

NEWSLETTER

An Initiative of ISAJ

Inside This Issue

Research Spotlight

Gallium oxide and its future – A Review

From the Pen of Young Mind

The catalytic efficacy of Ni-Cu-Al hydrotalcite catalysts on hydrogenation of furfural via thermo catalytic and electrocatalytic routes

Event Report

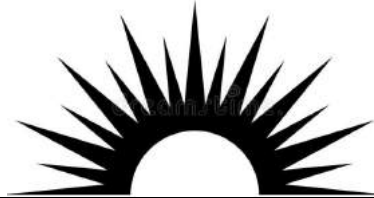
12th ISAJ Annual Symposium-2021

Photo Gallery

12th ISAJ Annual Symposium-2021



Venue of annual symposium-2021. See report and pictures inside.



Greetings and a warm welcome to the first issue of ISAJ Newsletter in 2022!

In this issue, we present you with three research articles and event report on 12th Annual ISAJ Symposium-2021. The Research articles are on the study on Gallium oxide nanowires and its prospects for power devices and the futuristic possibility of integrating electricity generation from renewable sources and converting biomass-based carbon sources for energy and fine chemicals. This issue also contains pictures of our 12th annual symposium held last year.

The review article discusses recent trends in materials development for power devices and emphasizes Gallium oxide (β -Ga₂O₃) nanowires as prospective material. This article has briefly discussed crystal structure, synthesis techniques, device applications, and future challenges for (β -Ga₂O₃) nanowires

The research article on biomass-based carbon sources for energy and fine chemicals discussed the thermal catalytic hydrogenation (TCH) and electrocatalytic hydrogenation (ECH) methods for hydrogenation of furfural using electrocatalyst for synthesizing synthetic chemicals and liquid fuels. This work has compared different catalytic approaches and catalyst efficacy of Ni-Cu-Al mixed oxide hydrotalcite catalysts for TCH and ECH of furfural.

ISAJ organized its 12h Annual Symposium on November 26 (Fri) and 27th (Sat), 2021, which was jointly organized with the School of Marine Science and Technology, Tokai University at Shimizu-Ku of Shizuoka City in hybrid mode. Symposium was held in the Marine Science Museum Auditorium of the university situated at a picturesque viewpoint giving the best known view of Mt. Fuji. The symposium theme was “Innovations in Science and Technology for New Issues and Challenges”. It had a special interest session on COVID-19. There were around 100 participants, including 8 plenary speakers, 26 invited speakers and 24 student presenters. We present an overview of the Annual Symposium in the Event Report section of this issue,

We hope you would find the present issue of our Newsletter interesting. We look forward to receiving your feedback. Any suggestions/ideas for improving the upcoming newsletters are welcome.

Swapnil Ghodke
Mahendra Kumar Pal
Editors

Gallium oxide and its future – A Review



Dr. D. Arun Kumar
Nagoya University
Email: arunku-
marphy@gmail.com

Currently, a post-doctoral researcher at Center for Low temperature Plasma Sciences of Nagoya University, Nagoya. Prior to this he was an Assistant Professor at Bannari Amman Institute of Technology, Sathyamangalam, India, from June 2015. He obtained his doctoral degree from University of Madras in October 2013. Dr D. Arun Kumar has expertise on metal oxides nanocomposites for dye sensitized solar cell applications, growth of III-V Nitride semiconductors for solar cell and HEMT device applications. Presently, he is engaged in the growth of gallium oxide by MBE for power device applications

Introduction

In the rapid development of electric power, industrial control, consumer electronics and automotive electronics industries, there is an ever-growing requirement for high performance power semiconductor devices, putting forward great demands on wide bandgap semiconductor materials. Such materials should be abundant, inexpensive, and easy to fabricate, and have high thermal and chemical stability. Compared to the conventional Si and later developed SiC and GaN, recently developed gallium oxide (Ga_2O_3) has attracted much interest for high power device applications, due to its ultra-wide bandgap of 4.8 eV, high theoretical breakdown field up to 8 MVcm⁻¹. Fig. 1 shows the bandgap dependences of the breakdown field. Accordingly, Ga_2O_3 shows much larger Baliga's figure of merit (FOM) of 3888, which is about ten times and four times larger than that of SiC and GaN respectively. This is because Baliga's figure-of-merit is proportional to the cube of the breakdown electric field but only linearly proportional to the electron mobility. These estimates indicate that Ga_2O_3 power devices would outperform SiC and GaN ones. These features have led to the evaluation of Ga_2O_3 nanowire as a mate-

