

Inkjet Printing of Functional Materials

Henning Sirringhaus and Tatsuya Shimoda,
Guest Editors

Abstract

This article introduces the November 2003 issue of *MRS Bulletin* on Inkjet Printing of Functional Materials. The issue is devoted to the emerging non-graphic-arts uses of inkjet printing as a technique for depositing and patterning functional materials in the liquid phase onto a substrate. The articles provide an overview of a selected range of representative applications in the field of structural ceramics, polymer electronics, and protein chips, and address some of the key challenges that face the broad scientific and industrial community as it attempts to apply a mature and well-developed graphic arts printing technique to the deposition of functional materials.

Keywords: functional materials, inkjet printing.

There are a growing number of applications that require the delivery of small quantities of functional materials with specific electrical, optical, chemical, biological, or structural functionalities into well-defined locations on a substrate. In many cases, these materials are most suitably processed from a liquid solution, dispersion, or melt, rather than from the vapor phase. Many functional materials, such as polymers or large biomolecules, are not amenable to vacuum deposition techniques. The need for solution processing may also be dictated by the nature and properties of the substrate; the need to distribute the materials over a large substrate area, or only to certain locations of the substrate and not to others (e.g., to induce a local chemical reaction); or simply to keep the material in a liquid environment at all times, such as for some biological applications. This issue of *MRS Bulletin* is devoted to the emerging non-graphic-arts uses of inkjet printing as a technique for depositing and patterning functional materials in the liquid phase. The articles provide an overview of representative applications in the field of structural ceramics, polymer electronics, and protein chips, and address some of the key challenges that face the broad scientific and industrial community as it attempts to apply a mature and well-developed graphic arts printing technique to the deposition of functional materials.

Inkjet printing has become one of the most widespread printing techniques in the home and office desktop printing market. Advances in inkjet technology now allow the printing of full-color, high-resolution photographs. In the commercial printing arena, inkjet technology is widely used for digital proofing prior to running a print job on a press; for short-run, wide-format digital printing such as posters for outdoor advertising; and for applications that require printing onto nonpaper substrates such as rigid display boards. Inkjet printers are being developed for integration with offset presses to print customized information in magazines, such as tailored advertising. In industry, inkjet technology is the dominant technology for printing variable information such as "sell-by" dates or product identification codes, as part of production or packaging processes.

Since the original observation by Lord Rayleigh in 1878 that a liquid stream is unstable and tends to break up into individual droplets, a large number of inkjet technologies have been developed. Continuous inkjet (CIJ) technology is based on inducing an electrical charge to the liquid by ejecting a jet of conductive ink from an orifice through a region with an external electric field. After the jet breaks up into isolated droplets, the charge remains on the droplets and can be used to deflect them either toward the substrate or into an ink collection and recirculation system.

In drop-on-demand (DOD) inkjet technology, ink droplets are formed only when required. The two dominant techniques in this area are thermal and piezoelectric DOD printing. In thermal DOD printing, droplets are generated by heating the wall of the ink chamber, causing the formation of vapor bubbles and the ejection of droplets through a nozzle orifice. In piezoelectric DOD printing, a pressure wave in the ink chamber is generated by applying a voltage pulse to a piezoelectric stack or plate, resulting in the formation of droplets at the nozzles. (For a more extensive review of these and other inkjet technologies and their applications in graphic arts printing, see, for example, Reference 1.)

