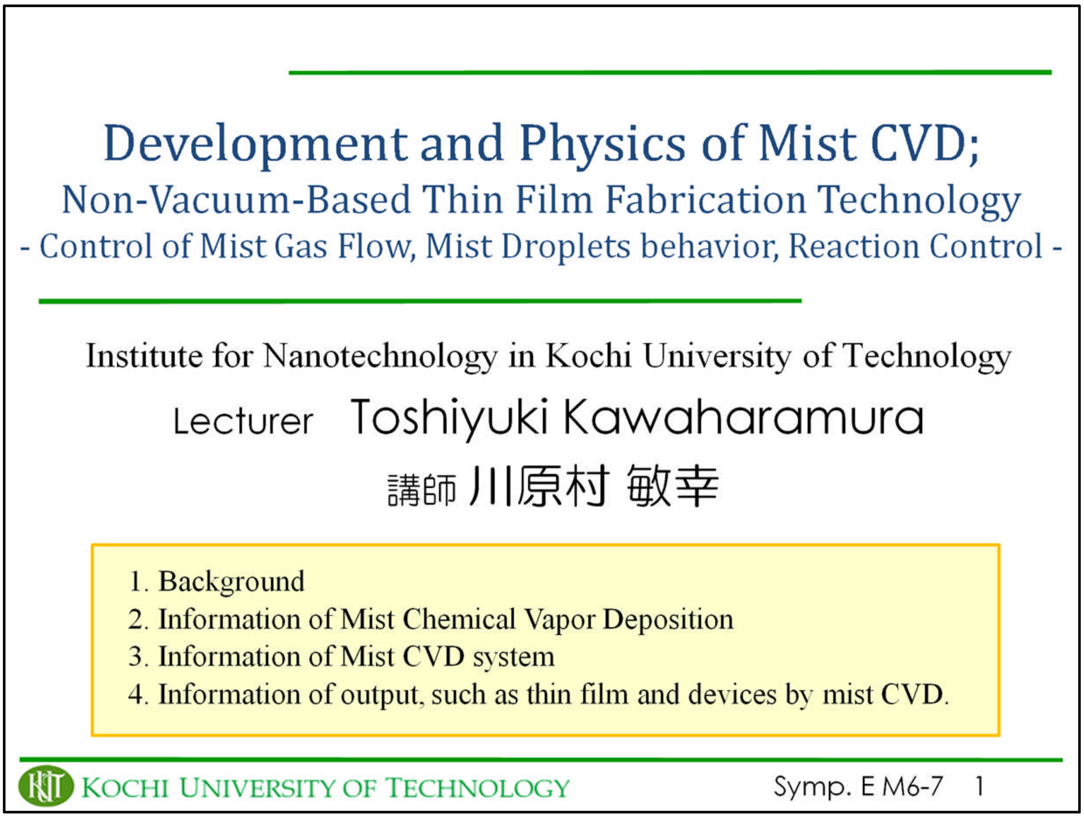

Development and Physics of Mist CVD;
Non-Vacuum-Based Thin Film Fabrication Technology
- Control of Mist Gas Flow, Mist Droplets behavior, Reaction Control -

Institute for Nanotechnology in Kochi University of Technology
Lecturer Toshiyuki Kawaharamura
講師 川原村 敏幸

1. Background
2. Information of Mist Chemical Vapor Deposition
3. Information of Mist CVD system
4. Information of output, such as thin film and devices by mist CVD.

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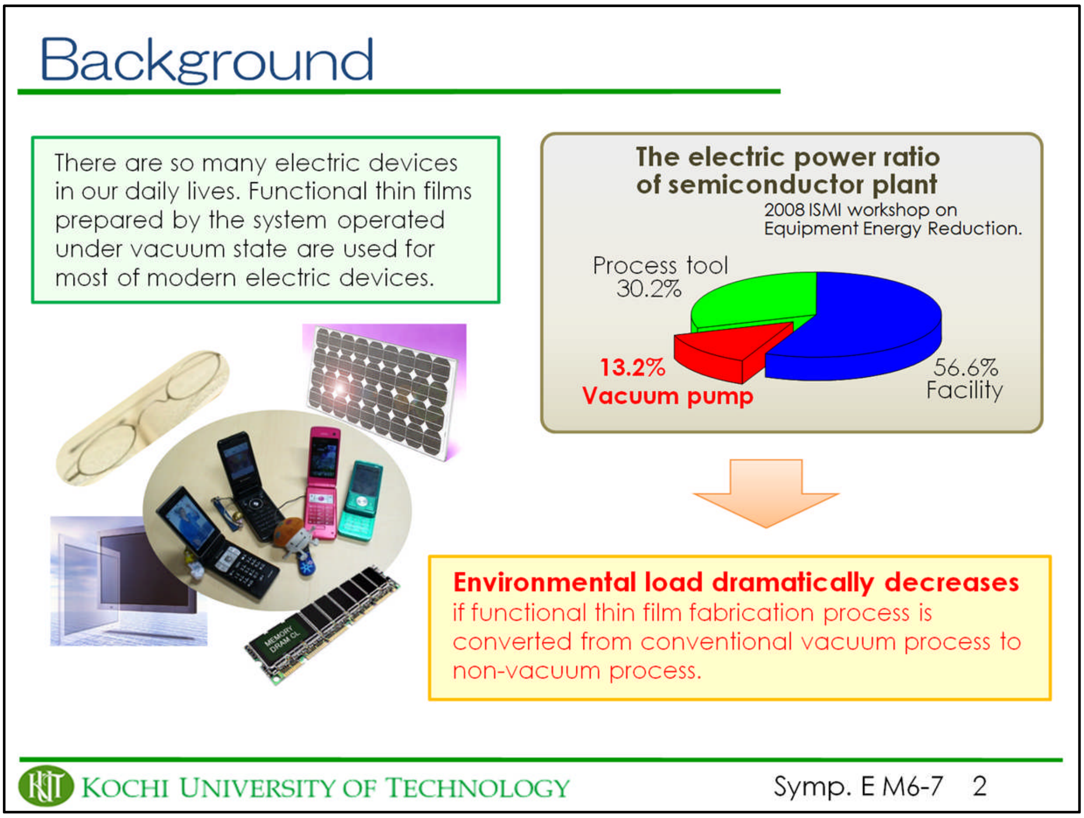
Thank you for your information. I appreciate that you’ve given me an opportunity. My name is Toshiyuki Kawaharamura. I belong to Institute for Nanotechnology in Kochi University of Technology. Today, I would like to introduce “mist CVD” which is one of the functional thin film fabrication techniques under atmospheric pressure.

ご紹介ありがとうございます。高知工科大学　ナノテクノロジー研究所の川原村です。この発表では、大気圧下で機能性薄膜を作製する為の技術「ミストCVD」についてお話します。



Background

There are so many electric devices in our daily lives. Functional thin films prepared by the system operated under vacuum state are used for most of modern electric devices.

The electric power ratio of semiconductor plant

2008 ISMI workshop on Equipment Energy Reduction.

Environmental load dramatically decreases if functional thin film fabrication process is converted from conventional vacuum process to non-vacuum process.

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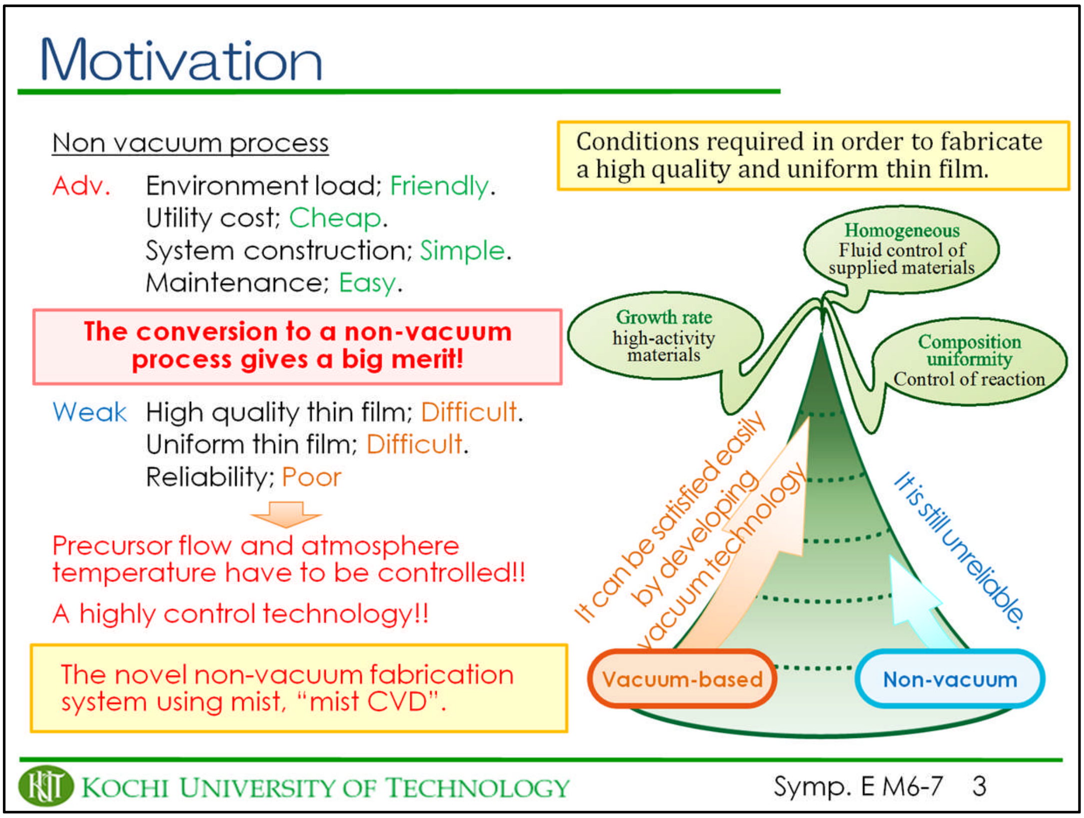
There are so many electric devices in our daily lives. Functional thin films prepared by the system operated under vacuum state are used for most of modern electric devices. This figure shows the report of the electric power ratio of semiconductor plant. From this figure, over 13% energy in the plant is used to just operate vacuum pump. As you can easily understand, if functional thin films fabrication process is converted from conventional vacuum process to non-vacuum process, environmental load dramatically decreases.

世の中は電子機器があふれています。近年、ほぼ全ての電子デバイスには真空プロセスによって作製された「機能薄膜」が用いられています。こちらの図は、半導体工場の電力割合を調べた報告です。この図からも分かるように、半導体工場では13.2%ものエネルギーが真空を保つために使用されております。つまり、もし薄膜作製プロセスを真空を用いない技術にすることが出来れば、環境負荷を劇的に減らせることが、分かると思います。



Motivation

Non vacuum process

Adv. Environment load; Friendly.
Utility cost; Cheap.
System construction; Simple.
Maintenance; Easy.

The conversion to a non-vacuum process gives a big merit!

Weak High quality thin film; Difficult.
Uniform thin film; Difficult.
Reliability; Poor

Precursor flow and atmosphere temperature have to be controlled!!

A highly control technology!!

The novel non-vacuum fabrication system using mist, "mist CVD".

Conditions required in order to fabricate a high quality and uniform thin film.

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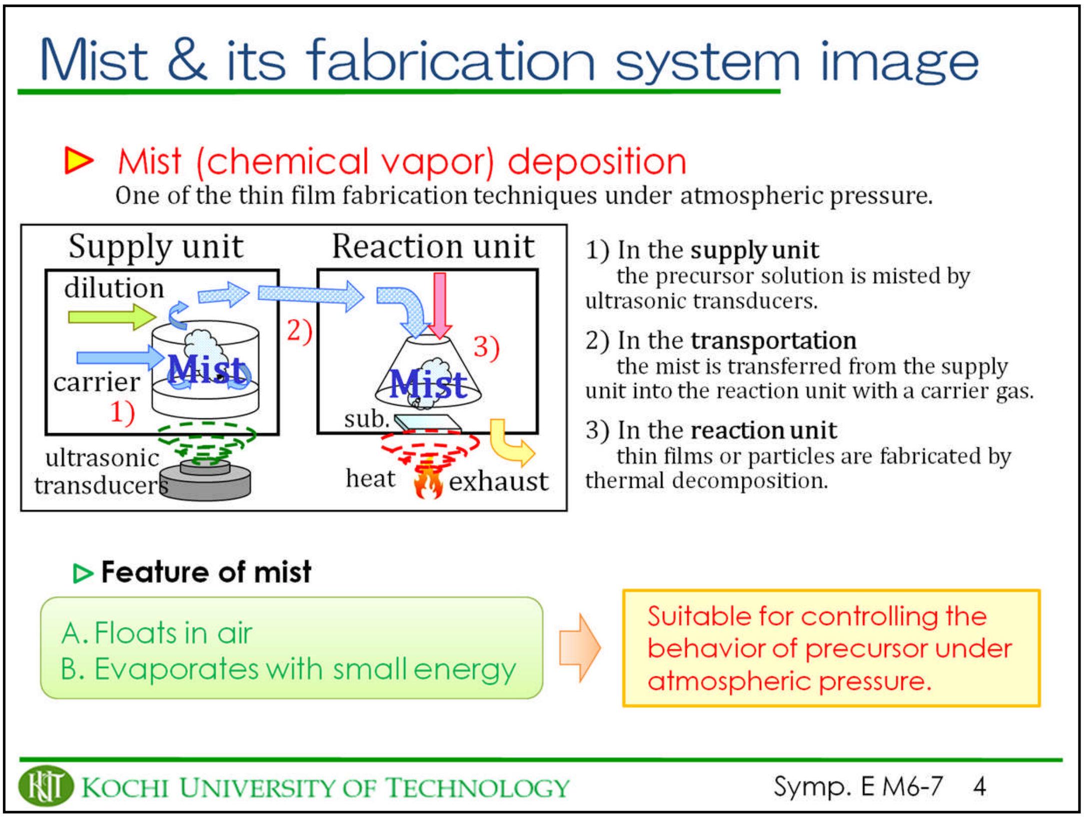
Additionally, in non-vacuum system, there are a lot of advantages, compared with the vacuum process. Environmental load is friendly, utility cost is cheap, system construction is simple, and maintenance is easy. So, the system conversion from vacuum process to a non-vacuum process gives a big merit! However, in non-vacuum system, precursor flow and atmosphere temperature have to be controlled in order to obtain high quality thin film and uniform thin film. So, we need a highly control technology. But now, there is no system with highly control technology under atmospheric pressure.

That is the reason why we have developed the novel non-vacuum fabrication system using mist. That name is mist CVD!

加えて、非真空プロセスには、真空プロセスに比べ多くの利点があります。環境への負荷が小さい。運転コストが安い。システム構造が簡易。メンテナンスが容易。つまり、真空から非真空プロセスへのシステム転換のメリットは非常に大きい。しかしながら、非真空システムでは、高品質で均一な薄膜を作製する為には、原料の挙動や雰囲気温度を高度に制御する必要がある。そうです、高度な制御技術が必要なのです。しかし、未だにそのような非真空プロセス技術は無いと言えます。

そこで、我々はミストを用いた新たな薄膜作製システム「ミスト化学気相成長(CVD)法」を開発してきました。



Mist & its fabrication system image

▷ Mist (chemical vapor) deposition

One of the thin film fabrication techniques under atmospheric pressure.

1) In the **supply unit**
the precursor solution is misted by ultrasonic transducers.

2) In the **transportation**
the mist is transferred from the supply unit into the reaction unit with a carrier gas.

3) In the **reaction unit**
thin films or particles are fabricated by thermal decomposition.

▷ **Feature of mist**

A. Floats in air
B. Evaporates with small energy

Suitable for controlling the behavior of precursor under atmospheric pressure.

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Mist deposition is one of the functional thin film fabrication techniques under atmospheric pressure. This figure is schematic image of mist deposition. In mist deposition system, there are two parts, supply unit and reaction unit. Supply unit consists of a solution tank and a few ultrasonic transducers. Reaction unit consists of a reactor chamber and a heater.

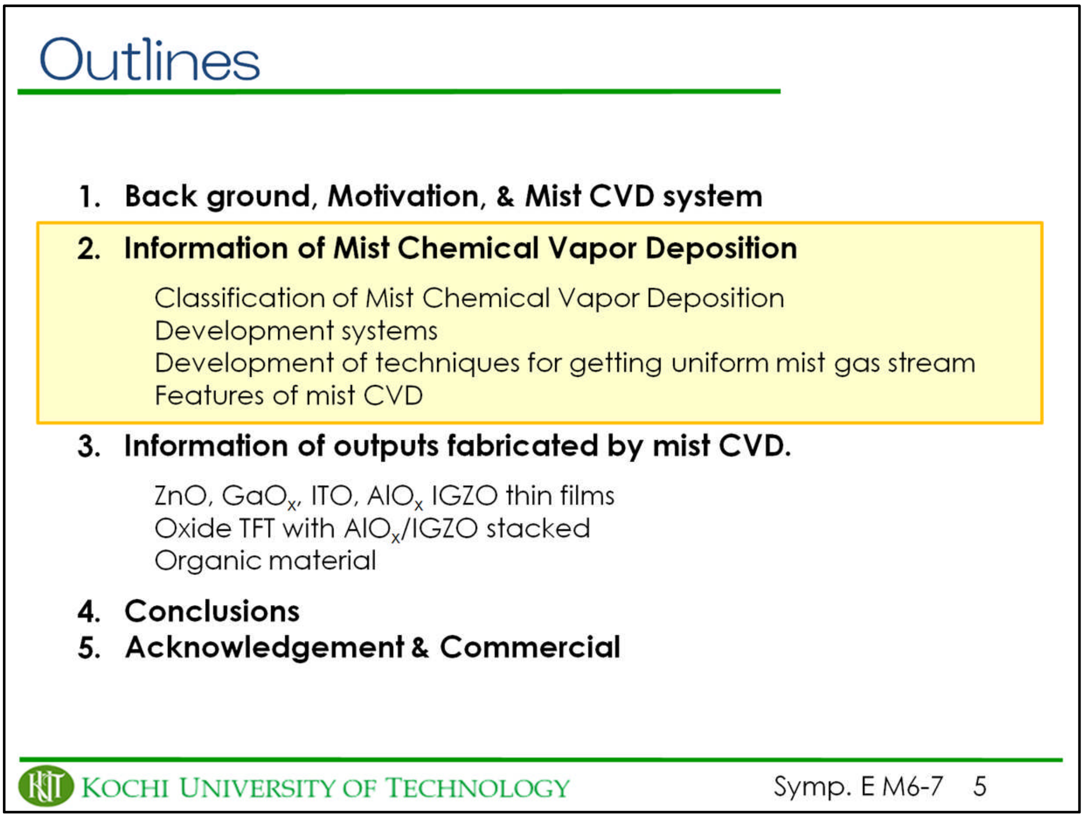
First, we prepare the precursor solution and it is misted by ultrasonic transducers in the supply unit. And next, the mist is transferred from the supply unit into the reaction unit with a carrier gas. At last, thin films or particles are fabricated by the thermal decomposition in the reaction unit.

