Photochemical Machining:
From Manufacturing's Best Kept Secret to a
$6 Billion per annum, Rapid Manufacturing Process

A Research Paper by

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Photochemical Machining: from 'manufacturing's best kept secret' to a $6 billion per annum, rapid manufacturing process

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Abstract

Photochemical machining (PCM) is one of the least well-known non-conventional machining processes. It employs chemical etching through a photoresist stencil as the method of material removal over selected areas. The technique is relatively modern and became established as a manufacturing process about fifty years ago. The processing technology has been kept a closely-guarded secret within a small number of industrial companies but despite this, the sales of parts made by PCM at the end of the twentieth century was approximately US$ 6 billion. This paper examines the state of the art of PCM, the PCM Roadmap and the newly-developed products made by PCM especially relevant to Microengineering, Microfluidics and Microsystems Technology, economic aspects and current challenges requiring research within the PCM industry.

Keywords: Photochemical machining technology, Products, Economics.

1 INTRODUCTION

Very few papers on the topic of photochemical machining (PCM) are available in the Annals of the CIRP or elsewhere and this is the first time that PCM has been the subject of a CIRP Keynote Paper. It therefore appears that PCM is not as well understood or publicised as many of the other non-conventional machining techniques such as electrodischarge machining (EDM), electrochemical machining (ECM) and laser beam machining (LBM) that receive regular coverage in the Annals.

Using techniques similar to those employed for the production of copper printed circuit boards and silicon integrated circuits (see Table 1), the PCM industry currently plays a valuable role worldwide in the production of a very wide range of precision parts and decorative items [1].

1.1 Process Outline

In the multi-stage PCM process illustrated in Figure 1, the use of photoresists enables fabrication of high resolution parts with complex, plan view geometry or with large arrays of variable aperture profiles in thin (< 2mm thick) flat metal sheet and thereby often bestows technical and economic advantages over:

- traditional metal cutting techniques [2]
- chemical milling used for lower resolution applications over larger areas [3]
- other non-traditional machining techniques such as laser cutting, wire-EDM and stamping [4].

1.2 Relationship with other chemical etching processes

PCM is closely allied to several other techniques that utilize etching technology to produce parts. The differences in the techniques are shown in Table 1. It should be noted that PCM is also known as photoetching, photochemical milling, photomilling, photofabrication, photochemical etching and (in the USA) chemical blanking.

PCM can be carried out on a very wide range of materials. Table 2 shows the main etchants used in PCM and some of the materials that can be etched in them. It should be noted that PCM does not involve the use of an external power supply as required in ECM. While much work in this field has been carried out by CIRP members McGeough, De Silva, Altena and Rajurkar amongst others [5], the method of material removal in PCM is based on the redox chemistry of etchant reduction effecting metal oxidation resulting in material dissolution with the formation of soluble byproducts that diffuse away from the reaction site.

1.3 Attributes

One of the important aspects of PCM is that the cross-sectional profile of etched features can be varied through the material thickness. Use of this attribute is made particularly in the fabrication of TV shadow aperture masks and hybrid circuit pack lids. The cross-sectional profiles can be varied as shown in Figure 2.

1.4 Limitations

The main limitation of PCM is to be found in the characteristics of isotropic etching whereby the etchant will attack not only downwards into the metal but also sideways beneath the resist stencil layer. The ratio of the depth to the undercut is termed the 'etch factor' (see Figure 3) and it limits the minimum hole diameter (ϕ_{min}) that can be etched through a metal sheet of thickness T, such that in general $\phi_{min} > T$.

2 BRIEF HISTORY OF PCM

Although the first photoresist was developed in 1826, the start of the photochemical machining industry seemed to coincide with the development of the highly successful KPR family of photoresists marketed by Kodak in the mid-1950s [1]. These photoresists were presensitised and therefore easy to use.