rial in semiconductor research fields; it is less expensive and easier to fabricate than Si, GaN and SiC. Compared to thin films, nanowires have a higher surface-to-volume ratio, which increases their sensitivity in detection. $\beta\text{-Ga}_2\text{O}_3$ nanowire based devices are very attractive for use as gas sensors due to their stability, moisture resistance, fast response, and long lifetime. Research interest in Ga_2O_3 nanowires has been increasing, and it has obtained recognition among other wide-bandgap materials. This short letter will mainly focus on crystal structure, synthesis techniques, device applications, and future challenges for $\beta\text{-Ga}_2\text{O}_3$ nanowires.

Crystal Structure of $\beta\text{-Ga}_2\text{O}_3$

Among the five structures of Ga_2O_3 single crystal, monoclinic β -phase Ga_2O_3 is the most stable one. $\beta\text{-Ga}_2\text{O}_3$ crystal also has some unique properties, for example, its (100) surface has a large lattice constant of 12.23 Å along [100] direction. $\beta\text{-Ga}_2\text{O}_3$ is part of the C2/m space group and has a base-centered arrangement with four lattice parameters. The unit cell of $\beta\text{-Ga}_2\text{O}_3$ has two different Ga atoms [Ga(I) and Ga(II)] and three different O atoms [O(I), O(II) and O(III)].

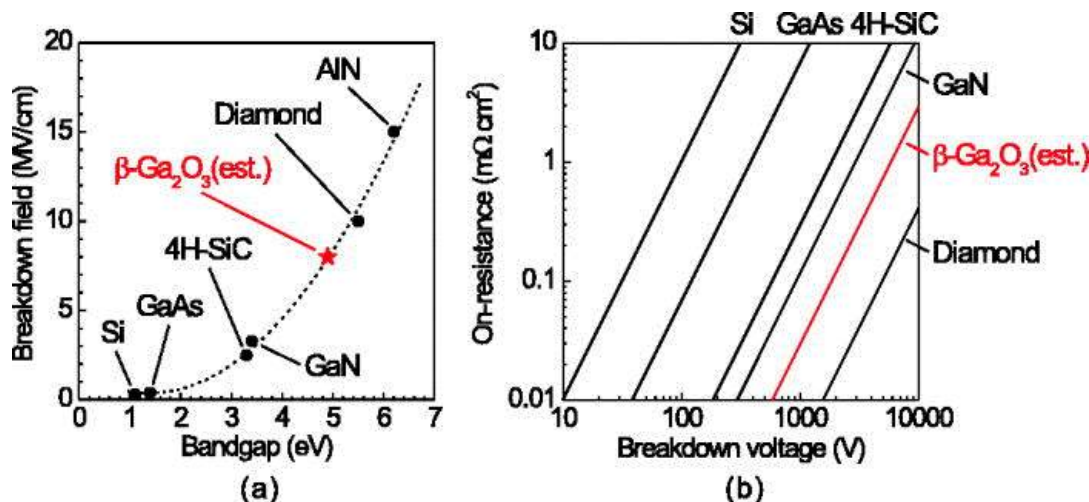


Fig. 1 (a) Bandgap dependences of the breakdown field and (b) theoretical limits of on-resistances as a function of breakdown voltage for major semiconductors and $\beta\text{-Ga}_2\text{O}_3$.

Electrical Properties

Energy bandgap for Ga_2O_3

$\beta\text{-Ga}_2\text{O}_3$ has an indirect bandgap of 4.83 eV, with a valence-band maximum (VBM), which is marginally less than the direct bandgap of 4.87 eV. Research has confirmed that $\beta\text{-Ga}_2\text{O}_3$ is an indirect bandgap material, but due to the weakness of the indirect transitions and the small energy difference between indirect and direct gaps, it is effectively a direct bandgap material.