The greatest feature of the mist deposition is using mist. Mist floats in air and evaporates with small energy. These features are suitable for controlling the behavior of precursor under atmospheric pressure.

ミストデポジション、ミストCVDは、大気圧下で薄膜を作製する為の技術の一つです。こちらに示す図は、ミストデポジションの概略図です。一般的なミストデポジションシステムには二つのパートがあります。供給部と反応部です。供給部は、溶液タンクと超音波振動子から構成されます。反応部は、反応炉とヒータから構成されます。

まず、原料溶液を用意し、超音波エネルギーを用いてミスト化します。キャリアガスによって原料ミストを供給部から反応部へ搬送します。そして、薄膜や粒子を熱分解などによって作製します。

ミスト法の最大の特徴は、ミストを扱う事である。ミストは、空中に浮遊し、ちょっとしたエネルギーでガス化するという特徴を有する。これらの特徴は、我々が原料の挙動を制御するにあたって、もってこいである。



Outlines

1. **Back ground, Motivation, & Mist CVD system**
2. **Information of Mist Chemical Vapor Deposition**
    Classification of Mist Chemical Vapor Deposition
    Development systems
    Development of techniques for getting uniform mist gas stream
    Features of mist CVD
3. **Information of outputs fabricated by mist CVD.**
    ZnO, GaO$_x$, ITO, AlO$_x$ IGZO thin films
    Oxide TFT with AlO$_x$/IGZO stacked
    Organic material
4. **Conclusions**
5. **Acknowledgement & Commercial**

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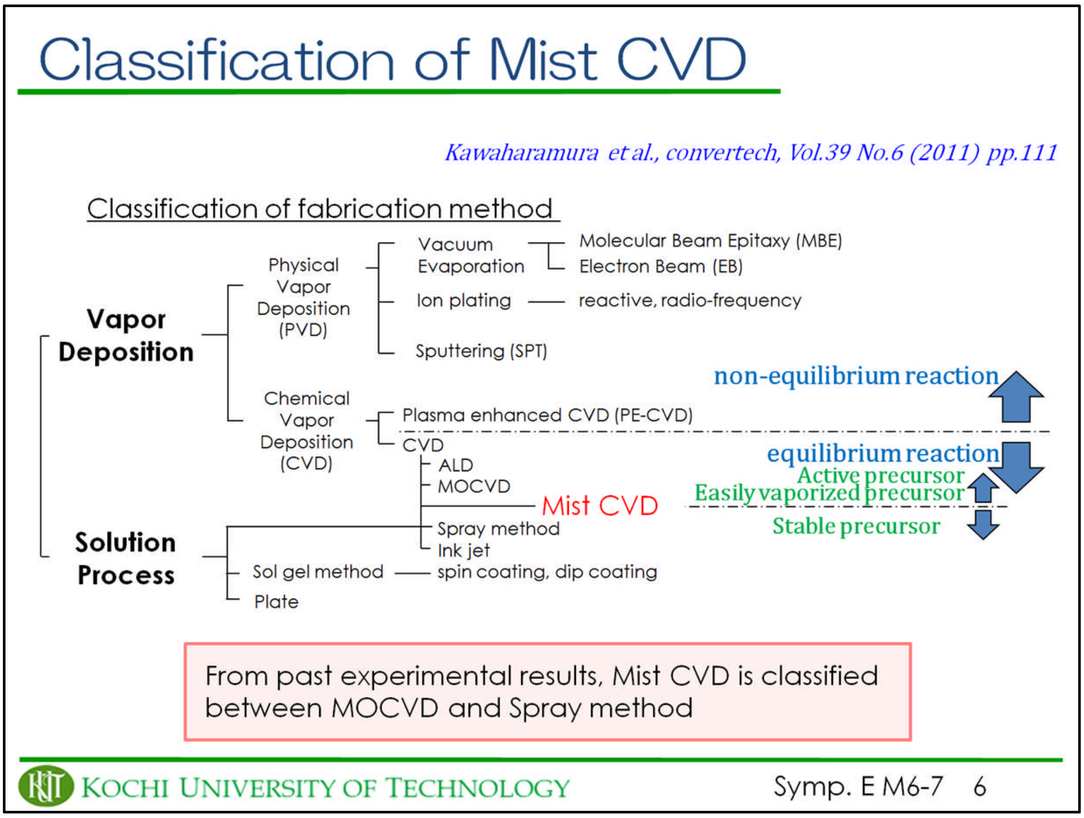
So, in this presentation, I am to explain a classification of mist deposition in the film fabrication method and to introduce development systems. Then I am to deliver the development of techniques for getting uniform mist gas stream under atmospheric pressure and to announce the features of mist CVD. After that, I am to report on the outputs fabricated by mist CVD.

そこで本発表では、ミストCVD法の位置付けを説明し、現在開発済みのシステムを紹介し、大気圧下でミストを含むガスを整流する技術やミストCVD法の特徴を説明した後、作製した機能薄膜やデバイスについて簡単に報告する。



Classification of Mist CVD

Kawaharamura et al., convertech, Vol.39 No.6 (2011) pp.111

Classification of fabrication method

Vapor Deposition
Physical Vapor Deposition (PVD)
Vacuum Evaporation
Molecular Beam Epitaxy (MBE)
Electron Beam (EB)
Ion plating
reactive, radio-frequency
Sputtering (SPT)
Chemical Vapor Deposition (CVD)
Plasma enhanced CVD (PE-CVD)
CVD
ALD
MOCVD
Mist CVD
Spray method
Ink jet
Solution Process
Sol gel method
spin coating, dip coating
Plate

non-equilibrium reaction
equilibrium reaction
Active precursor
Easily vaporized precursor
Stable precursor

From past experimental results, Mist CVD is classified between MOCVD and Spray method

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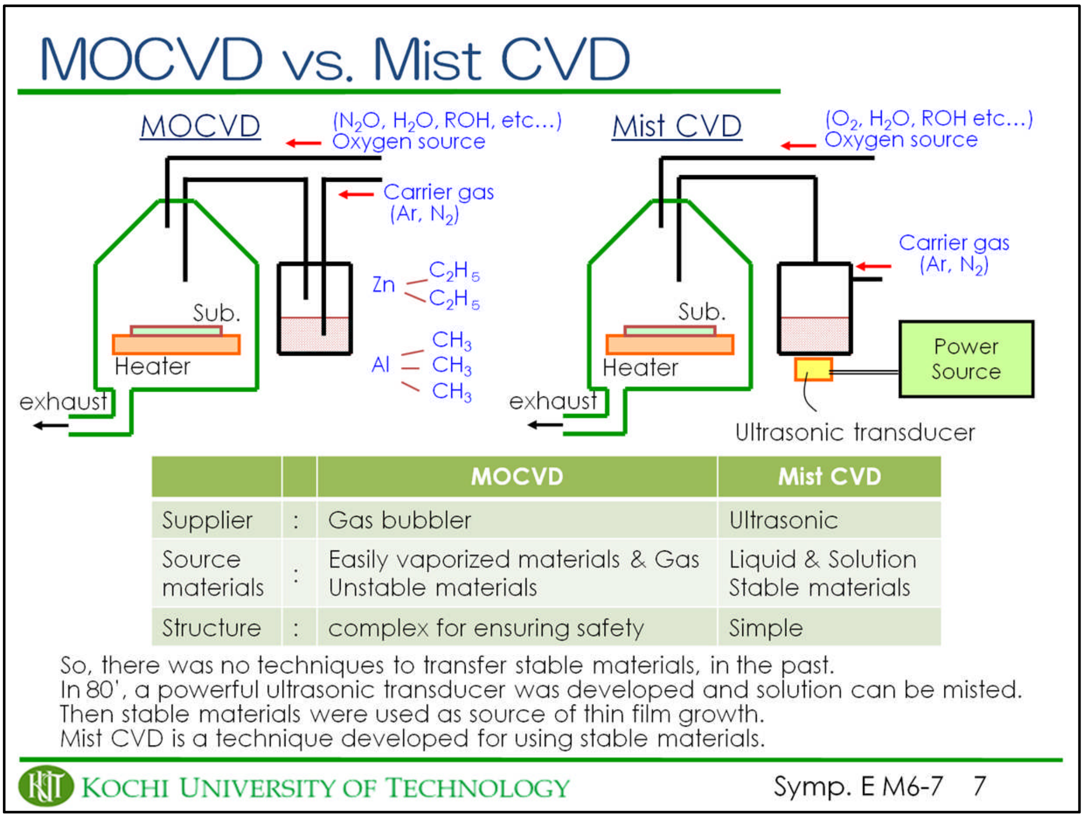
This is a classification map of fabrication method. From past experimental results, Mist CVD is classified between MOCVD and Spray method. I am to explain it, comparing mist CVD with MOCVD and Spray.

まずは、ミスト法がどこに分類されるかに関して説明します。こちらは、教科書に記載される薄膜作製法の分類図です。これまでの研究成果から、ミストCVD法は、MOCVD法とスプレー法の丁度中間的手法として分類されます。この点に関して、それぞれと比較しながら、簡単に説明します。



MOCVD vs. Mist CVD

		MOCVD	Mist CVD
Supplier	:	Gas bubbler	Ultrasonic
Source materials	:	Easily vaporized materials & Gas Unstable materials	Liquid & Solution Stable materials
Structure	:	complex for ensuring safety	Simple

So, there was no techniques to transfer stable materials, in the past.
In 80', a powerful ultrasonic transducer was developed and solution can be misted.
Then stable materials were used as source of thin film growth.
Mist CVD is a technique developed for using stable materials.

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Schematic images of MOCVD and mist CVD are shown in this sheet. Both compositions are almost same. Only source materials used and supplier are different.

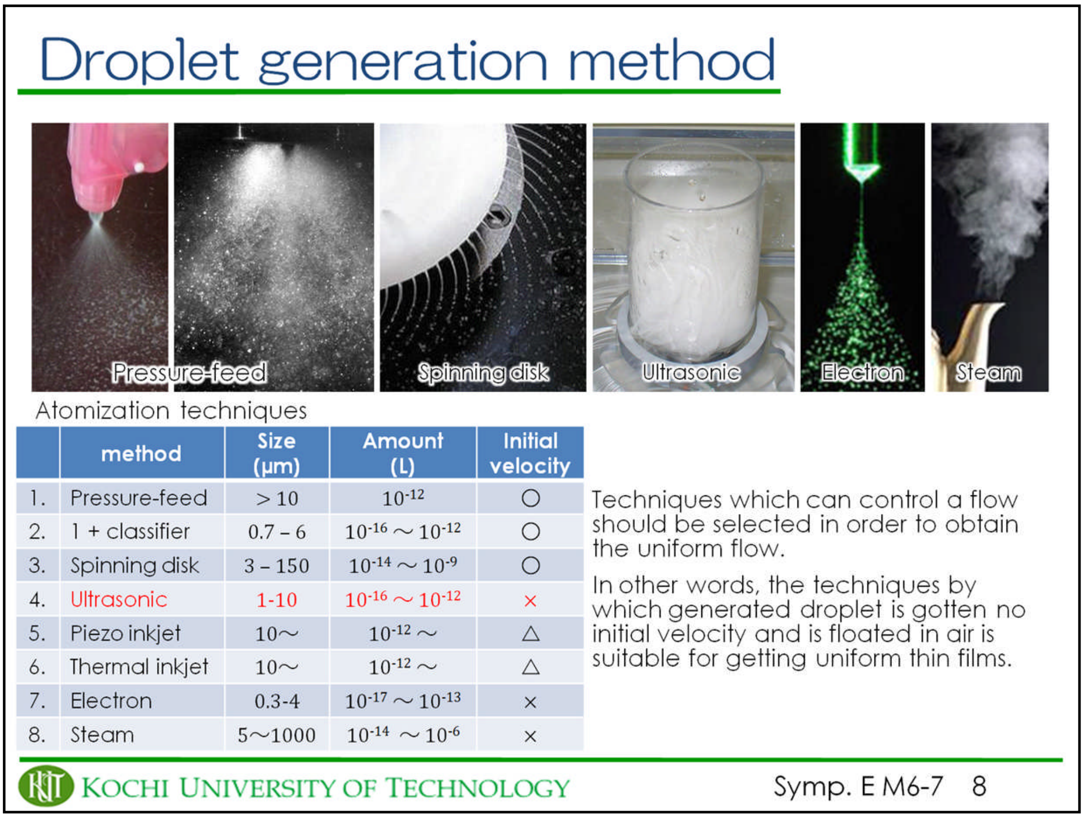
In MOCVD, easily vaporized materials or gas are used as source. In other word, unstable materials are used as source. Therefore, in MOCVD, complex structure for ensuing safety is needed.

So, there was no techniques to transfer stable materials, in the past. Around 1980, a powerful ultrasonic transducer was developed and solution could be misted. Then stable materials were used as source of thin film growth. In a word, mist CVD is a technique developed for using stable materials. So, the system is very simple structure, in mist CVD.

ここにはMOCVDとMist CVD法を並べました。どちらもその構成はほとんど同じです。唯一、使用する原料と原料供給手段だけ異なります。

MOCVD法では、ガスや蒸発しやすい材料を原料として利用します。つまり不安定な材料を原料として利用します。そのため、MOCVDでは、高度な安全機構が必要になる。

これまで安定な原料は搬送手段がありませんでした。1980年頃、強力な超音波振動子が開発され、溶液をミスト化する事が出来る様になりました。安定な原料を溶媒に溶解し、ミスト化する。そうすることによって初めて、ガス状にして搬送する事が可能になりました。つまり、ミストCVD法は、安定な材料を原料として利用する為に開発を進めた技術です。それゆえミストCVD法は非常に簡単な構造です。



Droplet generation method

Atomization techniques

	method	Size (μm)	Amount (L)	Initial velocity
1.	Pressure-feed	> 10	10^{-12}	○
2.	1 + classifier	0.7 – 6	$10^{-16} \sim 10^{-12}$	○
3.	Spinning disk	3 – 150	$10^{-14} \sim 10^{-9}$	○
4.	Ultrasonic	1-10	$10^{-16} \sim 10^{-12}$	×
5.	Piezo inkjet	10～	$10^{-12} \sim$	△
6.	Thermal inkjet	10～	$10^{-12} \sim$	△
7.	Electron	0.3-4	$10^{-17} \sim 10^{-13}$	×
8.	Steam	5～1000	$10^{-14} \sim 10^{-6}$	×

Techniques which can control a flow should be selected in order to obtain the uniform flow.

In other words, the techniques by which generated droplet is gotten no initial velocity and is floated in air is suitable for getting uniform thin films.

