マテリアル先端リサーチインフラ利用報告書
ARIM User's Report

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課題データ / Project Data

課題番号 Project Issue Number	22HK0095
利用課題名 Title	Fabricating NiO photocathode under strong coupling for photoreduction reaction
利用した実施機関 Support Institute	北海道大学 / Hokkaido Univ.
機関外・機関内の利用 External or Internal Use	外部利用/External Use
ARIM半導体基盤PF 関連課題 Related to ARIM-SETI	指定なし / No Designation
横断技術領域 Cross-Technology Area	加工・デバイスプロセス/Nanofabrication 計測・分析/Advanced Characterization
重要技術領域 Important Technology Area	量子・電子制御により革新的な機能を発現するマテリアル/Materials using quantum and electronic control to perform innovative functions
キーワード Keywords	電子顕微鏡/Electron microscopy,スパッタリング/Sputtering,蒸着・成膜/Evaporation and Deposition,ALD,フォトニクス/ Photonics

利用者と利用形態 / User and Support Type

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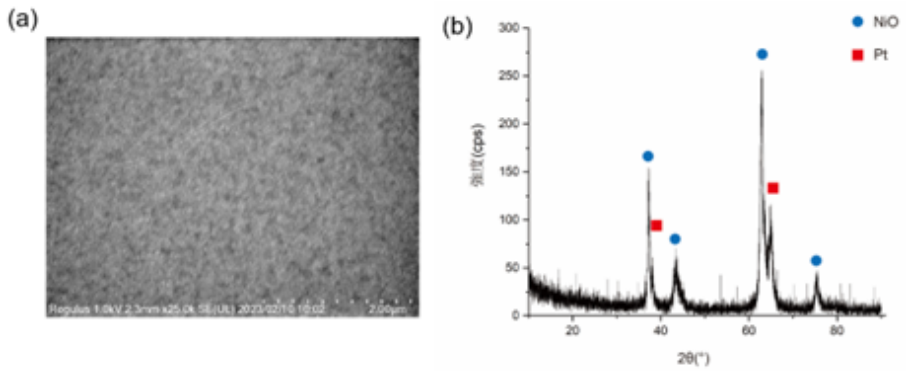
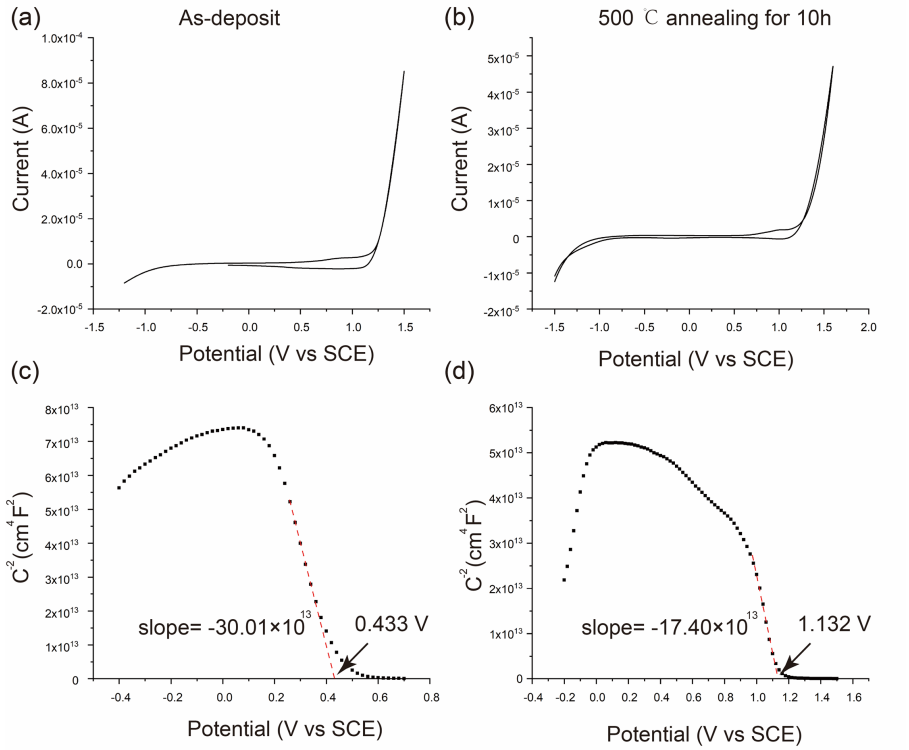
共同利用者氏名 Names of Collaborators Excluding Supporters in the Hub and Spoke Institutes	
ARIM実施機関支援担当者 Names of Supporters in the Hub and Spoke Institutes	三澤 弘明,松尾 保孝,石 旭
利用形態 Support Type	機器利用/Equipment Utilization

