кеуектілікке ие екенін көрсетті, бұл жарық сіңіруді және заряд тасымалын жақсартады. Нәтижесінде, мұндай қабықтар жоғары фототоқ тығыздығын және жетілдірілген электрохимиялық сипаттамаларды көрсетті. Алынған нәтижелер WO_3 негізіндегі ФЭХ жүйелерінің тиімділігін арттыруда шөктіру параметрлерін оңтайландырудың маңыздылығын айқындайды. Бұл зерттеу жұқа қабық морфологиясын басқару арқылы ФЭХ тиімділігін арттыруға ықпал етіп, су ыдырату технологияларын дамытуға үлес қосады.

Түйін сөздер: вольфрам триоксиді, фотоэлектрохимиялық су ыдырауы, магнитрондық шашырату, қиғаш бұрышпен шөктіру, жұқа қабықты жабындар, наноқұрылымды фотоанодтар.

А. Абдувалов*, Ж. Таубалдиева, К. Байгарин
Назарбаев Университет, Астана, Казахстан
*e-mail: alshyn.abduvalov@nu.edu.kz

Влияние параметров осаждения на морфологию поверхности и фотокаталитические свойства тонких пленок WO_3, полученных методом магнетронного распыления при скользящем угле осаждения

Возрастающая потребность в возобновляемых источниках энергии стимулирует активные исследования фотоэлектрохимического (ФЭХ) расщепления воды для производства водорода. Триоксид вольфрама (WO_3) является перспективным материалом для фотоанода благодаря своей химической стабильности, оптимальной ширине запрещенной зоны (~2,4–2,8 эВ) и высокой поглощающей способности в видимом диапазоне. Однако его эффективность ограничивается малой длиной диффузии дырок и высокой скоростью рекомбинации фотогенерированных носителей заряда. В данной работе исследуется влияние скорости вращения подложки при магнетронном распылении на морфологию и ФЭХ свойства тонких пленок WO_3 с применением метода осаждения при скользящем угле (glancing angle deposition) для формирования наноструктурированной поверхности, улучшающей поглощение света.

Анализ сканирующей электронной микроскопии (СЭМ) показал, что пленки, осажденные без вращения подложки, обладают большей пористостью, что способствует повышенному поглощению света и улучшению транспорта заряда. В результате такие пленки имеют более высокую плотность фототока и улучшенные электрохимические характеристики. Полученные результаты демонстрируют важность выбора параметров осаждения для оптимизации свойств WO_3 в ФЭХ приложениях. Проведенное нами исследование вносит вклад в развитие методов формирования тонкопленочных материалов, способствуя созданию более эффективных систем для расщепления воды с целью генерации водорода.

Ключевые слова: триоксид вольфрама, фотоэлектрохимическое расщепление воды, магнетронное распыление, осаждение при скользящем угле, тонкопленочные покрытия, наноструктурированные фотоаноды.

Introduction

The increasing demand for clean and sustainable energy sources has driven extensive research into photoelectrochemical (PEC) water splitting as a promising method for hydrogen production.

Among the various metal oxide semiconductor materials investigated for PEC applications, tungsten trioxide (WO_3) has emerged as a highly attractive candidate due to its comparable chemical stability, suitable bandgap (~2.4–2.8 eV), and strong visible-light absorption [1,2]. WO_3 serves as an efficient photoanode in PEC systems, facilitating water oxidation under solar illumination [3,4]. Its relatively deep valence band edge enables sufficient driving force for oxygen evolution, while its good electron mobility minimizes charge recombination losses. However, despite these advantages, WO_3 suffers from challenges such as weak absorbance in visible region (more than 450 nm), poor long-term stability in alkaline conditions, short hole diffusion length, and fast recombination of photogenerated carriers [5,6].