Dopants for Ga_2O_3

As Ga_2O_3 is an insulator, it needs to be doped to increase its electrical conductivity. Doping enables control of sheet resistance and facilitates the formation of ohmic contacts. Doping can even be used to tune the optical band gap and introduce defect levels. Dopants can be added by ion implantation. $\beta\text{-Ga}_2\text{O}_3$ is assumed to be an n-type semiconductor due to its shallow donor oxygen vacancies. Furthermore, these oxygen vacancies are deep donors and hence cannot contribute to the n-type conductivity. Other dopants such as Si, Ge, Sn, F, and Cl behave like shallow donors and enhance n-type conductivity. Mg, Cu, Zn and N are the potential dopants for p-type conductivity in $\beta\text{-Ga}_2\text{O}_3$.

Optical properties

The absorption spectra of Ga_2O_3 show cut off absorption edges at around 255-260 nm and slightly

around 270 nm. The band at 260 nm was due to the intrinsic band-to-band transition while the one at 270 nm was caused by Ga^{3+} vacancies in the conduction band. The absorption range (255-260 nm) can be obtained because of the transition from the valence band to the conduction band.

Ga_2O_3 synthesis techniques

A wide variety of methods have been used to grow Ga_2O_3 . These include molecular beam epitaxy, laser ablation, thermal oxidation, metalorganic chemical vapor deposition, pulsed laser deposition, arc discharge, sputtering, thermal evaporation, carbothermal reduction, microwave plasma, vapor-liquid-solid mechanism and the hydrothermal method. There are the advantages and disadvantages of these methods. Further research is necessary to determine the best method to grow high-quality Ga_2O_3 at low cost.

Molecular Beam Epitaxy

Molecular beam epitaxy has also been used to grow Ga_2O_3 on Ga_2O_3 substrates. The Ga flux is supplied to a heated substrate by evaporating high-purity molten Ga metal from a conventional Knudsen cell (K-cell). O radicals is provided by passing a controlled flow of oxygen (in units of standard cubic centimeter per minute, SCCM) through an RF plasma source run at a certain power (typically 200–500 W), which are produced by an RF-plasma cell. Figure 2 shows growth rate vs angle between the substrate surface and the (100) plane. It was found that the epitaxial growth rate can be increased by more than

ten times by changing from the (100) plane to the (010) or (310) plane.

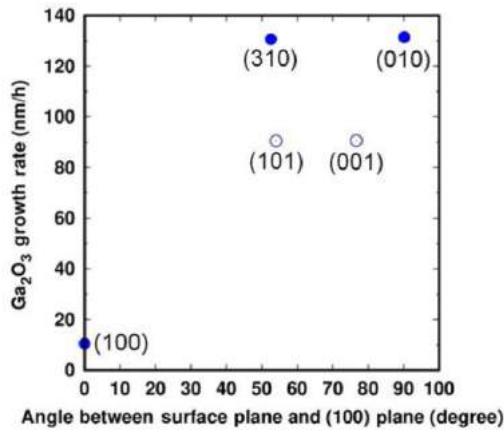


Fig. 2 Growth rate vs angle between the substrate surface and the (100) plane

Ga₂O₃ nanowire applications

The Ga₂O₃ nanostructures provide a path to a new generation of devices, but most Ga₂O₃ nanostructure-based devices are limited to a single nanowire, and the integration of individual devices on a single chip is still a real challenge. Another crucial issue is controlled doping in nanostructures and the formation of high-quality ohmic contacts between nanostructures and electrodes. Therefore, the construction of a device via a simple and cost-effective method is still a great challenge. In spite of these difficulties, Ga₂O₃ nanowire finds many applications such as Ga₂O₃ nanowire-based FETs, temperature/gas sensors and UV photodetectors (Photoconductors, MSM photodiodes, Schottky diodes, p-n junctions, p-i-n junctions, and avalanche photodiodes) are reported.

