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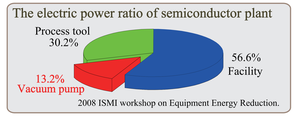
Electrical Properties of Oxide TFT with an IGZO/AlOx Stack Grown by Solution-Based Non-Vacuum Mist Chemical Vapour Deposition

Toshiyuki Kawaharamura, Dapeng Wang, Mamoru Furuta
Institute for Nanotechnology, Kochi University of Technology
高知工科大学 KOCHI UNIVERSITY OF TECHNOLOGY

– Motivations –



A lot of electric power is needed in order to keep vacuum state. The burdens of the environment can be directly reduced by shifting vacuum process to atmospheric pressure process.

Therefore, the conversion of TFT fabrication process to a non-vacuum process is attempted for environmentally friendly. The IGZO or IZO TFTs fabricated by spin coating method or sol-gel method have been reported in Ref. 1-4.

Source materials	Insulator	Channel layer	Post annealed	TFT properties	Ref.
$ZnAc_2$, $In(NO_3)_3$, (0.2:0.2 mol), 2ME	SiN_x, 400 nm, (PECVD), 150°C	IZO, 15 nm	300°C(5 min) 450°C(3 h), Air	μ = 6.57, on/off = 10^9, V_{on} = -1.5, V_{off} = -0.3, S = 0.15	[1]
$ZnAc_2$, $In(NO_3)_3$, $Ga(NO_3)_3$, ETA in 2ME	ATO, 220 nm, (ALD), ??°C	IGZO (In:Ga:Zn), 2:1:1-3, = 25 nm	(80°C(5 min)+ 400°C(10 min), Air)×2, 400°C(1 h), Air	In:Ga:Zn = 3:1:1, μ = 5.8, on/off = 10^7, V_t = 8.1, S = 0.28	[2]
$ZnAc_2$, $SnCl_2$, $ZrCl_4$, 2ME	Th-SiO_2, (SiO_2/p+-Si sub.)	ZrSnZnO (Zr:Sn:Zn), 0-1:7-4, ? nm,	500°C(2 h)	Zr:Sn:Zn = 0.3:7:4, μ = 4.02, on/off = 3.6×10^6, V_t = 3.1, S = 0.94	[3]
$ZnAc_2$, $In(NO_3)_3$, $Ga(NO_3)_3$, EMA in 2ME (1:25)	SiN_x, (? nm)	IGZO (In:Ga:Zn), 1-5:1:2, 50 nm	400°C(3 h)	In:Ga:Zn = 5:1:2, μ = 1.25, on/off = 4×10^6, V_t = -5.09, S = 1.05	[4]

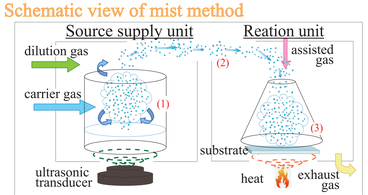
1) K-B. Park, et al., IEEE Electron Device Lett., Vol.31 (2010) pp.311.
2) P.K. Nayak, et al., Appl. Phys. Lett., Vol.97 (2010) pp.183504.
3) Y.S. Rim, et al., Appl. Phys. Lett.Vol.97 (2010) pp.233502.
4) G.H. Kim, et al., Appl. Phys. Lett., Vol.94 (2009) pp.233501.

However, in these reports, the gate insulator was prepared by vacuum process such as plasma-enhanced chemical vapour deposition (CVD). It is very important for the non-vacuum process conversion of TFT fabrication process to fabricate both a gate insulator and a semiconductor film by a non-vacuum process. Thus, we had attempted to convert TFT fabrication process to non-vacuum process with gate insulator and channel layer grown by mist CVD.

– Mist Chemical Vapour deposition (Mist CVD) –

A technique promising as an atmospheric pressure process!

Schematic view of mist method

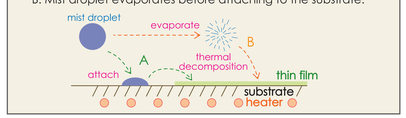


Advantage of mist method

A. "Stable materials" can be treated as "gas".
B. Selection operation of CVD and spray.
C. High experimental efficiency.
D. Less oxide-defect oxide thin film can be grown.

B. Selection operation of CVD & Spray.

A. Mist droplet directly attach to the substrate
B. Mist droplet evaporates before attaching to the substrate.



There is a big merit that stacked films can be continuously grown because the source solution does not directly attach to surface of the target film [5].

5) T. Kawaharamura, et al., Convertech, Vol.39 (2011) pp.111 [in Japanese].