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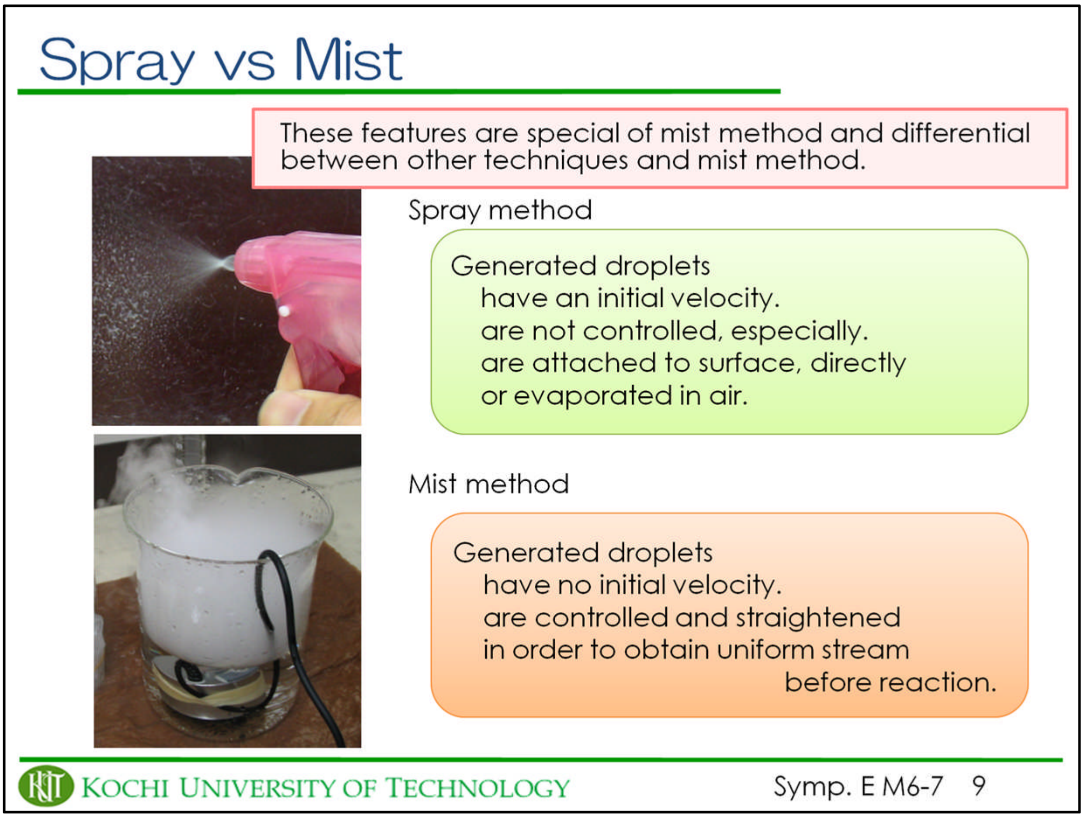
Now, the atomization technologies are shown in here. There are many kinds of atomization technologies. Techniques which can control a flow should be selected in order to obtain the uniform thin films. In other words, the techniques by which generated droplet is gotten no initial velocity and is floated in air is suitable for getting uniform thin films. For example, ultrasonic atomization is perfect for it.

さて、こちらに、液滴発生法を列挙しました。均質な薄膜を作製する為には、流れを制御出来る技術でなければなりません。その為には、液滴に初速度を持たせず空中に浮遊させる事が可能な液滴発生法が適していると言えます。例えば、超音波噴霧です。



Spray vs Mist

These features are special of mist method and differential between other techniques and mist method.

Spray method

Generated droplets
have an initial velocity.
are not controlled, especially.
are attached to surface, directly
or evaporated in air.

Mist method

Generated droplets
have no initial velocity.
are controlled and straightened
in order to obtain uniform stream
before reaction.

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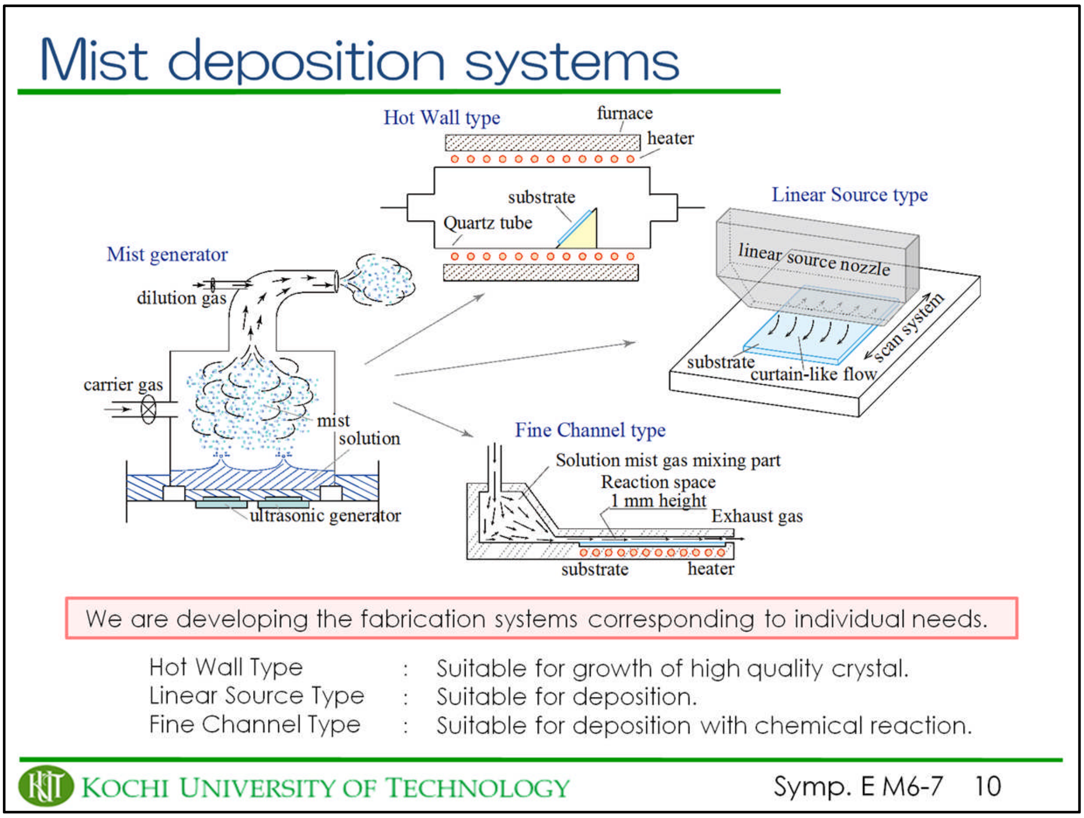
In a word, in spray method, generated droplets are not controlled especially, and are reacted or evaporated directly on the substrate. On the other hand, in mist method, generated droplets are controlled and straightened in order to obtain uniform stream before reaction.

つまり、スプレー法とミスト法の違いは、そこにあります。スプレー法では発生した液滴を含む流れを特に制御する事はなく反応や蒸発させ、薄膜を作製する手法です。しかしミスト法では発生した液滴を含む流れを制御して、均質な薄膜を作製する手法なのです。



Mist deposition systems

We are developing the fabrication systems corresponding to individual needs.

Hot Wall Type : Suitable for growth of high quality crystal.
Linear Source Type : Suitable for deposition.
Fine Channel Type : Suitable for deposition with chemical reaction.

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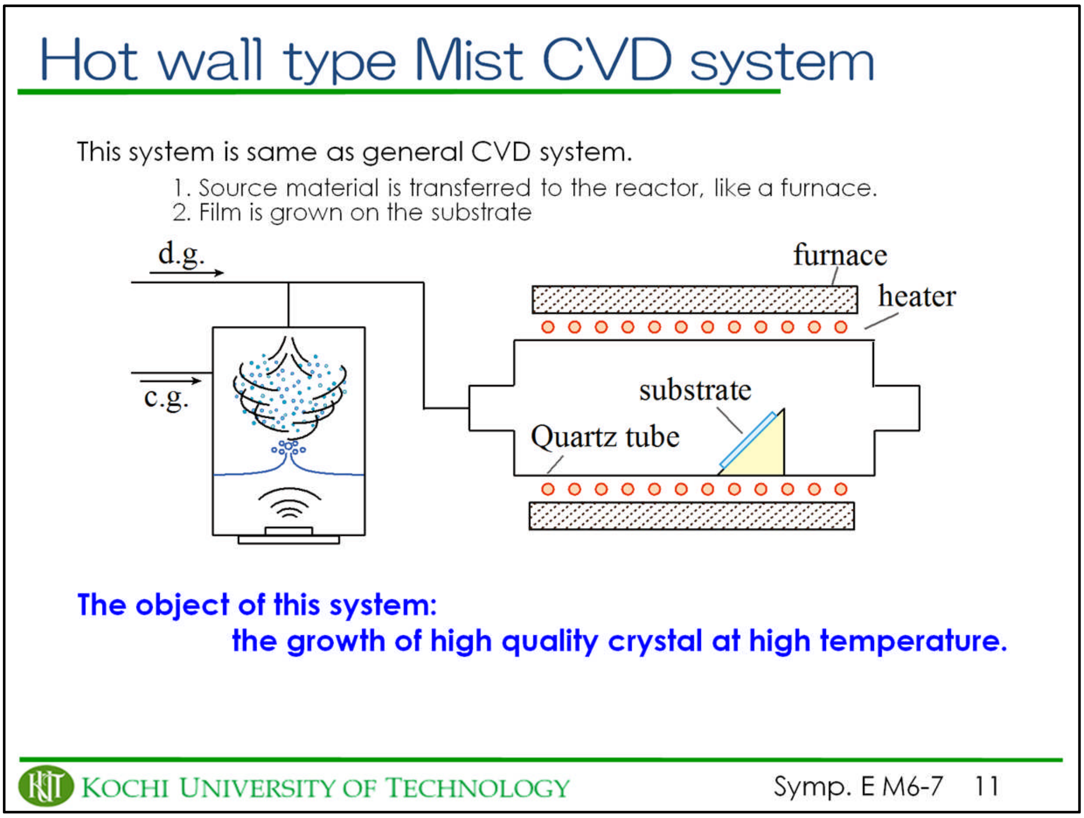
These features are special of mist method and differential between other techniques and the mist method.

In mist deposition, the ultrasonic transducer is used in supply unit. And, we are developing the fabrication systems corresponding to individual needs. For example, Hot wall, Fine Channel, and Linear Source. Hot wall type is suitable for growth of high quality crystal. Fine channel type is suitable for deposition with chemical reaction. Linear Source type is suitable for deposition.

これらの特徴が、ミスト法の他の手法との違いです。

ミスト法では、超音波噴霧を採用した原料供給装置を作りました。また、ミストの特徴を活かし、それぞれの用途に適した装置を開発しています。ホットウォール式は、高品質な結晶を作製する場合に適しており、ファインチャネル式は、化学反応を伴う場合に適しており、リニアソース式は、塗布に適しています。それぞれについて簡単に説明します。



Hot wall type Mist CVD system

This system is same as general CVD system.

1. Source material is transferred to the reactor, like a furnace.
2. Film is grown on the substrate

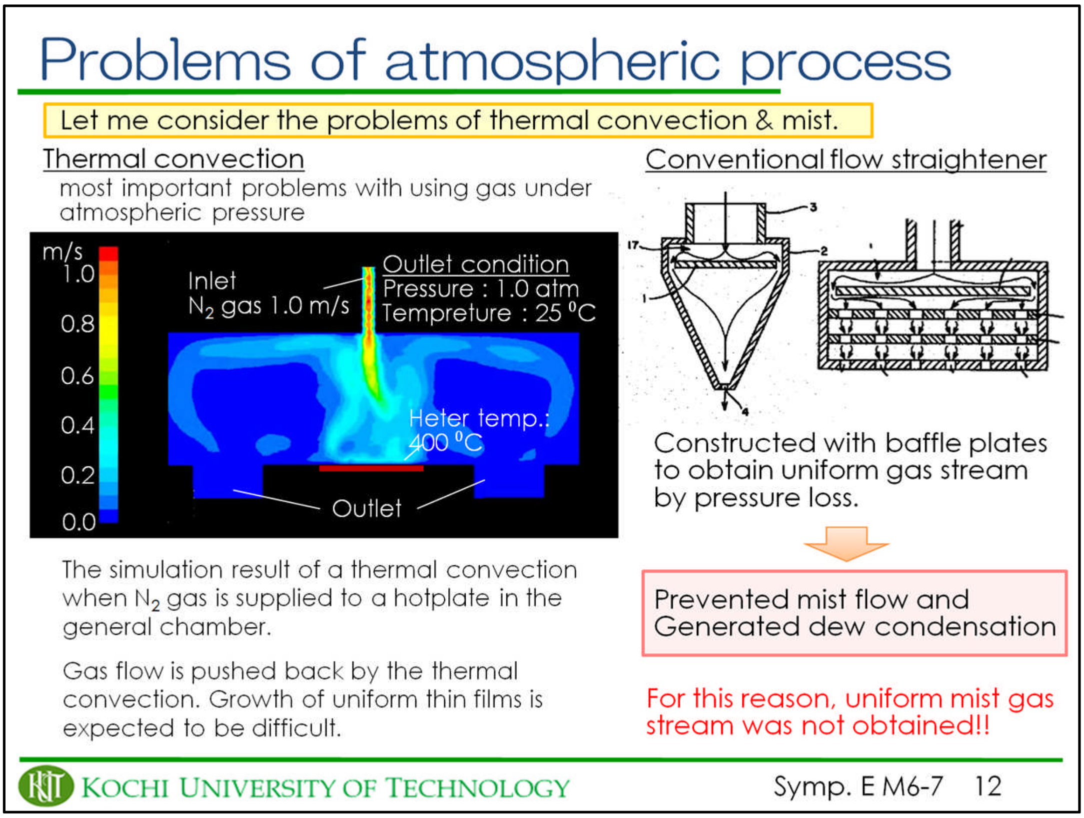
The object of this system:
the growth of high quality crystal at high temperature.

This is the schematic image of Hot wall type mist CVD system. This system is same as general CVD system. Source material is transferred to the reactor like a furnace. And film is grown on the substrate. The object of this system is the growth of high quality crystal at high temperature.

Next, I would like to explain about linear source type and fine channel type which is suitable for continuous production on large size substrate.

ホットウォール型のミストCVDシステムの概略図を示します。このシステムは、一般的なCVDシステムとほぼ同じです。原料を熱処理炉に搬送し、基板上に薄膜を成長させます。高温で高品質な薄膜を作製するのがこのシステムの目的です。

次に、より大面積基板への薄膜成長や連続的な生産が可能なリニアソース式とファインチャネル式について説明したいと思います。



Problems of atmospheric process

Let me consider the problems of thermal convection & mist.

Thermal convection

most important problems with using gas under atmospheric pressure

The simulation result of a thermal convection when N_2 gas is supplied to a hotplate in the general chamber.

Gas flow is pushed back by the thermal convection. Growth of uniform thin films is expected to be difficult.

Conventional flow straightener

Constructed with baffle plates to obtain uniform gas stream by pressure loss.

Prevented mist flow and
Generated dew condensation

For this reason, uniform mist gas stream was not obtained!!

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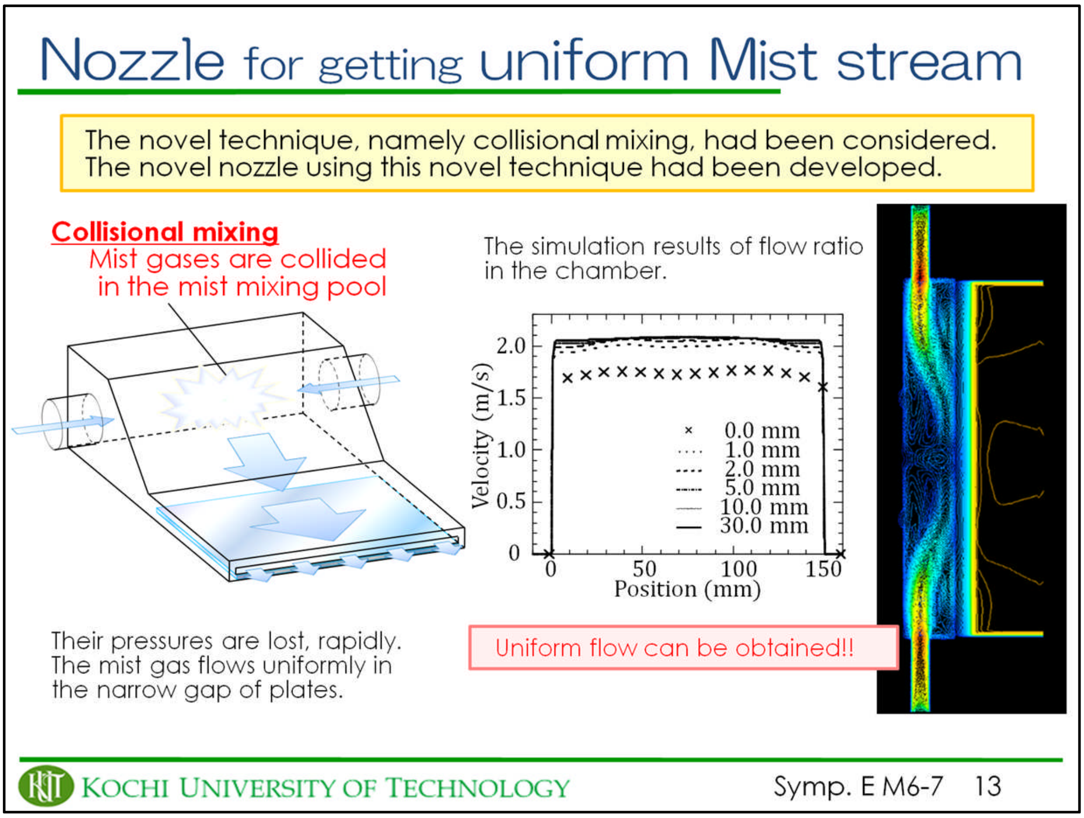
First of all, thermal convection is most important problems with using gas under atmospheric pressure. The simulation result of a thermal convection when N_2 gas is supplied to a hot plate in the general chamber is shown in here. Heater set at 400ºC and supplied gas was 1.0 m/s N_2. According to the simulation, gas flow is pushed back by the thermal convection. Growth of uniform thin films is expected to be difficult.

Then, we used conventional flow straighteners in order to obtain an uniform stream of gas including mist. However, the general flow straighteners are constructed with baffle plates to obtain uniform gas stream by pressure loss. In fact, baffle plates prevented mist flow and dew condensation was seen. For this reason, the uniform mist gas stream was not obtained by the general straighteners.