The application of inkjet technology to the delivery of functional materials poses a range of important challenges in terms of ink formulation, print head and print system design, substrate choice and preparation, and control of solvent evaporation. The inks need to be formulated in a narrow viscosity range compatible with the specific print head used. In many cases, the additives that are routinely used in graphic arts printing to modify, for example, ink viscosity, cannot be used for functional materials, as they will adversely affect the materials' performance. It is necessary to ensure that the ink does not in any way chemically interact with or dissolve any of the components inside the print head or the ink feed system. Nor should the ink's properties degrade under the high mechanical shear of a piezoelectric head or the high-temperature conditions of a thermal inkjet head. The ejection of droplets from the array of nozzles needs to be stable and reliable. Nozzles can become clogged by the evaporation of ink on the nozzle plate or the presence of particulates in the ink. Fluctuations in droplet volume can lead to undesirable variations in the amount of material deposited onto the substrate. For many applications, the velocity and direction of the droplets ejected from the array of nozzles must be highly uniform in order to ensure highly accurate positioning of a large number of droplets in well-defined substrate locations. For many nontraditional inkjet applications, the requirements for droplet positioning accuracy are significantly more demanding than for graphic arts printing. Finally, the spreading and drying of ink droplets on the substrate must be carefully controlled in order that the droplets arrive at the desired position and the desired structure and profile of the material on the substrate are achieved.

Solving these challenges through the design of specialized print heads and ink formulation is not made easier by the fact

that inkjet technology is still regarded by many experts in the field as "black magic." Although several groups have attempted to model theoretically the hydrodynamical processes occurring in the ink chamber and at the nozzle plate (e.g., see Reference 2), in many cases ink formulation and print head design are still based on empirical experience and trials. A better theoretical understanding of the inkjet process would be of great help to print head designers and ink formulators. Similarly, a theoretical understanding of the process of spreading and drying of a microliquid deposited onto a substrate is challenging because a microliquid exhibits specific size effects arising from its high surface-to-volume ratio, such as different drying kinetics, that are not observed for bulk liquids.

This issue of *MRS Bulletin* is organized in the following way. The first article, by Creagh and McDonald, is devoted to the design of specialized piezoelectric DOD print heads for non-graphic-arts applications, in particular, for manufacturing flat-panel displays based on light-emitting polymers. Although inkjet techniques such as CIJ or thermal DOD have many attractive attributes, a lot of the nontraditional inkjet printing to date has been done with piezoelectric DOD. This is at least partly due to the ability of piezoelectric DOD to deposit a broad range of water- and solvent-based inks, as well as both conductive and nonconductive inks. The article discusses some of the design principles for high-performance piezoelectric DOD print heads. It presents the state of the art of piezoelectric DOD print head technology in terms of droplet volume, variations of droplet volume between nozzles, achievable uniformity in droplet speed and directionality, and materials compatibility.

The second article, by Derby and Reis, is devoted to the formulation of jettable inks with a focus on the important class of particulate suspensions. Concentrated liquid suspensions of powders need to be printed in a range of applications, such as suspensions of metallic particles for the printing of high-conductivity metallic interconnects. Suspensions of ceramic particles are needed for the deposition of high-performance dielectrics and for printing three-dimensional objects formed from structural ceramics (e.g., for rapid-prototyping applications). The article re-

views the requirements for the rheology of such suspensions to be printable by inkjet technology and shows how basic fluid dynamics properties affect droplet formation and droplet spreading upon impact. The authors discuss in particular the requirements for inkjet printing of alumina ceramic suspensions for the fabrication of three-dimensional objects.

The next three articles are devoted to representative applications of inkjet printing in the area of displays, microelectronics, and biology, respectively.

The article by Shimoda et al. is devoted to the development of a microliquid manufacturing process based on inkjet technology and its application to the fabrication of full-color emissive-polymer displays. In such applications, inkjet technology is used to pattern the red, green, and blue emissive polymers, as well as charge injection and transport layers, into the respective pixel locations of the display. The article focuses on the effects of key process parameters such as the droplet positioning accuracy and the drying mode on the performance of inkjet-fabricated polymer light-emitting diodes (PLEDs). It also describes the inkjet-based manufacturing process for active-matrix PLED displays on top of polycrystalline silicon transistor active-matrix arrays.