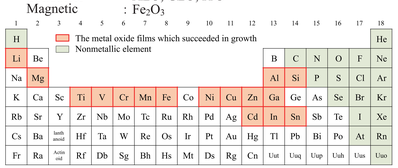
Outlines of mist method

1) The source supply unit
The material solution is atomized to form mist droplets in the diameter scale of several micrometers with ultrasonic transducer.
2) The transportation unit
The mist droplets was transferred by carrier gas and dilution gas from the source supply unit to the reaction unit.
3) The reaction unit
The thin films or particles are formed by the thermal decomposition.

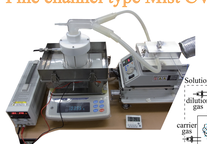
Producible films

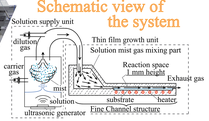
Metal oxide & organic films

Insulator : Al_2O_3, SiO
Semiconductor : ZnO, IGZO, Ga_2O_3, TiO_2
Conductor : AZO, GZO, ITO
Magnetic : Fe_2O_3



Fine channel type Mist CVD system in our lab.





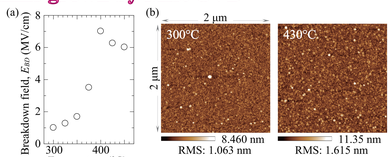
Please refer **"Study on mist CVD and its application to the growth of ZnO thin films"**
T. Kawaharamura,, Ph.D. Thesis, Faculty of Engineering, Kyoto-Univ., 2008 [in Japanese]
http://repository.kulib.kyoto-u.ac.jp/dspace/bitstream/2433/57270/1/26041.pdf

– Properties of AlOx thin films grown by Mist CVD –

Table 1. Deposition conditions of AlO_X thin films

Solute	Aluminum acetylacetonate ($AlAcac_3$)*2
Solvent (mixing ratio)	Distillated water*3, Methanol*4 (10 : 90)
Solution concentration	0.020 mol/L
Thickness	≈ 50 nm, 200 nm
Substrate temperature	300, 350, 400, 430 °C
Substrate	p+-Si*5
Growth system	φ100 mm ver. FC type mist CVD system*6
Carrier gas / flow rate	Air, 2.5 L/min × 2
Dilution gas / flow rate	Air, 10.0 L/min × 2
Ultrasonic transducer*1	2.4 MHz, 24 V×0.625 A, 6

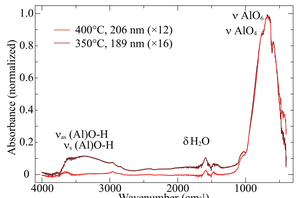
*1 HONDA ELECTRONICS, HM-2412
*2 Aluminum acetylacetonate, 99%, Sigma-Aldrich
*3 Wako Pure Chemical Industries
*4 Methanol, 99.8%, Wako Pure Chemical Industries
*5 Advantec
*6 Refs. 9 and 16.



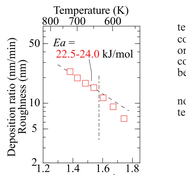
(a) Breakdown field (E_{BD}), and (b) surface structure of AlO_x thin films grown by mist CVD.

T > 400°C
E_{BD} > 6.0 MV/cm
k > 6.1
RMS =1.6 nm

The AlO_x thin films grown over 400°C exhibited the breakdown field and the dielectric constant of 6.0 MV/cm and 6.1, respectively. However, the E_{BD} of AlO_x thin film grown at temperatures below 350°C was dramatically declined.



FT-IR spectra of 200 nm thick AlO_x thin films grown by mist CVD.



Deposition rate and surface roughness of AlO_x thin films grown by mist CVD.

Compared with the AlO_x thin films deposited at various temperature, the difference of the shoulder around 1100 cm^{-1} corresponding to the bending vibration of Al-O-H (ν_s (Al)O-H or ν_{as} (Al)O-H) and the difference of peak around 2350 cm^{-1} corresponding to the stretching vibration of CO_2 adsorbed can be seen.

The logarithm of deposition ratio and surface roughness are not directly proportion to the reciprocal of the substrate temperature. The line has changed around 350°C.

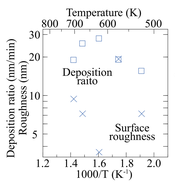
It is suggested that a residual as boehmite (γ-AlO(OH)) remains in the AlO_x thin film grown at the temperature below 350°C. It is thought that that is one of the reasons why the E_{BD} dramatically declines.