そもそも、大気中でガスを扱うと、熱対流が大きな問題となる。一般的なチャンバーを用いて加熱基板上にガスを供給した場合のガスの流れをシミュレートした結果を示す。基板温度は400ºC、供給ガスは、N2、1.0m/sである。図から分かるように、熱対流によりガスが押し戻されていることが分かる。均質な流れを作り出すことが難しいことが予想される。

そこで、整流器を用いて均質な流れを作り出そうと、一般的な整流器を用いて実験を行った。しかしながら、一般的な整流器は、圧力損失によりガスの整流を行っている為、邪魔板を用いる事が多い。ところがその邪魔板は、ミストを整流する場合、邪魔板に液滴が結露を起こしてしまう。その為もありうまく整流出来ず均質な薄膜を作製する事が困難であった。



Nozzle for getting uniform Mist stream

The novel technique, namely collisional mixing, had been considered.
The novel nozzle using this novel technique had been developed.

Collisional mixing
Mist gases are collided
in the mist mixing pool

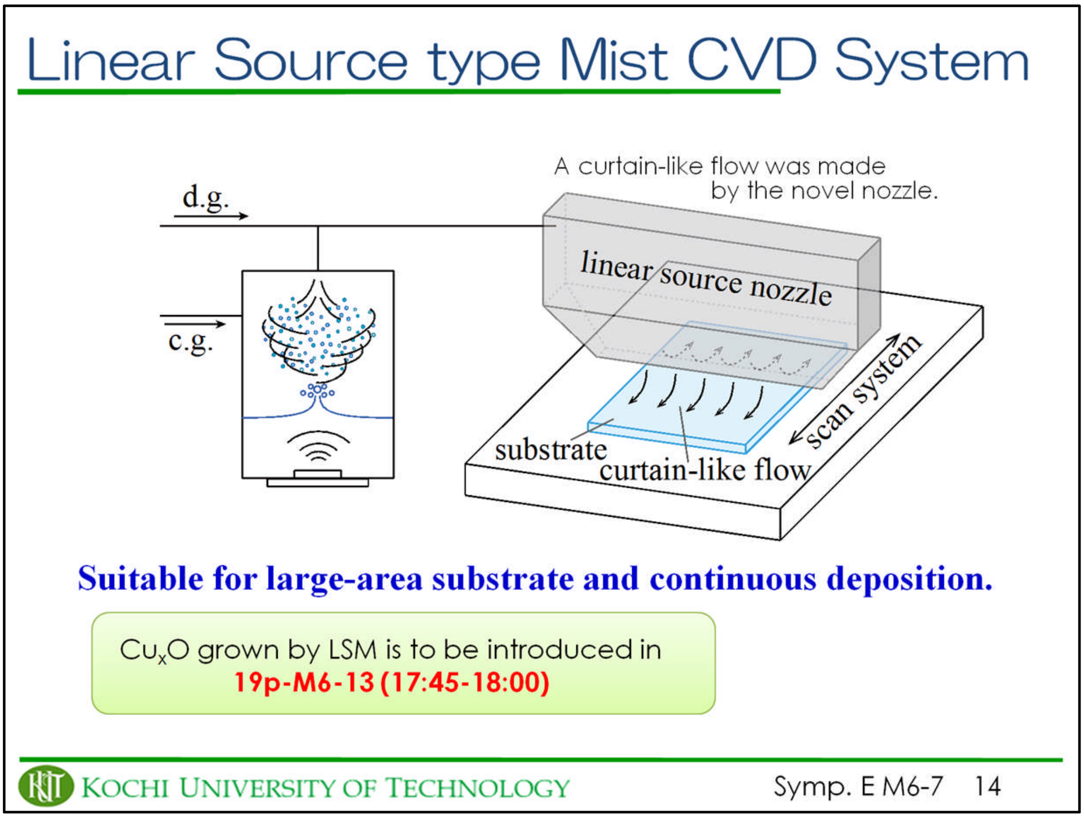
The simulation results of flow ratio
in the chamber.

Their pressures are lost, rapidly.
The mist gas flows uniformly in
the narrow gap of plates.

Uniform flow can be obtained!!

Then, the novel technology, namely collisional mixing, had been considered and the novel nozzle using this novel technique had been developed. This is the schematic image of the nozzle. The mist gas is collided by their own in the mist mixing pool and its pressure is lost rapidly. And the mist gas flows in the narrow gap of plates uniformly. The simulation results of flow ratio in the chamber are shown in these figures. The uniform flow can be obtained with this nozzle, as you can see.

そこで、ミスト流を整流する為に、ミスト流同士で圧力損失を生み出し整流させる技術、衝突混合と言う手法を考案し、均一なミスト流を生み出す装置を発明した。こちらが、その装置の概略図である。ミスト溜まり部でミスト流を衝突させ、流れの圧力を急激に損失させることにより、細い流路全面に亘り均一に流れるように工夫した装置である。この装置のガスの流れを数値計算により算出した。こちらが、流路の付け根からの距離に依存した速度分布で、こちらの図が、等速線図です。流路が狭まっているツバ部がある程度の長さになると、全面に亘って均一な速度を生じていることが分かります。



Linear Source type Mist CVD System

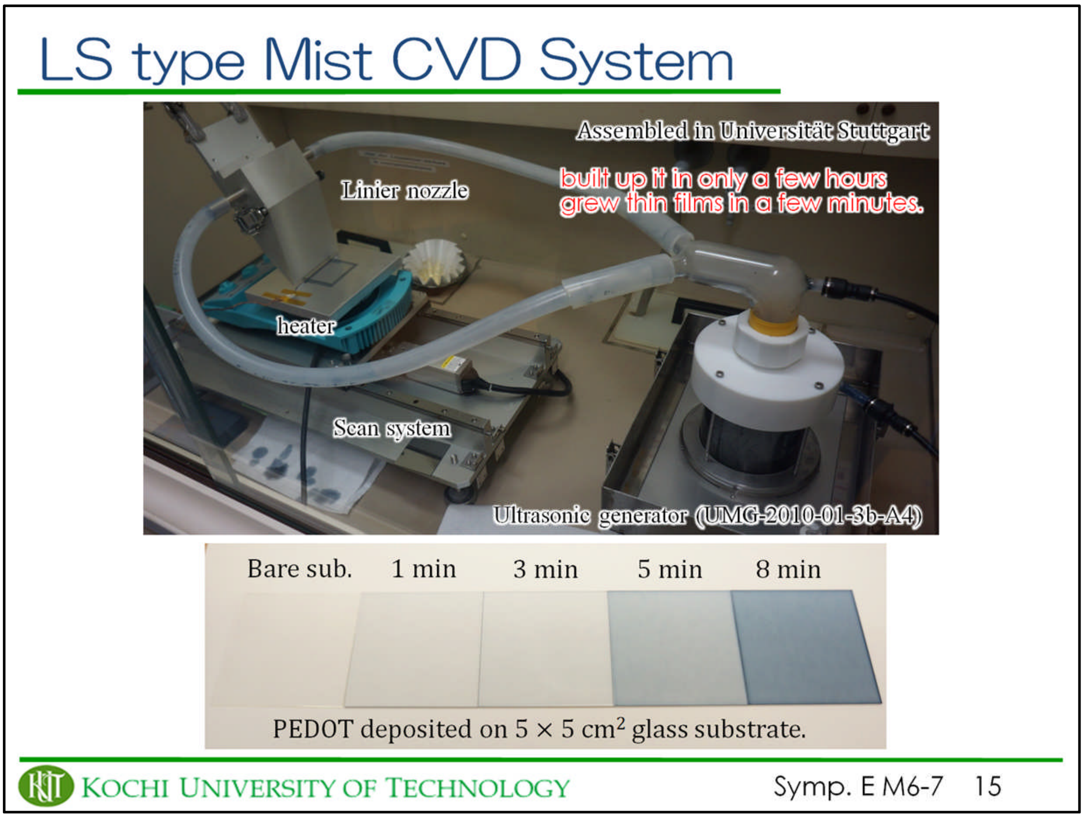
A curtain-like flow was made by the novel nozzle.

Suitable for large-area substrate and continuous deposition.

Cu_xO grown by LSM is to be introduced in
19p-M6-13 (17:45-18:00)

The schematic image of Linier Source type mist CVD system is shown in this sheet. A curtain-like flow was made by the novel nozzle. This system is suitable for large-scale substrate and continuous deposition.

この技術を用いたミストCVDシステムの一つが、このリニアソース型のミストCVDシステムです。リニアソース型のミストCVDシステムの概略図を示します。このノズルは、カーテン状の流れを作れます。このシステムは、大面積基板と連続プロセスに適しています。



LS type Mist CVD System

built up it in only a few hours
grew thin films in a few minutes.

PEDOT deposited on 5 × 5 cm^2 glass substrate.

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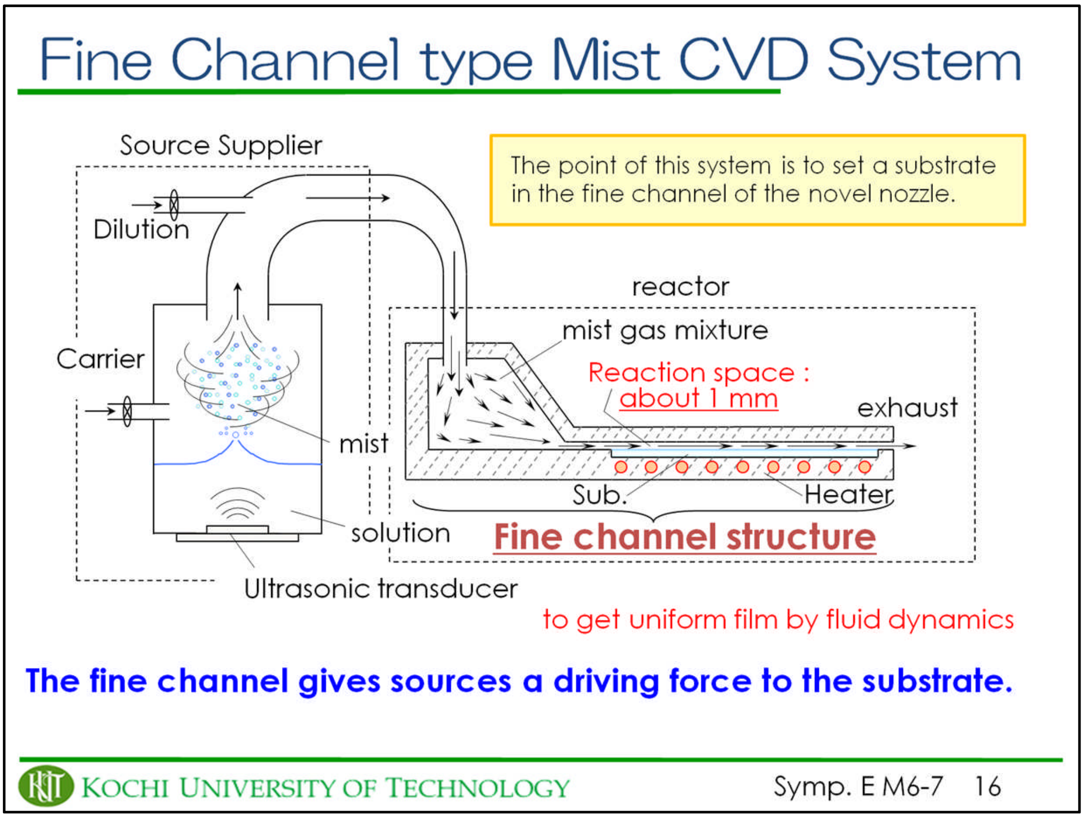
This is the linear source type mist CVD system carried and assembled in Universität Stuttgart by myself. I built up it in only a few hours and grew thin films in a few minutes. As you can see, uniform PEDOT film are deposited on the 5 cm^2 glass substrate.

これは私が、ストットガルド大学に持ち込んで組み立てた装置です。数時間で立ち上げ、均質な薄膜を数分で作り上げました。こちらに示しますように、PEDOTの均質膜が作製出来ている事が分かります。



Fine Channel type Mist CVD System

The point of this system is to set a substrate in the fine channel of the novel nozzle.

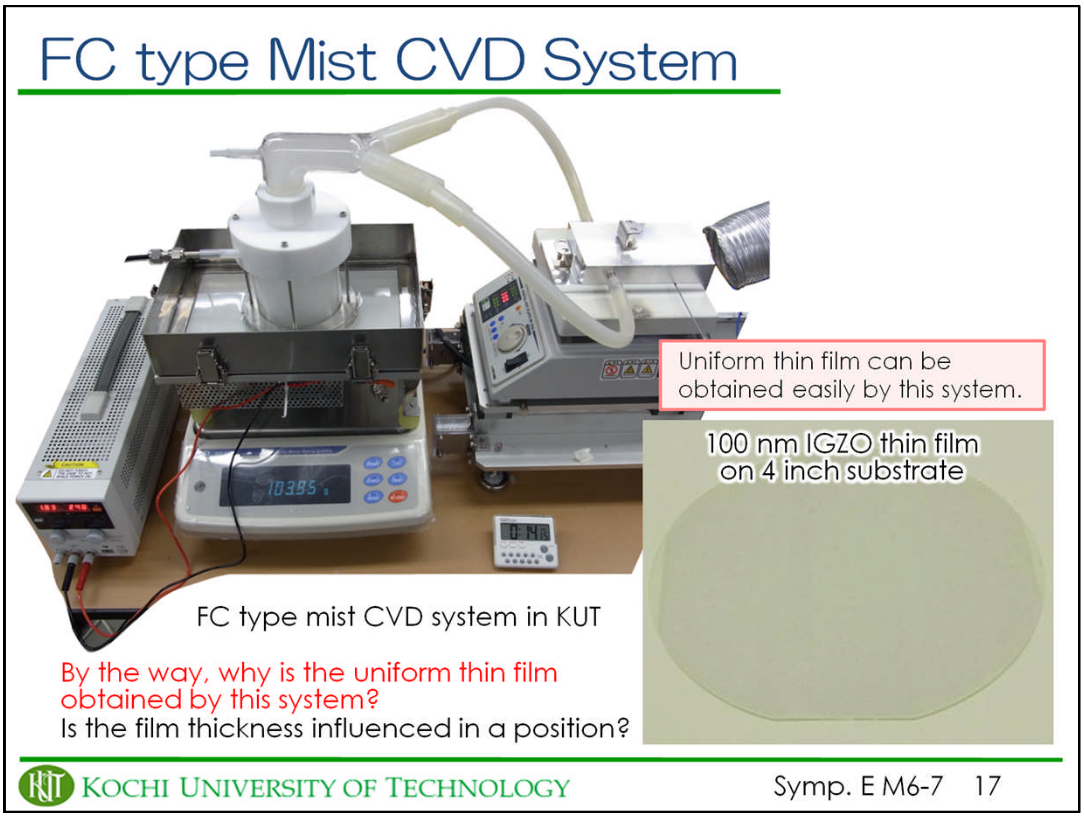
to get uniform film by fluid dynamics

The fine channel gives sources a driving force to the substrate.

KOCHI UNIVERSITY OF TECHNOLOGY Symp. E M6-7 16

And another is a Fine channel type mist CVD system. The point of this system is to set a substrate in the fine channel of the novel nozzle. The fine channel gives sources a driving force to the substrate.

また、もう一つが、ファインチャネル型のミストCVDシステムです。ファインチャネル型のミストCVDシステムの概略図を示します。このシステムのポイントはファインチャネル内に基板を設置しているところです。ファインチャネルは、原料の基板への押しつけ効果が期待されます。



FC type Mist CVD System

Uniform thin film can be obtained easily by this system.

100 nm IGZO thin film on 4 inch substrate

FC type mist CVD system in KUT

By the way, why is the uniform thin film obtained by this system?
Is the film thickness influenced in a position?

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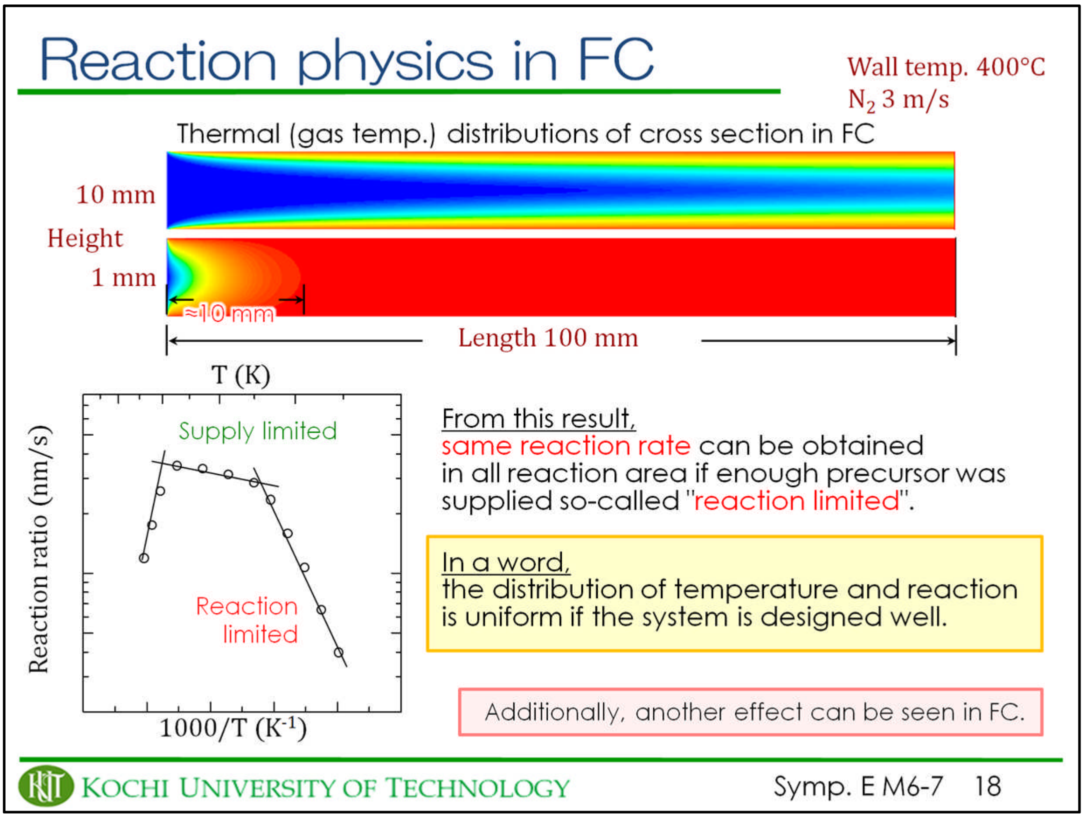
This is the fine channel type mist CVD system in KUT. This is a photo of 100 nm IGZO thin film on non-alkaline glass substrate. As you can see, uniform thin film can be obtained easily by this system.

