

# On the Use of Silver Nanoparticles for Direct Micropatterning on Polyimide Substrates

Jack H.-G. Ng, David E. G. Watson, Joachim Sigwarth, Aongus McCarthy, Kevin A. Prior, Duncan P. Hand, Weixing Yu, Robert W. Kay, Changqing Liu, *Senior Member, IEEE*, and Marc P. Y. Desmulliez, *Member, IEEE*

**Abstract**—This paper proposes a direct micropatterning process based on the growth of photoreduced silver nanoparticles onto polyimide substrates. The silver nanoparticles are found to have sufficient catalytic efficiency for subsequent electroless plating. Characterization of the process indicates that UV energy dose and heat treatment have to be traded off against photo and thermal degradation of the polymer substrate. Factors affecting the adhesion of the final electroless metal deposit are also discussed.

**Index Terms**—Direct writing, electroless plating, flexible substrate, interconnections, metallization, micropatterning, packaging, photolithography, polyimide, silver nanoparticles.

## I. INTRODUCTION

THE metallization of polyimide substrates has been the subject of intense studies over the last few years as evidenced by the large range of different processes proposed and the number of research groups working in this field worldwide [1]–[9]. With the increasing industrial relevance of plastic electronics, the race is on for the development of a fast, low cost, and reproducible manufacturing process that could replace the current-processing techniques such as those used in the printed circuit board industry [10].

Our group has recently demonstrated a “bottom-up” technique based on the growth of silver nanoclusters onto an ion-doped polyimide substrate as shown in Fig. 1 and described

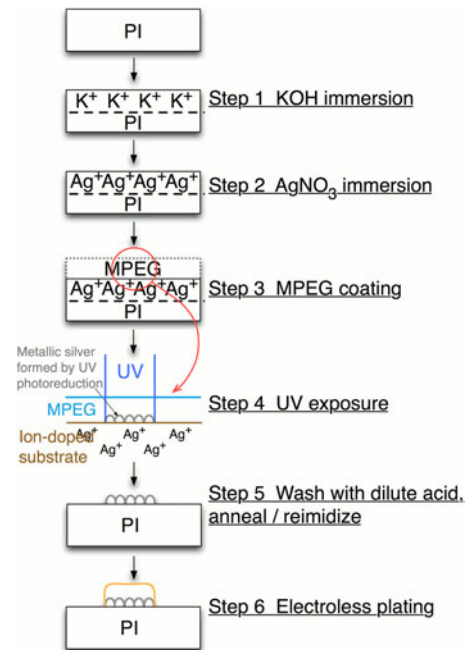


Fig. 1. Process steps of the direct metallization.

in detail in Section II. The growth was further enhanced by a photochemically assistive polymer coating [11]. The resulting deposition process offers several advantages compared to other fabrication routes. Waste materials are drastically reduced compared to traditional subtractive processes. No photoresist and developer materials are necessary, therefore, reducing the process running costs. Unlike other mechanical printing techniques, no premanufactured silver nanoparticles or inks are required since the silver nanoclusters are produced by *in situ* photoreduction. Therefore, the dependence on expensive proprietary products during the fabrication stage is eliminated. Another key advantage is the rigid interface created by these silver nanoparticles mechanically interlocked with the polymer substrate [12], thereby allowing good adhesion of subsequent metalized patterns with the substrate. Sequential laser write or full exposure through a photomask is also possible. Fine pitch lines down to around 15  $\mu\text{m}$  have been demonstrated using a continuous-wave laser [11] and around 40  $\mu\text{m}$  using UV-exposure through a photomask [1]. Finally, the patterning step can be carried out in a dry phase environment and at atmospheric pressure, demonstrating its potential for reel-to-reel manufacturing.

Silver nanoparticles are suitable catalysts for the electroless deposition of copper, silver, or gold. As well as emerging as a

Manuscript received February 9, 2011; revised; accepted May 15, 2011. Date of publication June 20, 2011; date of current version January 11, 2012. This work was supported in part by the U.K. Engineering Physical Sciences Research Council Project SMART MICROSYSTEMS, referenced FS/01/02/10 and funded by the IeMRC. The work was also financed under the Scottish Funding Council funded SRDG Initiative SCIMPS, Scottish Consortium for Integrated MicroPhotonic Systems. The review of this paper was arranged by Associate Editor M. M. De Souza.

J. H.-G. Ng, D. E. G. Watson, R. W. Kay, and M. P. Y. Desmulliez are with the Microsystems Engineering Centre, Heriot-Watt University, Edinburgh, EH14 4AS, U.K. (e-mail: j.h.ng@hw.ac.uk; degw1@hw.ac.uk; R.W.Kay@hw.ac.uk; M.Desmulliez@hw.ac.uk).

J. Sigwarth was with the Microsystems Engineering Centre, Heriot-Watt University, Edinburgh, EH14 4AS, U.K. He is now with Albert-Ludwigs-Universität Freiburg, Freiburg 79098, Germany (e-mail: js208@hw.ac.uk).

A. McCarthy, K. A. Prior, and D. P. Hand are with the Department of Physics, Heriot-Watt University (e-mail: A.McCarthy@hw.ac.uk; K.A.Prior@hw.ac.uk; D.P.Hand@hw.ac.uk).

W. Yu is with the Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun City 130033, China (e-mail: yuwx17@hotmail.com).

C. Liu is with the Wolfson School of Manufacturing and Mechanical Engineering, Loughborough University, Loughborough, LE11 3TU, U.K. (e-mail: C.Liu@lboro.ac.uk).

Color versions of one or more of the figures in this paper are available online at <http://ieeexplore.ieee.org>.

Digital Object Identifier 10.1109/TNANO.2011.2160092

cheaper and easier to prepare alternative to palladium (traditionally used as the catalyst for electroless plating to achieve greater thickness and thus good finishing layer electrical conductivity), processes are being developed that allow fine control over silver nanoparticle size [13]. The micropatterns of active silver surfaces produced from the UV-photomask exposure have a surface morphology that is the result of coalescence or agglomeration of silver nanoparticles. A post-exposure heat treatment step is required to allow the isolated silver particles in the polymer matrix to increase their surface catalytic activity. Higher particle densities and greater surface roughness of the silver seed layer should be produced by higher rates of photoreduction and longer heat treatment times, respectively. These process conditions are desirable for the initiation of subsequent electroless plating. However, prolonged UV irradiation and high-temperature treatment can have detrimental effects on the polymer substrate and the process needs optimization to determine the best conditions to generate dense, rough seed metal layers. To date, only preliminary results have been reported [1], [11] and in Section III, we give a more detailed characterization of the effects of UV energy dose and heat treatment time on the evolution of the silver nanoparticles seed layer and the polyimide substrate. This section also describes the catalytic activity of the nanoparticles for initiation of electroless plating along with a discussion on the adhesion of the deposited electroless metal.