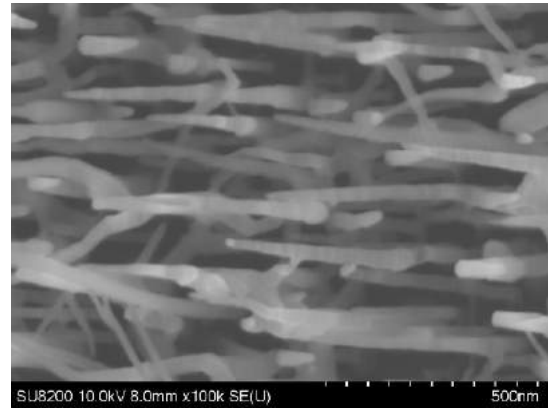


Fig. 3 SEM image of Ga₂O₃ nanowire grown by MBE

Challenges & future perspectives

β -Ga₂O₃ have unique properties like wide bandgap, high chemical and thermal stability. Thus, Ga₂O₃ could be excellent for device applications in the future. However, a number of challenges associated with Ga₂O₃ and need to be addressed are

1. More research is required to identify the different factors that affects Ga₂O₃ growth and study how it affects their optical, structural, thermal and electrical properties.
2. Lattice mismatch needs to be considered when selecting a substrate for growth.
3. More investigation is required for ohmic and Schottky contacts in Ga₂O₃ devices.
4. Research should also be performed on ways to improve carrier mobility and reduce contact resistance at the device level, and to lower costs to enable large-scale production.

Conclusions

From a materials point of view, the wide bandgap of Ga₂O₃ makes it more sensitive to UV light than other wide-bandgap materials such as GaN and SiC and allows it to handle higher power device applications. Thus, Ga₂O₃ nanowires are expected to play a key role in power devices and sensors of the next generation.

The catalytic efficacy of Ni-Cu-Al hydroxalcalcite catalysts on hydrogenation of furfural via thermo catalytic and electrocatalytic routes

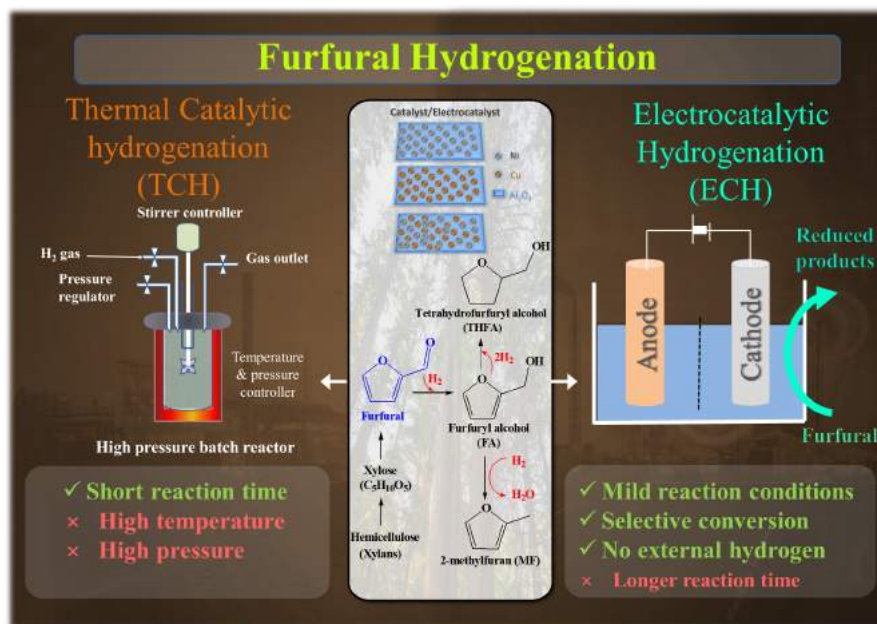


**Upender Rao
Thuppatti**

Nagoya University
Email: thuppatti.upender.rao@i.mbox.nagoya-u.ac.jp

Pursuing his doctorate at the Nori Lab, Nagoya University, Japan. Upender obtained a master's degree from IIT Hyderabad in 2019.

His interests lie in the domain of Carbon resource utilization, Catalyst development, atmospheric CO₂ capturing and conversion.



Graphical abstract

Introduction

The sustainable energy sector has been exploring possible renewable resources for energy and chemicals production to negate the adverse effects of climate change and depletion of fossil fuels. This transition also will diminish the environmental impact of the chemical and refinery industries. Biomass is an abundant resource that resembles actual fossil feedstocks. The futuristic possibility of integrating electricity generation from renewable sources and converting biomass-based carbon sources could make it feasible for energy and fine chemi-

cals production from biomass. In this regard, the hydrogenation of biomass-derived platform chemicals improves the efficiency of producing fine chemicals and provides a much-needed understanding of the primary reaction mechanism for the efficacious utilization of biomass. However, the traditional conversion processes of biomass-derived components such as thermal catalytic hydrogenation (TCH) and catalytic transfer hydrogenation (CTH) are involved with harsh treating conditions and energy-intensive processes. Hence, the immanent path forward is to use electrochemistry charged by renewable electricity to accommodate electrocatalytic hydrogenation (ECH).