By the way, why can the uniform thin film be obtained by this system? Don’t you think that the film thickness is influenced in a position? For example, it is thick in the inlet part and it is thin in the outlet part.

これらの技術を用いて、作製した装置が、このミストCVDシステムである。このシステムを用いれば、非常に簡単に均質な膜を作製する事ができる。こちらに示す膜は、無アルカリガラス基板上に成長した100 nmのIGZO薄膜である。

ところで、上流側と下流側で分布が出来ないか疑問に思うのではないでしょうか？それに関して簡単に説明します。



Reaction physics in FC

Wall temp. 400°C
N_2 3 m/s

Thermal (gas temp.) distributions of cross section in FC

From this result,
same reaction rate can be obtained
in all reaction area if enough precursor was
supplied so-called "reaction limited".

In a word,
the distribution of temperature and reaction
is uniform if the system is designed well.

Additionally, another effect can be seen in FC.

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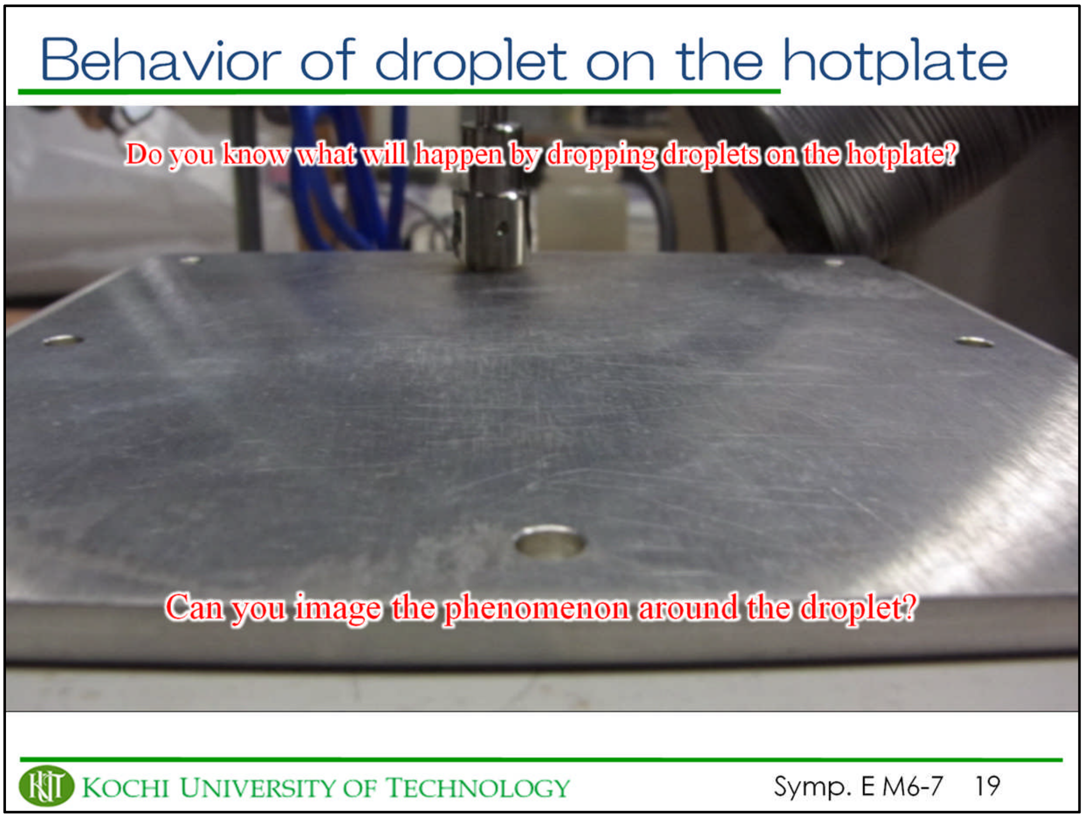
Thermal distribution of cross section in FC is shown in here. In the 10 mm height reactor, the gas temperature near wall is increasing immediately but the gas temperature of center area is not increasing. On the other hand, the gas temperature of all area is increasing soon at even pass 10 mm in the case of 1 mm height reactor. From this result, same reaction rate can be obtained in all reaction area if enough precursor was supplied so-called "reaction limited". In a word, the distribution of temperature and reaction is uniform if the system is designed well.

Additionally, another effect can be seen in FC.

ファインチャネル内の温度分布をこちらに示します。10mmの場合は、壁面近傍はすぐに昇温しますが、真ん中部分は、温度がなかなか昇温しません。一方で、流路高が1mmの場合は、流入したガスは一気に加熱され、10mm程度進んだところで、全面一定温度になっている事が分かります。このことから、反応時に原料が十分にある状態を保つ事が出来れば、いわゆる反応律速状態にすれば、全面に亘って同じ反応率を保つことが出来る分けです。つまり、上手に装置を作製すれば、温度ムラも反応ムラもなくなります。

実はこれだけでなく、ファインチャネルでは、もう一つ面白い効果が見られました。



Behavior of droplet on the hotplate

Do you know what will happen by dropping droplets on the hotplate?

Can you image the phenomenon around the droplet?

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Do you know what will happen by dropping droplets on the hotplate. Hotplate temperature is 150ºC.

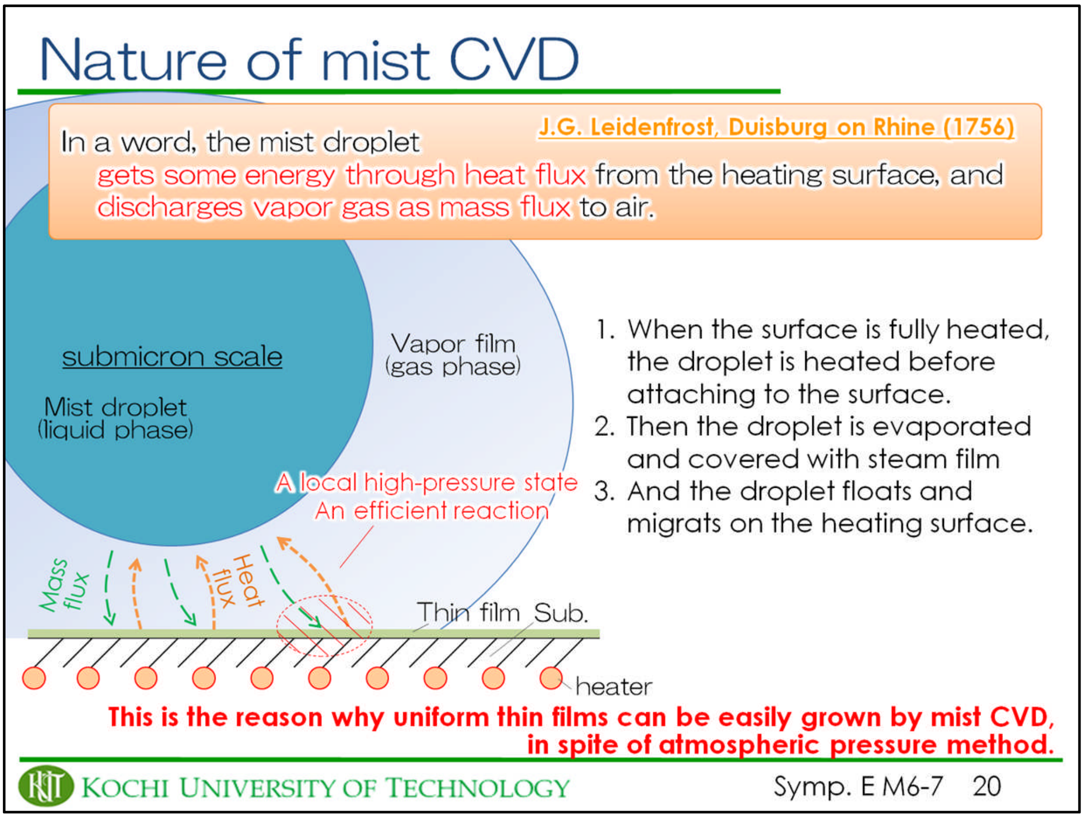
1. So, as you know, some droplets are evaporated soon.
2. But, some droplets are not evaporated soon, with jumping up and down or float in air.

Can you image the phenomenon around the droplet?

ホットプレートの上に、液滴を落とすと何が起こるかご存じでしょうか。ホットプレートは150ºCに加熱されています。

1. ある液滴は、ホットプレートの上ですぐに蒸発します。
2. しかし、ある液滴は、飛び跳ねますが、すぐには蒸発しません。

貴方はこの時に起こっている現象についてイメージできますか？



Nature of mist CVD

J.G. Leidenfrost, Duisburg on Rhine (1756)

In a word, the mist droplet
gets some energy through heat flux from the heating surface, and
discharges vapor gas as mass flux to air.

1. When the surface is fully heated, the droplet is heated before attaching to the surface.
2. Then the droplet is evaporated and covered with steam film
3. And the droplet floats and migrats on the heating surface.

This is the reason why uniform thin films can be easily grown by mist CVD, in spite of atmospheric pressure method.

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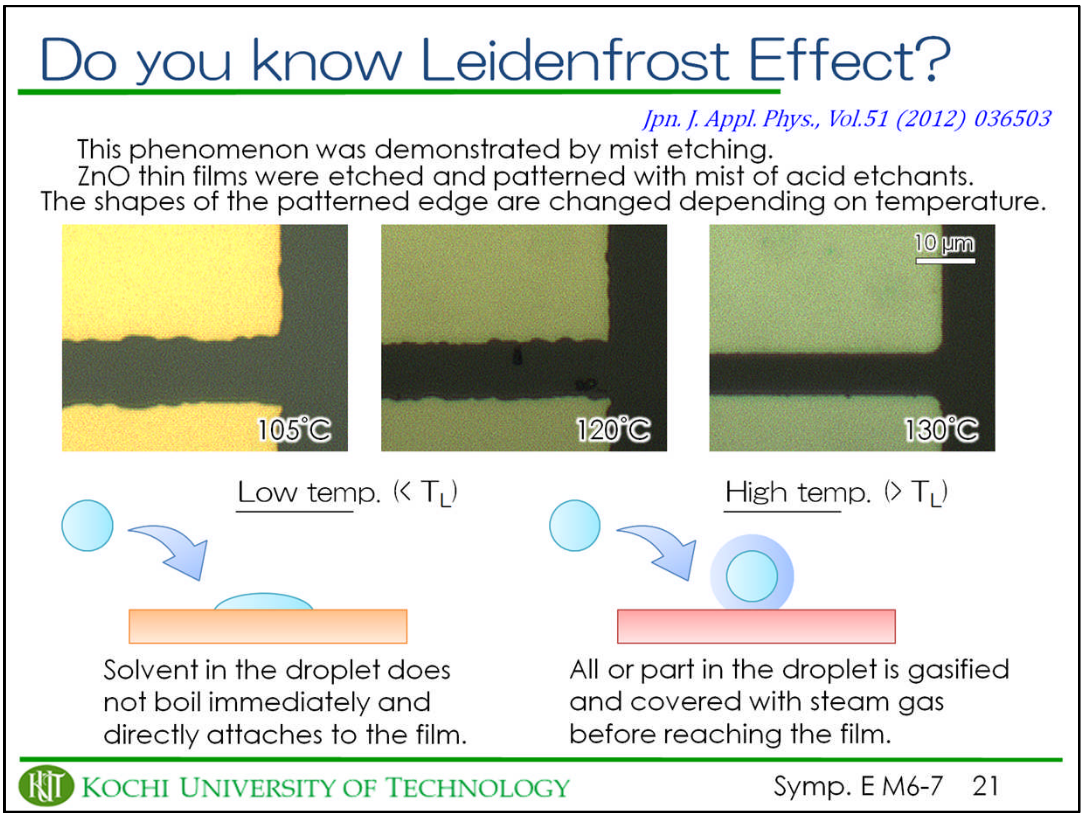
This phenomenon is named Leidenfrost Effect, which was reported by Dr. Leidenfrost in 1756. When the surface is fully heated, the droplet is heated before attaching to the surface. Then the droplet is evaporated from the surface, covered with steam film and migrated on the surface. In the word, the droplet gets some energy through heat flux from the heating surface, and discharges vapor gas as mass flux to air. This is Leidenfrost Effect. And this is the reason why uniform thin films can be easily grown by mist CVD, in spite of atmospheric pressure method.

これは、ライデンフロスト効果といわれる現象で、1756年にライデンフロストさんによって発表されています。壁面が充分に加熱されていると、液滴が壁面に当たる前に暖められ、暖められた液滴は表面から蒸発し、蒸気膜に覆われます。つまり、壁面から発生した熱流速により液滴が加熱され、液滴からの物質流速により液滴は浮遊することになります。これが、ライデンフロスト効果です。これが、大気圧手法にも係わらず、こんなにも簡単にミストCVD法で均質な薄膜が作製出来る理由です。

ミストCVD法では、この原理を利用して、上流から下流にかけて、均質な薄膜を作製する事が出来ます。

＊ミスト法の中でも、ミスト化学気相成長(CVD)法が成り立つのは、この原理を利用して薄膜を作製している時です。



Do you know Leidenfrost Effect?

Jpn. J. Appl. Phys., Vol.51 (2012) 036503

This phenomenon was demonstrated by mist etching.
ZnO thin films were etched and patterned with mist of acid etchants.
The shapes of the patterned edge are changed depending on temperature.

Low temp. (< T_L)

Solvent in the droplet does not boil immediately and directly attaches to the film.

High temp. (> T_L)

All or part in the droplet is gasified and covered with steam gas before reaching the film.

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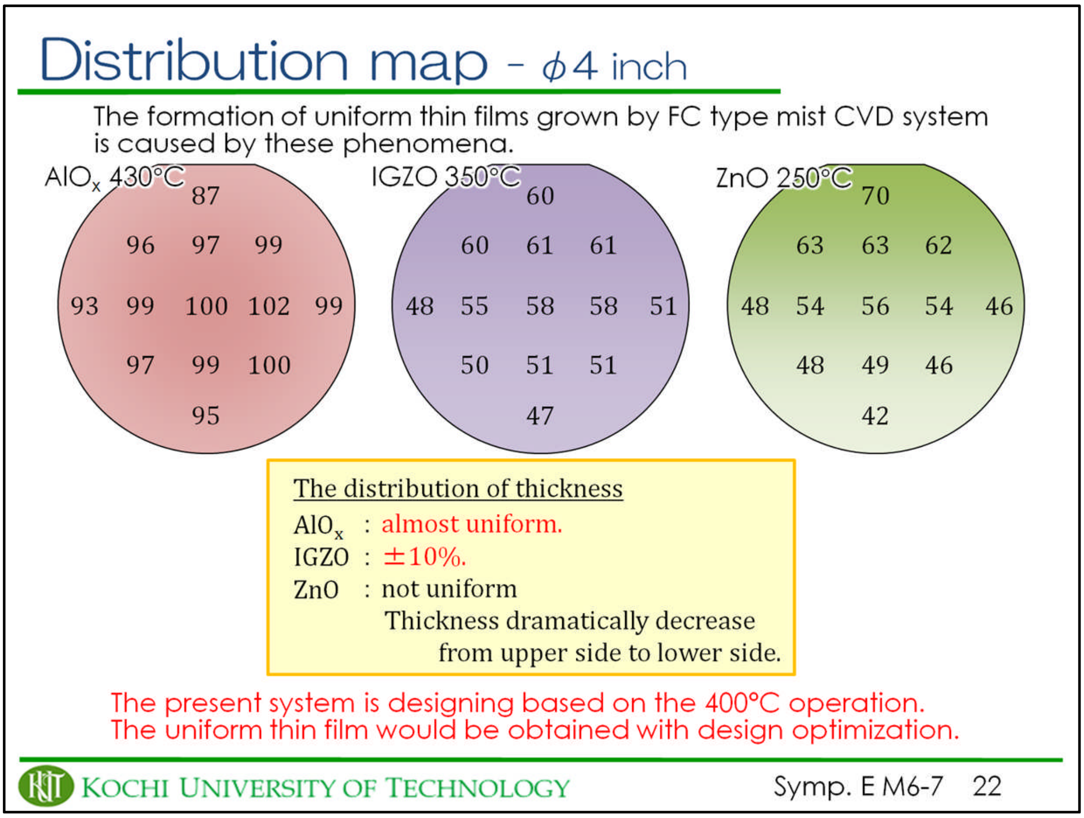
In fact, this phenomenon is demonstrated by mist etching. In this experiment, ZnO thin films were etched with misted acid etchants.

Please look these figures. ZnO thin films were patterned by mist etching. As you can see, the shapes of the patterned edge are changed depending on temperature. At low temperature, solvent in the droplet does not boil immediately and directly attaches to the film. On the other hand, at high temperature, all or part in the droplet is gasified and covered with steam gas before reaching the film.