## II. EXPERIMENTAL

### A. Fabrication Process

Fig. 1 shows a schematic process flow of the direct metal micropatterning using UV irradiation on a pretreated polyimide substrate. The Kapton 200 HN 50- $\mu\text{m}$ -thick polyimide films have been obtained from DuPont, Inc., and are doped with silver ions through a two-step immersion process. First, the films are immersed in a 1 M KOH solution at 50 °C for 5 min without stirring (step 1). Hydrolysis takes place and a thin surface layer of the polyimide is converted into potassium polyammate. After rinsing with deionized water (DI), the films are then immersed in a 0.1 M  $\text{AgNO}_3$  solution at room temperature with mild agitation (step 2). The  $\text{Ag}^+$  ions from the solution cause ion-exchange with the  $\text{K}^+$  ions within the modified surface. After rinsing with DI and drying, the silver ion-doped polyimide films are spray coated with a photoactive polymer, methoxy poly(ethylene glycol), (MPEG), using a handheld airbrush (step 3). The MPEG, of 100 g.l<sup>-1</sup> concentration, used absolute ethanol as the solvent, and the solution is heated to completely dissolve the polymer before coating. After coating the MPEG layer, UV-photomask exposure is carried out on the samples with duration ranging from 1 to 8 h under a power intensity of approximately 50 mW.cm<sup>-2</sup>. The exposure is performed using a broad-band mercury arc lamp with roughly collimated light output (step 4). The doped silver ions in the UV exposed areas are photoreduced to zero valence state silver. Subsequently, the MPEG layer is washed off with DI and the samples are then washed in a 1% w/w  $\text{H}_2\text{SO}_4$  solution. The dilute acid solution allows a second ion-exchange reaction where the  $\text{H}^+$  ions from the solution replace the unreacted  $\text{Ag}^+$  ions in the unexposed areas of



Fig. 2. Photograph of directly metalized micropatterns using a range of UV energy dose irradiations without any heat treatment applied.

the samples, turning the modified surface layer into poly(amic acid). Finally, the patterned samples are annealed at 300 °C for 1 to 8 h in a furnace to induce coalescence of the silver particles (step 5). During annealing, the poly(amic acid) layer also reimidizes back into the original polyimide molecular structure. Once the desired pattern of the seed silver nanoparticle layer is obtained, electroless plating can proceed (step 6). A commercial autocatalytic electroless silver bath ESM 100 from Polymer Kompositer AB, Sweden, has been used in this study for optimized bath performance in terms of bath stability, components monitoring, and plating rate.

### B. Characterization

The silver nanoparticles and aggregates have been compared using a Leo 1530 VP Field Emission Gun Scanning Electron Microscope (FEGSEM). The samples produced from varying UV doses and varying anneal times were also imaged by optical microscopy using an SZX10 Olympus stereomicroscope, and reflectivity measurements were carried out using a continuous-wave HeNe gas laser at 632.8 nm (NEC Corporation, Model GLG 5380) and a Newport 1830-C optical power meter at various angles. The etching effect on the polymer substrate was measured by a Veeco Dektak 3 stylus profilometer and a white light phase shifting interferometer (Zygo Viewmeter 5200). The Fourier transform infrared (FTIR) analysis was performed with a Perkin Elmer Spectrum 100.

## III. RESULTS AND DISCUSSION

### A. Effects of UV Exposure Dose on the Silver Particles

The photoreduction of silver ions results in the formation of silver atoms within the polymer matrix at the surface of the substrate, which can then immediately nucleate into bigger particles. The applied optimum light dose should, therefore, be high enough so that all silver ions in the exposed areas can be used for photoreduction. With no annealing and at a relatively low UV energy dose of approximately 260 J.cm<sup>-2</sup>, faint patterns in the exposed areas are observed while above 345 J.cm<sup>-2</sup>, a more prominent silver color is produced. The silver nanoparticles generally display a silvery color tinged with green or purple as shown in Fig. 2.

The FEGSEM images in Fig. 3 show that increasing energy doses increased the density of silver particles formed as expected. Without annealing, the silver particles have a narrow distribution of particle size. However, at UV energy doses above

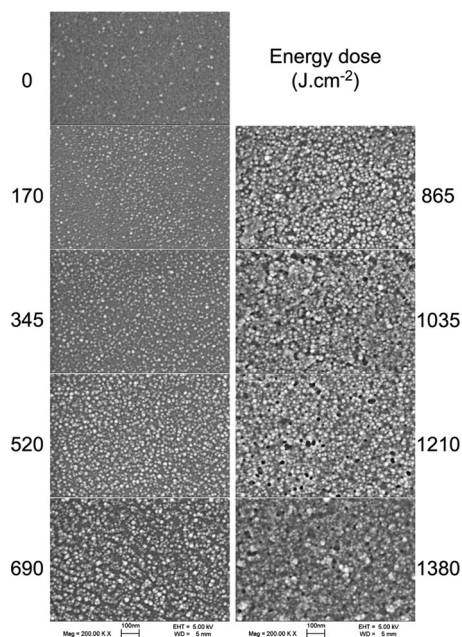


Fig. 3. FEGSEM images of a silver ion-exchanged sample subjected to UV irradiation with different energy dose.

$690 \text{ J.cm}^{-2}$ , the polymer substrate becomes degraded and small holes appear on the substrate amongst the silver nanoparticles. The particle density is found to peak at a UV dose of  $865 \text{ J.cm}^{-2}$  although some polymer degradation on the substrate has already occurred by this stage. No clear differences in the particle density can be observed, when the UV dose is increased up to  $1210 \text{ J.cm}^{-2}$  although the polymer substrate becomes increasingly degraded with prominent pores appearing. This plateau of particle density indicates that the source of silver ion source incorporated in the polymer substrate has been depleted. At a dose of  $1380 \text{ J.cm}^{-2}$ , the polymer is noticeably degraded with a rough surface containing fewer silver nanoparticles than with doses in the range from  $865$  to  $1210 \text{ J.cm}^{-2}$ .