To address these limitations, researchers have explored various strategies, including nano-structuring [7], doping [8,9], heterojunction or composite formation [10], and phase changes [11–13], to improve the PEC performance of WO_3 thin films. Nanostructuring of WO_3 thin films plays a critical role in enhancing their performance PEC water splitting applications. The efficiency of PEC processes largely depends on the material's ability to absorb light. Nanostructured WO_3 films, such as those with porous or columnar architectures, offer several advantages in this context [14]. First,

increased surface area resulting from porosity provides more active sites for water oxidation reactions, improving photocurrent generation. Second, nanostructuring enhances light trapping and scattering, leading to improved optical absorbance, especially in the visible spectrum where WO_3 is active. This higher absorbance increases the number of photogenerated electron–hole pairs available for redox reactions. Additionally, the porous structure shortens the diffusion paths for photogenerated holes, thereby reducing recombination losses and enhancing charge separation efficiency. Together, these effects contribute to higher photocurrent density and better overall PEC behavior, making controlled nanostructuring a key strategy in the design of efficient WO_3-based photoanodes.

In previous reported works, using "glancing angle deposition" method (GLAD) [15], Limwichean et al. studied dependence of PEC properties of sputter deposited WO_3 thin films on substrate positions from target material [14]. They reported growth of more porous WO_3 nanoforest thin films at higher glancing angle and at closer distance between substrate and target. However, they observed better PEC activity on sample deposited at GLAD 61.9° and 85-mm substrate-target distance. Another most important parameter that may affect the growth and PEC of sculptured WO3 is substrate rotation speed.

This report aims to check effect of the "substrate rotation speed" of WO_3 thin films to its photoactivity and thin film growth while sputter depositing. Surface, morphology and crystalline structures of obtained WO_3 thin films deposited by glancing angle magnetron sputtering under stationary (0 rpm) and rotating substrate (15 rpm) conditions were thoroughly studied and analyzed using electron microscopy and x-ray diffractometer. PEC properties are evaluated and discussed. Substrate rotation plays a crucial role in magnetron sputtering deposition of WO_3 thin films by ensuring uniform thickness. Without rotation, the deposition rate varies across the substrate, leading to non-uniform film thickness and inconsistent PEC performance.

Methodology

Synthesis. Initially, commercial FTO/Glass substrates were cleaned in ethanol by ultrasonic bath for 15 minutes. After, they were held for 15 minutes under UV-Ozone cleaner to remove organic contaminants from the surface. WO_3 nanoforest thin films were synthesized using Kurt Lesker magnetron sputtering system using W target (pure W, 99.9 %). The deposition was carried out under reactive sputtering using oxygen and argon gases in the chamber at overall 5 mTorr pressure. O_2/Ar flow rates were 21/33 sccm. The substrate-target distance was 13 cm. Before deposition, magnetron chamber was pumped down to $9*10^{-7}$ mTorr pressure to ensure high vacuum conditions and experiment contamination prevention. After deposition, all samples were annealed at 500 °C for 1 h on hotplate in air to make them crystalline.

For the experiment, "glancing angle deposition" method is used [15]. It helps to achieve nanostructured (nanoforest) WO_3 thin films that are beneficial for light trapping. Two sets of samples were prepared to study growth morphology and photocatalytic properties depending on substrate holder rotational speed: 0 rpm and 15 rpm. It is worth noting that grown thin films at 0 and 15 rpm have identical thickness to ensure elimination coming from thickness difference.

Characterization. Scanning electron microscopy (SEM) imaging was performed using a Carl Zeiss Crossbeam 540 GEMINI II system. The crystallographic phases of the samples were identified using a Rigaku SmartLab multifunctional X-ray diffractometer (XRD) equipped with CuKα radiation (λ = 0.1541 nm). Optical properties were evaluated using an Evolution 300 UV-Vis spectrophotometer.

For PEC, linear sweep voltammetry (LSV) measurements of the photoanodes were conducted using a CHI660E potentiostat in a standard three-electrode configuration, employing an Ag/AgCl reference electrode (3.5 M KCl). The electrolyte solution consisted of 0.16 M Na_2SO_4 at pH 7. A PLS-FX300HU solar simulator (AM 1.5, 100 mW/cm^2) was used to simulate solar illumination during all PEC experiments. The applied potentials were converted to the reversible hydrogen electrode (RHE) scale using the equation:

$$V_{RHE}=V_{Ag/AgCl}+0.059\cdot pH+0.205$$

where $V_{Ag/AgCl}$ is the measured potential and 0.205 V corresponds to the standard potential of the Ag/AgCl electrode (3.5 M KCl).