Electrochemistry provides a smooth technology for chemical processing (a mild, green, and atom efficient route) and offers much-needed insights into the electron transfer mechanism, including new reaction pathways. Despite the fascinating interest, widespread challenges of adopting this technology are driven by extra knowledge and the equipment setup. Nonetheless, the ECH process offers the following prospects (1) simple operating conditions, (2) requirement of no external H₂ source, (3) cleaner process, and easy product separation (higher carbon recovery and improved H/C ratios).

Furfural is a platform chemical derived from acid-catalyzed hemicellulose reaction, which has a broad range of conversion to synthetic chemicals and liquid fuels[1]. Direct hydrogenation of furfural to tetrahydro furfuryl alcohol (THFA) via furfuryl alcohol (FAL) has attracted much attention to produce the green solvent. In this work, furfural hydrogenation is intended to be carried out using Ni-Cu-Al hydrotalcite (HT) mixed oxides as the catalysts in TCH and as electrocatalysts in ECH to report the efficacy of these mixed oxides. Cu has an excellent affinity for furfural conversion to FAL, and Ni has shown remarkable selectivity towards THFA from FAL. Combining these two metals at an appropriate ratio on Al₂O₃ facilitates the complete conversion of furfural to FAL and further hydrogenation to THFA.

Preparation of catalysts

Three hydrotalcite catalysts (Ni-Al₂O₃ HT, Cu-Al₂O₃ HT, Ni-Cu-Al₂O₃ HT) with Ni or Cu to Al molar ratio of 2:1 have been prepared by the coprecipitation method mentioned elsewhere [2]. In a typical procedure, the aqueous metal precursor solutions were added dropwise to a precipitating solution of Na₂CO₃ and NaOH at vigorous stirring conditions. The resulting solution was stirred for 1 hour maintain the pH at 10 by adding 3M NaOH solution. After that, the precipitated mixture was aged at 65 °C in a Parr reactor for 18 hours to develop the hydrotalcite-like structure. Finally, the solid precipitate was filtered out before multiple washes with ultrapure water to bring down the pH to neutral. Thus, obtained solid was dried at 110 °C overnight, and further calcination and reduction were carried out at 500 °C in air and 5% H₂/N₂ gas, respectively.

Preparation of electrocatalyst

First, a mixed solution of 50 μL of 5 wt % Nafion, 475 μL of water, and 475 μL of ethanol was prepared. In this solution, 20 mg of prepared catalysts were dispersed by sonication. Finally, the working electrode was prepared by dropping 50 μL of a catalyst ink onto the carbon paper with a geometric area of 1 cm²[3].

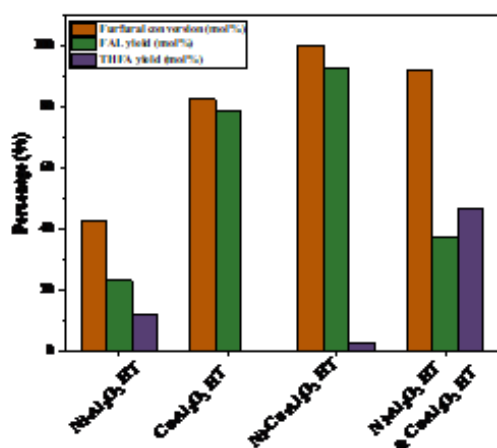
Hydrogenation of furfural

Thermal catalytic hydrogenation of furfural was investigated in a 100 ml Parr reactor equipped with a pressure and a temperature controller. The reactions were carried out at specific reaction conditions (130 °C, 20 bar H₂, 3 hours). Electrocatalytic hydrogenation was conducted in a 100 ml H-type divided cell with a three-electrode setup using 0.5M H₂SO₄ as catholyte. A Pt wire was used as a counter electrode and an Ag/AgCl as a reference electrode. Nafion-117 cation exchange membrane was used to allow the passage of electrons from the anolyte compartment to the catholyte. The products were isolated and analyzed by GC-FID and identified by GC-MS equipment.