### B. Effects of Heat Treatment

To produce a silver layer with high surface catalytic activity suitable for subsequent electroless plating, a combination of sufficient dose of light energy and duration of heat treatment is required. The thermal treatment allows the coalescence of the silver particles within the polymer matrix. As a consequence, the silver layer develops a bright silver appearance as shown in Fig. 4(a) compared to Fig. 4(b). Fig. 5 shows a reflectivity measurement of the samples prepared with a fixed UV exposure dose of  $690 \text{ J.cm}^{-2}$  and annealing times varying from 2 to 5 h. The measurements have been carried out at different incident angles with a laser light source of  $632.8 \text{ nm}$  wavelength with maximum power of  $0.95 \text{ mW}$ . The reflectivity of the samples increases as the annealing time is increased, especially for samples heated for more than 1 h. However beyond 4 h of annealing time, the reflectivity decreases. With 5 h of heat treatment, the exposed areas where silver nanoparticles/polymer composite should have turned into a brown color as shown in Fig. 4(b). It can be

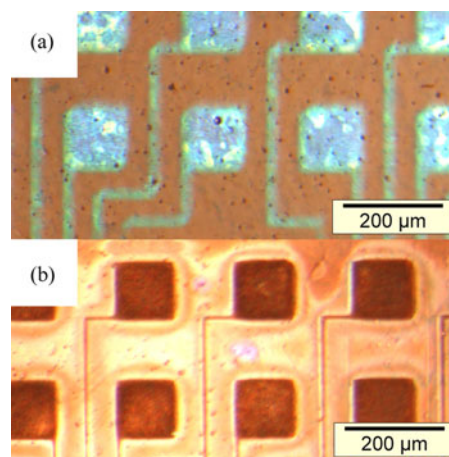


Fig. 4. Optical microscopy images of a sample after photoreduction with  $690 \text{ J.cm}^{-2}$ . (a) 4-h heat treatment. (b) 5-h heat treatment.

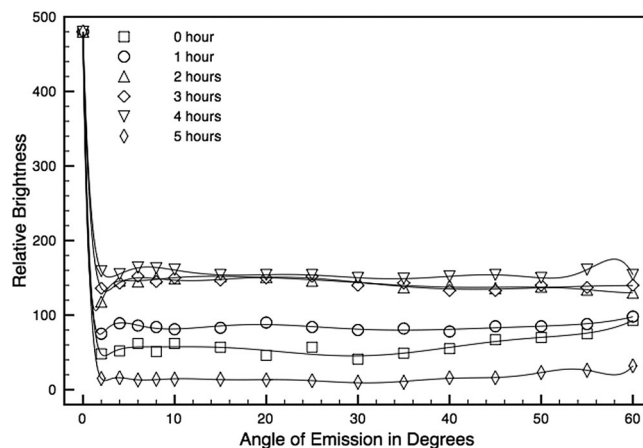


Fig. 5. Reflectivity measurements of a set of samples with fixed UV dose of energy of  $690 \text{ J.cm}^{-2}$  and varying heat treatment times.

clearly seen that the polymer regions surrounding the degraded brown patterns also exhibit some changes. This indicates that a thermal effect certainly plays a role in the degradation of the areas that have been exposed to UV radiation. The brown patterns have a roughened surface, which shows an even poorer reflectivity than the sample without heat treatment.

Although it is advantageous to choose as short a heat treatment time as possible, the most desirable treatment conditions for these samples are determined by the subsequent electroless plating tests.

The coalescence of the silver particles and degradation of the surface of the substrate occur concomitantly. The evolution of the morphology of the silver nanoparticles can be observed in Fig. 6 from the FEGSEM images of samples with approximately  $690 \text{ J.cm}^{-2}$  UV exposure energy dose and varying annealing times. A virgin polyimide control sample with no chemical pre-treatment is also used to isolate any contribution to the substrate of the UV exposure and subsequent annealing. As the duration of the heat treatment increases, the silver treated sample [see sample (iii) in Fig. 6] displays silver particles with increasing average particle size. When no heat treatment is applied, there



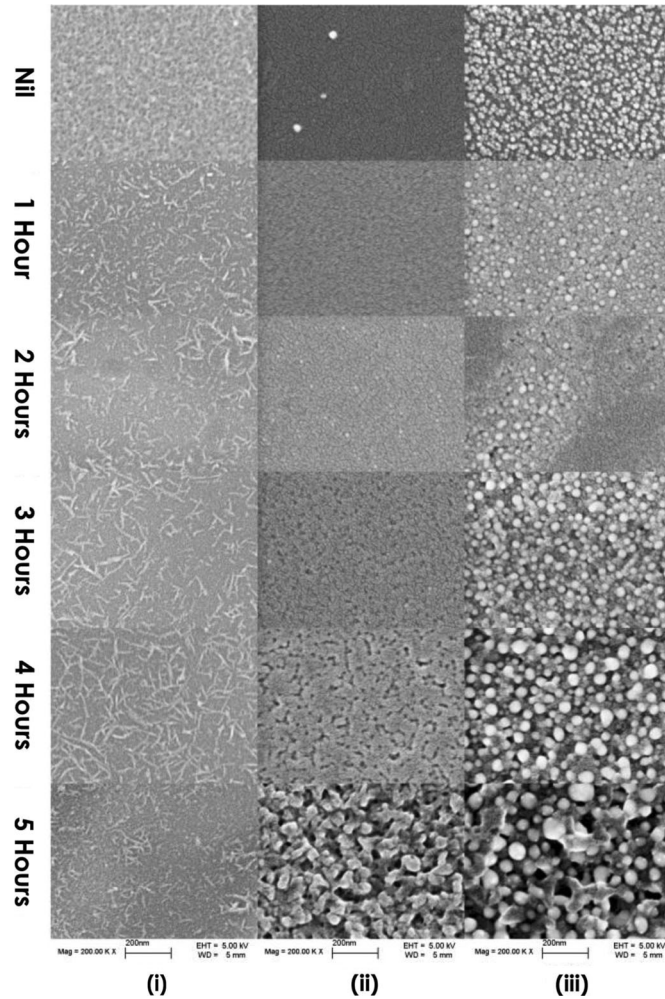


Fig. 6. FEGSEM images of the surface degradation and silver particle coalescence of the samples submitted to different treatment conditions under varying heat treatment times. Samples: (i) KOH surface-modified polyimide with UV exposure, (ii) silver ion-exchanged polyimide, and (iii) silver ion-exchanged polyimide with UV exposure. A constant UV energy dose of approximately  $690 \text{ J.cm}^{-2}$  is employed for the exposed samples.

is a reasonably regular distribution of silver particles formed by photoreduction on top of the substrate.