Electrochemical impedance spectroscopy (EIS) was performed under illumination using a frequency range of 1 Hz to 10 kHz with an AC amplitude of 50 mV at a DC bias of 0.68 V vs Ag/AgCl. The data were fitted to equivalent circuit models using the EIS Spectrum Analyzer software [16].

Results and discussions

Figure 1 shows the SEM images of WO_3 thin films that have a columnar microstructure with vertically aligned grains, characteristic of sputter-deposited films. The cross-sectional views (a, c) reveal a relatively dense structure with some gaps between columns, which may affect charge transport and film stability. The top-view images (b, d) display a cracked, granular morphology with well-defined grains, suggesting good surface coverage but potential mechanical instability due to the presence of cracks. The surface coverage of the WO_3 thin film deposited at 0 rpm in image (b) is approximately 76.19%, meaning that about 23.81% of the surface consists of cracks or voids. WO_3 thin film deposited at 15 rpm has 77.04% surface coverage indicating 22.96% of cracks or voids. The main difference in growth is density of columnar microstructure: thin films deposited at 15 rpm show accumulated bigger packs of columns with less distance between each column compared to more separated columns of sample grown at 0 rpm at same scale of area.

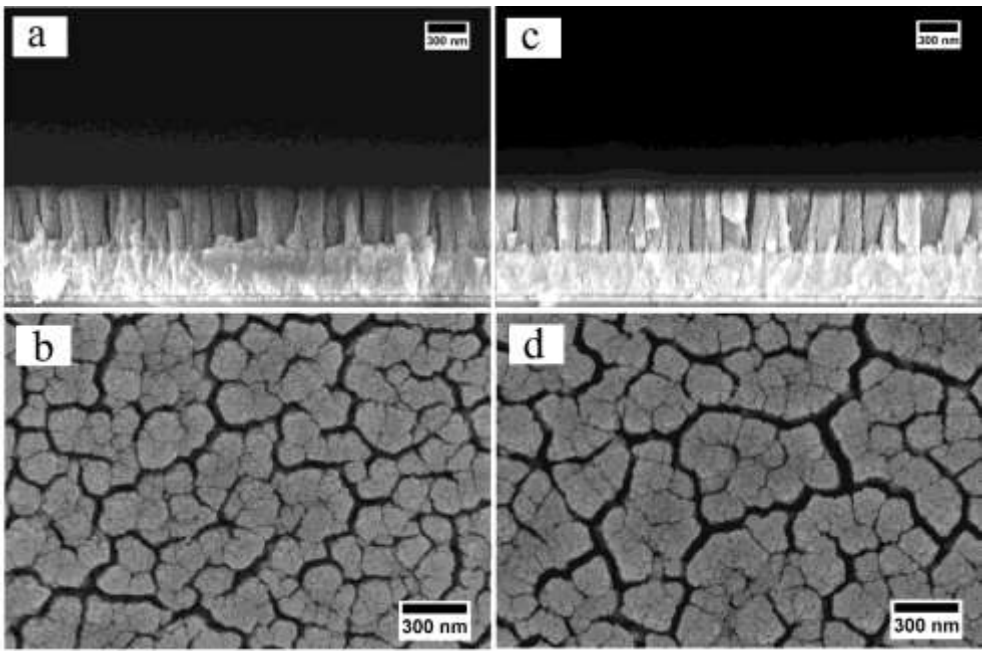

Figure 1 – Cross-sectional and surface SEM images of WO_3 thin films deposited by glancing angle magnetron sputtering under stationary - 0 rpm (a, b) and rotating substrate - 15 rpm (c, d) conditions

The crystalline structure of WO_3 thin films deposited by magnetron sputtering at different substrate holder rotational speeds (0 and 15 rpm) was examined using X-ray diffraction (XRD), and the results are shown in Figure 2. The XRD patterns of both samples display well-defined diffraction peaks corresponding to the triclinic phase of WO_3, in accordance with JCPDS card no. 00-032-1395. Prominent peaks are observed at 2θ values around 23.18°, 23.68°, 24.33°, 26.62°, 28.7°, 33.69° which correspond to the (002), (020), (200), (1-20), (1-1-2), (022) and FTO (200) planes of substrate respectively.