Results and discussion

The results of thermal catalytic hydrogenation of furfural at moderate reaction conditions are shown in Fig.1. The reaction with the Ni-Al₂O₃ HT catalyst resulted in only 42% furfural conversion, whereas Cu-Al₂O₃ HT displayed 82 mol% of furfural conversions. However, the affinity of Cu metal was limited to the hydroxyl group of the furfural structure to form FAL. Meanwhile, the Ni metal has shown the affinity to both the hydroxyl group and the ring structure of furfural to further hydrogenate it to THFA. The conversion of furfural with Ni-Al₂O₃ HT catalyst was limited because in-situ formed FAL occupied the active sites of the catalyst with forming THFA. The mixed oxide hydrotalcite catalyst (Ni-Cu-Al₂O₃) converted furfural completely, but the end product yield was limited to 93% of FAL. This could be due to the dominant activity of Cu metal to engage with the hydroxyl group of the furfural. The physical mixing of Ni and Cu catalysts improved the THFA yield to 47 mol% inferring to the tandem hydrogenation of furfural and FAL on Cu and Ni metals

during the reaction.



Thermal hydrogenation of furfural Reaction conditions: 5 mmol Furfural, 30 ml 2-Butanol, 100 mg catalyst, 130 °C, 20 bar H₂, 3 hours

The role of electrocatalyst is crucial to achieving high selectivity and yield of furfural hydrogenation products and high faradaic efficiency. In this regard, a catalyst with high catalytic activity for thermal hydrogenation of furfural could be advantageous given appropriate reacting conditions. The electrocatalytic hydrogenation of furfural is still in adjusting the instrumental setup and the optimal selection of reaction parameters (applied voltage, electrolyte pH, suitable current density, substrate concentration, solvent selection). The preliminary runs of the ECH of furfural have shown the catalyst's abil-

ity in hydrogen evolution reaction (HER). All the three electrocatalysts were active to form FAL and 2-methyl furan (2-MF) so slightly, but HER was dominant, which resulted in poor faradaic efficiency for furfural conversion.

Summary

This work focussed on the catalyst efficacy of Ni-Cu-Al mixed oxide hydrotalcite catalysts for TCH and ECH of furfural to compare different catalytic approaches. The catalysts have shown superior activity at moderate reaction conditions for TCH of furfural, although the product selectivity varied with varying metal oxide. The further work is to provide suitable ECH conditions for Ni-Cu-Al mixed oxide catalysts to obtain the maximum yields of THFA.

References

1. S. Peleteiro, S. Rivas, J. L. Alonso, V. Santos, and J. C. Parajó, "Furfural production using ionic liquids: A review," *Bioresour. Technol.*, vol. 202, pp. 181–191, 2016.
2. H. L. Huynh and Z. Yu, "CO₂ Methanation on Hydrotalcite-Derived Catalysts and Structured Reactors: A Review," *Energy Technol.*, vol. 8, no. 5, 2020.
3. X. Hao et al., "Biomass-Derived N-Doped Carbon for Efficient Electrocatalytic CO₂ Reduction to CO and Zn-CO₂ Batteries," *ACS Appl. Mater. Interfaces*, vol. 13, no. 3, pp. 3738–3747, 2021.

12th ISAJ Annual Symposium-2021

Conveners: Dr. Kedarnath Mahapatra, Tokkai University
Dr. Santosh Ghothwal, Kyoto University
Dr. Manjiri Kulkarni-Deshpande
Dr. Swapnil Ghodke, Nagoya University

The Indian Scientists Association in Japan (ISAJ) organized its 12th annual hybrid (on-site and virtual) symposium on “Science-Technology-Innovation (STI) Towards a Sustainable World” on November 26-27, 2021 at Tokai University, Shimizu campus Shizuoka.

Through this year’s symposium, we have celebrated the first year of the United Nations Decade of Ocean Science for Sustainable Development (2021-2030) and the 70 years of India-Japan diplomatic relations. The convener of the symposium and the General Secretary of ISAJ Dr. Kedarnath Mahapatra commenced the ceremony with the conveners’ message. Prof. Hiroshi Saito, Dean, School of Marine Science and Technology Tokai University has welcomed the guest with warm greetings.