To determine whether the UV exposure or the annealing step is responsible for the degradation of the substrate, samples annealed for different lengths of time and various treatment conditions and their levels of degradation are shown in Table I. A control sample with no chemical pretreatment on the polyimide substrate is also used to isolate any contribution to the substrate of the UV exposure and subsequent annealing. These samples, denoted as (1–6) are as follows: 1) polyimide with no subsequent chemical processing; 2) polyimide with UV exposure and no subsequent chemical processing; 3) KOH surface-modified polyimide with no UV exposure; 4) KOH surface-modified polyimide with UV exposure; 5) silver ion-exchanged polyimide with no UV exposure; 6) silver ion-exchanged polyimide with UV exposure. All samples subjected to UV exposure (samples 2, 4, and 6) have been coated with the MPEG polymer. FEGSEM images of these samples can be seen in Fig. 6. As expected,

TABLE I  
LEVELS OF DEGRADATION OF THE SURFACE OF THE SUBSTRATE BASED ON FEGSEM IMAGES

Heat treatment time	(a) PI	(b) PI + UV	(c) KOH/PI	(d) KOH/PI + UV	(e) Ag <sup>+</sup> /PI	(f) Ag <sup>+</sup> /PI + UV
None	no	no	no	textured	no	no
1 hour	no	no	no	textured	some	some
2 hours	no	no	no	textured	some	some
3 hours	no	no	no	textured	moderate	moderate
4 hours	no	no	no	textured	moderate	moderate
5 hours	no	no	no	textured	severe	severe

Samples: (a) unmodified polyimide, (b) unmodified polyimide with UV exposure, (c) KOH surface-modified polyimide, (d) KOH surface-modified polyimide with UV exposure, (e) silver ion-exchanged polyimide, and (f) silver ion-exchanged polyimide with UV exposure. A constant UV energy dose of around  $690 \text{ J.cm}^{-2}$  was employed for the exposed samples.

samples (1–3) did not exhibit any significant change in appearance and are, therefore, not shown here. Columns (d)–(f) in Table I correspond to samples (i)–(iii) of Fig. 6, respectively. A constant UV energy dose of approximately  $690 \text{ J.cm}^{-2}$  was used. All samples with surface modification (samples 3–6) have been washed with 1% w/w  $\text{H}_2\text{SO}_4$  solution prior to anneal. The two polyimide samples with only MPEG coating, no subsequent chemical processing (samples 1, 2), either with or without UV irradiation both also show no degradation at 5-h heat treatment.

Without UV irradiation, the KOH surface-modified sample (sample 3) does not exhibit any morphology changes upon heat treatment up to 5 h. This sample has a similar appearance to the control sample (sample 1).

With UV exposure, the same hydrolyzed surface (sample 4) shows a “nest-like” texture when no heat treatment is applied, providing thereby a clear indication that the UV irradiation produces the morphology of the surface. When heat treatment is applied, the sample does not exhibit any degradation as observed for samples 4 and 5, but maintains a similar texture throughout the 1- to 5-h heat treatment.

Without UV exposure, the silver ion-exchanged sample (sample 5) starts exhibiting some surface morphological changes at 3-h annealing time and after 5 h, significant degradation of the polymer substrate is observed. Therefore, without UV irradiation the silver ion-exchange and subsequent dilute acid washing must play a role in inducing the thermal degradation of the polymer substrate.

The silver ion-exchanged sample with UV irradiation (sample 6) is the only sample that produces silver nanoparticles. The coalescence of the silver particles and degradation of the surface of the substrate occur concomitantly. The evolution of the morphology of the silver nanoparticles can be observed as the duration of the heat treatment increases. When no heat treatment is applied, there is a reasonably regular distribution of silver particles formed by photoreduction on top of the substrate without any coalescence taken place. At 1- and 2-h heat treatment, the coalescence of the silver nanoparticles is not very pronounced. After 3, 4, and 5 h of annealing times, the average particle size increases with heat treatment times.

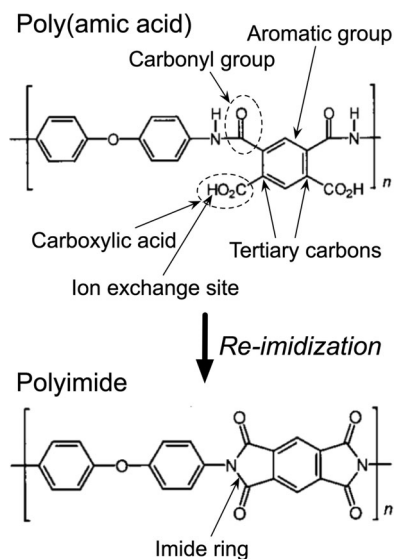


Fig. 7. Structural formulae of poly(amic acid) and polyimide of the type pyromellitic dianhydride oxydianiline (PMDA-ODA).

At the same time, the polymer substrate develops leaf-like structures for annealing times above 3 h. Since no morphology changes are observed for the control sample which underwent the same UV exposure and thermal annealing (sample 2), the transformation of the polymer substrate must be due to the chemical treatments. The level of polymer degradation can be seen to be increasing for annealing times between 3 and 5 h. After 5-h heat treatment, the degraded polymer shows a leaf-like structure. The silver particles are found on the surface or in the gaps of the fragmented polymer substrate.

The degradation of the surface of the substrate can be explained in terms of oxidative degradation due to UV irradiation and heat treatment in air.

The surface of the substrate is an amorphous polymer containing mobile metal ions, namely, potassium polyamate and silver polyamate for the KOH surface-modified samples and silver ion-exchanged samples, respectively. After washing in dilute  $\text{H}_2\text{SO}_4$ , hydrogen ions are exchanged with the potassium or silver ions in these samples, forming polyamic acid. These amorphous polymer layers do not exhibit the same considerable thermal stability of the unmodified polyimide as seen in the samples at 5-h anneal without UV irradiation. The extent of degradation is also dependent on the UV energy dose when UV irradiation is applied.

This suggests that during the heat treatment, oxygen attacks the amorphous layer, which contains tertiary carbon atoms and carboxylic acid, as illustrated by Fig. 7. At elevated temperatures, free radicals formed at tertiary carbon atoms are more stable and longer lasting, making them more susceptible to attack by oxygen. Consequently, there is a possibility that the following two reactions can take place together: 1) carbonyl groups can be formed from the oxidation of the tertiary carbon which can then be further oxidized; and 2) the neighboring carboxylic acid, composed of a carbonyl group and a hydroxyl group, is already in a high oxidation state and further oxidation removes

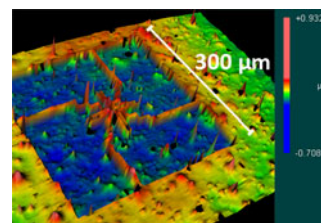


Fig. 8. Height profiles measured by Zygo.

the carboxyl carbon as carbon dioxide. As a result, some carbon atoms are lost and/or some polymer chains are broken and thereby weakening the poly(amic acid) structure [14].

When continuous UV irradiation is applied, the presence of aromatic groups in the poly(amic acid) molecule can act as an effective UV absorbing agent. More free radicals can be formed by the interactions of UV photons with the aromatic groups or the tertiary carbon bonds, which then again react further with oxygen in the atmosphere, increasing the oxidative degradation described earlier. Therefore, additional damage is observed on the surface-modified UV irradiated samples after heat treatment compared to those not submitted to UV irradiation.

