

Nanomaterials

Kazunori Yamamoto

New Business Development Headquarters
Tsukuba Research Laboratory
Advanced Fundamental Technology Development Center

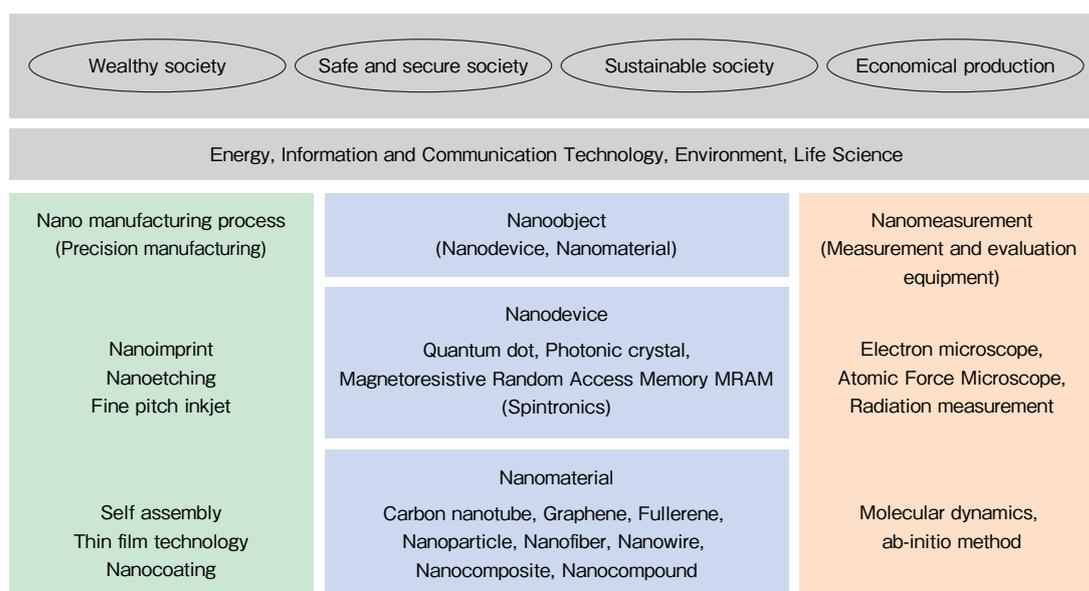
Nanotechnologies, major fields of which include Nano manufacturing process, Nanomaterials, Nanodevices, and Nanomeasurement, are expected to become fundamental technologies for manufacturing in a wide range of industries. In this paper, Cu ink for Printed Electronics is introduced as a typical Nanomaterial with which Hitachi Chemical is familiar. The scope also includes our efforts to attain the international standard and cooperate with partners to overcome inconsistencies in advanced technologies. We, Hitachi Chemical, will apply those advanced technologies to applications in the near future, expanding next generation ICT (Information and Communication Technology) and other industries.

1 Introduction

R&D of nanotechnology has been accelerated worldwide since the U.S. announced its National Nanotechnology Initiative strategic plan in 2000. In Europe, the EU increased its budget for nanotechnology in the 6th R&D Program Framework, while in Asia, South Korea set up a 10-year master plan for nanotechnology in 2001. Japan has taken the lead in basic technology, for example, the discovery of Carbon NanoTubes in 1991, and producing an Atomic Force Microscope and Magnetoresistive Random Access Memory (MRAM) by the 10-year Atom Technology Project launched in 1992¹⁾.

Nanotechnology can be roughly classified into three categories. They are nano manufacturing processes, nanomaterials and nanodevices for new features of high performance, and nanomeasurement (**Table 1**). Hitachi Chemical deals with all of these technologies and nanomaterials in particular. Focusing on nanomaterials, this paper reports typical applications, general international standardization trends and future prospects.

Table 1 Technology Map of Nanotechnologies



Source: Created based on a Technology Map of Nanotechnologies 2009, METI

2 Nanomaterials, Applied Technologies and Products

The maximum size at least one direction of nanomaterial is defined as 100 nm in size in at least one direction^{2), 3), 4), 5)}. A carbon nanotube (CNT) is a typical nanomaterial, comprising a hollow nanofiber formulated in the six-membered ring network composed of carbon atoms and featuring e.g. high mechanical strength, low electrical resistance and high thermal conductivity. Commercialization of multi-walled CNTs is underway for specific applications. Single-walled CNTs (SWCNTs) are in the basic study phase, and separation and refinement technologies have recently been reported.

The copper-clad laminates with low CTE (Coefficient of Thermal Expansion) for semiconductor package substrate are typical applications of nanomaterials commercialized by Hitachi Chemical. Copper-clad laminates are manufactured using nanosilica as fillers. The material is slurried after surface treatment with nanocoat technology, dispersed in epoxy resin varnish and sent to a common coating process⁶⁾. Nanomaterials such as CNTs, plate-like nanoparticles, nanofilms, and the conductive component of Cu ink for printed electronics (PE) are currently under R&D. CNTs and Cu ink will be described later in this report.