The article by Burns et al. focuses on the use of inkjet printing in the solution-based manufacturing of integrated circuits for thin-film transistors (TFTs). This application is characterized by the need to integrate a range of different materials, including solution-processable conductors, polymer semiconductors, and polymer dielectrics, into multilayer assemblies with good control of interfaces. It also has very stringent requirements for printing resolution, droplet volume, and droplet-placement accuracy in order to achieve critical feature sizes (of several micrometers) and high uniformity of transistor performance. The article describes the use of surface-energy-assisted inkjet printing to enable transistor devices with channel lengths of micrometer and even submicrometer dimension with high device uniformity. The application of this inkjet-based manufacturing process to the fabrication of polymer-dispersed liquid-crystal and electronic paper displays driven by an active matrix of printed TFTs is discussed.

The last article, by Zaugg and Wagner, reviews the fabrication of protein biochips,

which have recently gained a lot of attention as emerging bioanalytical tools for clinical diagnostics as well as drug development. The creation of such devices was possible by merging scientific approaches and methodologies in microfabrication, organic interface chemistry, biochemistry, and—last but not least—advances in depositing minute amounts of protein-containing solutions precisely onto small micron-sized areas of biochip substrates. The extremely fragile nature of the biomolecules in these solutions (which ultimately become the active ingredients on the biochips) imposes special demands on the design of the corresponding arraying technology that are very different from standard inkjet printing applications. This article presents a comparison of different DOD and alternative arraying technologies that are currently under development or already commercialized.

The articles in this issue have been selected to provide a representative, but in no way comprehensive, overview of the many important applications that inkjet technology is finding outside the graphic arts printing field. Important application areas such as textile printing, printing of photoresist layers, patterning of printed circuit boards, and the delivery of liquids to induce local chemical reactions had to be omitted. All of these areas constitute important fields of research and development and provide a broad spectrum of interesting scientific challenges for a wide range of functional materials. Similarly, due to space limitations, no attempt has been made to include alternative, viable printing techniques capable of controlled delivery of small fluid volumes to well-defined locations. Techniques such as microdispensing, screen, offset, and gravure printing, and spray and aerosol coating using small nozzles, have many attractive attributes that rival those of inkjet technology and make them viable alternatives for many applications.

References

1. H.P. Le, in *Recent Progress in Inkjet Technologies II*, edited by E. Hanson (Society for Imaging Science and Technology, Springfield, VA, 1999) p. 1.
2. Y. Zhou, in *Recent Progress in Inkjet Technologies II*, edited by E. Hanson (Society for Imaging Science and Technology, Springfield, VA, 1999) p. 175. □

The Materials Gateway: www.mrs.org

Henning Sirringhaus, Guest Editor for this issue of the *MRS Bulletin*, is vice president of research at Plastic Logic Ltd. (Cambridge, U.K.) and also a Reader in Physics at the Cavendish Laboratory of the University of Cambridge. His current research interests include the charge transport physics and materials science of polymer semiconductors, their application in thin-film transistor devices and circuits, the development of novel microstructuring and printing techniques for solution-processable functional materials, and the application of scanning probe microscopy techniques to the study of electronic properties of soft condensed matter.

Sirringhaus received his diploma and PhD degrees in physics from the Swiss Federal Institute of Technology in Zurich in 1991 and 1995, respectively. From 1996 to 1997, he did post-doctoral work in the Department of Electrical Engineering at Princeton University on amorphous silicon thin-film transistors. He has been working in the field of polymer electronics since 1997 and co-founded Plastic Logic in 2000.

Sirringhaus can be reached at Plastic Logic Ltd., 34 Cambridge Science Park, Milton Road, Cambridge, CB4 0FX United Kingdom; tel. 44-122-370-6000, fax 44-122-370-6006, and e-mail henning.sirringhaus@plasticlogic.com.

Tatsuya Shimoda, Guest Editor for this issue of the *MRS Bulletin*, is director of the Technology Platform

Research Center at Seiko-Epson Corp. in Nagano, Japan, and a visiting professor at the Japan Advanced Institute of Science and Technology. Shimoda has been a member of the research staff at Seiko-Epson since 1977. Until 1994, Shimoda was engaged in research and development work on magnetic materials and their applications; since then, he specialized in R&D work on thin-film devices and novel processes including a microliquid technology for inkjet printing of displays and semiconductor components.