The reaction of poly(amic acid) reforming the C-N-C imide rings upon heat treatment, known as reimidization, also takes place. Some of the imide rings are indeed reformed after 30 min of heat treatment [1]. However, the completeness of this reimidization process has not been quantified. While reimidization is taking place, some oxidative degradation effects have already occurred, i.e., some carbon atoms are already removed or the polymer chains are already shortened, especially in the UV irradiated regions of the samples. This could affect the crosslinking of the reformed polyimide molecules, and hence, the layer of polyimide recovered from the modified material may not possess the same physical properties as those of the unmodified polyimide in the bulk of the substrate.

### C. Further Degradation Effects on the UV Irradiated and Annealed Areas

The silver patterns on the UV exposed and annealed samples were found to be recessed into the substrate as shown in the Zygo white light interferometer height profile in Fig. 8. This phenomenon may be attributed to polymer deterioration due to the oxidative degradation described in the previous section. The depth of the recession is quite uniform across the whole microstructure exposed to UV light. The Dektak stylus profiler measurements across a UV exposed pattern, shown in Fig. 9, confirms that the recessed areas are up to a few hundred nanometers deep with silver nanoparticles residing at the bottom of the recessed patterns.

As discussed earlier, the oxidative degradation on the substrate is believed to be due to a combination of heat treatment and UV irradiation. To obtain further evidence for this hypothesis, the influence of the annealing time and UV energy dose on the size of the recess has been investigated.

The graph in Fig. 10 shows that the depth of recess increases with annealing time for a range of different UV exposure times.

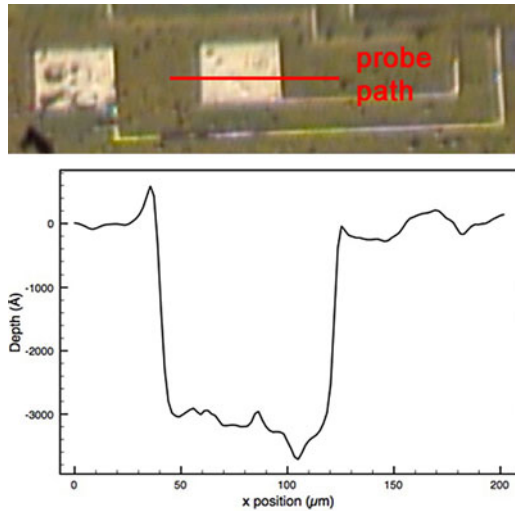


Fig. 9. Dektak stylus profiler measurement across an  $80 \times 80 \mu\text{m}^2$  contact pad with silver seed layer fabricated by  $690 \text{ J}\cdot\text{cm}^{-2}$  UV dose and 4-h anneal time.

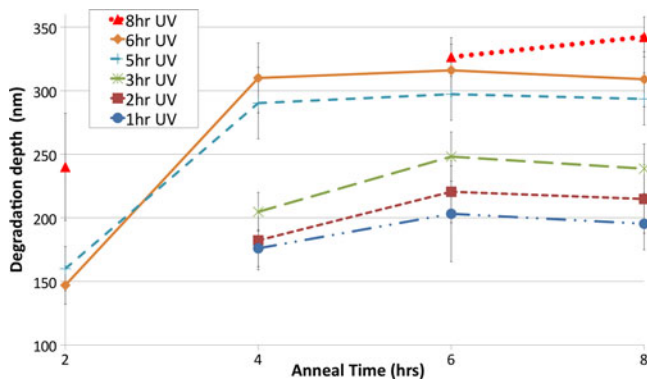


Fig. 10. Effect of annealing time on depth of substrate degradation for selected UV exposure times.

Clearly, the longer a sample is annealed for, the greater the recess depth. However, it appears that no further degradation occurs after between approximately 4 to 6 h, depending on the previous UV energy exposure time, where a plateau is reached. The shorter UV exposure times, i.e., the samples with the lower energy doses before annealing, take longer to reach a plateau than those given a higher UV energy dose. It is also evident from Fig. 10 that the UV exposure plays a part in the degradation, with recess depth from an 8-h UV exposure being approximately 50% greater than a 2-h exposure. These results clearly indicate that the polymer shrinkage can be attributed to a combination of both photo and thermal effects.

To articulate how these effects combine to produce this phenomenon, we present a tentative hypothesis of the physical mechanisms at molecular level. The longer the UV exposure time, the more silver nanoparticles will coalesce [12]. Also, it has been shown that incompletely imidized polyimide is liable to break down into smaller molecules, mainly in the form of carbon monoxide and carbon dioxide [14]–[17]. Furthermore, it has been reported that the presence of silver on a polyamic acid interface can inhibit reimidization [18]. It is possible that this

effect, combined with the silver particles acting as thermal radiators, during both the photochemical and thermal steps of the process, will accelerate the decomposition of the Kapton substrate. Attenuated total reflection FTIR spectroscopy has been measured on the recessed areas. The spectra (results not shown) were found to be almost identical to pristine polyimide. The degraded polymer top layer is believed to be too thin such that the surrounding unmodified polyimide molecules contribute to the FTIR signals collected.

Since the samples with heat treatment only and without UV irradiation did not have any pattern, whether this recession effect took place on those samples was not investigated and will need to be the study of further research.

#### D. Electroless Plating

Electroless plating has the advantage of not requiring an applied voltage since it is a chemically driven process, eliminating the use of electrical contacts and the need to determine the electrical field distribution. This plating method is also useful for the metallization onto nonconducting surfaces or 3-D structures.

An electroless bath solution is composed of specially selected chemical components with determined concentrations. For effective electroless plating, the pH and the temperature of the bath are also carefully monitored. Bath stability is maintained until electron transfer is initiated. Initiation of electroless plating is usually achieved by the presence of suitable catalysts on the surface of the substrate. The catalysts can serve as metal nucleation sites, adsorbing the target metal ions, reducing molecules from the plating solution onto their surfaces, and lowering the activation energy of the plating reactions.

In order to create sufficient numbers of catalytic sites for the initiation of electroless plating, samples with UV irradiation of  $690 \text{ J}\cdot\text{cm}^{-2}$  have been processed to ensure that the photoreduction process used up all the available silver ions for the production of silver nanoparticles. Subsequent heat treatment has increased the catalytic activity of the silver surfaces by allowing the nanoparticles to coalesce into larger particles. Samples with different heat treatment times are compared to test their performances in the electroless bath. The electroless silver bath ESM 100 chosen for this study is autocatalytic. The deposited layer acts as the catalyst for further plating, once the initial catalysts on the substrate are covered by the plated silver.

