Extended Abstracts of the 2013 International Conference on Solid State Devices and Materials, Fukuoka, 2013, pp1210-1211

# Ultrasonic-Assisted Mist Deposition for Green Materials and Devices

Shizuo Fujita[1], Kentaro Kaneko[2], Shigetaka Katori[3], Toshiyuki Kawaharamura[4] and Mamoru Furuta[4]

[1] Kyoto University
Photonics and Electronics Science and Engineering Center, Katsura, Kyoto 615-8520, Japan
Phone: +81-75-383-3075 E-mail: fujitasz@kuee.kyoto-u.ac.jp
[2] Kyoto University
Department of Materials Chemistry, Katsura, Kyoto 615-8510, Japan
[3] Tsuyama National College of Technology
Department of Electrical and Electronic Engineering, Tsuyama, Okayama, 708-8509, Japan
[4] Kochi University of Technology
Research Institute for Nanotechnology, Kami, Kochi 782-8502, Japan

**Abstract**

**We report the fabrication of green materials, oxide and organic semiconductors, by green chemistry, i.e., safe, low-energy-consumption, and cost-effective solution-based non-vacuum fabrication technology, for green device applications. Successful formation of various materials demonstrates promising potential of this technology for promotion of future sustainable society.**

## 1. Introduction

Recent worldwide interests for environment remind us the necessity of developing green materials, which are safe and abundant, achieving green applications such as energy-saving devices and solar cells. Oxide semiconductors and organic semiconductors are the main target of green materials for active applications. For their fabrication, towards the future sustainable society, careful consideration is desirable for the cost and energy necessary. Different from arsenides or nitrides, oxides are suitable for non-vacuum and solution-based fabrication methods, meeting the above purpose, because one do not need to be so nervous on oxygen contamination which is a fatal problem for non-oxide materials. For organic semiconductors, increasing efforts have been carried out for non-vacuum processes such as inkjet printing and spraying.

We have developed ultrasonic-assisted mist deposition technology as a safe and cost-effective fabrication technology for the fabrication of oxide and organic semiconductors. In this presentation we show and discuss the potentials and advantages of this technology from the recent results.

## 2. Deposition Technology

The basic concept of ultrasonic-assisted mist deposition method is to utilize ultrasonically-atomized mist particles of solution source as a reaction precursor transferred like a gas. An example of a mist generator is given in Fig.1. For the deposition of oxides, we use water or alcohol solution of such as acetyl or acetylacetonato complexes of metals. The role of mist generator is equivalent to a metalorganic (MO) source but markedly enhances safety. Mist particles are sent to a deposition system and the formation of metal-oxides is caused by heat[1,2]. Hence the deposition process is the chemical vapor deposition (CVD) mode similarly to MOCVD.

For the deposition of organic thin films, we prepare organic solutions of the target material. The mist particles reach above the substrate surface, where the solution is vaporized and the solute remains on the substrate[3]. This mechanism is the vaporized deposition mode similar to spin-coating.

## 3. Thin Films Fabricated by Mist Deposition

*Transparent Conductive Oxides*

This mist CVD has originally been developed for the deposition of transparent conducting oxide thin films such as ZnO and ITO. The most up-to-date result obtained by our industrial collaborator shows the formation of ZnO thin films with sheet resistance of 10 Ω/□ at 200$^{o}$C. This low sheet resistivity, together with the soft deposition technology hardly giving damage to the underlying layers, may be applicable to transparent electrodes in emerging devices.

*$Al_2O_3$/InGaZnO Thin Films and Transistors*

A variety of amorphous and polycrystalline oxide films have been fabrication by the mist CVD. $Al_2O_3$ and InGaZnO thin films were successfully fabricated by the mist CVD and this allowed formation of $Al_2O_3$/InGaZnO thin film transistors with reasonable device properties for display applications, as shown in Fig.2,.

*Single Crystalline Oxides*

For single-crystalline oxide semiconductors, layer-by-layer growth of ZnO, which has been difficult by MOCVD, was successfully achieved[3]. The electron mobility close to 100 cm$^2$/Vs was realized. Recent reports suggesting promising potential of $Ga_2O_3$ for power devices[4,5] encourage the growth of $Ga_2O_3$ by the mist deposition method for more effective saving of energy. Corundum-structured $Ga_2O_3$ single crystals were grown on sapphire by the mist CVD, and the X-ray diffraction ω-scan rocking curves exhibited as small as 40 arcsec, suggesting excellent crystallinity. No remarkable dislocations were seen in the cross sectional TEM image, as shown in Fig.3. Band gap engineering by alloying with $Al_2O_3$ or $In_2O_3$, conductivity control by doping Sn, function engineering, as shown in Fig.4, by alloying with $Fe_2O_3$ have also been achieved.