実際に、これは、ミストを用いて薄膜のエッチングを行った実験結果から明らかになりました。こちらの写真をご覧下さい。酸化亜鉛薄膜をミストエッチングでパターン化した結果です。低温では液滴に跡が見られますが、高温になると液滴の跡が見られません。つまり、低温では、液滴が直接膜に接触していると考えられます。一方で、高温では、液滴は直接膜に接触することなく、ガス化もしくは蒸気膜に覆われ浮いている状態になります。



Distribution map - ϕ4 inch

The formation of uniform thin films grown by FC type mist CVD system is caused by these phenomena.

The distribution of thickness

AlO$_x$: almost uniform.
IGZO : ±10%.
ZnO : not uniform
Thickness dramatically decrease
from upper side to lower side.

The present system is designing based on the 400°C operation.
The uniform thin film would be obtained with design optimization.

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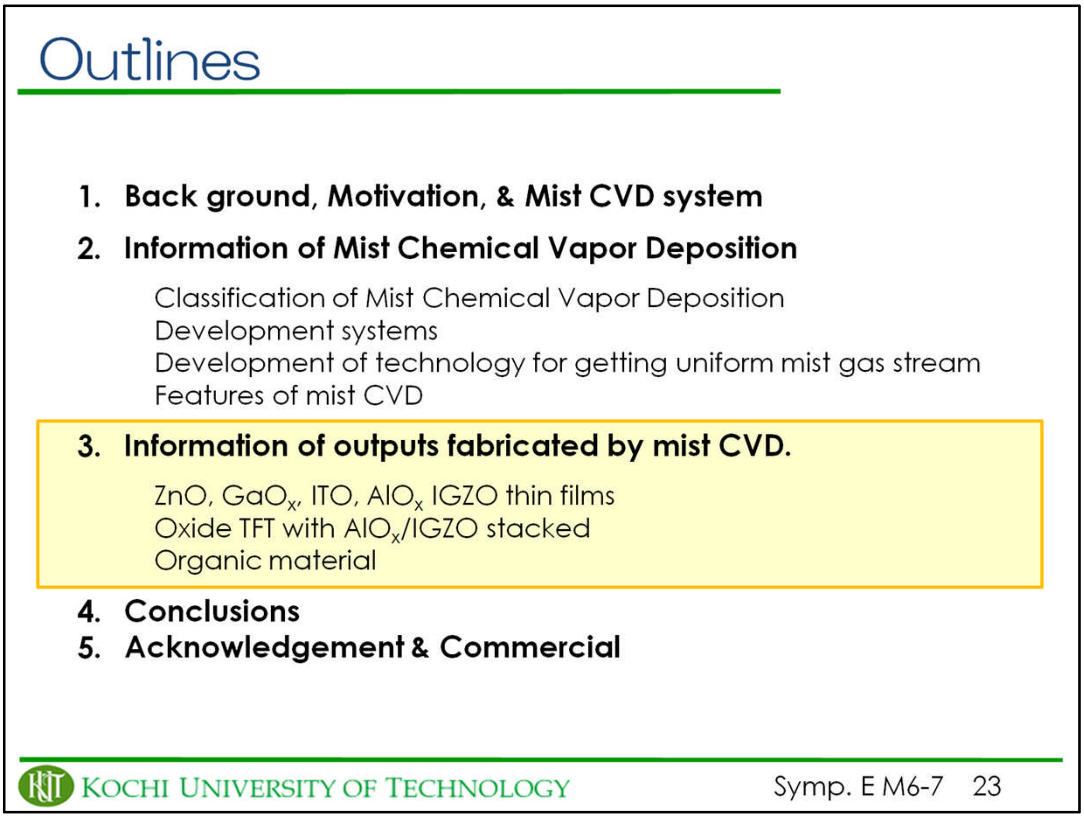
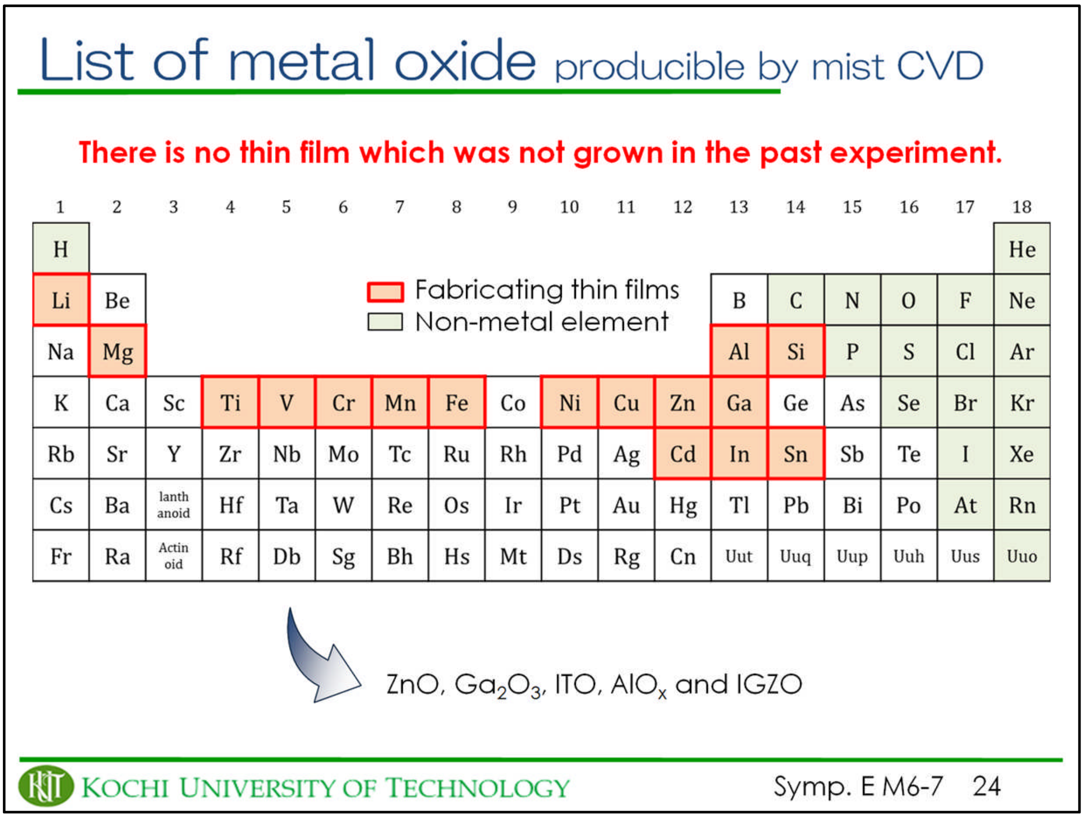
The formation of uniform thin films grown by fine channel type mist CVD system is caused by these phenomena. For examples, there are the distribution maps of AlO$_x$, IGZO, and ZnO thin films on φ 100 mm substrates. AlO$_x$ and IGZO thin films are almost uniform. But ZnO thin films are not uniform. The present system is designing based on the 400ºC operation. The uniform thin film would be obtained with design optimization.

これらの現象が、ミストCVD法で均一膜を簡単に得られる理屈です。実際にどの程度均質な膜が得られるのでしょうか。アルミナとIGZOと酸化亜鉛薄膜を作製した時の、膜厚分布図がこちらになります。アルミナとIGZO薄膜はほとんど均一ですが、酸化亜鉛は均一ではありません。現在の装置が400ºCを目安に設計しており、装置最適化を行えば、均一な薄膜を得られるでしょう。



Outlines

1. **Back ground, Motivation, & Mist CVD system**
2. **Information of Mist Chemical Vapor Deposition**
   - Classification of Mist Chemical Vapor Deposition
   - Development systems
   - Development of technology for getting uniform mist gas stream
   - Features of mist CVD
3. **Information of outputs fabricated by mist CVD.**
   - ZnO, GaO_x, ITO, AlO_x IGZO thin films
   - Oxide TFT with AlO_x/IGZO stacked
   - Organic material
4. **Conclusions**
5. **Acknowledgement & Commercial**



List of metal oxide producible by mist CVD

There is no thin film which was not grown in the past experiment.

🟥 Fabricating thin films

▭ Non-metal element

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	lanthanoid	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Actinoid	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo

ZnO, Ga_2O_3, ITO, AlO_x and IGZO

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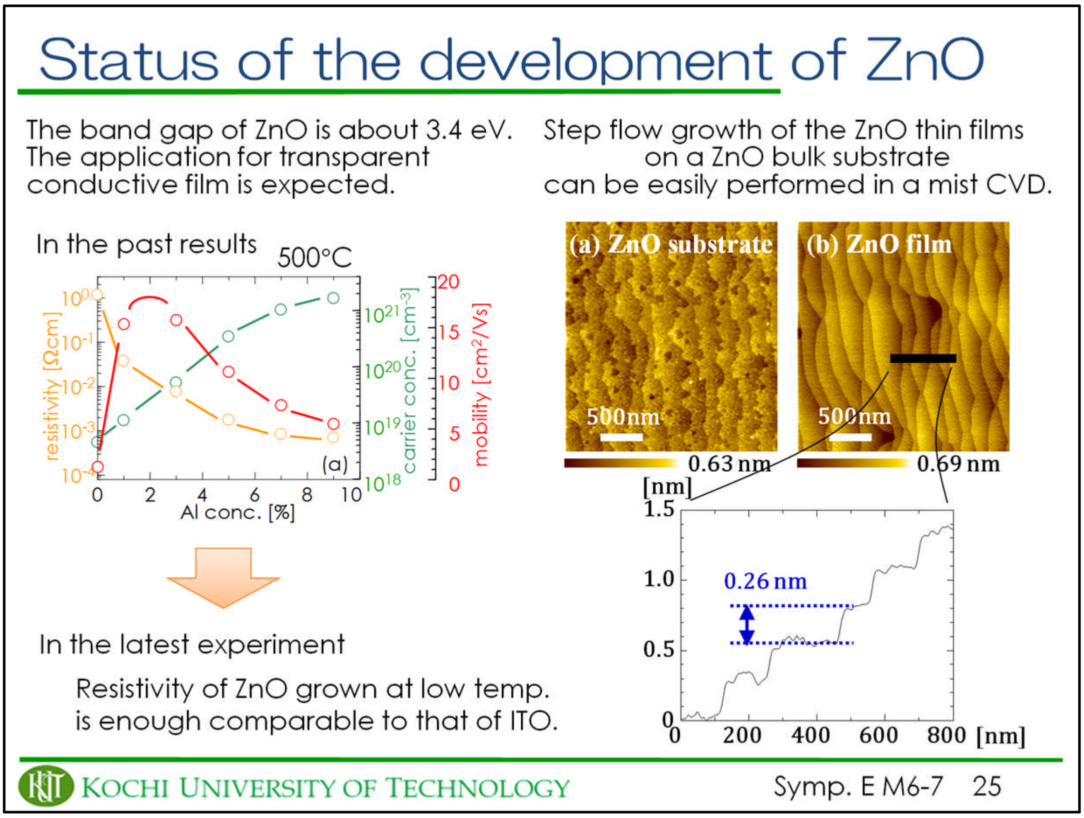
It is the list of metal oxide thin films producible by mist CVD. There is no thin film which was not grown in the past experiment.

Today, I briefly inform you about ZnO, Ga_2O_3, ITO, AlO_x and IGZO thin films

ここには、ミストCVD法で作製可能な金属酸化物薄膜の一覧を載せてあります。これまでの実験で出来なかった薄膜はありません。本日は簡単に、酸化亜鉛と、酸化ガリウム、酸化アルミニウム、酸化インジウム錫、酸化アルミニウム、酸化インジウムガリウム亜鉛について紹介します。



Status of the development of ZnO

The band gap of ZnO is about 3.4 eV.
The application for transparent
conductive film is expected.

Step flow growth of the ZnO thin films
on a ZnO bulk substrate
can be easily performed in a mist CVD.

In the past results 500°C

In the latest experiment

Resistivity of ZnO grown at low temp.
is enough comparable to that of ITO.

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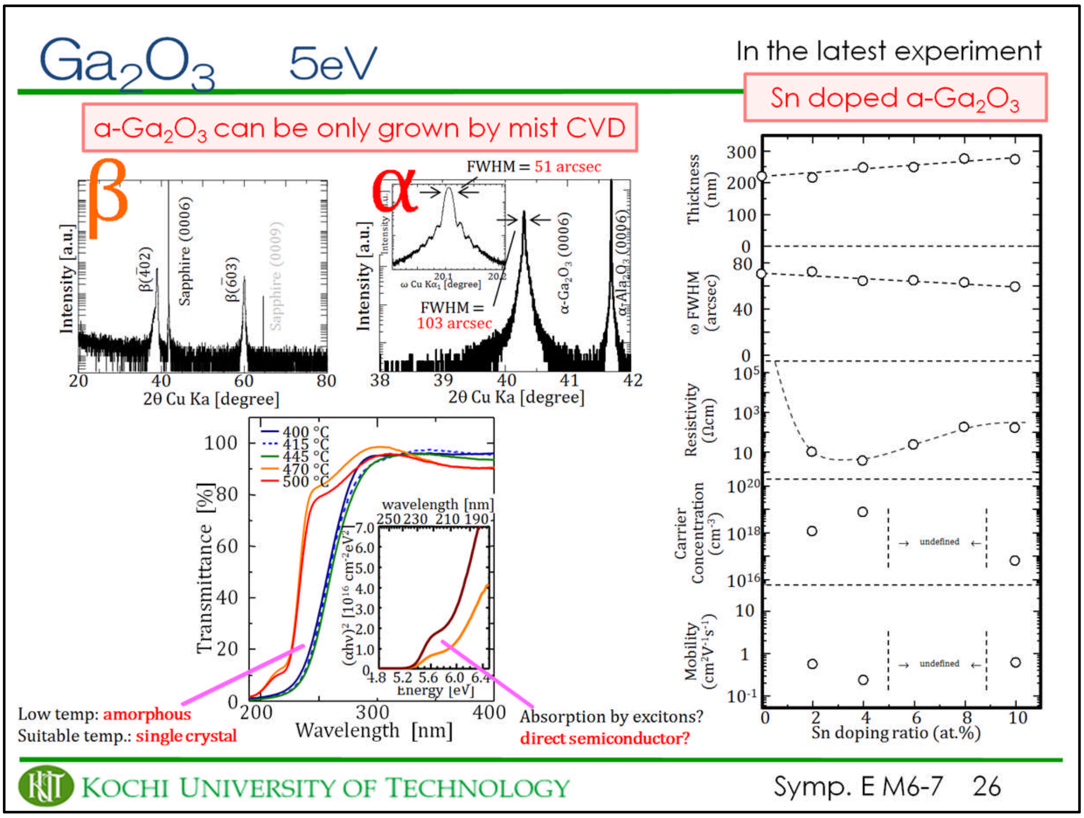
The band gap of ZnO is about 3.4 eV. The application for transparent conductive film is expected.

In the past results, Al doped ZnO thin films grown by mist CVD at 500ºC exhibited the resistivity of 10^{-4} Ωcm. In the latest experiment, resistivity of ZnO grown at 200ºC is enough comparable to that of ITO.

Moreover, step flow growth of the ZnO thin films on a ZnO bulk substrate can be easily performed in mist CVD. This experiment is difficult in MOCVD.

酸化亜鉛薄膜のバンドギャップは3.4eV程で、透明導電膜としての用途が期待されています。
ミストCVD法の実績としては、アルミニウムをドーパント剤として500ºCで作製したところ、10^{-4} Ωcmの抵抗値を得ることに成功しました。最近の結果では、200ºCで作製した酸化亜鉛の導電性は十数Ω/□ということです。また、MOCVDでは難しい酸化亜鉛基板上への酸化亜鉛薄膜のステップフロー成長がミストCVD法では、簡単にできます。



Ga_2O_3 5eV

α-Ga_2O_3 can be only grown by mist CVD

In the latest experiment

Sn doped α-Ga_2O_3

Low temp: amorphous
Suitable temp.: single crystal

Absorption by excitons?
direct semiconductor?