The key parameters for controlling this bath are the cyanide to silver ion ratio (CN:Ag), pH, and temperature. They can be tuned to suit the catalytic activity of the silver nanoparticles; however, any adjustments need to be within the range of operating limits engineered for the various chemical reactions in the bath. Cyanide is a ligand which prohibits the release of the silver ions in the bath, and therefore, if the CN:Ag ratio is too high, no plating occurs while if it is too low, overplating occurs and the rapidly plated layer detaches itself easily from the substrate. Moreover, the substrate areas without any catalysts can nucleate a plated area during overplating. CN:Ag ratios of 0.79–1.1 were tested. The optimum operating temperature of the bath was  $67^\circ\text{C}$ , but temperatures as low as  $55^\circ\text{C}$  were tested, and it was found that when the temperature is too low, the plating will not



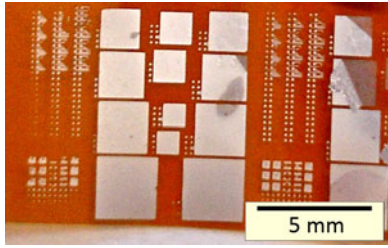


Fig. 11. Optical micrograph of the 4-h heat treatment sample plated with electroless silver.

occur. Similarly, variations of pH between 9.8 and 10.3 were also tested and the optimum pH was 10.

In any case, it is preferable to increase the catalytic activity of the silver nanoparticles rather than adjusting the bath parameters away from their optimum operating conditions. This ensures the best qualities of the deposited layer including hardness and adhesion, while minimizing the number of parameters to be configured.

To increase the catalytic activity of the silver nanoparticles, heat treatment time has been increased to allow further coalescence. Evidence of the transformation of the silver nanoparticles was described earlier in the reflectivity measurements and the FEGSEM images. The 2–4 h heat treated samples exhibit the highest reflectivity and have been tested against the electroless bath for their catalytic activity performance.

With no heat treatment, all silver nanoparticles dissolved into the plating solution, suggesting that without any heat treatment, no reimidization takes place so the modified layer is susceptible to attack by the plating solution.

After 2-h heat treatment, the plating is not initiated within 10 min. For a seed layer with high catalytic activity, the electroless plating should proceed within a minute with the deposited layer visibly observable.

After 3-h heat treatment, plating is initiated and proceeds selectively onto the regions containing silver nanoparticles. However, the plated layer soon detaches from the substrate into the bath.

The best plating result is found to be with 4-h heat treatment, with bath parameters of  $\text{CN:Ag} = 1.06$ ,  $\text{pH} = 9.9$ , and temperature of  $67^\circ\text{C}$ . The deposited electroless silver has a rough white appearance as shown in Fig. 11. A magnified image of the sample under an optical microscope is shown in Fig. 12. The minimum feature size that allowed the deposited electroless silver layer to remain on the sample was about  $30\text{ }\mu\text{m}$ . The tracks with linewidth between 10 and  $20\text{ }\mu\text{m}$  appeared to have been attacked by the plating bath. Not only was no plated layer found on those patterns, but the original silver nanoparticle seed layer had also disappeared. It is believed that with such narrow linewidth the plating solution could more readily attack the degraded polymer underneath the silver nanoparticle layer, resulting in the detachment of the seed layer. Fig. 12(b) shows that when the sample was immersed in the plating bath for a longer period, the electroless silver layer deposited on the bigger feature patterns also starts to disappear. It can be seen that the detachment was not between the electroless silver layer and

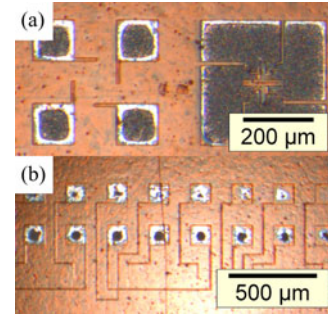


Fig. 12. Magnified optical micrographs of the sample shown in Fig. 11. (a) Disappearance of the narrow tracks. (b) Electroless silver deposited on the bigger features also disappeared with longer immersion period in the plating bath.

the silver nanoparticle seed layer. There is no seed layer like that shown in Fig. 4(a) left behind. The degradation of the polymer substrate, clearly seen in the FEGSEM image in Fig. 6, causes a severe impediment to the mechanical interlocking between the polymer and the silver nanoparticles, and as a consequence, poor adhesion of the deposited metal results.

In addition, it can also be observed from the FEGSEM images that the silver nanoparticles are not closely packed together in any of the samples. In fact, the silver nanoparticles only occupied no more than 50% of the substrate with areas of polymer gaps in between them. The low density of the silver nanoparticles would provide a weak adhesion strength to any electroless layer plated on top, and it also exposes more of the degraded polymer to the attack of the plating solution.

The maximum density of the silver nanoparticles on the substrate produced by the photoreduction can only be increased by increasing the loading of silver ions in the substrate. This can be achieved by increasing the degree of KOH surface modification initially, and thus, a larger volume of silver ions can be exchanged into the substrate. However, a high degree of surface modification on polyimide using high concentration of KOH solution has been shown to cause severe degradation to the rigidity of the polyimide film [1]. Therefore, a balance needs to be established between sufficient loading of silver ions for effective subsequent electroless plating and degree of KOH surface modification.

#### IV. CONCLUSION

This paper has presented the various process parameters affecting the production of a suitable silver seed conductive layer generated on top of a polyimide substrate. The conditions for substrate preparation, photoreduction, initiation of electroless plating, and adhesion of the deposited metal have been reviewed and their competing effects explained.

The applications of various UV energy doses and heat treatment times have been presented in the context of the surface modification of the polyimide substrate. Increasing the UV energy dose increases the amount of silver nanoparticles formed. When a critical UV energy dose is employed, all the silver ions available in the exposed areas of the substrate are used for photoreduction. At energy dose above  $690\text{ J}\cdot\text{cm}^{-2}$ , degradation of

the surface-modified polymer substrate is observed. UV irradiation was also shown to cause morphology changes to the sample with KOH surface modification only without incorporation of silver ions. This change remained constant upon increasing heat treatment times. Heat treatment of silver nanoparticles induced two antagonistic effects: particle growth and polymer degradation. Possible causes of the oxidative degradation of the polymer substrate have been suggested.

Suitable catalytic activity of the silver nanoparticles is required for the initiation of electroless plating. Such an activity has been shown to increase with increased heat treatment time.

Adhesion of the electroless metal deposits has been shown to be affected by the degradation of the polymer substrate due to heat treatment and also the insufficient density of the silver nanoparticles as a seed layer.

Increases of both the catalytic activity of the silver nanoparticles by longer heat treatment and of the density of the silver nanoparticles by higher loading of silver ions in the substrate are recommended to optimize the performance of the final electroless plating. However, a compromise must be reached between such measures and the degradation of the substrate due to the heating of the modified polymer and/or the high surface modification due to increased KOH concentration. To reduce the processing times for industrial adaptation, flash exposure lamps [19] or various types of lasers can be employed, and this is currently being pursued by our group.

