2025年度 第1回ARIM量子・電子マテリアル領域セミナー （オンライン開催）

GaCp*を用いた結晶性GaN膜の原子層堆積

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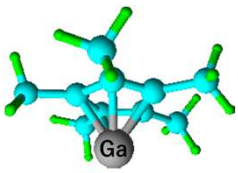
ALD用ガリウムプリカーサー

広く用いられているプリカーサー; TMG (Trimethylgallium), TEG (Triethylgallium)
新規プリカーサー; GaCp* (Pentamethylcyclopentadienylgallium)

Precursor	TMG	TEG	GaCp*
Chemical Formula	$Ga(CH_3)_3$	$Ga(C_2H_5)_3$	$GaC_5(CH_3)_5$
Molecular Weight	114.8	156.9	204.9
Appearance at 23 °C	Liquid	Liquid	Liquid
Vapor Pressure	23.7 kPa (20 °C)	0.58 kPa (20 °C)	0.16 kPa (50 °C)
Pyrophoric	Yes	Yes	No*
Valence	III	III	I



* 消防法危険物第3類に該当するが、室温で大気開放しても発火しない

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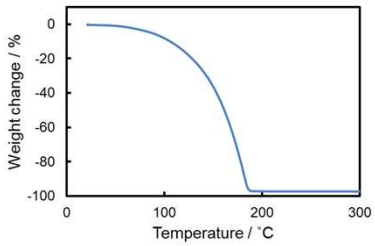
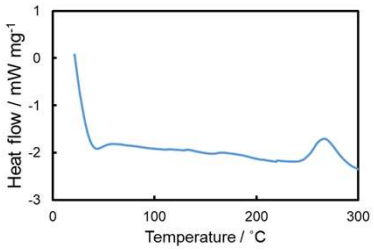
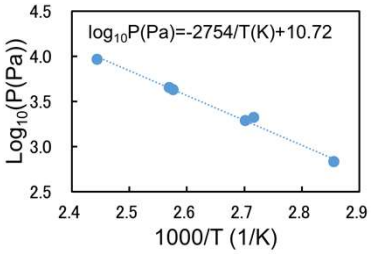
GaCp*の物性



TG（Thermogravimetry）



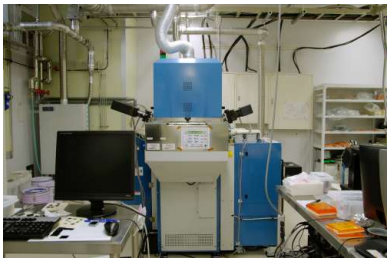
SC-DSC
（Sealed cell differential scanning calorimetry）



Clausius-Clapeyron plot

新規プリカーサーによるGaNのALDの評価

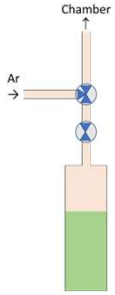
- GaCp*はGa_2O_3のALD用に開発した
- GaCp*はI価のプリカーサーなので結晶性のGaNが成膜可能と思われたが、当時は社内にプラズマALDの装置がなかったため、NPFで成膜実験を行うこととした
- 【NPF031】原子層堆積装置_1[FlexAL]（in-situ 分光エリプソ付属）を技術代行で利用



NPFのWebsiteより

実験方法

- **ALD procedures**
  - Precursor: GaCp* (Pentamethylcyclopentadienyl gallium)
  - Co-reactant: remote NH_3/H_2 plasma and remote N_2 plasma
  - Substrate: Si wafer with native oxide
  - Precursor delivery: Baking type
  - Precursor temperature: 80 °C
  - Deposition temperature: 200 °C
  - Process of one ALD cycle:
    GaCp* → NH_3/H_2 plasma → N_2 plasma



- **Film thickness measurement**
  - Spectroscopic ellipsometer

- **Film analysis**
  - HR-RBS (High-resolution Rutherford backscattering spectrometry)
  - rf-GDOES (Radio frequency glow discharge optical emission spectroscopy)
  - XTEM (Cross-sectional transmission electron microscopy)