Shimoda can be reached at Seiko-Epson Corp., 281 Fujimi, Fujimi-machi, Suwagun, Nagano-ken, 339-0293 Japan; tel. 81-266-62-8444, fax 81-266-62-8998, and e-mail shimoda.tatsuya@exc.epson.co.jp.

Seamus E. Burns is manager of the display projects at Plastic Logic Ltd. (Cambridge, U.K.), where he has been since March 2001. He received his degree in physics from the University of Sheffield and then earned his PhD degree at Cambridge University under the supervision of Richard Friend. Burns' research involved the development of solution-processable semiconductor device structures such as organic semiconductor light-emitting diodes and lasers and the modeling of the photonic properties of those devices. He then worked as a consultant for three years before joining Plastic Logic.

Burns can be reached at Plastic Logic Ltd., 34 Cambridge Science Park, Milton Road,



Henning Sirringhaus



Tatsuya Shimoda



Seamus E. Burns



Hiroshi Kiguchi



Marlene McDonald



John Mills

Cambridge, CB4 0FX United Kingdom; e-mail seamus.burns@plasticlogic.com.

Paul Cain is an engineer at Plastic Logic Ltd. (Cambridge, U.K.) and works on research into laser processing methods for digitally printed thin-film transistors and circuit components, as well as logic-circuit design and fabrication methods for organic electronics. Cain received a BSc degree in physics from Nottingham University in 1998 and a PhD degree in semiconductor physics from the University of Cambridge and Hitachi Cambridge Laboratory in 2001 for work on the design, fabrication, and measurement of single-electron devices and electron transport in coupled quantum dots.

Cain can be reached at Plastic Logic Ltd., 34 Cambridge Science Park, Milton Road,

Cambridge, CB4 0FX United Kingdom; tel. 44-122-370-6017, fax 44-122-370-6006, and e-mail paul.cain@plasticlogic.com.

Linda T. Creagh is the business development director at Spectra Inc. in Lebanon, N.H. Spectra, an independent subsidiary of MARKEM, designs, manufactures, and markets inkjet print heads and inks for industrial, graphic arts, and commercial applications. Creagh joined Spectra in 1985 as director of ink development after 10 years of developing inkjet technologies with Xerox R&D. Before Xerox, she was involved in liquid display research at Texas Instruments. She has a number of technical publications and more than 15 U.S. and foreign patents in the fields of inkjet technology and liquid-crystal displays.

Creagh can be reached at Spectra Inc., 101 Etna Rd., Lebanon, NH 03766 USA; tel. 940-565-0027, fax 940-565-0027, and e-mail Lcreagh@Spectra-inc.com.

Brian Derby is a professor of materials science at the Manchester Materials Science Centre (Manchester, U.K.). His current research interests include inkjet printing as a fabrication tool in materials science and tissue engineering, mechanical properties of materials, novel fabrication methods, nanomechanical characterization, the properties of metal/ceramic interfaces, and the materials science of decorative metalwork. He received his BA (1978) and PhD (1981) degrees in materials science from the University of Cambridge. He has been a European Space Agency fellow in Grenoble, France, and a



Paul Cain



Linda T. Creagh



Brian Derby



Katsuyuki Morii



Nuno Reis



Shunichi Seki

Lecturer and Reader in materials engineering at the University of Oxford, where he was director of the Oxford Centre for Advanced Materials and Composites. He is the author of more than 200 papers.

Derby can be reached at the Manchester Materials Science Centre, Grosvenor Street, Manchester, M1 7HS United Kingdom; tel. 44-161-200-3569, fax 144-161-200-8877, and e-mail b.derby@umist.ac.uk.

Hiroshi Kiguchi is a development manager at Seiko-Epson Corp. in Nagano, Japan. He joined Seiko-Epson in 1989 after receiving his BS degree in chemistry from Shizuoka University. He has been working on applied development using inkjet technology for industry on the IJ Industrial Applications Project since 2000. He is

a member of the Chemical Society of Japan and the Society of Polymer Science, Japan.