Hitachi Chemical has participated in the Nanotechnology Program, Innovative Material Creation Program, Nanotechnology and Advanced Material Commercialization Program, and Quantity Synthesis of SWNCT and R&D of Transparent Electrodes launched by the New Energy and Industrial Technology Development Organization (NEDO). Our CNTs synthesized using the Chemical Vapor Deposition (CVD) method are characterized by millimeter-long length and high purity exceeding 98% (**Figure 1**, **Table 2**)⁷⁾. Its application as an additive for functionalization is expected, in addition to the use for transparent electrodes. In Cu ink, a dense conductor layer with low volume resistivity of 2 to 4 $\mu\Omega \cdot \text{cm}$, equivalent to electroless plating wiring, can be formulated in gas-phase treatment under atmospheric pressure at a temperatures below 190 °C using a Cu compound with an average particle diameter of 70 nm as the conductive component (**Table 3**). Because no dispersant is used, the reactive conditioning temperature required to remove the dispersant can be kept low, and gas-phase treatment eliminates the liquid control and waste treatment processes^{8), 9), 10), 11)}. Accordingly, the printing method using Cu ink is characterized by fewer processes and resources, and a more compact wiring space (**Figure 2**). PE meets the needs to break away from traditional technologies such as vacuum and photolithography processes, as well as thin semiconductor packaging and wiring on curved planes. Hitachi Chemical has participated in basic technology development projects to promote the commercialization of *Manufacturing technology for printed devices* and *flexible device technology* managed by the Japan Advanced Printed Electronics Technology Research Association, established in 2011, while striving to market PE for applications on next-generation information and communication equipment.

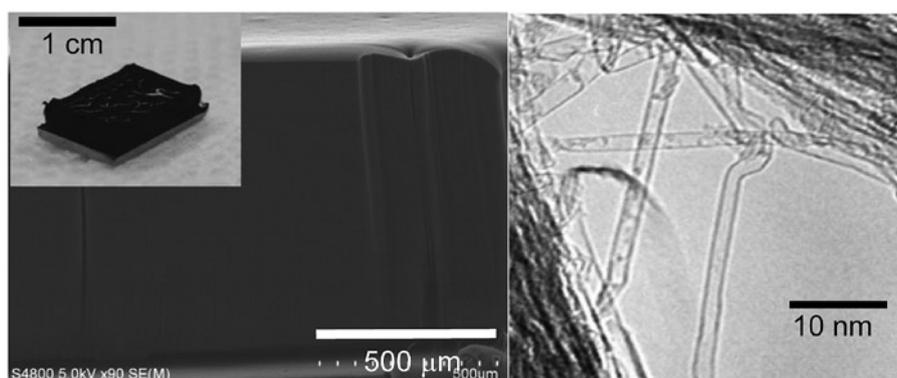
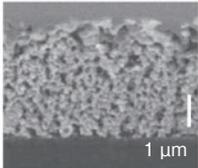
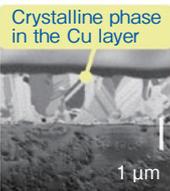
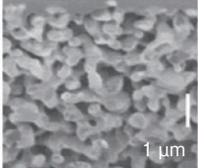


Figure 1 Electron Micrograph of CNT

Table 2 Comparison of CNT Properties by Various Synthetic Methods

Item	CVD method (Hitachi Chemical)	HiPCO method	CoMoCat method
Diameter	2-7 nm	1-2 nm	≈1 nm
Length	1-5 mm	2-3 μm	2-3 μm
Catalyst residue	<0.1%	30%	10-20%
Purity	≥99.8%	≤70%	≤10%
Raw material	Hydro Carbon	Carbon monoxide	Carbon monoxide

Table 3 Dependence of the Reactive Conditions on the Cu Layer Structure

Gas-phase treatment under reducing pressure ($6 \mu\Omega \cdot \text{cm}$)	Gas-phase treatment under atmospheric pressure ($3 \mu\Omega \cdot \text{cm}$)	Liquid-phase treatment under atmospheric pressure ($100 \mu\Omega \cdot \text{cm}$)
After reactive conditioning 		
Cross-sectional SIM image 	Cross-sectional SIM image 	Cross-sectional SIM image 

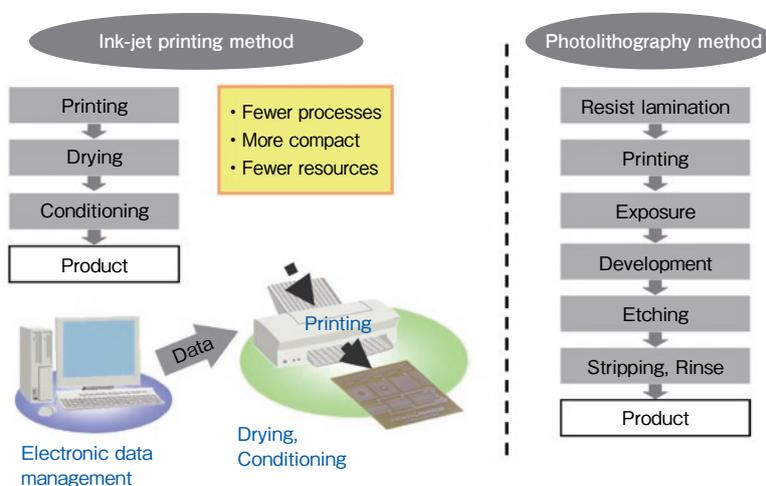


Figure 2 Comparison of the Manufacturing Process between Ink-jet Printing and Photolithography