It can be seen that both samples, regardless of rotation speed, exhibit the same set of diffraction peaks, indicating that the crystal phase of WO_3 is preserved under both deposition conditions. However, noticeable differences in peak intensity and sharpness can be observed between the two. The sample deposited at 15 rpm (red pattern) shows slightly higher peak intensities and narrower peaks compared to the 0-rpm sample (black pattern), particularly in the (020) and (202) reflections. Despite the increase in rotation speed, no significant shift in peak positions was observed, indicating that there is no substantial strain or phase transformation induced by rotation. This suggests that the microstructural evolution induced by substrate rotation primarily affects the film's crystallinity rather than its phase composition.

The optical properties of obtained samples analysed by UV-Vis spectroscopy. Figure 3 shows absorbance spectra (a) and Tauc plots (b) for samples deposited at 0 and 15 rpm. Despite the differences in surface morphology as seen in SEM images, optical properties of the samples stay the same. Tauc plot method was used to define the band gap of films [17], and it is estimated as 3.05 eV for both samples.

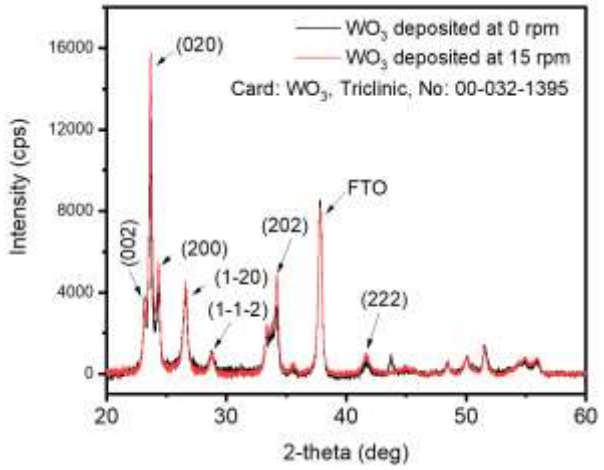

Figure 2 – XRD spectra of WO_3 thin films deposited by glancing angle magnetron sputtering under stationary and rotating substrate conditions