– Properties of IGZO thin films grown by Mist CVD –

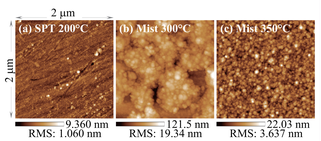
Table 2. Deposition conditions of IGZO thin films

Solute1	Indium acetylacetonate ($InAcac_3$)*2
Solute2	Gallium acetylacetonate ($GaAcac_3$)*3
Solute3	Zinc acetylacetonate ($ZnAcac_2$)*4
Solvent	Distillated water*5, Methanol*6 (mixing ratio: 10 : 90)
Solution concentration	0.030 (1:1:1)*7 mol/L
Thickness	≈ 200 nm
Substrate temperature	150, 200, 250, 300, 350, 400, 430 °C
Substrate	Quartz*8, Eagle XG*9
Growth system	φ100 mm ver. FC type mist CVD system*10
Carrier gas / flow rate	Air, 2.5 L/min × 2
Dilution gas / flow rate	Air, 10.0 L/min × 2
Ultrasonic transducer*1	2.4 MHz, 24 V×0.625 A, 6

*1 HONDA ELECTRONICS, HM-2412
*2 Indium(III) acetylacetonate, 99.99%, Sigma-Aldrich
*3 Gallium(III) acetylacetonate, 99.99%, Sigma-Aldrich
*4 Zinc acetylacetonate, >95%, nacalai tesque
*5 Wako Pure Chemical Industries
*6 Methanol, 99.8%, Wako Pure Chemical Industries
*7 In:Ga:Zn, atomic ratio
*8 Miorika Glass
*9 Corning
*10 Refs. 9 and 16.



Deposition ratio and surface roughness of the IGZO thin films grown by the mist CVD



Surface structure of the IGZO thin films.

Surface of M-IGZO is rough compared with that of SPT-IGZO. Especially, in this case, Surface of M-IGZO is roughest at 300°C.

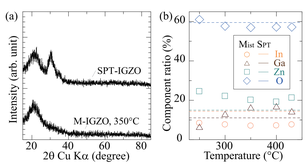
Deposition ratio of M-IGZO does not depend on temperature. This is because the dominant reaction shifts at each temperature domain due to each precursor with variant chemical reaction rate.

Both M-IGZO and SPT IGZO were amorphous since no diffraction peak was detected in XRD measurement.

From RBS measurement, the composition ratio of M-IGZO and SPT-IGZO were so different from ideal elemental ratio. In a SPT-IGZO, each metal composition ratio was 36:27:37 (In:Ga:Zn) owing to different sputtering ratio of each metal oxide contained in the target. In the mist CVD, composition ratio of films depends on growth temperature and mixture ratio of source materials at preparation. Hence, in a M-IGZO grown at 350°C, which is a same as the condition of IGZO thin film used for the channel layer of the oxide TFT, each metal composition ratio was 16:37:47 (In:Ga:Zn).

T=350°C
amorphous
deposition rate > 25 nm /min
In:Ga:Zn = 16:37:47

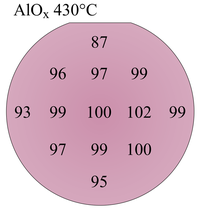
Change of dominant reaction depending on precursor is observed.



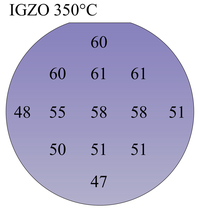
(a) XRD 2θ/ω spectra and (b) composition ratio of the IGZO thin films grown by the mist CVD

– Uniformity of thin film grown by Mist CVD –

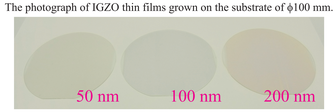
AlO_x 430°C



IGZO 350°C



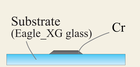
The photograph of IGZO thin films grown on the substrate of ϕ100 mm.



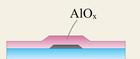
AlO_x : Approximately-uniformity
IGZO : ±10%

In mist CVD, uniformity thin films can be get.

– Fabrication process –

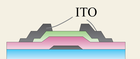


(1) Fabrication of gate electrode
sputtering, 50 nm 150°C
Patterning: Wet etching



(2) Fabrication of gate insulator
mist CVD (1 atm)
430°C, ≈ 100 nm
Patterning: Wet etching

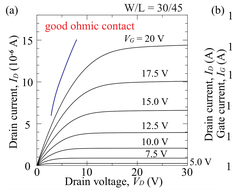
(3) Fabrication of channel layer
mist CVD (1 atm)
350°C, ≈ 50 nm
Patterning: Wet etching

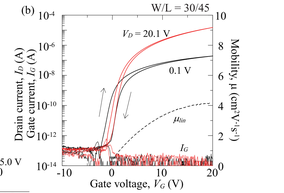


(4) Fabrication of source & drain electrode
sputtering, 50 nm, RT
Patterning: Wet etching
(lift-off)

(5) Post annealing
H_2(5%) + N_2, 350°C, 1 h

– The drive of the first prototype –





Mobility μ ($cm^2V^{-1}s^{-1}$)	linear	: 4.2
	saturation	: 4.0
V_{GS} at I_{DS} = 1 nA (V)		: 0.39
S (V/dec.) @ 10-100 pA		: 0.55
Hysteresis ΔV_H (V)		: 0.68
I_{on}/I_{off} at V_{GS} = 30/-10 V		: > 10^8
Gate leakage current @ V_G = 20V		: <10^{-12}

The oxide TFT was driven with low leakage current & good on/off ratio.