The first PCM companies were formed in North America and the UK but soon the technology was also being applied in mainland Europe and the Far East. Later, the technology spread to Central and South America, Australasia, Central Asia and Southern Africa. The European countries behind the Iron Curtain were active in

Fabrication method or *end product*	Typical material etched	Thickness of material etched	Underlying material or support
Photochemical machining (PCM)	Metals, glasses or ceramics	2mm (typical maximum)	Not applicable
Printed circuit boards (PCBs)	Electroformed copper foil (a conductor)	17.5μm (typical)	Rigid epoxy fibre glass or other insulator such as flexible polyimide
Integrated circuits (ICs)	Silicon dioxide or silicon nitride	0.01-0.1μm (typical)	Silicon
Chemical milling	Aluminium, titanium and aerospace alloys	0.1-10mm (typical)	Not applicable

Table 1: Comparisons of different etching technologies and products

Aqueous Etchants	Materials etched in the PCM process
Acidified ferric chloride	Aluminium, Alloy 42, copper and copper alloys, HyMu, Inconels, Invar, Kovar, Permalloy, Monel, Mumetal, nickel, Nimonics, phosphor bronze, stainless steels and other steels, tin.
Acidified cupric chloride	Beryllium copper, copper and copper alloys including brass and bronze, lead.
Alkaline potassium ferricyanide	Aluminium, molybdenum and tungsten.
Sodium hydroxide	Aluminium, anodized aluminium.
Hydrofluoric acid	Beryllium, columbium (niobium), titanium, zirconium, glasses and ceramics.

Table 2: PCM etchants

using PCM as part of their defence industry but, since the fall of the Berlin Wall in 1989, their PCM industry has been greatly contracted, especially in Russia and Bulgaria.

Many of the job-shop (sub-contract) PCM companies were started by entrepreneurs as small spin-off companies intent on manufacturing piece-parts as a rapid and economic alternative to stamping. Some larger companies believed that the PCM process was so critical to their production that it was brought in-house to gain competitive advantage and preserve confidentiality.

In the early days of commercial PCM, process technology was guarded jealously to the point that PCM was regarded as '*Manufacturing's Best Kept Secret*'. However, the formation in 1967 of a small, USA-based trade organisation, the Photo Chemical Machining Institute (PCMI), did provide a focus for industrial PCM companies and that has eventually led to more open discussion of

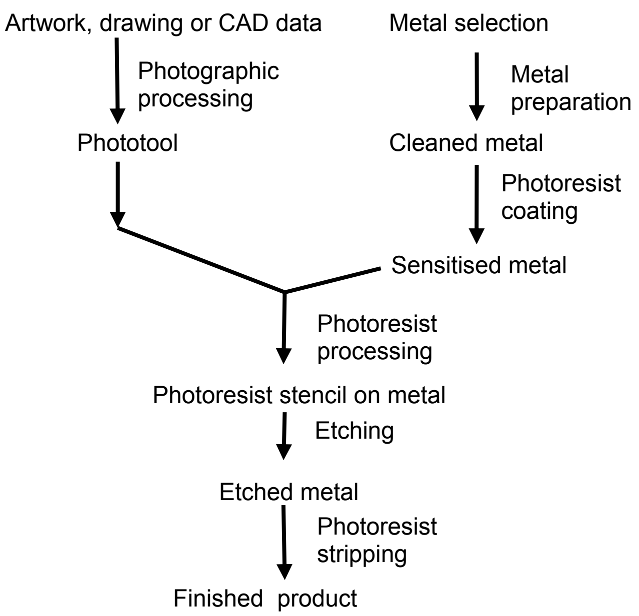

Figure 1: The current PCM process.

PCM technology and challenges. This organisation now has international membership with regional Chapters in the USA and Europe. The Japanese Photo Fabrication Association (JPFA), formed in the late 1970s, provided a similar focus for Japanese PCM companies.

Many PCM companies have also expanded their process capability within the past ten years by installing additional laser cutting, wire-EDM, CNC routing, waterjet cutting, forming, electroplating and/or photoelectroforming (PEF) processes to form 'one-stop shops'. The business philosophy is to utilise the best technique for both technical and financial benefit.

Research into PCM, outside company laboratories, has been concentrated since the mid-1970s into just a few universities and research institutes based in Europe (e.g. UK, Germany and The Netherlands), Japan and, more recently, China. Since 2000, with the cessation of PCM university research in mainland Europe and to further global pre-competitive research, Cranfield University has set up five PCM Research Consortia each of one year's duration. The Consortia comprise over a dozen rival commercial PCM companies from across the world with the common objective of investigating current industrial PCM challenges [6-10]. The formation of the consortia constituted the first occasion of PCM multi-collaboration across company and country boundaries.

3 PHOTORESISTS

One of the essential elements of PCM is the use of a photoresist. Since the mid-1950s, many different photoresists have been marketed with the options of being:

- positive- or negative-working (Figure 4)
- natural product- or synthetic polymer-based
- applied as a liquid (including electrophoretic deposition) or dry film
- organic solvent- or aqueous-based formulations.