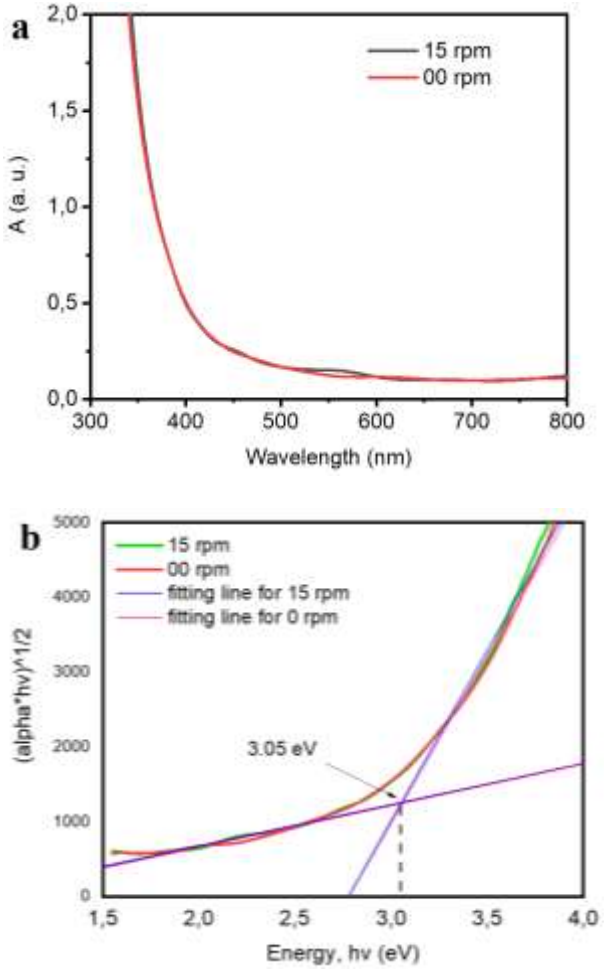

Figure 3 – Absorbance spectra (a) and Tauc plots (b) of WO_3 thin films deposited by glancing angle magnetron sputtering under stationary and rotating substrate conditions

The photoelectrochemical activity of the films was initially evaluated through LSV (Figure 4-a). Under illumination, the WO_3 thin film deposited at 0 rpm exhibited an 13 % enhanced photocurrent density compared to the film grown at 15 rpm at 1.23 V vs RHE scale (9.11^{-4} mA/cm^2 vs 8.05^{-4} mA/cm^2). The negligible current recorded under dark conditions for both samples confirmed the photo-induced nature of the observed responses. The improved photocurrent in the 0 rpm sample is indicative of enhanced charge separation and transport kinetics, which can be directly correlated with the superior surface morphology observed via SEM. To further assess the dynamic response of the electrodes under intermittent light conditions, chopped LSV measurements were conducted (Figure 4-b). The 0 rpm sample demonstrated a sharp and stable photocurrent response during light on/off cycles.

Electrochemical impedance spectroscopy was employed to probe the interfacial charge transfer properties under illumination (Figure 4-c). The Nyquist plots revealed that the 0 rpm film exhibited a smaller semicircle, indicative of lower charge transfer resistance (R_ct), compared to the 15 rpm counterpart. This observation suggests improved interfacial kinetics for the sample deposited at 0 rpm, and it agrees with the less photocurrent observed in the samples prepared at 15 rpm. Such correlation in dependence of charge transport properties on surface morphology is key factor that explains such PEC enhancement mechanisms. More packed structures on sample deposited at 15 rpm have longer distance for charge to reach surface and back contact than on sample deposited at 0 rpm. Close packed treelike structures deposited at 15 rpm show more charge transfer resistance at 2940 Ohm than 561 Ohm on more separated structures. Charge transfer resistance calculations were done using open-source EIS Spectrum Analyzer software by fitting the obtained data from EIS measurements.

The operational stability of the photoanodes was examined through chronoamperometry under continuous illumination at a fixed potential (Figure 4-d). The WO_3 sample deposited at 0 rpm more stable photocurrent generation over a 200-second duration. The enhanced stability of the 0 rpm sample can be attributed to its denser microstructure, which likely offers better protection against photocorrosion and mitigates charge trapping at defect sites.

Conclusion

The obtained data clearly demonstrate that substrate rotation during RF glancing angle magnetron sputtering significantly enhances the structural and functional properties of WO_3 thin films. Glancing angle magnetron deposition without rotation of substrate improved surface morphology,

leading to superior photocurrent generation, faster and more stable light response, and greater operational durability. These studies are critical for advancing and understanding growth and formation of WO_3-based photoelectrodes in solar-driven water splitting applications and other PEC systems. The findings highlight the importance of optimizing physical deposition parameters—particularly substrate motion—as a straightforward yet highly effective strategy for tuning the properties of metal oxide photoanodes.