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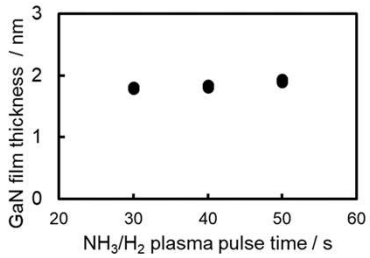
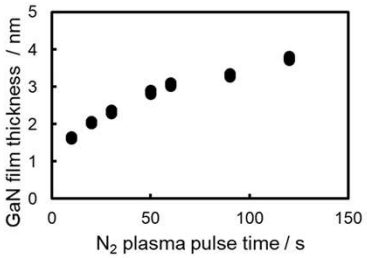
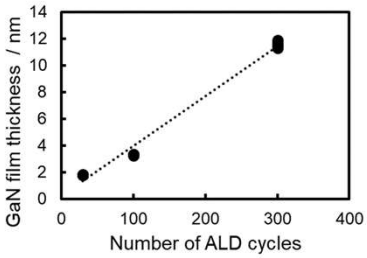
膜の成長（GaCp* → NH_3/H_2 plasma → N_2 plasma）



Basic condition
Growth temperature: 200 °C,
number of ALD cycles: 30,
GaCp* pulse time: 0.1 s,
N_2 plasma pulse time: 90 s.



Basic condition
Growth temperature: 200 °C,
number of ALD cycles: 100,
GaCp* pulse time: 0.1 s,
NH_3/N_2 plasma pulse time: 30 s.



ALD condition
Growth temperature: 200 °C,
GaCp* pulse time: 0.1 s,
NH_3/N_2 plasma pulse time: 30 s,
N_2 plasma pulse time: 90 s.

GaCp*の飽和は未確認

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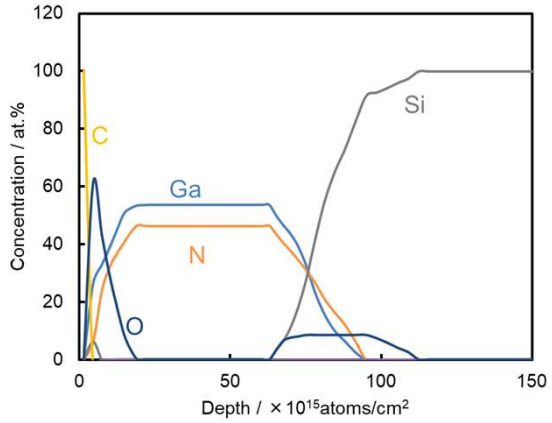
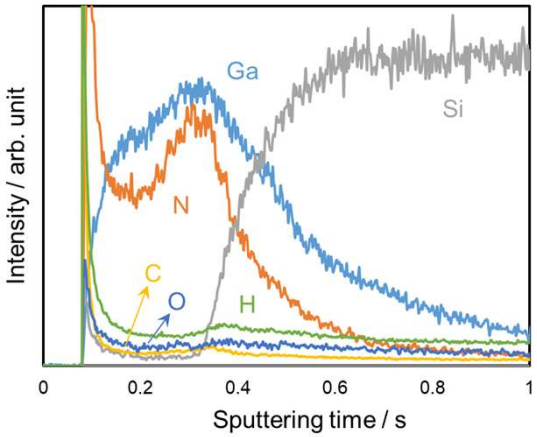
膜組成と不純物分析

HR-RBS



GD-OES



ALD condition Growth temperature: 200 °C, number of ALD cycles: 300, GaCp* pulse time: 0.1 s, NH_3/H_2 pulse time: 30 s, N_2 plasma pulse time: 90 s.

