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学位論文題目	Preparation of Li-Al-O and Na-Al-O System Oxide Films by Laser Chemical Vapor Deposition（レーザー化学気相析出法による Li-Al-O 系および Na-Al-O 系酸化物膜の合成）
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論文内容要旨

Chapter 1 Introduction

In this chapter, the composites in Li-Al-O and Na-Al-O systems were introduced and the objectives of this research were presented. The Li-Al-O system has three compounds of LiAl_5O_8 , LiAlO_2 and Li_5AlO_4 . LiAl_5O_8 doped with rare-earth or transition ions is fine color emitting phosphors. LiAlO_2 attracts increasing attention as a potential substrate for growing GaN semiconductor due to low lattice mismatch and removability. Li_5AlO_4 shows high reactivity with water (H_2O) and carbon dioxide (CO_2) in atmosphere because of high lithium content. It is deemed to be a suitable material for humidity sensor and CO_2 captor. NaAlO_2 , $\text{NaAl}_6\text{O}_{9.5}$ and Na- β -alumina are included in Na-Al-O system. NaAlO_2 received much attention as a heterogeneous base catalyst for production of biodiesel. $\text{NaAl}_6\text{O}_{9.5}$ is metastable and transforms toward the β -alumina at elevated temperatures. Na- β -alumina is well-known as an excellent solid electrolyte in Na-ion battery. My present study is aimed to preparing these useful materials in the form of film by laser CVD and investigating their electrical properties.

Chapter 2 Preliminary investigation

This chapter is focused on investigating the discovery history of β -alumina, crystal structures of Li-Al-O and Na-Al-O composites and previous preparations of them. The problems and solution on the preparation of Li-Al-O and Na-Al-O films for present status were expatiated. Beta alumina was first reported by Rankin and Merwin in 1916. Kummer et al. investigated the details of ionic diffusion in beta alumina and discovered the remarkably high conductivity of sodium ions in 1967, which directly inspired the concept of high-temperature sodium batteries. Reducing the beta alumina thickness to micron range will result in a significant drop in area specific resistance. However, β -alumina films have never been obtained by CVD because of high crystallization temperature, high vapor pressure of Li/Na and high reactivity of Li/Na precursor. Due to the same reasons, other Li-Al-O and Na-Al-O composites in the form of film have been never prepared.

Thus, decreasing the preparation temperature is probably a necessary step to prepare Li-Al-O and Na-Al-O films. Laser chemical vapor deposition (laser CVD) is a deposition technique for films of various materials by introducing activated field with laser irradiation for chemical reaction. The chemical reaction on the substrate surface was activated greatly by laser, which decreased the preparation temperature and accelerated the deposition of films.

Chapter 3 Preparation of Li-Al-O films by laser CVD

Li-Al-O films were prepared on AlN substrates by laser CVD, as shown in Figure 1. The parameters of deposition temperature (T_{dep}), molar ratio of Li/Al ($R_{\text{Li/Al}}$) and total pressure (P_{tot}) were adjusted to construct the specific films. Single-phase α -LiAl₅O₈ films were obtained at $T_{\text{dep}} = 1107$ –1280 K and $R_{\text{Li/Al}} = 0.1$ –2.9. By decreasing T_{dep} to 1003–1273 K and increasing $R_{\text{Li/Al}}$ to 0.4–6.1, the γ -LiAlO₂ phase was co-deposited with the α -LiAl₅O₈ phase. Single-phase γ -LiAlO₂ films were obtained at $T_{\text{dep}} = 984$ –1238 K and $R_{\text{Li/Al}} = 0.9$ –10.6. A further decrease in T_{dep} to 940–1060 K and increase in $R_{\text{Li/Al}}$ to 2.2–10.6 resulted in the co-deposition of γ -LiAlO₂ and β -Li₅AlO₄ phases. Single-phase β -Li₅AlO₄ films were obtained at $T_{\text{dep}} = 923$ K and $R_{\text{Li/Al}} = 11.4$. An amorphous film was prepared at $T_{\text{dep}} = 895$ –1023 K, which was crystallized to α -Al₂O₃ after annealing at 1273 K for 2 h. At 833 K, no film was obtained, irrespective of the $R_{\text{Li/Al}}$ value.

