先端科学技術研究科　博士論文要旨

<table>
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<tr><td>題目</td><td colspan="3">Perovskite thin film fabricated from radio frequency sputtering towards future solar cell applications

太陽電池応用に向けた RF スパッタリングによるペロブスカイト薄膜の作製</td></tr>
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Since the foundation of photovoltaic properties, metal-halide perovskite is well known as the young-potential material for solar cell application due to its such as a high absorption coefficient greater than 5.7 x 104 cm^{-1} at 600 nm, high carrier mobility exceeding 20 cm^2/Vs, low binding energy of exciton, and a broad absorption spectrum ranging from 400 to 800 nm. [1] These properties could lead to the swift-rise in power conversion efficiency demonstrated for this technology by reaching from 3.81% to over 26% by improving the fabrication processes, interface modifications, and controlling the perovskite compositions. [2] Moreover, the low-temperature process is developed for the flexible perovskite solar cells (PSCs) due to the ease of fabrication, thus, many state-of-art applications were expected for high efficiency solar cells.

Perovskite thin films are generally fabricated by solution-based process *via* single spin-coating method, which continues to attract many attentions due to its straightforward, simple, and efficient procedure. However, solution-based processes for fabricating PSCs face several challenges, including poor surface coverage, solvent residue, and significant material waste, raising concerns about environmental sustainability and production costs. [3-4] To address these issues, vacuum-based processes *via* radio frequency (RF) sputtering method have been developed for PSC fabrication. This method provides advantages in terms of precise film formation and high uniformity even on complex geometry substrates. [5] Moreover, the major advantage of RF-sputtering is the potential to tailor the morphological structure of the sputtered film by adjusting sputtering parameter, allowing the optimization of perovskite characteristics.

Motivated by the advancements and potential to further develop RF-sputtering-based method, the perovskite thin films fabricated from RF-sputtering and post-conversion through two-step gas-phase reaction were proposed in this thesis as shown in Fig. 1. The optimization of sputtering parameters and post-conversion processes was also studied to seek for the optimal structure for perovskite thin films towards PSCs applications. The outline and summary of each chapter are described as follows,

In chapter 2, perovskite thin films fabricated from RF-sputtering were proposed using lead sulfide as a perovskite precursor. Two-step gas-phase conversion were carried out to convert the lead sulfide film to lead iodide *via* iodine sublimation at room temperature for 60 h and methylammonium lead iodide ($MAPbI_3$) film *via* methylammonium (MAI) evaporation with the annealing temperature optimized at 140 °C for 2 h. The achieved films presented in great uniformity and excellent surface coverage over the textured silicon substrate with the pyramid shape. Furthermore, the substrate temperatures played an important role on the morphological change from porous-disordered to fibrous-interconnected grain to reduce the effects of grain-boundary defects. The change in the grain structure could promote less light scattering resulted

in more responsive in visible region, consequently, enhancing the carrier extraction and carrier lifetime.

In chapter 3, target-to-substrate distance and sputtering pressure was further varied to study the effects on the $MAPbI_3$ films fabricated from RF-sputtering. Although, the longer of target-to-substrate distance promote the grain-growth due to reduced kinetic energy, the films also presented significantly poor crystallinity regarded fewer perovskite crystal sites led to increase non-radiative recombination and reduced charge carrier generation. On the other hands, higher sputtering pressures transformed the films from dense to porous structure with more disordered crystal growth. Moreover, the higher sputtering pressures led to form the larger grain with fewer grain-boundaries to improving charge transport properties confirmed by higher absorption coefficients in the visible region to improve the light collection and reduced carrier recombination.

In chapter 4, planar-structured with n-i-p junction PSC devices were fabricated using the films achieved from chapter 2 and chapter 3 to study the potential and constrains of the perovskite thin film fabricated from RF-sputtering. The results showed significantly low current density-voltage (J-V) characteristics due to many factors: (i) Inappropriate PSCs structure due to p-type characteristics of the films; (ii) Poor interfacial properties between the $MAPbI_3$ led to high series resistance value; (iii) Poor crystallinity and grain-boundaries, which attributed to low current density in perovskite material.