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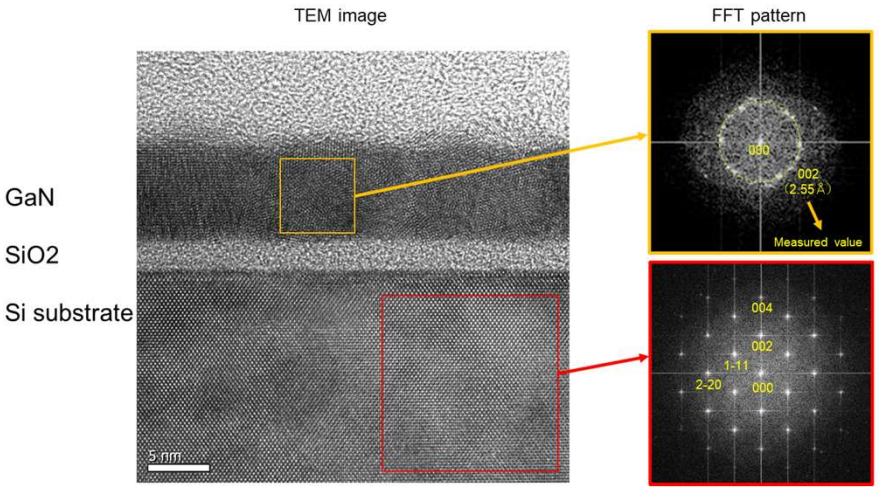
結晶性



GaN層は格子縞が確認できるため、結晶層と考えられる
FFT解析によりGaN(002)面を示すスポットが得られている

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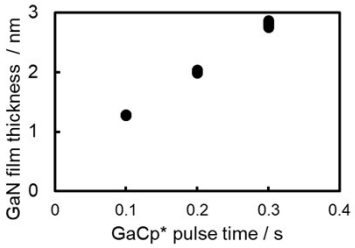
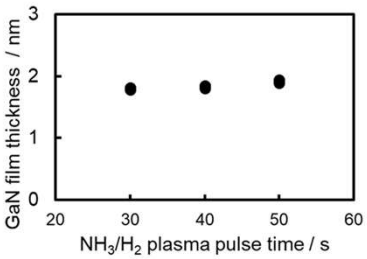
GaCp*パルスの飽和確認

2020年3月データ



Basic condition
Growth temperature: 200 °C,
number of ALD cycles: 30,
NH_3/N_2 plasma pulse time: 30 s,
N_2 plasma pulse time: 90 s.

2019年10月データ



Basic condition
Growth temperature: 200 °C,
number of ALD cycles: 30,
GaCp* pulse time: 0.1 s,
N_2 plasma pulse time: 90 s.

2020年3月成膜で、2019年10月の膜厚が再現しない
→ 80℃Baking方式では蒸気圧が足りない可能性
→ Vapor draw方式に変更

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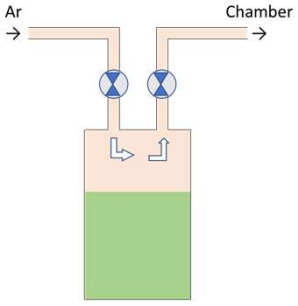
実験方法2

- **ALD procedures**
  - Precursor: GaCp* (Pentamethylcyclopentadienyl gallium)
  - Co-reactant: remote NH_3/H_2 plasma and remote N_2 plasma
  - Substrate: Si wafer with native oxide
  - Precursor delivery: Vapor draw type
  - Precursor temperature: 60 °C
  - Deposition temperature: 200 °C
  - Process of one ALD cycle:
    GaCp* → NH_3/H_2 plasma (pNH_3/H_2) → N_2 plasma (pN_2)
    GaCp* → N_2 plasma (pN_2)



- **Film thickness measurement**
  - Spectroscopic ellipsometer

- **Film analysis**
  - HR-RBS (High-resolution Rutherford backscattering spectrometry)
  - rf-GDOES (Radio frequency glow discharge optical emission spectroscopy)
  - XTEM (Cross-sectional transmission electron microscopy)