Kiguchi can be reached at Seiko-Epson Corp., 1010 Fujimi, Fujimi-machi, Suwa-gun, Nagano-ken, 399-0295 Japan; tel. 81-266-62-6817, fax 81-266-62-6826, and e-mail kiguchi.hiroshi@exc.epson.co.jp.

Marlene McDonald has worked as a development engineer at Spectra Inc. in Lebanon, N.H., since 1994. Her work is focused on computational modeling, jet design, and new product development. McDonald received her BA degree from Dartmouth College and her MSME in fluid mechanics from the University of Massachusetts at Amherst.

McDonald can be reached at Spectra Inc., 101 Etna Road, Lebanon, NH 03766 USA; tel. 603-442-4013,

fax 603-643-3079, and e-mail mmcdonald@spectra-inc.com.

John Mills is vice president of engineering at Plastic Logic Ltd. (Cambridge, U.K.). He holds a PhD degree in physics from the Defence Research Agency and a first degree in physics from the University of East Anglia. Mills has over seven years of management-level experience in research and development businesses. Before joining Plastic Logic in 2002, he was the director of development for the combined Commercial Printing and Product Identification divisions of Domino Printing Sciences.

Mills can be reached at Plastic Logic Ltd., 34 Cambridge Science Park, Milton Road, Cambridge, CB4 0FX United Kingdom; e-mail john.mills@plasticlogic.com.

Katsuyuki Morii graduated from Osaka Prefecture University, Japan, in 1993 and received MS and PhD degrees in materials science from the Japan Advanced Institute of Science and Technology (JAIST) in 1995 and 1998, respectively. After working as an associate in the department of physical materials science at JAIST, he joined Seiko-Epson Corp. in Nagano in 1999, where he has been working on basic research concerning inkjet phenomena and conductive polymers. He is now a chief researcher in the Technology Platform Research Center.

Morii can be reached at Seiko-Epson Corp., 281 Fujimi, Fujimi-machi, Suwa-gun, Nagano-ken, 399-0293 Japan; tel. 81-266-62-8444, fax 81-266-62-8998, and e-mail katsuyuki.morii@exc.epson.co.jp.

Nuno Reis is currently a postdoctoral research fellow at the Instituto Superior Tecnico in Lisbon, Portugal, and at the Manchester Materials Science Centre (Manchester, U.K.). He graduated from the Instituto Superior Tecnico in 1996 with a diploma in materials engineering, having worked toward his dissertation at Siemens Research Laboratories in Munich. He then obtained a DPhil degree in materials science at the University of Oxford in 2002. He is currently working on novel production methods for tissue engineering scaffolds, inkjet printing technologies, and photopolymerization studies by stray-field magnetic resonance imaging.

Reis can be reached at the Instituto Superior

Tecnico, Av. Rovisco Pais, Lisbon, 1049-001 Portugal; and by e-mail at nunoreis@ist.utl.pt.

Shunichi Seki received his BS and MS degrees in physics from the Science University of Tokyo in 1992 and 1994, respectively. In 1997, he joined Seiko-Epson Corp. in Nagano, Japan, where he has been working on the development of inkjet technology, especially its application to polymer light-emitting diodes in the OLED Product Development Department.

Seki can be reached at Seiko-Epson Corp., 281 Fujimi, Fujimi-machi, Suwa-gun, Nagano-ken, 399-0293 Japan; tel. 81-266-62-5607, fax 81-266-61-1545, and e-mail seki.shunichi@exc.epson.co.jp.