Various textures of Li-Al-O films were formed after deposition, as shown in Figure 2. The surface of a single-phase α -LiAl₅O₈ film prepared at $T_{\text{dep}} = 1280$ K and $R_{\text{Li/Al}} = 1.6$ showed faceted grains with pyramidal and polygonal shapes (Fig. 2(a)). The cross-section was columnar (Fig. 2(b)). At $T_{\text{dep}} = 1183$ K and $R_{\text{Li/Al}} = 1.9$, the surface of a single-phase (001)- γ -LiAlO₂ film consisted of pyramidal grains, and the cross-section was an elongated columnar structure (Fig. 2(c), (d)). At $T_{\text{dep}} = 923$ K and $R_{\text{Li/Al}} = 11.4$, a single-phase β -Li₅AlO₄ film had a rough fluffly surface and consisted of columns larger than 2 μm (Fig. 2(e), (f)).

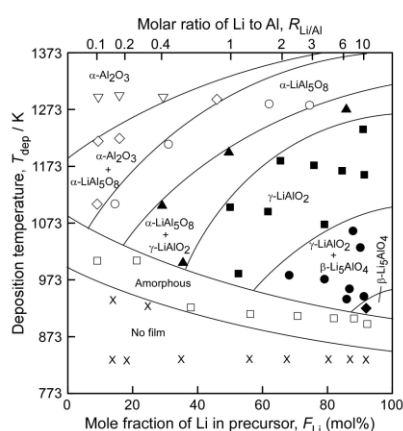


Fig. 1 Effects of T_{dep} and $R_{\text{Li/Al}}$ on the crystalline phases of Li-Al-O films prepared by LCVD.

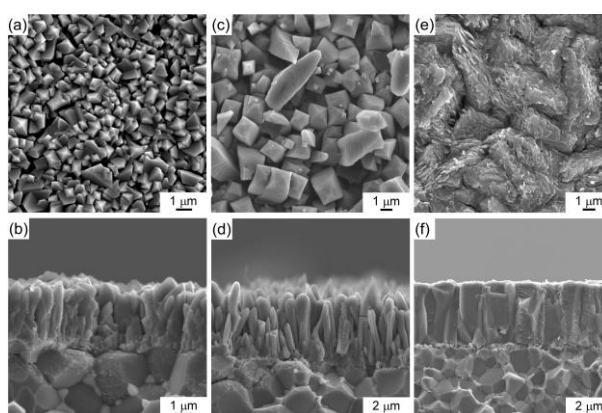


Fig. 2 Surface and cross-sectional microstructures of (a, b) LiAl₅O₈ film, (c, d) LiAlO₂ film, and (e, f) Li₅AlO₄ film.

Chapter 4 Preparation of Na-Al-O films by laser CVD

NaAlO₂, NaAl₆O_{9,5} and Na- β -alumina films were prepared on AlN substrate by laser CVD. To obtain as-deposited Na- β -alumina film, the disadvantage of high vapor pressure of Na was overcome by extremely increasing $R_{\text{Na/Al}}$ and P_{tot} , as shown in Figure 3. At $P_{\text{tot}} < 400$ Pa, Al₂O₃ films in a single phase were prepared although the amounts of Na(dpm) precursors consumed were much more than those of Al(acac)₃ so that $R_{\text{Na/Al}}$ reached 20–80. That could be due to the severe depletion of Na precursors. At high T_{dep} such as 1310–1360 K, the Na(dpm) precursor is highly reactive yielding premature reaction in a gas phase often causing powder formation (homogeneous reaction) and the Na(dpm) precursor could have been depleted. However, Na- β -alumina was co-deposited with Al₂O₃ by increasing P_{tot} to 400–600 Pa. It indicated the depletion of Na precursors was compensated by high P_{tot} because increasing P_{tot} also contributed to a rise of Na concentration in chamber, which favored the formation of Na-Al-O phases. With further increasing P_{tot} to 600–1000 Pa, the concentration of gaseous Na precursors in chamber was even raised, causing solitary deposition of Na- β -alumina films at $R_{\text{Na/Al}} = 20$ –80.

The (001)-oriented Na- β -alumina films deposited at $P_{\text{tot}} = 600$ Pa consisted of loose flakes. The (110)-oriented Na- β -alumina films deposited at $P_{\text{tot}} = 1000$ Pa had dense facets with polygonal shape. The bright field TEM image of the

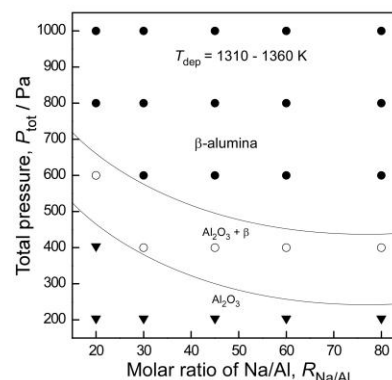


Fig. 3 Effects of P_{tot} and $R_{\text{Na/Al}}$ on the crystalline phases of Na-Al-O films prepared by LCVD.