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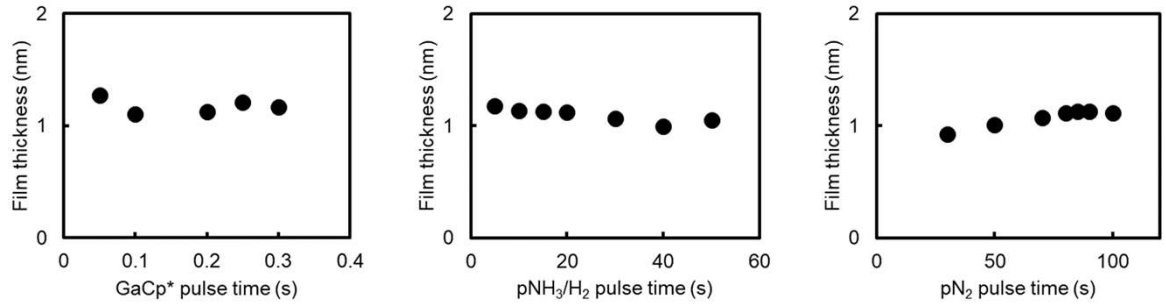
飽和確認（GaCp* → NH_3/H_2 plasma → N_2 plasma）



Basic condition
Growth temperature: 200 °C, number of ALD cycles: 30,
GaCp* pulse time: 0.2 s, NH_3/H_2 plasma pulse time: 15 s,
N_2 plasma pulse time: 90 s.

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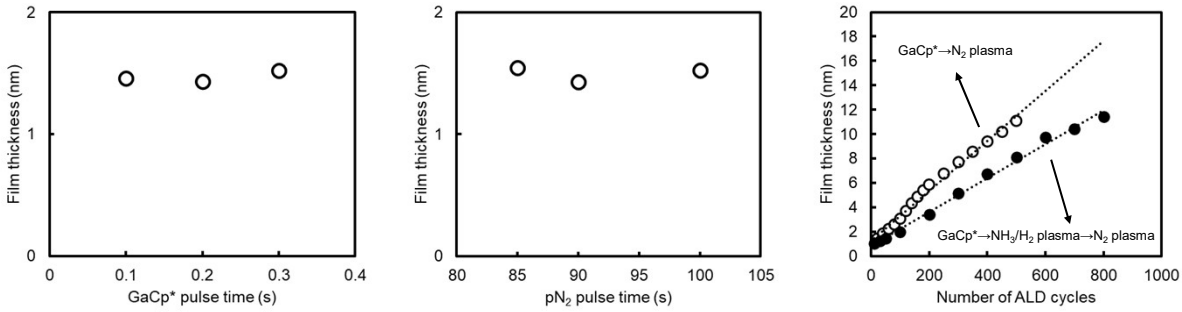
飽和確認（GaCp* → N_2 plasma）とGPC比較



Basic condition
Growth temperature: 200 °C, number of ALD cycles: 30,
GaCp* pulse time: 0.2 s, N_2 plasma pulse time: 90 s.

ALD condition = Basic conditon

NH_3/H_2 plasma の有無でGPCが異なる
→ NH_3/H_2 plasma によるエッチングの可能性

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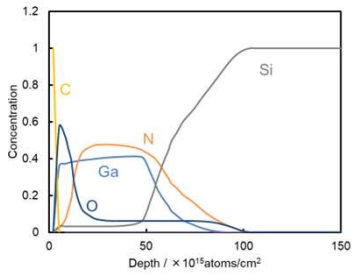
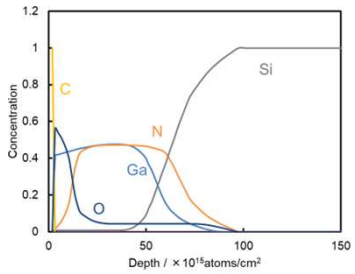
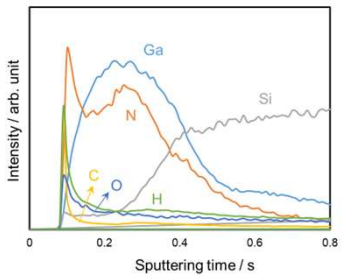
膜組成と不純物の分析

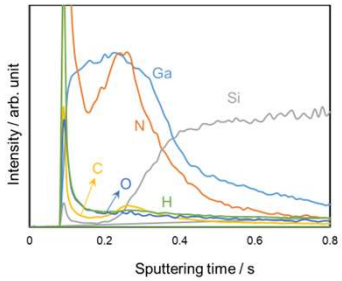
HR-RBS





GD-OES





ALD condition
Growth temperature: 200 °C,
number of ALD cycles: 1000,
GaCp* pulse time: 0.2 s,
NH_3/H_2 pulse time: 15 s,
N_2 plasma pulse time: 90 s.