Peter Wagner co-founded Zyomyx Inc. in Hayward, Calif., in 1998 and has since served as chief technology officer and as a member of the board of directors. Wagner has more than 15 years of experience in surface biochemistry and is one of the early pioneers in biological scanning probe microscopy. During the past decade, Wagner developed a number of new methodologies in single-molecule biophysics, nanotechnology, and surface chemistry. He has authored more than 100 scientific publications, book chapters, patents, and conference abstracts. Prior to joining Zyomyx, Wagner was awarded a Humboldt fellowship for research at Stanford University to develop ultrasensitive biosensors and to further integrate surface chemistry and biochemistry with a focus on

Thin Film Solutions from Experts in Deposition Control

The name **Sycon** and its logo are synonymous with quality Thin Film Depositions. With Sycon's full line of deposition components and world-class support, you're sure of getting a reliable instrument for your deposition requirement.



The **STC-2002** is the flexible multi-layer powerhouse. Expandable to 8 Channels of measurement & control for very demanding process applications.



The **STC-2000A** has the same high-speed precision measurement engine as the 2002. Two measurement channels, handle most deposition applications.



STM-100 / MF, Multi-film monitors. Easy to use, with large back-lit high visibility display. A World standard; 1000's in use.



VISIT MRS BOOTH NO
324

The **STM-1**, low cost, precision rate/thickness monitor. Single channel monitor with integrated oscillator on a compact pc board.



The **VSO-100**, Sycon's In-Vacuum Sensor / Oscillator. For large system applications.

Sycon instruments
Made in the U.S.A

v 315-463-5297 / f 315-463-5298
www.sycon.com

For more information, see <http://advertisers.mrs.org>

Inkjet Printing of Functional Materials



Peter Wagner



Jizheng Wang



Frank G. Zaugg

protein immobilization and micro- and nanostructuring. Prior to his work at Stanford, Wagner completed postdoctoral studies at the Swiss -- Federal Institute of Technology Zurich (ETH Zurich). He holds an MS degree in organic chemistry from the University of Stuttgart, an MS degree in biochemistry from the University of Berlin, and a PhD degree in surface biophysics from ETH Zurich.

Wagner can be reached at Zyomyx Inc., 26101 Research Rd., Hayward, CA 94545 USA; tel. 510-266-7503, fax 510-266-7792, and e-mail peter.wagner@zyomyx.com.

Jizheng Wang is currently working as a postdoctoral research associate in the Optoelectronics Group of the Cavendish Laboratory at the University of Cambridge. His areas of research include the development of nanometer-scale pat-

terning techniques and the fabrication of short-channel all-polymer field-effect transistors. He received his PhD degree in semiconductor materials from the Institute of Semiconductors, Chinese Academy of Sciences, where he concentrated on investigations of molecular-beam epitaxy growth of III-V quantum dots and quantum wells.

Wang can be reached by e-mail at jw360@cam.ac.uk.

Frank G. Zaugg is a senior research scientist in the Microsystem Technology Group of Zyomyx Inc. in Hayward, Calif. His current research interests include the development of novel technologies arising from the integration of microfabrication (MEMS), organic interface chemistry, and biochemistry. At Zyomyx, he is developing the biochip architecture as well as microfluidic de-

vices and robotic systems for manufacturing high-density protein-array biochips. Zaugg joined Zyomyx in 1999 after obtaining his PhD degree from the Swiss Federal Institute of Technology Zurich (ETH Zurich). During his thesis, he developed chemical and topographical nanofabrication techniques to produce substrates for the biochemical analysis of functional biomembranes, including proteins. Prior to his dissertation, Zaugg worked as a research assistant at the Institute of Biochemistry II (ETH Zurich) on bioconjugation and organic synthesis of bifunctional cross-linkers. Zaugg also holds an M.S. degree in biochemistry from ETH Zurich.

Zaugg can be reached at Zyomyx Inc., 26101 Research Rd., Hayward, CA 94545 USA; tel. 510-266-7507, fax 510-768-2847, and e-mail fzaugg@zyomyx.com. □

MRS 2003 FALL MEETING SPECIAL EVENT

THE COMING OF MATERIALS SCIENCE

Book Signing by Author **Robert W. Cahn**

Tuesday, December 2 • 2:30 pm – 3:30 pm
Publications Sales • Level 2, Hynes