利用した主な設備 / Equipment Used in This Project

利用した主な設備 Equipment ID & Name	HK-611：多元スパッタ装置 HK-618：プラズマ原子層堆積装置 HK-607：EB蒸着装置 HK-616：原子層堆積装置 HK-404：超高分解能電界放出形走査電子顕微鏡

報告書データ / Report

概要（目的・用途・実施内容） Abstract (Aim, Use Applications and Contents)	In this study, we fabricate nickel oxide (NiO) thin-film photocathodes under the modal strong coupling conditions to enhance the photochemical reaction efficiency, especially the carbon dioxide reduction reaction. Photoelectrode under modal strong coupling conditions was demonstrated to broaden the harvesting spectrum region, and even improve the internal quantum efficiency of chemical reactions.[1,2]Copper is one of the most attractive metals to synthesize hydrocarbons from CO_2 because of its optimal binding ability with CO_2 and the reaction intermediates.[3] Herein, we investigate a plasmonic photocathode system composed of Cu-Au alloy nanoparticles (CuAu-NPs)/NiO/Pt film, which utilizes the advantage of the coupling between the localized surface plasmon resonance (LSPR) and the Fabry-Pérot (FP) cavity for light absorption enhancement.
実験 Experimental	The CuAu-NPs/NiO/Pt structure was fabricated on a silica glass substrate with dimensions of 10×10×1.0 mm^3. The silica substrates were cleaned with acetone, methanol, and deionized water in an ultrasonic bath for 5 min and dried by nitrogen flow. A layer of Pt-film (˜100 nm) was deposited onto a silica glass substrate by a sputtering system (ULVAC, QAM-4-STS) with a 2-nm Ti adhesion layer. A 45-nm NiO film was deposited by sputtering in oxygen on the Pt-film at room temperature. Cu and Au thin film were sequentially evaporated by an electron-beam evaporator (EIKO, EB-580) at a deposition rate of 0.1 Å/s. Finally, the samples were annealed in a nitrogen atmosphere at 300˚C for 2 h, and CuAu-NPs appeared on the NiO film surfaces.
結果と考察 Results and Discussion	Figure 1 (a) shows the surface morphology of NiO film deposited on 100-nm Pt film. A smooth NiO surface was identified. Figure 1 (b) shows the XRD spectrum of 45-nm NiO/Pt-film. Characteristic NiO crystal peaks were observed, indicating a good crystallinity of NiO fabricated by the sputtering in oxygen. Before Cu-Au alloy nanoparticle deposition, we measured the photoelectrochemical properties of the NiO/Pt film. Figure 2(a) shows the C-V curve of NiO/Pt-film as fabricated. The flat-band potential was also measured by Mott-Schottky plot, as shown in Figure 2(c). The flat-band potential was calculated to be 0.433 V vs. SCE. A post-annealing treatment was performed to improve the photoelectrochemical properties of the NiO/Pt film. Figure 2(c) shows the C-V curve of NiO/Pt film after annealing at 500 ℃. It is noted that the flat band potential was increased to 1.132 V vs. SCE after annealing which is corresponding to the reference value. Based on the fabricated NiO/Pt film samples, we will deposit CuAu NPs on NiO/Pt film and apply them for CO_2 reduction by measuring the photocurrent conversion efficiency and the reaction products.

図・表・数式 1 Figures, Tables and Equations 1	 Figure 1. (a) SEM image of NiO surface. (b) XRD spectrum of NiO thin-film deposited on 100-nm Pt film.
図・表・数式 2 Figures, Tables and Equations 2	 Figure 2. C-V curves and mott-schottky curve of as-deposited NiO film (a,c) and annealed NiO film (b,d).
その他・特記事項（参考文献・謝辞等） Remarks(References and Acknowledgements)	References[1] Shi, X.; Ueno, K.; Oshikiri, T.; Sun, Q.; Sasaki, K.; Misawa, H., N*at. Nanotechnol.*, 2018, 13, 953-958.[2] Suganami, Y.; Oshikiri, T.; Shi, X.; Misawa, H., *Angew. Chem. Int. Ed.*, 2021, 60, 18438-18442.[3] Ross, M.B., De Luna, P., Li, Y. *et al. Nat. Catal.*, 2019, **2**, 648-658.

成果発表・成果利用 / Publication and Patents

DOI（論文・プロシーディング） DOI (Publication and Proceedings)	
口頭発表、ポスター発表および、その他の論文 Oral Presentations etc.	
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