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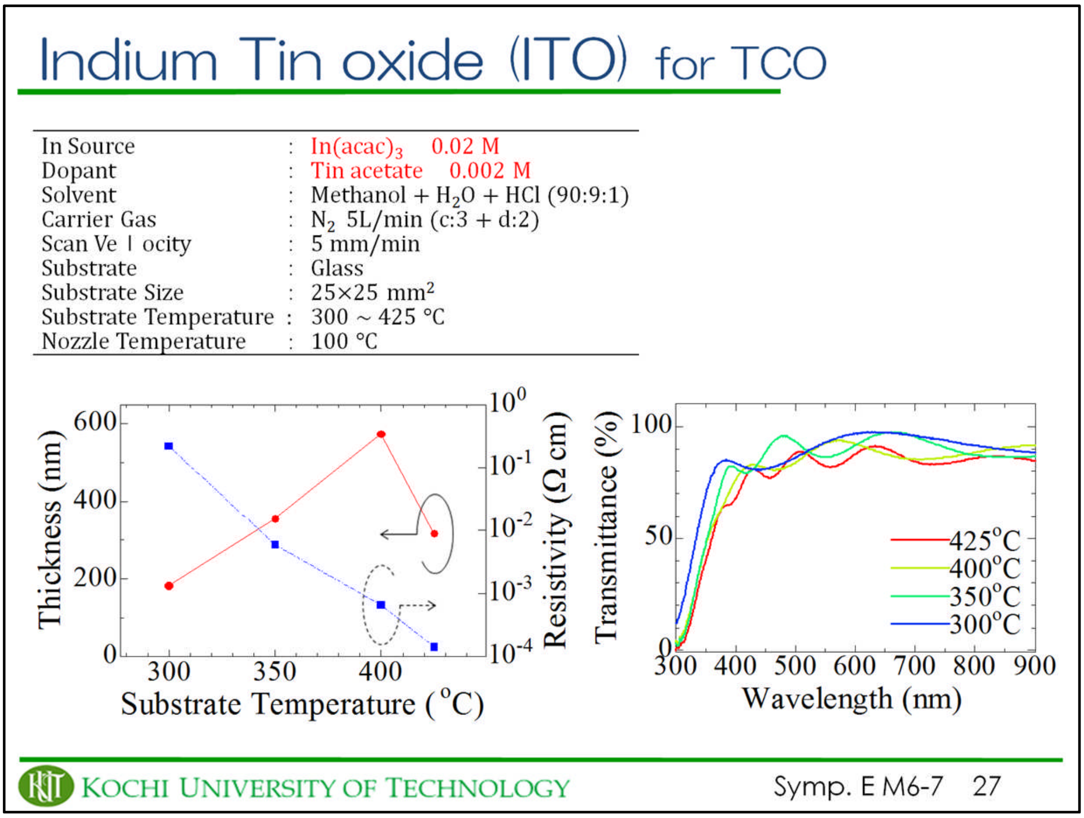
Next is gallium oxide (GaO_x) thin film. The band gap of GaO_x is about 5 eV.
α type Ga_2O_3 can be grown by mist CVD. It has never grown with other method. Additionally, its crystallinity is very fine! We can see Laue fringe in XRD measurement.
Moreover, in the latest experiment, Sn doped α type Ga_2O_3 thin film for transparent conductive film is successful growth.

次に、酸化ガリウム（GaOx)について紹介します。GaOxのバンドギャップは約5eVです。
ミストCVD法では、α型の酸化ガリウムが成長できます。α型の酸化ガリウムはこれまでに他の手法での成長に成功しておりません。つまりこの結果が世界初です。加えて、結晶性は非常に優れています。
また、最近の実験によって、その導電化にも成功しています。



Indium Tin oxide (ITO) for TCO

In Source	:	In(acac)$_3$ 0.02 M
Dopant	:	Tin acetate 0.002 M
Solvent	:	Methanol + H_2O + HCl (90:9:1)
Carrier Gas	:	N_2 5L/min (c:3 + d:2)
Scan Velocity	:	5 mm/min
Substrate	:	Glass
Substrate Size	:	25×25 mm^2
Substrate Temperature	:	300 ~ 425 ℃
Nozzle Temperature	:	100 ℃

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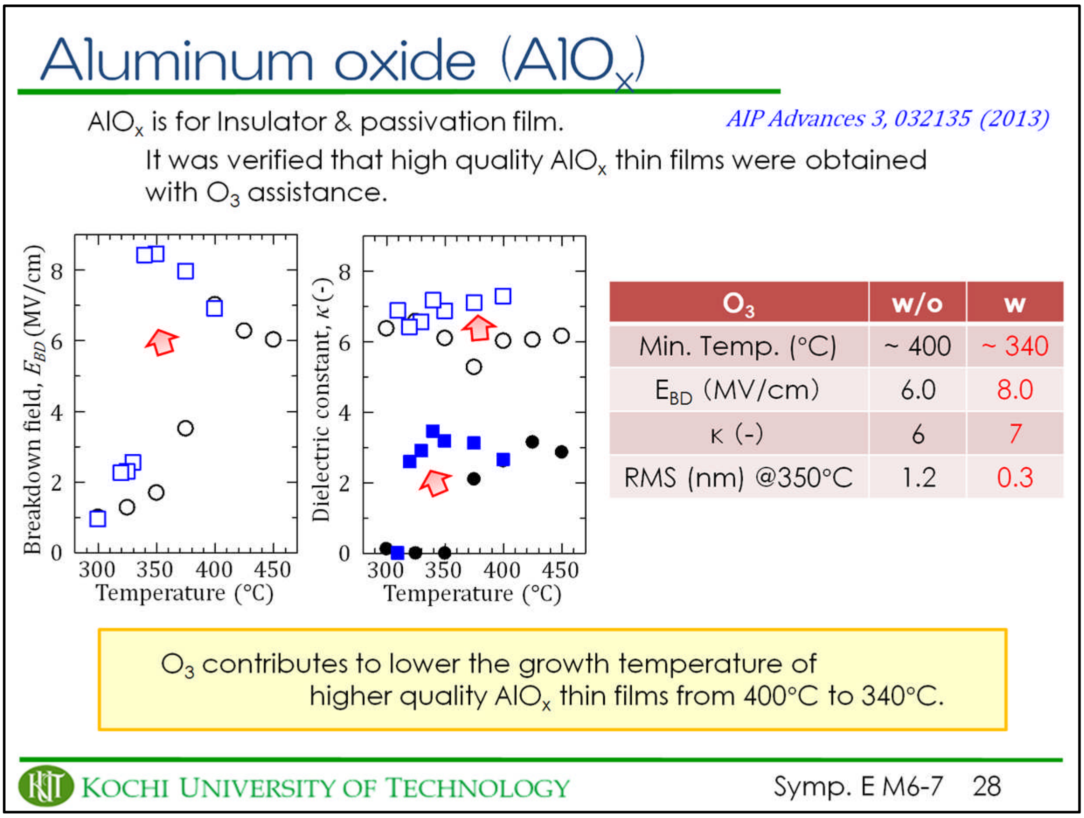
And in the case of ITO, the resistivity about 10^{-4} Ωcm.

透明導電膜として、ITO薄膜も作製出来ます。抵抗値は、10^{-4} Ωcm程度です。



Aluminum oxide (AlO_x)

AlO_x is for Insulator & passivation film.

AIP Advances 3, 032135 (2013)

It was verified that high quality AlO_x thin films were obtained with O_3 assistance.

O_3	w/o	w
Min. Temp. (°C)	~ 400	~ 340
E_{BD} (MV/cm)	6.0	8.0
κ (-)	6	7
RMS (nm) @350°C	1.2	0.3

O_3 contributes to lower the growth temperature of higher quality AlO_x thin films from 400°C to 340°C.

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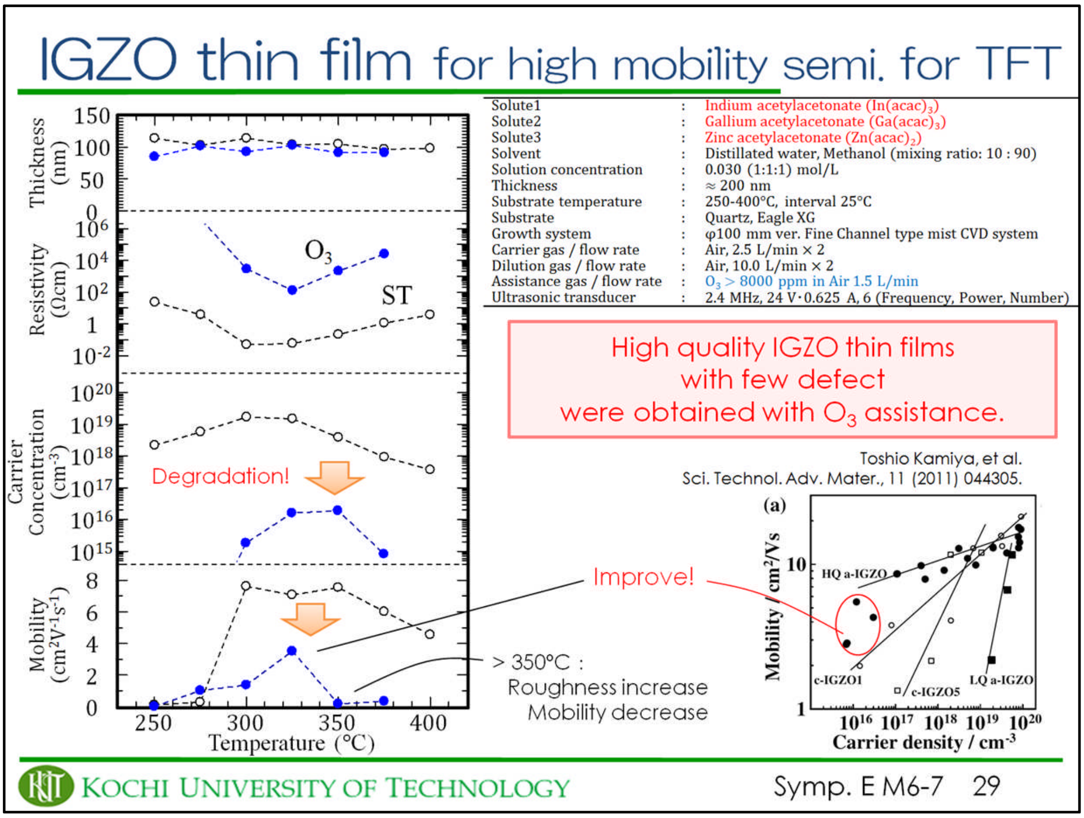
Aluminum oxide (AlO_x) thin films for insulator was successfully grown by mist CVD. In recent results, it was verified that high quality AlO_x thin films were obtained with O_3 assistance and O_3 contributed to lower the growth temperature of higher quality AlO_x thin films from 400ºC to 340ºC.

絶縁体としてのアルミナも作製出来ます。最近の結果では、O_3支援により、AlO_xの性能が向上、400ºCから340ºCと60ºCもの低温で作製できることが確認されました。



IGZO thin film for high mobility semi. for TFT

Solute1 : Indium acetylacetonate ($In(acac)_3$)
Solute2 : Gallium acetylacetonate ($Ga(acac)_3$)
Solute3 : Zinc acetylacetonate ($Zn(acac)_2$)
Solvent : Distilled water, Methanol (mixing ratio: 10 : 90)
Solution concentration : 0.030 (1:1:1) mol/L
Thickness : ≈ 200 nm
Substrate temperature : 250-400°C, interval 25°C
Substrate : Quartz, Eagle XG
Growth system : φ100 mm ver. Fine Channel type mist CVD system
Carrier gas / flow rate : Air, 2.5 L/min × 2
Dilution gas / flow rate : Air, 10.0 L/min × 2
Assistance gas / flow rate : $O_3 > 8000$ ppm in Air 1.5 L/min
Ultrasonic transducer : 2.4 MHz, 24 V·0.625 A, 6 (Frequency, Power, Number)

High quality IGZO thin films
with few defect
were obtained with O_3 assistance.

Toshio Kamiya, et al.
Sci. Technol. Adv. Mater., 11 (2011) 044305.

Degradation!

Improve!

> 350°C :
Roughness increase
Mobility decrease

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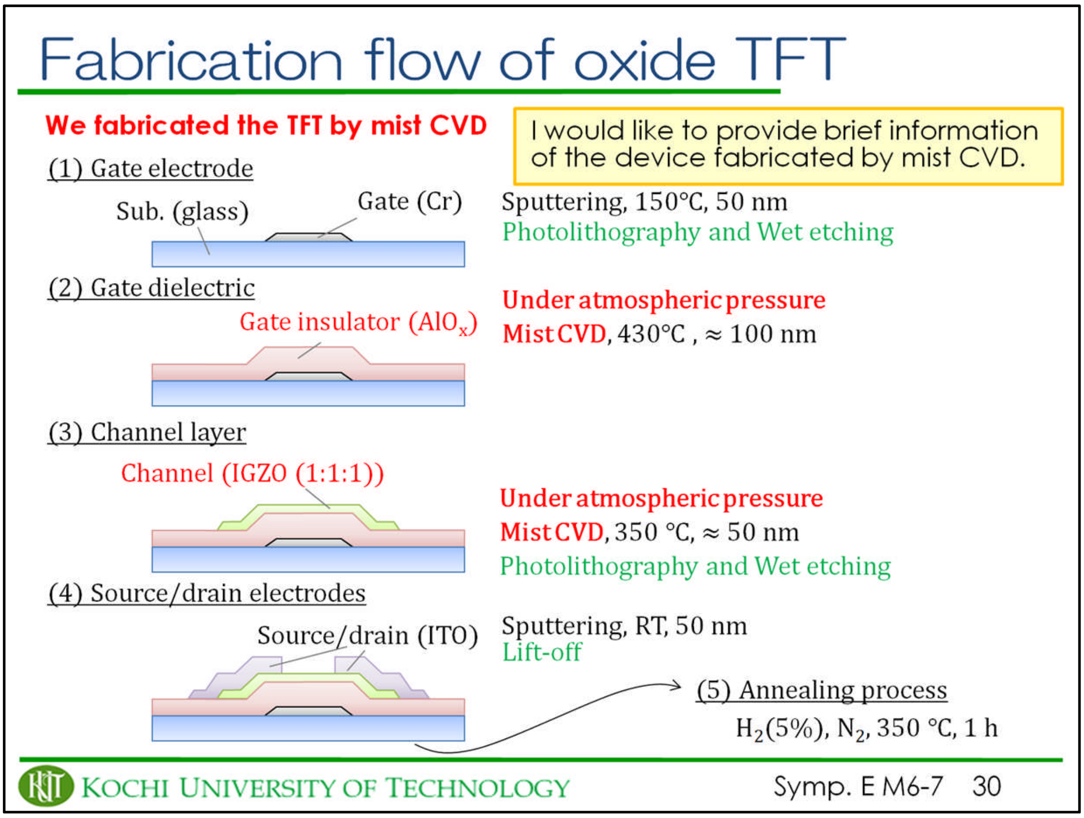
Symp. E M6-7 29

IGZO thin films can be grown. IGZO is expected as a high mobility semiconductor for TFT. In recent results, it was verified that high quality IGZO thin films with few oxide defect were obtained with O_3 assistance.

IGZO薄膜の作製も出来ます。IGZO薄膜は、TFT用の高移動度半導体材料として期待されています。最新の結果では、O3支援により欠陥の少ない高品質なIGZO薄膜を得らラーる事が判明した。



Fabrication flow of oxide TFT

We fabricated the TFT by mist CVD

I would like to provide brief information of the device fabricated by mist CVD.

(1) Gate electrode

Sputtering, 150°C, 50 nm
Photolithography and Wet etching

(2) Gate dielectric

Under atmospheric pressure
Mist CVD, 430°C , ≈ 100 nm

(3) Channel layer

Under atmospheric pressure
Mist CVD, 350 °C, ≈ 50 nm
Photolithography and Wet etching

(4) Source/drain electrodes

Sputtering, RT, 50 nm
Lift-off

(5) Annealing process
H_2(5%), N_2, 350 °C, 1 h

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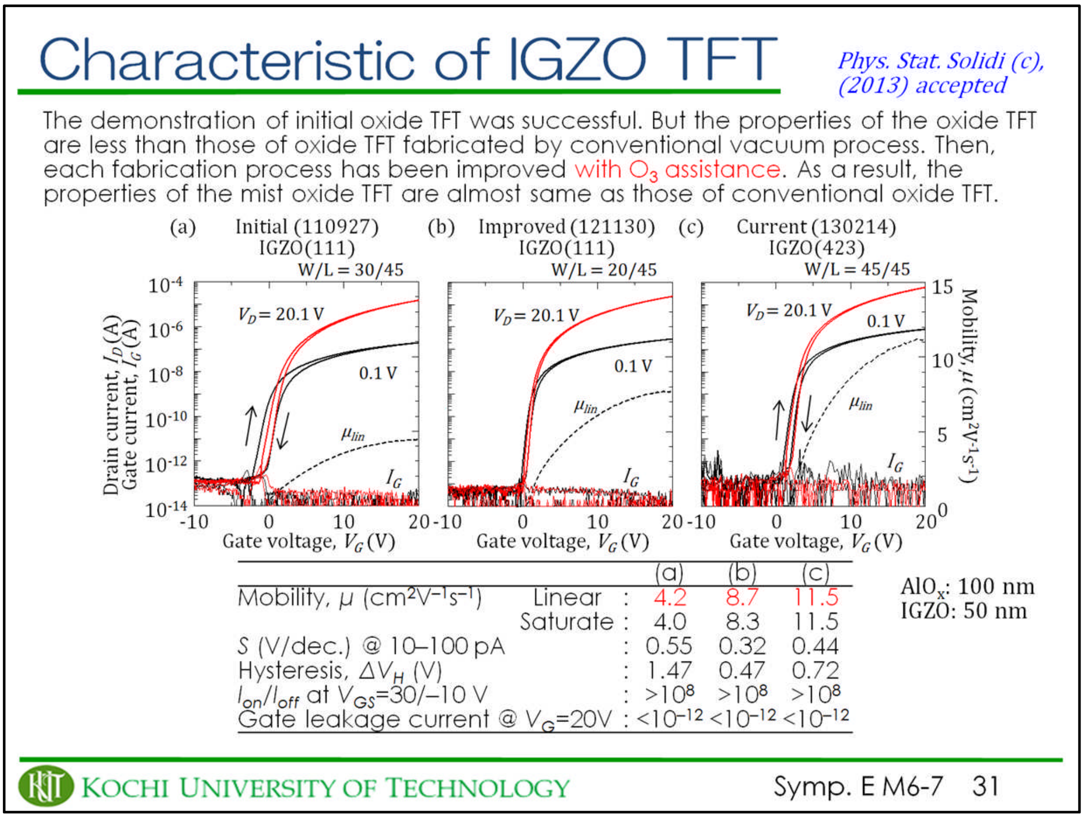
I would like to also provide brief information of the device fabricated by mist CVD.