HR-RBSで検出下限程度のF検出

ALD condition
Growth temperature: 200 °C,
number of ALD cycles: 500,
GaCp* pulse time: 0.2 s,
N_2 plasma pulse time: 90 s.

化学量論組成だが、微量のC検出

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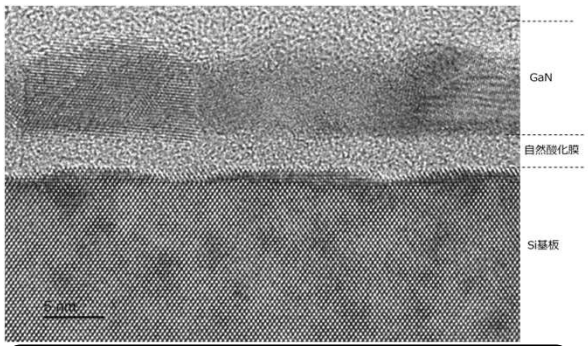
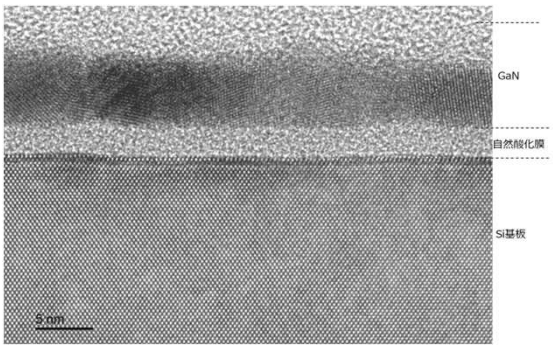
断面TEM





ALD condition Growth temperature: 200 °C, number of ALD cycles: 1000, GaCp* pulse time: 0.2 s, NH_3/H_2 pulse time: 15 s, N_2 plasma pulse time: 90 s.

ALD condition Growth temperature: 200 °C, number of ALD cycles: 500, GaCp* pulse time: 0.2 s, N_2 plasma pulse time: 90 s.

膜の平滑性を比較すると、NH_3/H_2 plasma ありの方が荒れているので
NH_3/H_2 plasma によるエッチングが疑われる
→ NH_3/H_2 plasma を H_2 plasma に変更

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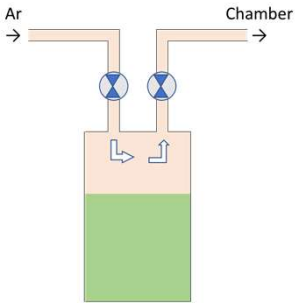
実験方法3

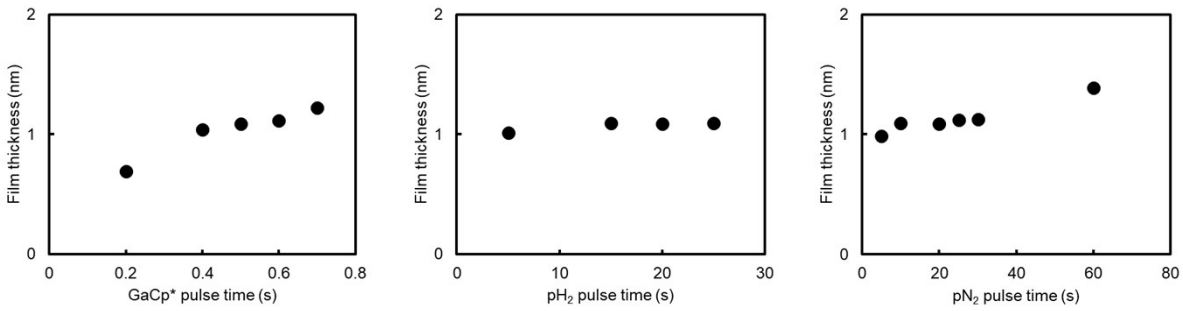
- **ALD procedures**
  - Precursor: GaCp* (Pentamethylcyclopentadienyl gallium)
  - Co-reactant: remote H_2 plasma and remote N_2 plasma
  - Substrate: Si wafer with native oxide
  - Precursor delivery: Vapor draw type
  - Precursor temperature: 60 °C
  - Deposition temperature: 200 °C
  - Process of one ALD cycle:
    GaCp* → NH_3/H_2 plasma (pH_2) → N_2 plasma (pN_2)
    GaCp* → N_2 plasma (pN_2)