3 Trends of International Standardization and Approaches of Hitachi Chemical

Prevention of inconsistencies, overlapped work, and uniformity of result tables, including terminology and evaluation methods, are part of the purposes for international standardization. Countries are striving to take the lead in standardization to gain competitive advantages. For the international standardization of nanotechnology, the International Organization for Standardization (ISO) launched a technical committee TC229 in 2005, while the Japanese Industrial Standards Committee (JISC) established the Japan National Committee for International Standardization of Nanotechnology¹²⁾. The role of Japan in standardization is to characterize measurement and the safety of CNTs in particular. For the international standardization of PE, the International Electrotechnical Commission (IEC) established a technical committee TC119 in 2011, and Japan is expected to be active as the organizer of the material working group. JISC set up a PE International Standardization ad hoc Committee in the Japan Electronics and Information Technology Industries Association, which is currently negotiating with the U.S.-based IPC (former Institute for Printed Circuits) for smooth standardization. Hitachi Chemical has actively participated in these international standardization projects.

4 Future Prospects

Hitachi Chemical has focused on four business domains: information and communication, and display, environment and energy, automobile, and life science. The information and communication, and display domain includes not only functionalization and upgrading of conventional technologies, but also R&D of PE, as explained in Section 2, and the promotion of organic electronics with technological trends such as cloud computing, Internet of Things (IoT), big data and electronics. As electronic

devices transform, new business opportunities may open up. In the environment and energy domain, it seems to be the time for us to enter new businesses because the large-scale development initiatives involving renewable energy, and innovation for building the next generation society such as smart cities that improve energy efficiency, are underway. Nevertheless, such clear technological trends accelerate global competition, the demand for materials remains considerable. Competing power comes of differentiated capabilities for enhancing customer value is important, therefore, combining and optimizing technologies alone will be insufficient to maintain an industry leading position. Nanomaterials are useful for differentiation, but nano-level structural control may be equally critical. Technology to produce nanofilms by stacking components with opposite electric charges alternately, and the polymer brush that grafts functional groups are included in this category. Open innovation is effective to make these fundamental technologies available in the short-term. Our objectives are to bring up unique technologies that differentiate our products from others by establishing good relationship with our partners through society activities and technology exchanges.

5 Conclusion

Nanotechnology that creates atomic-level functionality deviates from the progress of existing technologies, which may hinder its commercialization. Cooperation with partners for added value is therefore critical and why we implement international standardization to share globalized technologies. We are in an era where good unique technology alone does not ensure success. This report presented the features of our Cu ink products for PE as an example of nanotechnology application. We believe such cutting-edge technologies exceed conventional technologies, and will be commonly used.

[References]

- 1) Interim report of Nanotechnology Policy Study Group "Prescription for Value Creation with Nanotechnologies," Nanotechnology and Materials Strategy Office, Ministry of Economy Trade and Industry, March 31, 2005
- 2) The Royal Society & The Royal Academy of Engineering, UK, "Nanoscience and Nanotechnologies: opportunities and uncertainties." July, 2004
- 3) ISO TS 27687 "Nanotechnologies-Terminology and definitions for nanoobjects: Nanoparticles, nanofibers, and nanoplate"
- 4) Japan Industrial Standards JIS/TS Z0027 "Nanotechnologies and nanoobjects (nanoparticles, nanofibers and nanoplates) terminology and definition," 2010
- 5) Scientific Committee on Emerging and Newly Identified Health Risks, Scientific basis for the definition of the term "nanomaterials," European Union 2010
- 6) Yoshihiro Nakamura, et al, Investigation of Low Coefficient of Thermal Expansion Materials for Improving PoP Packaging Reliability, the 16th Japan Welding Society Symposium on Micro-joining and Assembly Technology in Electronics, Abstracts, 359-364, 2010
- 7) Eisuke Haba, et al, Transparent conductive properties of SWCNT films and dependency of its thickness, The 36th Fullerenes-Nanotubes General Symposium, 2P-20, 2009
- 8) Pub. No. 2011-140598, Method of Manufacturing of Nanoparticle Dispersion and Dispersion of Ink-jet printing
- 9) Yasushi Kumashiro, et al., "Printing Materials for Flexible Electronics Device", Proceedings of International Conference on Electronics Packaging 2010, TB3-1 (2010)
- 10) Maki Inada, et al., "Material Technology of Conductive Wiring for Ink-jet Print," Transactions of The Japan Institute of Electronics Packaging, Vol. 4, No. 1, p.114-118, (2011)
- 11) Kyoko Kuroda, et al, "Development of Copper Materials and Processing for Printed Electronics", Proceedings of International Conference on Electronics Packaging 2012, TB3-4 (2012)
- 12) News Letter of International Standardization for Nanotechnology, First Issue (2006)