Na- β -alumina film at $P_{\text{tot}} = 1000$ Pa is shown in Fig. 4(a). The platelet grains were elongated from the substrate. Fig. 4(b) depicts the selected area electron diffraction (SAED) pattern corresponding to the grain designated in Fig. 4(a). This indicated that (001) planes of the Na- β -alumina grain were steeply inclined from the substrate as illustrated in Fig. 4(c). The Na- β -alumina film included grains with the conduction planes vertical to the substrate surface, where Na ions were arrayed in the film thickness direction. Since Na ions can two-dimensionally migrate along the conduction planes under an electric field, the crystal orientations with the conduction planes parallel to current flows are desirable as electrolytes for batteries.

The maximum R_{dep} of NaAlO₂, NaAl₆O_{9.5} and Na- β -alumina films in a single phase were 131 $\mu\text{m h}^{-1}$ at $T_{\text{dep}} = 986$ K, 46 $\mu\text{m h}^{-1}$ at $T_{\text{dep}} = 1100$ K and 44 $\mu\text{m h}^{-1}$ at $T_{\text{dep}} = 1316$ K, respectively. The conductivity of Na- β -alumina film reached 1 $\text{S}\cdot\text{m}^{-1}\cdot\text{K}$ at 573 K.

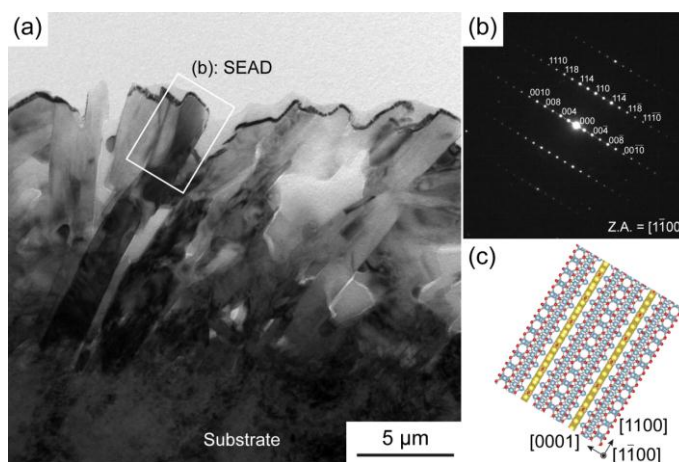


Fig. 4 TEM image (a), electron diffraction pattern (b) and crystal structure perpendicular to (1-10) (c) of Na- β -alumina film deposited at $T_{\text{dep}} = 1345$ K, $R_{\text{Na/Al}} = 30$ and $P_{\text{tot}} = 1000$ Pa.

Chapter 5 Preparation of Li-doped Na-Al-O films by laser CVD

In this chapter, variation of crystal phases of Li-doped Na-Al-O films deposited on AlN substrate as functions of T_{dep} and $R_{\text{Li/Al}}$ was investigated (Fig. 5). Without laser radiation, amorphous films were prepared at $T_{\text{dep}} < 750$ K. At $T_{\text{dep}} = 800$ –900 K and $R_{\text{Li/Al}} = 0$ –0.5, NaAlO₂ was co-deposited with Na₂CO₃ at $P_{\text{tot}} = 800$ Pa and $R_{\text{Na/Al}} = 1.5$. Increasing T_{dep} to 900–1100 K contributed to deposition of NaAlO₂ films in a single phase. With increasing $R_{\text{Li/Al}}$ to 0.5–1.0, the mixture film of NaAlO₂ and LiAlO₂ was prepared at $T_{\text{dep}} = 800$ –1100 K. Further increasing $R_{\text{Li/Al}}$ to 1.5 contributed to formation of LiAlO₂ films in a single phase. At $T_{\text{dep}} = 1100$ –1200 K and $R_{\text{Li/Al}} = 0.1$ –1.0, Li-doped Na- β -alumina was often co-deposited with NaAlO₂, LiAlO₂, LiAl₅O₈, Al₂O₃ or NaAl₆O_{9.5}. The strait T_{dep} range of 1165–1185 K contributed to independent deposition of Li-doped Na- β -alumina films at $R_{\text{Li/Al}} = 0.1$ –0.5. Single-phase Al₂O₃ films were prepared at $T_{\text{dep}} > 1200$ K.