- **Film thickness measurement**
  - Spectroscopic ellipsometer

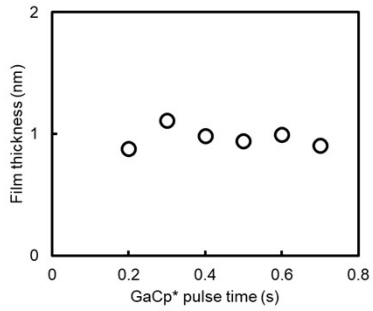
- **Film analysis**
  - HR-RBS (High-resolution Rutherford backscattering spectrometry)
  - rf-GDOES (Radio frequency glow discharge optical emission spectroscopy)
  - XTEM (Cross-sectional transmission electron microscopy)

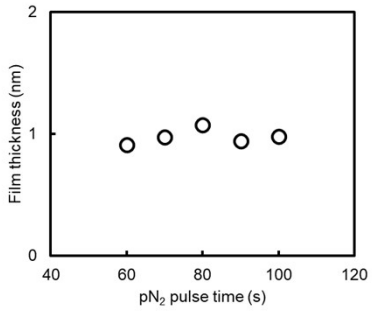
飽和確認（GaCp* → H_2 plasma → N_2 plasma）

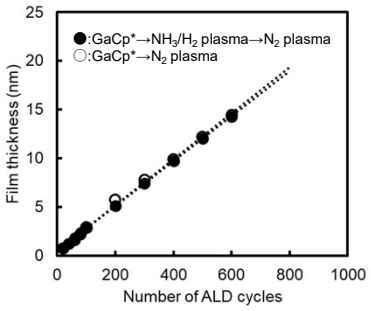


Basic condition
Growth temperature: 200 °C, number of ALD cycles: 30,
GaCp* pulse time: 0.5 s, H_2 plasma pulse time: 20 s,
N_2 plasma pulse time: 20 s.

飽和確認（ GaCp* → N_2 plasma ）とGPC比較







Basic condition
Growth temperature: 200 °C, number of ALD cycles: 30,
GaCp* pulse time: 0.5 s, N_2 plasma pulse time: 90 s.

ALD condition = Basic conditon

H_2 plasma の有無でGPCがほとんど同じ
→ NH_3/H_2 plasma によるエッチングが抑制された可能性

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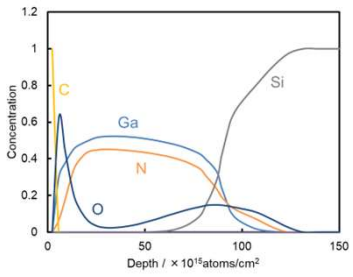
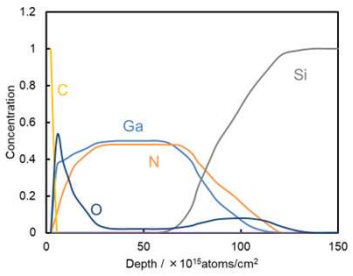
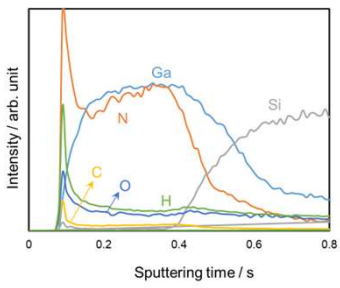
膜の分析