In the latest result, we fabricated the oxide TFT by mist CVD. This is the fabrication flow of oxide TFT. First, Cr gate electrode was deposited by sputtering. And, AlOx gate insulator and IGZO channel layer was grown by mist CVD under atmospheric pressure. And, ITO source/drain electrodes were deposited by sputtering. And finally, the TFT was annealed in Hydrogen or N_2 ambient. In this process, the wet etching are used.

加えて、ミストCVD法で作製したデバイスについても紹介したい。最近、ミストCVD法で酸化物トランジスターを作製しました。酸化物トランジスターの作製フローを示します。まず、スパッタリングでクロムゲートを作製し、ゲート絶縁膜と、チャネル層をミストCVD法で大気圧で作製しました。そして、ソース/ドレイン電極をスパッタリングで作製し、最後に、TFTを窒素や水素雰囲気下で熱処理しました。このプロセスでは全てウェットエッチングを使っています。



Characteristic of IGZO TFT

Phys. Stat. Solidi (c), (2013) accepted

The demonstration of initial oxide TFT was successful. But the properties of the oxide TFT are less than those of oxide TFT fabricated by conventional vacuum process. Then, each fabrication process has been improved with O_3 assistance. As a result, the properties of the mist oxide TFT are almost same as those of conventional oxide TFT.

		(a)	(b)	(c)
Mobility, μ (cm^{2}V^{-1}s^{-1})	Linear :	4.2	8.7	11.5
	Saturate :	4.0	8.3	11.5
S (V/dec.) @ 10–100 pA	:	0.55	0.32	0.44
Hysteresis, ΔV_H (V)	:	1.47	0.47	0.72
I_{on}/I_{off} at V_{GS}=30/–10 V	:	$>10^8$	$>10^8$	$>10^8$
Gate leakage current @ V_G=20V	:	$<10^{-12}$	$<10^{-12}$	$<10^{-12}$

AlO_x: 100 nm
IGZO: 50 nm

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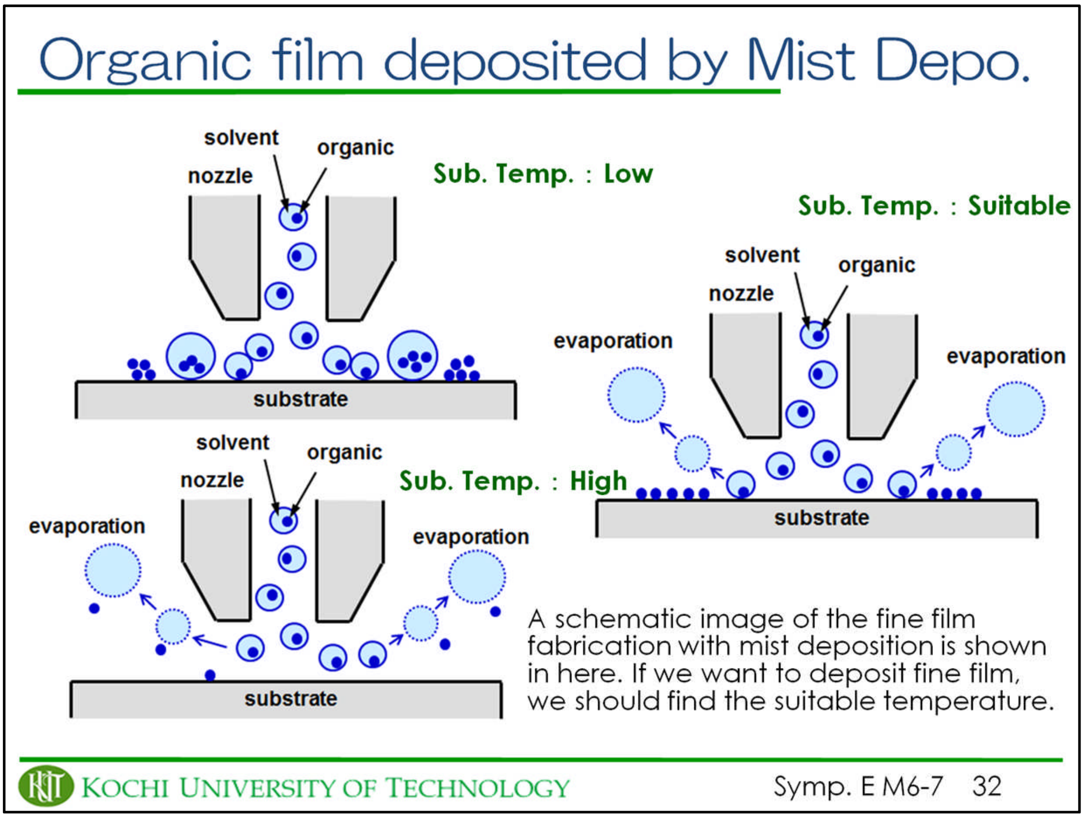
The characteristic of the oxide TFT were shown in here. The AlO_x insulator is around 100 nm and the IGZO channel layer is around 50 nm. Interestingly, the demonstration of initial oxide TFT was successful. But the properties of the oxide TFT are less than those of oxide TFT fabricated by conventional vacuum process. Then, each fabrication process has been improved with O_3 assistance. As a result, the properties of the oxide TFT fabricated by mist CVD are almost same as those of oxide TFT fabricated by conventional vacuum process. In latest results, mobility of oxide TFT fabricated by mist CVD is around 12 cm^2/Vs.

作製した酸化物TFTの特性をこちらに示します。酸化物TFTには、100 nmアルミナ絶縁膜と50nmのIGZO活性層を形成した。興味深いことに、初めて作製した酸化物TFTの駆動に成功しました。しかし、従来の真空手法で作製した酸化物TFTの特性と比較すると、ミストCVD法で作製した酸化物TFTの特性は劣っていた。そこで、O_3支援により作製工程を改善し、酸化物TFTの特性の向上を図った。その結果、ミストCVD法で作製した酸化物TFTの特性は、真空手法で作製した酸化物TFTの特性に匹敵するようになった。最新の結果では、移動度が12程度の値を示しています。



Organic film deposited by Mist Depo.

A schematic image of the fine film fabrication with mist deposition is shown in here. If we want to deposit fine film, we should find the suitable temperature.

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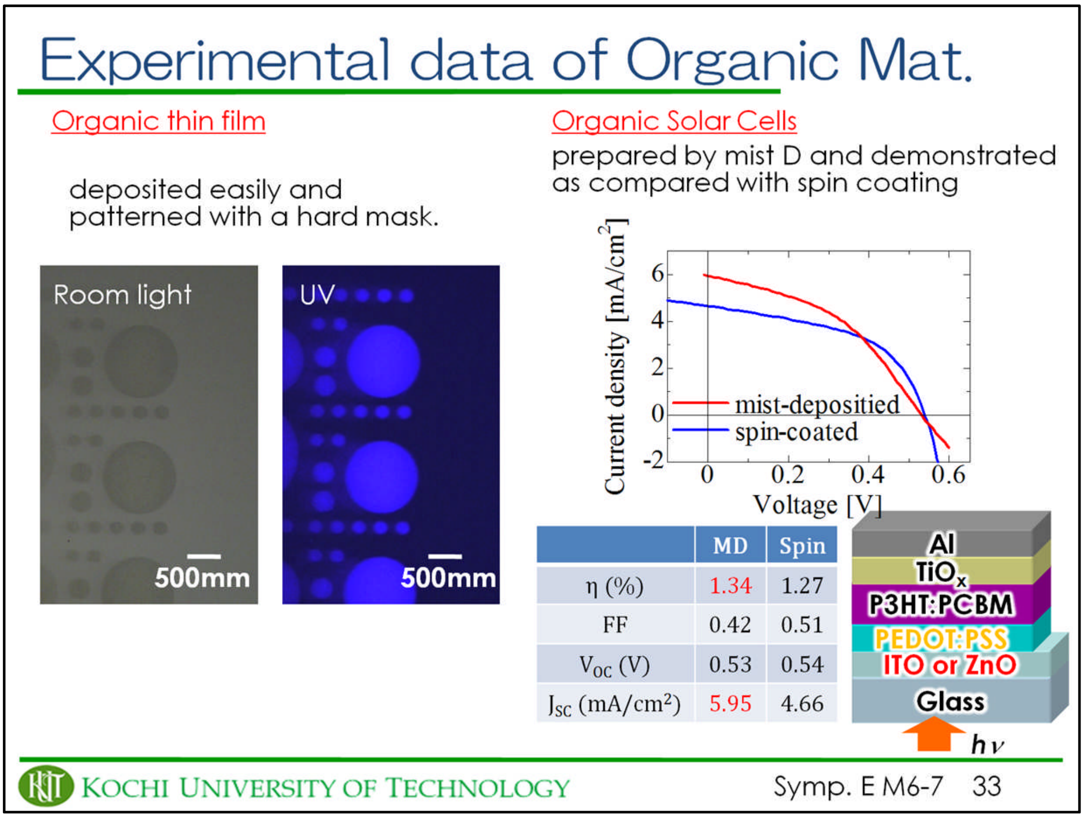
And finally, I would like to introduce organic films deposited by mist deposition.

A schematic image of the fine film fabrication with mist deposition is shown in here. If we want to deposit fine film, we should find the suitable temperature.

そして、ミスト法で塗布した誘起膜に関しても紹介したい。ミスト塗布法で均質な薄膜を作製する為の概念図をこちらに示します。均質な薄膜を作製する為には、適切な温度を見つけなければなりません。



Experimental data of Organic Mat.

Organic thin film

deposited easily and
patterned with a hard mask.

Organic Solar Cells

prepared by mist D and demonstrated as compared with spin coating

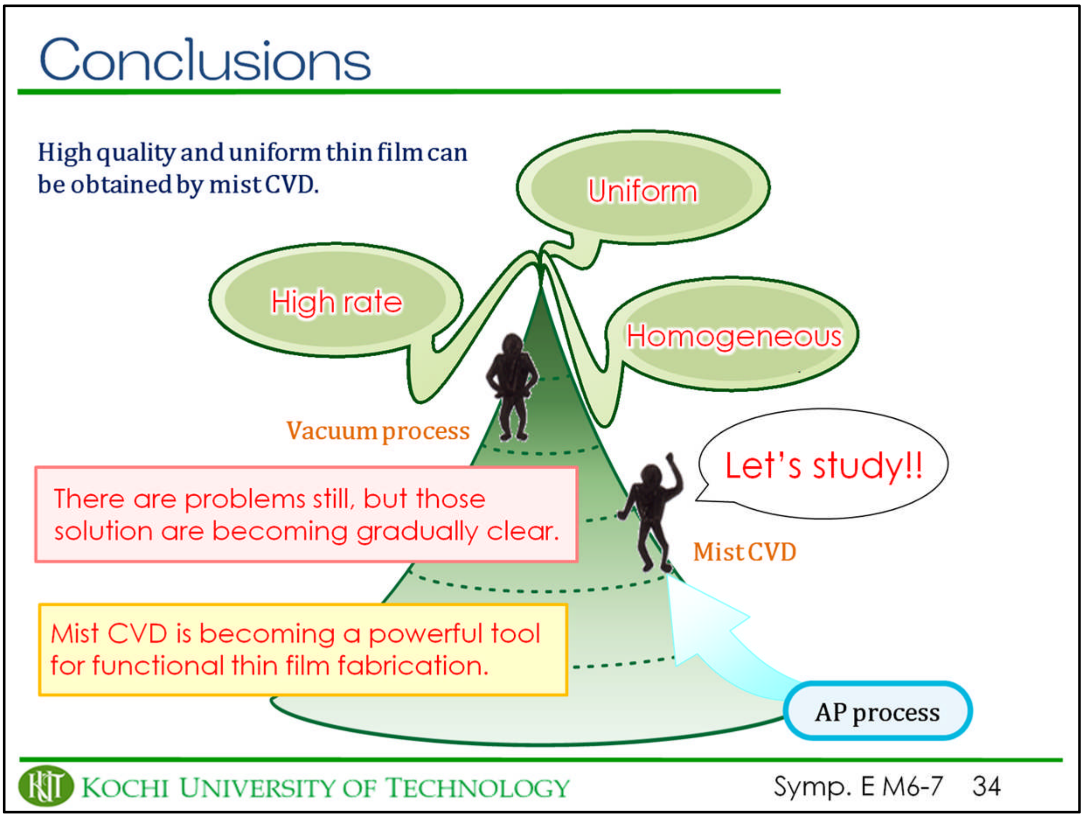
	MD	Spin
η (%)	1.34	1.27
FF	0.42	0.51
V_{OC} (V)	0.53	0.54
J_{SC} (mA/cm^2)	5.95	4.66

Uniform organic thin films were easily deposited and patterned with a hard mask.

And organic solar cells were prepared by mist deposition and demonstrated as compared with spin coating.

均質な有機薄膜はミスト塗布法で簡単に付けることができ、パターン化もハードマスクを用いて簡単にできます。

また、有機薄膜太陽電池をミスト塗布法で作製し、スピンコート法と比較して実証しました。



Conclusions

High quality and uniform thin film can be obtained by mist CVD.

Uniform

High rate

Homogeneous

Vacuum process

Let's study!!

Mist CVD

AP process

There are problems still, but those solution are becoming gradually clear.

Mist CVD is becoming a powerful tool for functional thin film fabrication.

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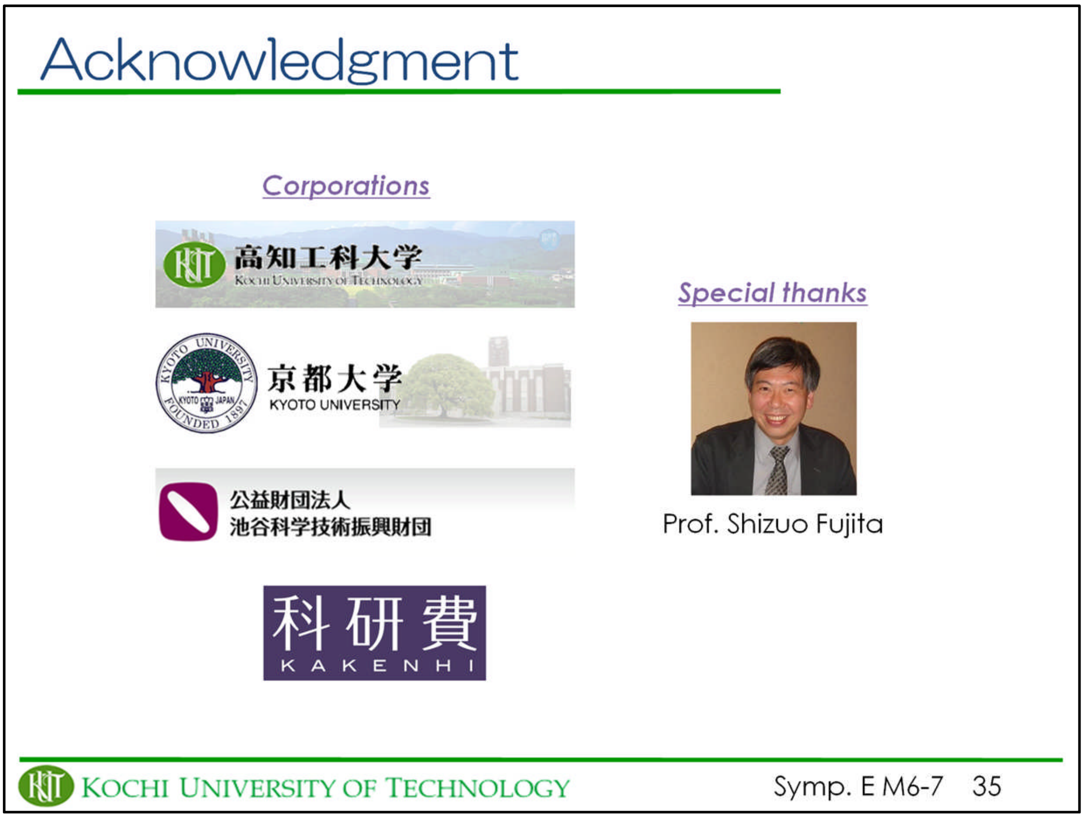
High quality and uniform thin film can be obtained by mist CVD recently. There are problems still. But, those solutions are becoming gradually clear. And mist CVD is becoming a powerful tool for functional thin film fabrication. Let's study on mist CVD together!

最後に、ミストCVD法では最近非常に品質の良い薄膜を作製出来るようになってきました。まだまだ問題もありますが、それらの解決手段も徐々に判明してきており、ミストCVD法は機能薄膜作製のための強力なツールになりつつあります。是非皆さん一緒に研究をしましょう。



Acknowledgment

Corporations

高知工科大学
Kochi University of Technology

京都大学
KYOTO UNIVERSITY

公益財団法人
池谷科学技術振興財団

科研費
KAKENHI

Special thanks

Prof. Shizuo Fujita

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Finally, I would like to thank to these corporations and Prof. Fujita.

最後に、これらの団体及び藤田先生に感謝をのべて、謝辞といたします。

Commercial

Could you please contact me if you would like to know the details?

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予定＆更新情報

日/Sun.	月/Mon.	火/Tue	水/Wen.	木/Thu	金/Fri.	土/Sat.
26	27	28	29	30	31	1
2012 MRS Fall Meeting & Exhibit (Boston, MA, USA)						
2	3	4 研支援（東京）	5	6	7	8
9	10	11	12	13	14	15
16	17	18	19	20	21	22

私のHPページアドレス

http://www.**nano**.kochi-tech.ac.jp/**tosiyuki**/index.html

Could you please contact me if you would like to know the details?
Thank you for your attention.

もし、さらに詳しく内容を知りたい方は、是非私に連絡を下さい。
ありがとうございました。