The mixed film of Li-doped Na- β -alumina and NaAl₆O_{9.5} showed pyramidal grains (Fig. 6(a), (d)). Li-doped Na- β -alumina film consisted of rectangular and triangular facets (Fig. 6(b), (e)). The mixed film of LiAl₅O₈ and Li-doped Na- β -alumina had clusters of pyramidal grains (Fig. 6(c), (f)). The maximum R_{dep} (deposition rate) of Li-doped Na- β -alumina films was 60 $\mu\text{m h}^{-1}$ at $T_{\text{dep}} = 1167$ K, $R_{\text{Li/Al}} = 0.5$ and $P_{\text{tot}} = 800$ Pa. The as-deposited Li-doped Na- β -alumina film always showed (001) orientation and had low electrical conductivity because the closely-packed spinel structure in the crystal blocked ion movement along c -axis.

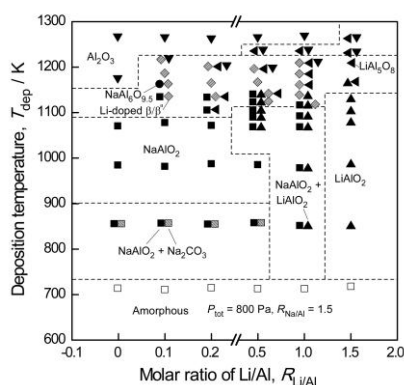


Fig. 5 Effects of T_{dep} and $R_{\text{Li/Al}}$ on the crystalline phases of Li-Na-Al-O films prepared by LCVD.

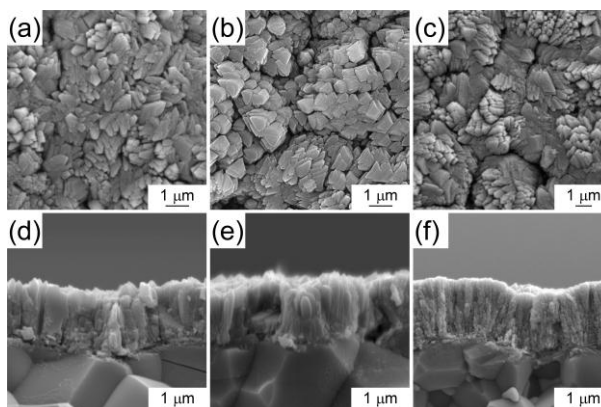


Fig. 6 Microstructures of (a, d) mixture of NaAl₆O_{9.5} and Li-doped β -alumina; (b, e) Li-doped β -alumina film; (c, f) mixture of LiAl₅O₈ and Li-doped β -alumina.

Chapter 6 Conclusions

Li-Al-O films including LiAl_5O_8 , LiAlO_2 and Li_5AlO_4 were prepared by laser chemical vapor deposition (LCVD). (110)-oriented LiAl_5O_8 films had flake-like grains while (100)-oriented LiAl_5O_8 films consisted of polygonally faceted grains. (001)-oriented LiAlO_2 films showed pyramidal grains and (110)-oriented LiAlO_2 films had granular grains. Non-oriented Li_5AlO_4 films had dense and rough fluffy morphology. The R_{dep} reached $98 \mu\text{m h}^{-1}$ at 944 K, where a LiAlO_2 and Li_5AlO_4 mixed phase was observed. The electrical conductivity of LiAlO_2 film is 5 times higher than those of LiAlO_2 single crystals and polycrystalline sintered sample at the same temperature.

Na-Al-O films including $\text{NaAl}_6\text{O}_{9.5}$ and NaAlO_2 were prepared by laser CVD. (041)-oriented $\text{NaAl}_6\text{O}_{9.5}$ films had polygonal and pyramidal facets. (100)-oriented NaAlO_2 films had finely faceted grains while (110)-oriented NaAlO_2 films showed roof-like grains. The maximum R_{dep} of NaAlO_2 and $\text{NaAl}_6\text{O}_{9.5}$ in a single phase were $131 \mu\text{m h}^{-1}$ at $T_{\text{dep}} = 986 \text{ K}$ and $46 \mu\text{m h}^{-1}$ at $T_{\text{dep}} = 1100 \text{ K}$, respectively.