*Organic Thin Films*

The mist deposition technique was also applied for the fabrication of organic thin films such as organic LED materials of aluminum-quinoline ($Alq_3$) and triphenyldiamine (TPD), as well as a solar cell material of P3HT:PCBM and a conductive polymer PEDOT:PSS. A solar cell fabricated by the mist deposition with the heterojunction of P3HT:PCBM and PEDOT:PSS resulted in good device efficiency compared to the conventional spin-coating deposition. All these materials were deposited at the substrate temperature lower than $200^{o}$C, so they may be integrated on flexible substrates.

*Devices with Single Deposition Process*

Due to wide application of the mist deposition technique, it is plausible that multilayered structures constituting a device can successively fabricated by this process, allowing simple and roll-to-roll technology. An example is a PEDOT:PSS/ZnMgO/ZnO(TCO)/glass ultraviolet photodetector, where all layers are fabricated by the mist deposition. We sincerely expect that the mist deposition method can give marked contribution for the development of various devices with low energy consumption.

## 4. Conclusions

Mist deposition is a promising technology for fabrication of oxide and organic semiconductors with safe and cost-effective way, opening new and wide application of oxide materials for novel devices supporting the future environment. We expect that green applications by green materials with green chemistry markedly contribute to future sustainable society of our planet.


## Acknowledgements

This work was supported by a Scientific Grant-in-Aid for Scientific Research from the Japan Society of Promotion of Science, a Regional Innovation Strategy Support Program "Kyoto Environmental Nanotechnology Cluster" from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and “The research and development project for innovation technique of energy conservation” of the New Energy and Industrial Technology Development Organization (NEDO).


## References


[1] Y. Kamada, T. Kawaharamura, H. Nishinaka, and S. Fujita: Jpn. J. Appl. Phys. **45** (2006) L857.

[2] H. Nishinaka, Y. Kamada, N. Kameyama, and S. Fujita: Jpn. J. Appl. Phys. **48** (2009) 121103.

[3] J. Piao, S. Katori, T. Ikenoue, and S. Fujita: Jpn. J. Appl. Phys. **50** (2011) 020204.

[4] M. Higashiwaki, K. Sasaki, A. Kuramata, T. Masui, and S. Yamakoshi: Appl. Phys. Lett, **100** (2012) 013504.

[5] K. Sasaki, A. Kuramata, T. Masui, E. G. Vıllora, K. Shimamura, and S. Yamakoshi: Appl. Phys. Express **5** (2012) 035502.


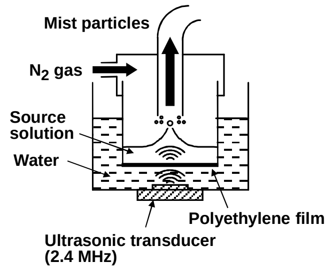


Fig.1 Schematic illustration of mist generator.

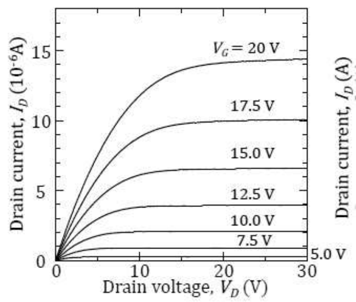


Fig.2 Drain characteristics of InGaZnO TFTs whose active (InGaZnO) and insulating ($Al_2O_3$) layers were deposited by the mist deposition (CVD mode) technique. The on/off ratio was $>10^8$, leakage current was <1pA, and channel mobility was 4.2 $cm^2$/Vs, which were nearly the standards tor display applications.

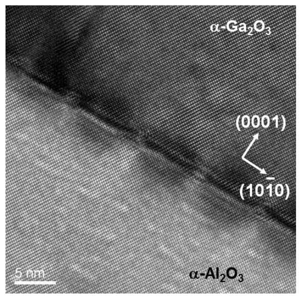


Fig.3 TEM cross sectional view of corundum-structured $Ga_2O_3$ grown by the mist deposition (CVD mode) on sapphire ($Al_2O_3$) substrates, showing no severe dislocation lines originating from the interface.

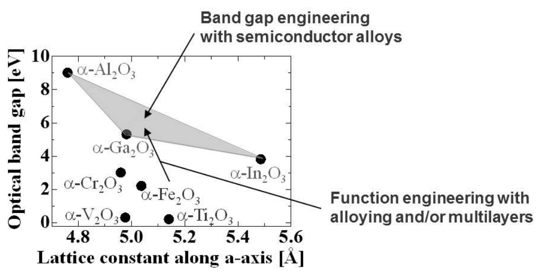


Fig.4 Concept of band gap engineering and function engineering. Alloying of corundum-structured $Al_2O_3$, $Ga_2O_3$, and $In_2O_3$ will make a wide band gap semiconductor system $(Al,Ga,In)_2O_3$, similar to (Al,Ga,In)N, allowing coherent multi-layered structures for devices. The $(Al,Ga,In)_2O_3$ may be alloyed with corundum-structured transition-metal-oxides like $Cr_2O_3$, $Fe_2O_3$, $V_2O_3$, and $Ti_2O_3$, adding new functions to the $(Al,Ga,In)_2O_3$ semiconductor alloys. A variety of multi-layered structures are expected by the above corundum-structured material system.