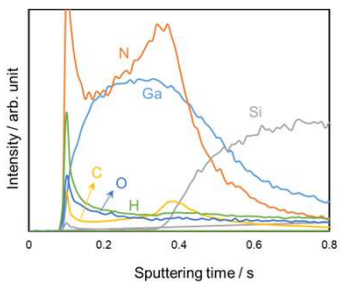
HR-RBS





GD-OES





ALD condition
Growth temperature: 200 °C,
number of ALD cycles: 600,
GaCp* pulse time: 0.5 s,
H_2 pulse time: 20 s,
N_2 plasma pulse time: 20 s.

表面荒れの可能性

ALD condition
Growth temperature: 200 °C,
number of ALD cycles: 600,
GaCp* pulse time: 0.5 s,
N_2 plasma pulse time: 90 s.

ほぼ化学量論組成だが、
微量のC検出

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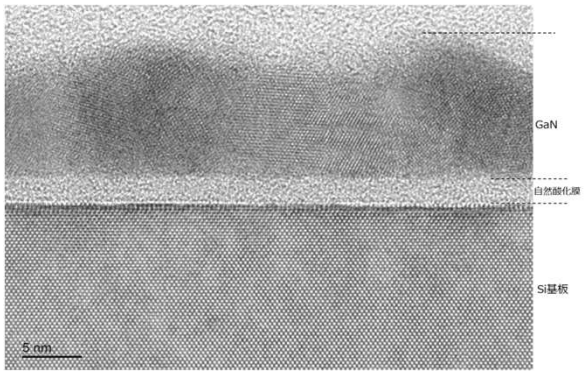
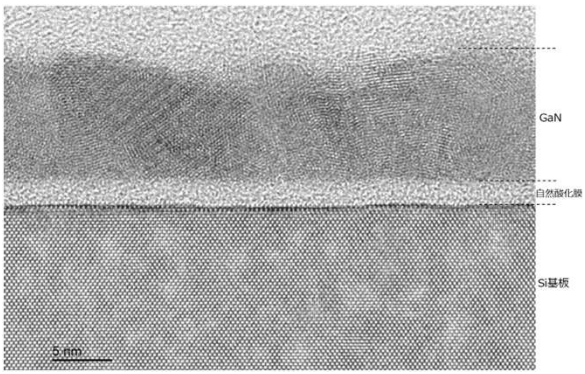
断面TEM



ALD condition Growth temperature: 200 °C, number of ALD cycles: 600, GaCp* pulse time: 0.5 s, H_2 pulse time: 20 s, N_2 plasma pulse time: 20 s.



ALD condition Growth temperature: 200 °C, number of ALD cycles: 600, GaCp* pulse time: 0.5 s, N_2 plasma pulse time: 90 s.

膜の平滑性を比較すると、H_2 plasma ありの方がやや荒れている
→ H_2 plasma 20 s が長すぎた可能性

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まとめ

- Ga_2O_3のALD用に開発したGaCp*はI価のプリカーサーなので結晶性のGaNが成膜可能と思われたので、【NPF031】原子層堆積装置_1[FlexAL]（in-situ 分光エリプソ付属）を技術代行で利用して評価実験を行った
- 最初にBaking方式の原料供給で、GaCp*→NH_3/H_2プラズマ→N_2プラズマのALDによって、期待通りの結晶性のGaN膜が得られたが、GaCp*パルスの飽和条件が不安定だったので、Vapor draw方式に変更した
- Vapor draw方式を用いることによって、GaCp*パルスの飽和条件は安定したが、次にNH_3/H_2プラズマの影響とみられるF汚染の問題が発生し、成膜結果が安定しなかった
- NH_3/H_2プラズマをH_2プラズマに変えることで、F汚染はかなり抑えられ、良い結果が得られた

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