Photoresists based on natural products (such as casein) are still used, especially in Japan, for mass production of IC leadframes and TV shadow masks due to the favourable economics. However, as batch-to-batch consistency can vary with natural products, replacement with synthetic polymers having consistent properties has

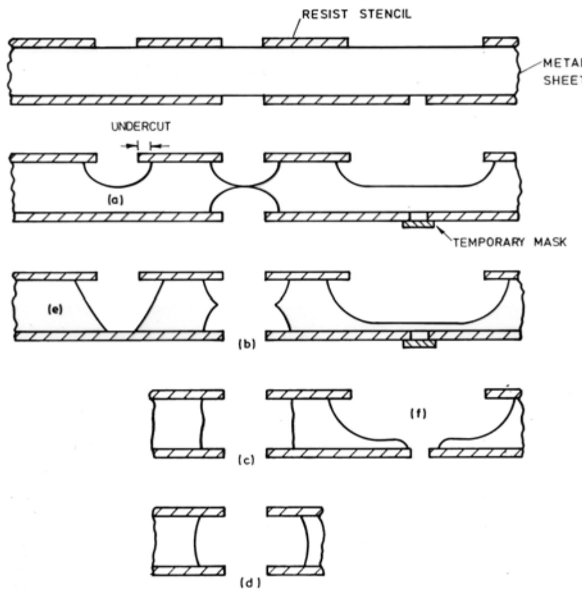

Figure 2: Etch profile development (from top to bottom) as etching time increases.

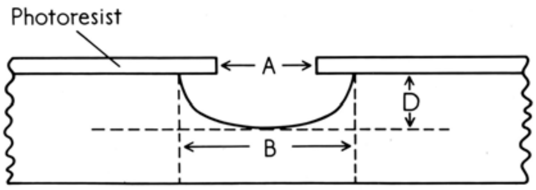

Figure 3: Etch factor = Depth of etch (D) / Undercut where undercut = ½ (B-A).

proved to be advantageous in certain industrial applications.

The challenge of preventing pinholes occurring in thin liquid resist coatings was solved by hot lamination of resists as thicker dry films. This significant advance in coating technology was first used industrially around 1968 [1]. These films were initially developed in solvents but as the environmental consequences of volatile organic compounds (VOCs) became a concern, development evolved as a totally aqueous process.

The range of photoresist products and manufacturers has therefore been bewilderingly complex. In 2000, a major shake-out in the resist world resulted in Rohm and Haas acquiring Shipley, Morton International and Lea Ronal. This has rationalised their product ranges and achieved synergy across them. Du Pont and MacDermid are major USA dry film photoresist manufacturers with additional facilities in Europe and other liquid, USA-based, photoresists are marketed by Fry Metals and Arch Chemicals. In the rest of the world, photoresists are supplied mainly by Hitech Photopolymere and Vantico (Switzerland), Tokyo Ohka Kogyo, Asahi, Fuji and Hitachi (Japan).

4 MATERIALS

Virtually all materials can be etched, although some are etched more easily than others. Etching is basically rapid, controlled corrosion. Thus corrosion-resistant materials are difficult to etch and require extremely corrosive etchants. Some metals (e.g. tantalum, gold and titanium), special alloys, ceramics, glass and plastics fall into this category. However, many materials used commonly in manufacturing can be etched readily by using aqueous solutions comprising ferric chloride, cupric chloride, ferric nitrate, potassium ferricyanide or dilute acids or alkalis.

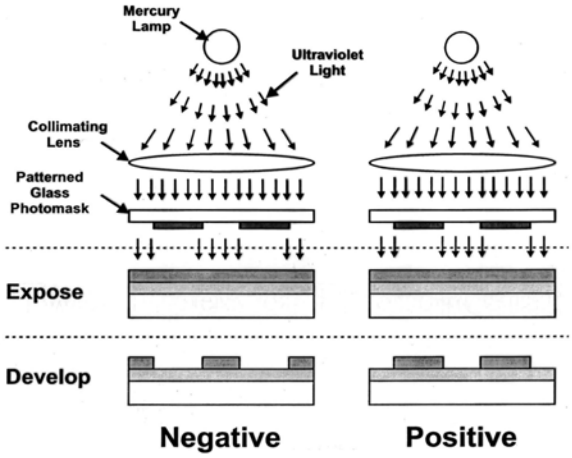

Figure 4: Positive and negative photoresists.