The Chairman of ISAJ, Dr. Sunil Kaul gave an overview of the ISAJ activities in his welcoming address. His Excellency Mr. Sanjay Kumar Verma, The Ambassador of India to Japan kindly inaugurated the symposium with his inspiring and encouraging speech followed by overwhelming messages by Prof. Kiyoshi Yamada, Chancellor Tokai University and Mr. Nobuhiro Tanabe, Mayor of Shizuoka city. Dr. Usha Dixit, Counsellor (S&T), Embassy of India, Tokyo has motivated us by her kind address, A special address was given by Dr. Yoshiro Kaku, Chief representative of The New Energy and Industrial Technology Development Organization, India.

The Ambassador of India handed over awards for ISAJ Life time Achievement Award to Dr. Renu Wadhwa of AIST Tsukuba and Distinguished Mentor Award to Dr. Toshio Yamagata (formerly) of JAMSTEC. By congratulating the awardees we continued with the distinguished keynote lecture by Prof. Asahiko Taira, Ex-President, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), presently the Executive Director of Tokai University Institute of Oceanic Research and Development. The inaugural session was then concluded

by a vote of thanks from the Vice Chairman of ISAJ, Dr., Alok Singh who thanked all the participants, members of the organizing committee, Tokai University and sponsors for their support in making this symposium a success. In the afternoon session, a numbers of plenary and invited talks were given by senior scientists across the globe on ocean Science and Technology.

On the second day November 27, 2021, the symposium showcased the most recent advances in scientific research performed in Japan by Indian scientists and their colleagues in various field of research, such as biology and medicine, power and structural engineering, energy and environment, material Science and physical sciences.

The hybrid format of the symposium has attracted an overwhelming number of abstracts for both in-person and online presentations, the largest in the 12-year history of the Symposium, including keynote, plenary, invited lectures, short presentations by the young scientists, and almost one-third of them have presented in person. The overwhelming response of participants from institutes across Japan and outside Japan: India, South Korea, Indonesia, Germany, etc. was appreciable. Very senior as well as young scientists gave a total of 65 talks.

Marine Science Museum Auditorium and Beach Hotel Gosea’s in Shimizu made an excellent venue for the symposium because the city has a wonderful coastal lines on one side and a giant Fujisan view on the other. About 100 participants attended the symposium from broad range of disciplines of science and technology. In concluding session at the end, Dr. Sunil Kaul, Dr. Alok Singh and Dr. Kedarnath Mahapatra presented awards to the poster and presentation awardees.

We value the support and encouragement received from all the participants, the Embassy of India and the City Government of Shizuoka for this epoch-making event to become a reality.

12th ISAJ Annual Symposium-2021



Dr. Sunul Kaul presenting a memento to His Excellency Mr. Sanjay Kumar Verma in appreciation for his full support to our association.



Dr. Renu Wadhwa (AIST TSukuba) receives Life Time Achievement Award from His Excellency. Dr. Alok Singh read the citation of the award.



Prof. Kiyoshi Yamada, Chancellor Tokai University, addresses the symposium through web link.



The Ambassador meets the Mayor of the Shizuoka city Mr. Nobuhiro Tanabe (third from left).



Welcome Address by Dr. Kedar Mahapatra (ISAJ General Secretary and a symposium convener) of Tokai University, .



Visiting under-sea floor drilling ship Chikyu (at the back) of JAMSTEC, on invitation of former President of JAMSTEC Dr. Asahiko Taira.



Group picture of the on-site participants at the end of the two day symposium.

Editors

Dr. Swapnil Ghodke

Nagoya University, Nagoya, Japan
swapneelghodke@gmail.com

Dr. Mahendra Kumar Pal

Indian Institute of Technology (BHU), Varanasi, India
mail.mahendra.jpn@gmail.com

About ISAJ

The Indian Scientists' Association in Japan (ISAJ) is a Non-Profit Organization (NPO) aimed at networking and promoting Science and Technology Cooperation between India and Japan.

Contact Us:

Feel free to write to us

For any information about ISAJ and membership: isaj@gmail.com

To subscribe our newsletter: isaj.newsletter@gmail.com

Visit us on the web at www.isaj.org