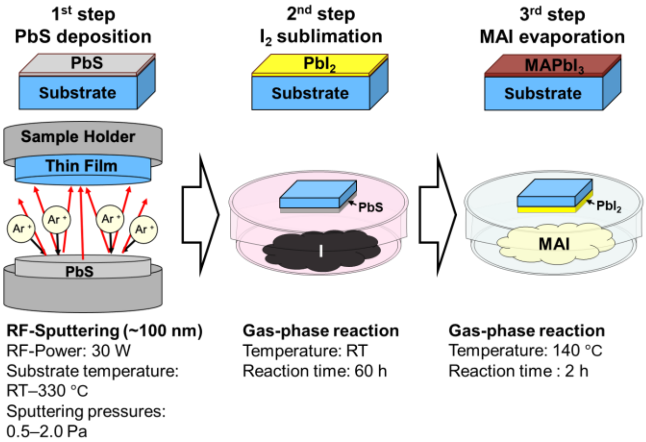

Figure 1 Fabrication flow of perovskite thin films fabricated from RF-sputtering.

Overall, this thesis proposed complete fabrication of perovskite films *via* RF-sputtering, which provided advantages onto the morphological control to enhance properties of the perovskite films. However, PSCs using these films remained significant low performance, indicating the necessity to improve the quality of the films to reach higher potential to be appropriate for the PSC devices.

References:

[1] Noman, M., el al, *RSC Adv.* **14**, 5085–5131 (2024)

[2] Raifuku, I. et al, *Appl. Phys. Express* **10** (2017).

[3] Wang, J. F. et al, *Sci. Rep.* **7** (2017).

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[5] Filho, D. S. et al, *Sci. Rep.* **8**, (2018).

論文審査結果の要旨

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金属ハロゲン化ペロブスカイトは、その高い吸収係数、高いキャリア移動度、低い励起子結合エネルギーといった優れた特性から、太陽電池応用において有望な材料として注目されている。しかし、従来の溶液プロセスによるペロブスカイト薄膜の製造方法は、表面カバレッジの低さ、残留溶媒、材料の無駄といった課題を抱えており、環境の持続可能性や製造コストの観点からも問題がある。
本論文では、ペロブスカイト薄膜の製造において、ラジオ周波数スパッタリング（RFスパッタリング）を用いる新たなアプローチを提案している。RFスパッタリングは、複雑な形状の基板にも高い均一性と精密な膜形成を可能にする。研究では、スパッタリングパラメータとその後の変換プロセスを最適化し、ペロブスカイト薄膜の形態構造を改善し、太陽電池応用における特性を向上させることを目指した。
RFスパッタリングにおいて硫化鉛を前駆体として用い、二段階のガス相変換を行い、メチルアンモニウム鉛ヨウ化物（MAPbI3）薄膜を形成するプロセスについて述べた。このプロセスで得られた薄膜は、優れた表面カバレッジと均一性を示し、基板温度が粒界欠陥の低減とキャリア抽出および寿命の向上に重要な役割を果たした。
MAPbI3薄膜のターゲットから基板までの距離とスパッタリング圧力の影響を探求した。その結果、ターゲットから基板までの距離が長くなると結晶性が低下し、非放射再結合が増加する一方、スパッタリング圧力が高い場合には、粒界を減少させ、光の集光とキャリア再結合の抑制に寄与する特性向上が確認された。
以上に述べたように、本論文は、ペロブスカイト薄膜の形態制御におけるRFスパッタリングの潜在能力を示しているが、実用的な太陽電池応用に向けた性能向上のためには、さらなる改良が必要であることを明らかにしている。本研究は、次世代のペロブスカイト型太陽電池の実現に向けて有益な手法を提供しているとして、審査員一同は、本論文が博士（工学）として十分に価値があるものと判定した。