#### ACKNOWLEDGMENT

J. H.-G. Ng thanks A. Remgård and C. Göransson of Polymer Kompositer AB, Sweden, for the useful discussions and advice on the operation of the ESM electroless bath. The authors would also like to thank J. Bates from Loughborough University for carrying out the FEGSEM microscopy.

#### REFERENCES

- [1] J. H.-G. Ng, M. P. Y. Desmulliez, M. Lamponi, B. G. Moffat, A. McCarthy, H. Suyal, A. C. Walker, K. A. Prior, and D. P. Hand, "A direct-writing approach to the micropatterning of copper onto polyimide," *Circuit World*, vol. 35, no. 2, pp. 3–17, Apr. 2009.
- [2] J. H.-G. Ng, D. E. G. Watson, J. Sigwarth, A. McCarthy, H. Suyal, D. P. Hand, T. Y. Hin, and M. P. Y. Desmulliez, "An additive method for photopatterning of metals on flexible substrates," in *Proc. 36th Int. MATADOR Conf.*, vol. 9-6, pp. 389–392, Jul. 2010.
- [3] M. Tagawa, K. Maeda, T. Kajita, K. Yokota, K. Akamatsu, and H. Nawafune, "Atomic beam-induced fluorination of polyimide and its application to site-selective Cu metallization," *Langmuir*, vol. 23, pp. 11351–11354, Nov. 2007.
- [4] Y. Matsumura, Y. Enomoto, T. Tsuruoka, K. Akamatsu, and H. Nawafune, "Fabrication of copper damascene patterns on polyimide using direct metallization on trench templates generated by imprint lithography," *Langmuir*, vol. 26, no. 14, pp. 12448–12454, Jul. 2010.
- [5] S. C. Park and Y. B. Park, "Effect of temperature/humidity treatment conditions on interfacial adhesion energy between inkjet-printed Ag and polyimide," *Jpn. J. Appl. Phys.*, vol. 48, no. 8, pp. 08HL02-1–08HL02-6, Aug. 2009.
- [6] O. Berkh, A. Inberg, B. Sorokov, N. Fishelson, R. O. Almog, L. Burstein, and Y. Shacham-Diamand, "Fabrication of flexible microelectrodes using Cold HV sputtering," *J. Optoelectron. Adv. Mater.*, vol. 12, no. 5, pp. 1176–1182, May 2010.
- [7] Y. Liao, B. Cao, W. Wang, L. Zhang, D. Wu, and R. Jin, "A facile method for preparing highly conductive and reflective surface-silvered polyimide films," *Appl. Surf. Sci.*, vol. 255, no. 19, pp. 8207–8212, Jul. 2009.
- [8] S. H. Yoon, J. H. Lee, P. C. Lee, J. D. Nam, H. C. Jung, Y. S. Oh, T. S. Kim, and Y. K. Lee, "Sintering and consolidation of silver nanoparticles printed on polyimide substrate films," *Macromolecular Res.*, vol. 17, no. 8, pp. 568–574, Aug. 2009.
- [9] H. J. Kim, Y. J. Park, J. H. Choi, H. S. Han, and Y. T. Hong, "Surface modification of polyimide film by coupling reaction for copper metallization," *J. Ind. Eng. Chem.*, vol. 15, no. 1, pp. 23–30, Jan. 2009.
- [10] N.-S. Kim and K. N. Han, "Future direction of direct writing," *J. Appl. Phys.*, vol. 108, no. 10, pp. 102801–102806, Nov. 2010.
- [11] J. H.-G. Ng, M. P. Y. Desmulliez, K. A. Prior, and D. P. Hand, "UV direct patterning of metal on polyimide," *IET Micro Nano Lett.*, vol. 3, no. 3, pp. 82–89, Sep. 2008.
- [12] K. Akamatsu, S. Ikeda, and H. Nawafune, "Site-selective direct silver metallization on surface-modified polyimide layers," *Langmuir*, vol. 19, no. 24, pp. 10366–10371, Nov. 2003.
- [13] S. Jradi, L. Balan, X. H. Zeng, J. Plain, D. J. Lougnot, P. Royer, R. Bachelot, S. Akil, O. Soppera, and L. Vidal, "Spatially controlled synthesis of silver nanoparticles and nanowires by photosensitized reduction," *Nanotechnology*, vol. 21, no. 9, 095605, (7 pp.), Mar. 2010.
- [14] R. Srinivasan, R. R. Hall, W. D. Loehle, W. D. Wilson, and D. C. Allbee, "Chemical Transformations of the polyimide Kapton brought about by ultraviolet-laser radiation," *J. Appl. Phys.*, vol. 78, no. 8, pp. 4881–4887, Oct. 1995.
- [15] S. F. Dinietz, E. J. Bird, R. L. Wagner, and A. W. Fountain, III, "A comparative study of the gaseous products generated by thermal and ultra-violet laser pyrolyses of the polyimide PMDA-ODA," *J. Anal. Appl. Pyrolysis*, vol. 63, no. 2, pp. 241–249, Jun. 2002.
- [16] Y. N. Sazanov, A. V. Gribanov, and V. A. Lysenko, "The role of nitrogen atoms in forming the carbon structure in the carbonization of polymer composites," *Fibre Chem.*, vol. 40, no. 4, pp. 355–364, Jul. 2008.
- [17] E. E. Ortelli, F. Geiger, T. Lippert, J. Wei, and A. Wokaun, "UV-laser-induced decomposition of Kapton studied by infrared spectroscopy," *Macromolecules*, vol. 33, no. 14, pp. 5090–5097, Jul. 2000.
- [18] J. T. Young, W. H. Tsai, and F. J. Boerio, "Characterization of the interface between pyromellitic dianhydride oxydianiline polyimide and silver using surface-enhanced Raman-scattering," *Macromolecules*, vol. 25, no. 2, pp. 887–894, Jan. 1992.
- [19] D. E. O'Hara and W. F. Bueschel, "Flash exposure system for thin photoresist films," *Polymer Eng. Sci.*, vol. 14, no. 7, pp. 509–512, 1974.

**Jack H.-G. Ng** was born in Hong Kong and has lived in Scotland since childhood. He received the B.Sc. (Hons.) degree in physics from the University of Edinburgh, Edinburgh, U.K. where he developed interests in micro/nanoscale sciences, and the M.Sc. (by research) degree in nanomaterials from the University of Central Lancashire, Lancashire, U.K. He is currently working toward the Ph.D. degree in the Microsystems Engineering Centre (MISEC), Heriot-Watt University, Edinburgh, U.K.

He joined the MISEC under the supervision of Prof. M. Desmulliez and Prof. D. Hand, where he is currently a Research Associate. His research interests include deposition and patterning of metals on non-conducting surfaces, wet chemical surface modification, electroless plating, failure modes and up-scaling of microfabrication, laser direct-write applications, flexible electronics, and packaging of medical devices.