S & ΔV_H are worse than previous reports

(a) Output and (b) transfer characteristics of oxide TFT with a IGZO/AlOx stack fabricated by mist CVD.

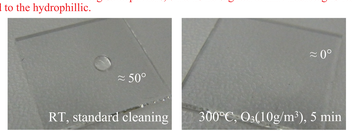
In this experiment, for the system construction of mist CVD, TFT was left under atmosphere for several hours after growing AlO_x insulator before growing IGZO channel layer. Therefore, the creation of defects or traps in the IGZO channel layer or in interface between the AlO_x insulator and the IGZO channel layer is not denied.

Moreover, in this research, the oxide TFT has no passivation film.

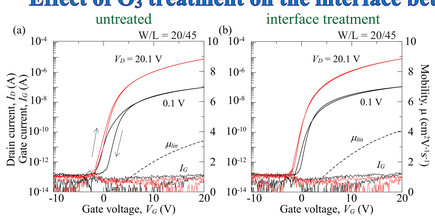
S & ΔV_H may be improved with continuous process and interface treatment.

– Effect of O_3 treatment on the AlO_x –

Treatment process of the AlO_x thin film surface was added for 5 min at 300°C under O_3 ambient, after growth of AlO_x and just before growth of IGZO. After the O_3 treatment, the surface of AlO_x thin films was cleaned with eliminating of impurities, such as an organic matter adhering to the surface and was changed to the hydrophillic.

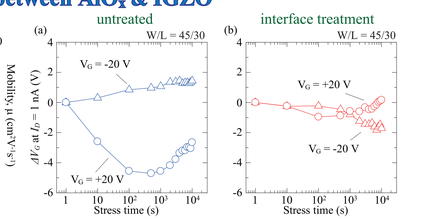


– Effect of O_3 treatment on the interface between AlO_x & IGZO –



		untreated	interface treatment
I_{on}/I_{off} at V_{GS} = 30/-10 V		: > 10^8	: > 10^8
Gate leakage current @ V_G = 20V		: <10^{-12}	: <10^{-12}
Mobility μ ($cm^2V^{-1}s^{-1}$)	linear	: 3.4	: 4.1
S (V/dec.) @ 10-100 pA		: 0.77	: 0.67
Hysteresis ΔV_H (V)		: 0.74	: -0.11

Transfer characteristics of oxide TFT with a IGZO/AlOx stack (a) without and (b) with interface treatment.



Bias conditions: V_G = ±20 V, V_D = 0 V, T = RT, t = 10000 s

Life time of oxide TFT with a IGZO/AlOx stack (a) without and (b) with interface treatment.

The improvement of μ and ΔH was found with the O_3 treatment.
The effect of the O_3 treatment is clearly seen in the life time evaluation.

S is still worse than previous reports.

Conclusion

1) Oxide TFT consisting of both channel layer (IGZO) and gate insulator (AlO_x) grown by mist CVD which is one of suitable techniques for growing thin films continuously under atmosphere was fabricated.
2) The improvement of μ and ΔH was seen with introduction of the interface treatment under O_3 ambient.
3) The index of non-vacuum process conversion of the TFT fabrication process was demonstrated with fabricating the oxide TFT with an IGZO/AlO_x stack grown by the mist CVD.

Please refer
"Electrical Properties of the Thin-Film Transistor With an Indium–Gallium–Zinc Oxide Channel and an Aluminium Oxide Gate Dielectric Stack Formed by Solution-Based Atmospheric Pressure Deposition"
M. Furuta, T. Kawaharamura, D. Wang, T. Toda, and T. Hirao,
IEEE Electron Device Lett. Vol.33 (2012) pp.851-853.

Contact me!
Affiliation: Institute for Nanotechnology, Kochi University of Technology
Address: 185 Miyanokuti Tosayamada-chou Kami-city, Kochi, 782-8502, Japan
Tel., Fax.: +81-887-57-2747, +81-887-57-2714
E-mail: kawaharamura.toshiyuki@kochi-tech.ac.jp
Web page http://www.nano.kochi-tech.ac.jp/tosiyuki/index.html