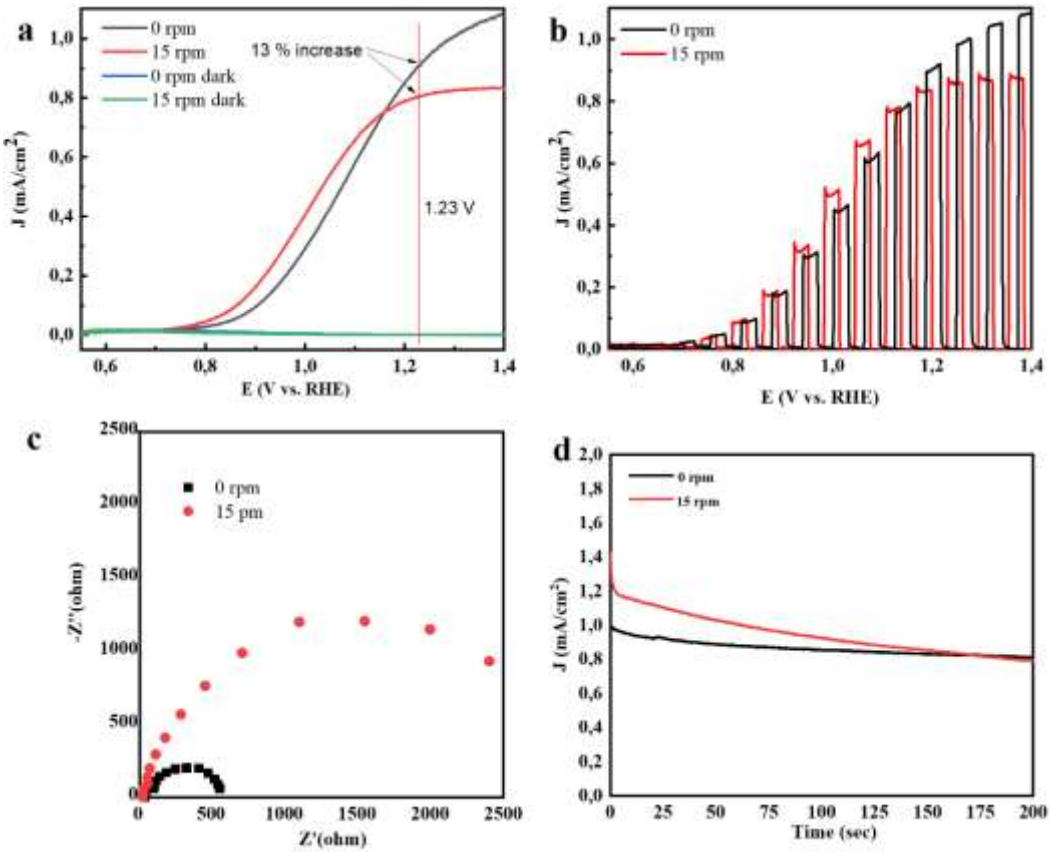

Figure 4 – LSV (a), chopped LSV (b), EIS (c) and current-time (d) plots of WO_3 thin films deposited by glancing angle magnetron sputtering under stationary and rotating substrate conditions

Gratitude, conflict of interest

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Information about authors:

1. **Alshyn Abduvalov** (corresponding author) – PhD in Physics, Researcher at Nazarbayev University, Astana, Kazakhstan, e-mail: alshyn.abduvalov@nu.edu.kz

2. **Zhamilya Taubaldiyeva** – MSc student at Nazarbayev University, Astana, Kazakhstan, e-mail: zhamilya.taubaldiyeva@nu.edu.kz

3. **Kanat Baigarin** – PhD in plasma physics and chemistry, Chief Officer for Sustainable Development at Nazarbayev University, Project PI, Astana, Kazakhstan, e-mail: kbaigarin@nu.edu.kz

Авторлар туралы мәлімет:

1. **Абдувалов Алшын** (автор корреспондент) – физика бойыншша PhD, Назарбаев Университетінің ғылыми қызметкері, Астана, Қазақстан, e-mail: alshyn.abduvalov@nu.edu.kz

2. **Таубалдиева Жәмиля –** Назарбаев университетінің магистранты, Астана, Қазақстан, e-mail: zhamilya.taubaldiyeva@nu.edu.kz

3. **Байғарин Қанат –** плазма физикасы және химия бойыншша PhD, Назарбаев Университетінің тұрақты даму жөніндегі бас директоры, PI жобасы, Астана, Қазақстан, e-mail: kbaigarin@nu.edu.kz