**David E. G. Watson** was born in Aberdeen, Scotland, U.K. He received the B.Eng. degree in electronic and software engineering from Aberdeen University, Aberdeen, U.K., in 2005, and the M.Sc. in microsystems engineering from Heriot-Watt University, Edinburgh, U.K., in 2008, where he is currently working toward the Ph.D. degree in microsystems in the MISEC group.

His main research interests include flexible electronics and microelectromechanical systems packaging.



**Joachim Sigwarth** was born in Lenzkirch, Germany. He worked as an Internship at the Microsystems Engineering Centre, Heriot-Watt University, Edinburgh, U.K., in 2009 on novel fabrication of flexible electronics and process development and characterizations. He is currently working toward the M.Sc. degree in microsystems engineering at the Albert-Ludwigs-Universität Freiburg, Freiburg, Germany.

**Aongus McCarthy** is from Ferbane, Co. Offaly, Ireland. He received the B.Sc. degree from University College Galway, Co. Galway, Ireland, in 1989, the Diploma degree in electronic engineering from the Institute of Technology, Carlow, Ireland in 1990 and the B.Sc. degree in physical optoelectronics from Essex University, Colchester, U.K., in 1991. He received the Ph.D. degree in physics from Heriot-Watt University, Edinburgh, U.K., in 2002. He is currently with Heriot-Watt University.

His research interests include optical interconnects (free-space and guided-wave), optical and optomechanical design, direct laser-writing techniques, and microscope systems.

Dr. McCarthy is a member of the Optical Society of America and the IEEE Laser and Electro-Optics Society.

**Kevin A. Prior** received the degree in natural sciences and the Ph.D. degree in physical chemistry for studies of single crystal metal surfaces from Cambridge University, Cambridge, U.K., in 1976 and 1979, respectively.

After working as a Research Assistant at Cambridge University, in 1980, he joined the Molecular Beam Epitaxy (MBE) Group at the Post Office (subsequently British Telecom) Research Labs at Martlesham Heath, Suffolk, U.K. From 1980 to 1988, he was involved in the research on the growth of GaAs, AlGaAs, and InP by MBE and also on the thermodynamics of MBE growth. In 1988, he moved to Heriot-Watt University, Edinburgh, U.K., setting up an MBE facility for the growth of wide bandgap II–VI semiconductors. The MBE group worked initially on the development of II–VI semiconductor lasers, and subsequently on the growth, characterization, and processing of novel II–VI materials including MgS, MnS, and CrS, and have published more than 150 papers.

**Duncan P. Hand** received the B.Sc. degree in physics and electronics from the University of St. Andrews, U.K., in 1986 and the Ph.D. degree in centred around fibre bragg gratings from the University of Southampton (Optical Fibre Group), U.K., in 1991.

He is currently a Professor of applied photonics and the Head of physics at Heriot-Watt University, Edinburgh, U.K. His research interests include a range of applications of high-power lasers, primarily in manufacturing and sensing. His research in manufacturing includes laser micro-joining, laser precision machining, and fiber-optic delivery of high-power laser light, and is a key component of the SMI, an Innovative Manufacturing Research Centre based at Heriot-Watt, which recently received £7.2 m funding from the U.K. Engineering and Physical Sciences Research Council.

**Weixing Yu** was born in Xi'an, China, in 1975. He received the Ph.D. degree in microelectronics from Nanyang Technological University, Singapore, in 2005.

After two years working as a Senior Engineer in a microelectronic packaging industry and a Research Scientist in R&D Department in Schott, he moved to Heriot-Watt University, Edinburgh, U.K., as a Postdoctoral Researcher and worked with Prof. Desmulliez on "3-D Mintegration" Project financed by Engineering and Physical Sciences Research Council. In 2009, he moved back to China and is currently a Research Professor in Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun City, China. He is the author or coauthor of more than 30 journal papers. His current research interests include micro/nanooptics, microelectric packaging, surface plasmonics for super-resolution nanolithography, and so on.

**Robert W. Kay** received the B.Eng. (Hons.) degree in electrical and electrical engineering and the Ph.D. degree in the fabrication of microengineered stencils for flip-chip bonding and wafer level packaging from Heriot-Watt University, Edinburgh, U.K., in 2001 and 2008, respectively.

He is currently with Heriot-Watt University. As a result of his Ph.D. research, he cofounded the start-up company MicroStencil, Ltd., Singapore, which now sells its precision electroformed solder paste stencils to the global electronics market. In 2010, he started as Postdoctoral Research Associate on a project looking at postprocessing of CMOS devices.

**Changqing Liu** (M'02–SM'06) received the B.Eng. degree from the Nanjing University of Science and Technology, Nanjing, China, in 1985, the M.Sc. degree from the Chinese Academy of Science, Beijing, China, in 1988, and the Ph.D. degree from Hull University, Hull, U.K., in 1998.

He has worked as an Assistant Professor in the Institute of Metals Research of Academia Sinica and as a Postdoctoral Researcher at the Interdisciplinary Research Centre in Materials, Birmingham University. In 2000, he joined the Wolfson School of Mechanical and Manufacturing Engineering, Loughborough University, Loughborough, U.K., where he is currently a Professor of electronics manufacture. He is the author or coauthor of more than 150 technical papers. His current research interests include novel materials and manufacturing processes to enable multifunctional devices and miniaturization by elaborating the fundamental issues that are primarily associated with the multimaterial, multifunctional, miniaturization, and reliability aspects of electronics-enabled products.

**Marc P. Y. Desmulliez** (M'08) was born in Lille, France, in 1963. He received the Dip.d'Ing. degree from the Ecole Supérieure d'Electricité de Paris, Paris, France, in 1987. He received two College Diplomas in microwave and modern optics from University College London, London, U.K. and in theoretical physics from the University of Cambridge, Cambridge, U.K., in 1987 and 1989, respectively. He received the Ph.D. degree in optoelectronics from Heriot-Watt University, Edinburgh, U.K., in 1995.

He is currently a Research Coordinator in the Department of Electrical, Electronic and Computer Engineering, Heriot-Watt University, and has been directing the Microsystems Engineering Centre since 1999. This Centre regroups six academic members of staff and more than 30 Ph.D. students and Researchers, specialized in all aspects of microelectromechanical systems (MEMS) manufacturing, packaging, and testing. His major fields of study are MEMS, advanced packaging and manufacturing technologies. His current research interests include the post-CMOS processing of MEMS and advanced 3-D manufacturing technologies.

Dr. Desmulliez is a Fellow of the Institute of Engineering and Technology. He is a Chartered Engineer and a Chartered Physicist from the U.K. Institute of Physics.