Beta alumina films including Na- β -alumina and Li-doped Na- β -alumina were obtained by laser CVD. Na- β -alumina films were obtained at $T_{\text{dep}} = 1310\text{--}1390 \text{ K}$, $R_{\text{Na/Al}} = 20\text{--}80$ and $P_{\text{tot}} = 600\text{--}1000 \text{ Pa}$. The Na- β -alumina films deposited at $P_{\text{tot}} = 600 \text{ Pa}$ consisted of loose flakes. The (110)-oriented Na- β -alumina films deposited at $P_{\text{tot}} = 1000 \text{ Pa}$ had dense facets with polygonal shape. The maximum R_{dep} of Na- β -alumina films were $44 \mu\text{m h}^{-1}$ at $T_{\text{dep}} = 1316 \text{ K}$. The electrical conductivity of Na- β -alumina film reached $1 \text{ S}\cdot\text{m}^{-1}\cdot\text{K}$ at 573 K. (001)-oriented Li-doped Na- β -alumina films were prepared at $T_{\text{dep}} = 1165\text{--}1185 \text{ K}$, $R_{\text{Li/Al}} = 0.1\text{--}0.5$, $R_{\text{Na/Al}} = 1.5$ and $P_{\text{tot}} = 800 \text{ Pa}$. The Li-doped Na- β -alumina films consisted of rectangular and triangular facets. The R_{dep} of Li-doped Na- β -alumina films reached $60 \mu\text{m/h}$ at $T_{\text{dep}} = 1167 \text{ K}$, $R_{\text{Li/Al}} = 0.5$ and $P_{\text{tot}} = 800 \text{ Pa}$.

論文審査結果の要旨

本論文は、レーザー化学気相析出法 (Chemical Vapor Deposition、CVD) を用い Li-Al-O および Na-Al-O 系の酸化物セラミックス材料を合成し、 β/β'' -alumina 構造を有する膜、およびこれらの系に存在する種々の化合物膜を合成し、その合成条件と結晶構造、微細組織および電気的性質を明らかにすることを目的とした研究であり、全6章からなる。

第1章および第2章では、研究の背景を述べ、本論文の目的と構成を記した。

第3章では、Li-dipivaloylmethanate (Li(dpm)) および Al-acetylacetonate (Al(acac)₃) の有機錯体金属原料を用い、Li-Al-O 膜をレーザー照射場において CVD を行い、CVD 条件が結晶相、微細組織、成膜速度および電気的性質に及ぼす影響を調べた。成膜温度やレーザー強度、炉内圧力や Li/Al 原料供給比を広範な条件で膜を作製し、非晶質 Li-Al-O、LiAlO₂、LiAl₅O₈ および Li₅AlO₄ の各種単相膜およびコンポジット膜が得られた。これらレーザー照射場では、(110)-および(100)-LiAlO₂ 膜や(001)-および(110)-LiAl₅O₈ 膜など、配向成長することを明らかにした。また、微細組織の炉内圧力や Li/Al 原料供給比による影響を系統的に調べ、粒状組織、ピラミッド自形組織、多角形組織、カリフラワー状組織の Li-Al-O 膜を最大成膜速度約 50 $\mu\text{m}/\text{h}$ で合成した。得られた膜の電気的性質を調べ、LiAlO₂、LiAl₅O₈ および Li₅AlO₄ がイオン伝導性を示すを明らかにした。

第4章では、Li(dpm) および Al(acac)₃ 有機錯体金属原料を用い、Na-Al-O 膜をレーザーCVD により合成し、CVD 条件が結晶相、微細組織、成膜速度および電気的性質に及ぼす影響を調べた。Na/Al 原料供給比 0-3.5 とし、広範な成膜温度および炉内圧力条件で成膜し、非晶質 Na-Al-O、NaAlO₂、NaAl₆O_{9.5} および Al₂O₃ の単相膜およびコンポジット膜が最大 100 $\mu\text{m}/\text{h}$ 以上で高速成長した。NaAlO₂ および NaAl₆O_{9.5} 膜を成膜後に 1373-1573 K で大気焼鈍することで、Na β/β'' -alumina 膜が得られた。また、Na/Al 原料供給比 20-80、成膜温度 1260 K 以上、炉内圧力 400 Pa 以上の Na 過剰雰囲気下におけるレーザーCVD により Na β/β'' -alumina が得られることを明らかにした。NaAlO₂、NaAl₆O_{9.5} および β/β'' -alumina 膜はイオン伝導性を示した。

第5章では、第3および4章で得られた結果を基に、Li 置換した Na β/β'' -alumina 膜の合成を目的とし、レーザーCVD により Li-Na-Al-O 膜を合成した。Na β/β'' -alumina 膜を得るためには Na 過剰雰囲気下で 1260 K 以上の高温での合成が必要であったが、では(Li+Na)/Al 原料供給比が 1 以下、成膜温度 1100-1200 K の条件で Li 置換 Na β/β'' -alumina 膜が得られることを明らかにした。Li 置換 Na β/β'' -alumina 膜は、c 軸が基材表面に平行な板状組織をもち、成膜速度は最大で 100 $\mu\text{m}/\text{h}$ 以上であり、イオン伝導を示すことを明らかにした。

第6章では、本論文を総括した。

よって、本論文は博士(工学)の学位論文として合格と認める。