4.1 Metals

The metals most commonly etched by 31 PCM companies in 2000 were as follows (with an estimate of the % of companies that etch the particular metals in parentheses) [11]:

- stainless steels (94%)
- copper and its alloys (especially brass) (84%)
- nickel and its iron alloys (66%)
- aluminium and its alloys (55%)
- mild, carbon and silicon steels (52%)
- molybdenum (32%)

4.2 Glasses and photosensitive glasses

The etching of glasses involves aqueous solutions of hydrofluoric acid (HF). This extremely aggressive etchant poses health and safety challenges [12] but there has been a resurgence of interest in glass etching in the last few years due to new applications of microfluidics in micro chemical reactors, lab-on-a-chip technology, micro Total Analysis Systems (micro-TAS) and ink jet printing.

It should be noted that photosensitive glasses up to 2mm in thickness **do not require a photoresist imaging process** as the glasses themselves are UV light sensitive. The exposure dosage to UV light is required to be very high in comparison to that required for photoresist exposure; 1mm thick glass requires 2 Jcm^{-2} [13].

4.3 Polymers

The etching of polymers through polymeric photoresist stencils is a challenge in itself to determine etchant compatibility. However, poly(methylmethacrylate), polyimide and a few other plastics have been etched successfully to form devices such as flexible circuits and replacement lens haptics (Figure 5) for cataract patients.

5 PRODUCTS

5.1 Precision products

PCM has provided a major, rapid-response service to supply components to the microelectronics, electrical and mechanical engineering industries over the past fifty years. The demand has been for relatively thin (< 2mm thick), complex, precision parts at an economic price. Prime examples are TV shadow aperture masks (Figure 6),

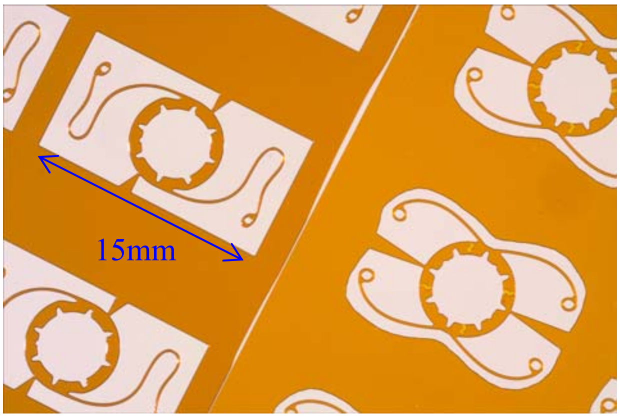

Figure 5: Lens haptics etched from 0.125 mm thick Kapton™ polyimide film (Courtesy of Tech-Etch Inc., MA, USA).

Figure 6: Low resolution TV shadow aperture mask (Courtesy of PCMI).

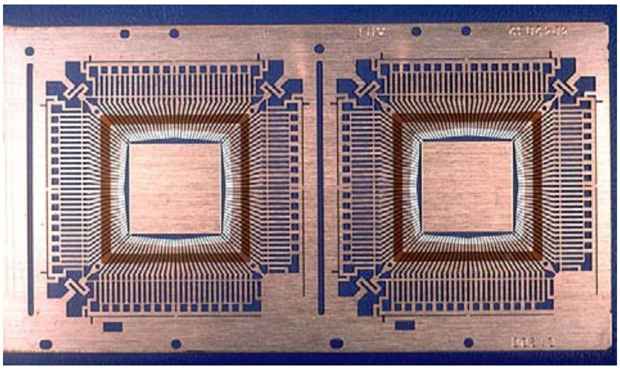

Figure 7: 60 mm wide integrated circuit leadframes (Courtesy of Microponent Ltd, Birmingham, UK).

integrated circuit leadframes (Figure 7), disk drive suspension head assemblies (Figure 8), fine screens, sieves and meshes, shims, washers, laminations, optical shutters and light chopper discs, scales, filters, EMC/RFI enclosures (folded boxes), cutting blades and hybrid circuit pack lids. More recent developments include the use of etched gaskets in mobile telephones (Figure 9).

Three traditional, state of the art, high-volume products made by PCM are examined in more detail below:

TV shadow aperture masks

Shadow masks (Figure 6) are an essential component in conventional TV colour picture tubes (CPTs) and computer monitor colour display tubes (CDTs), comprising arrays of holes or slots through which electron beams are scanned

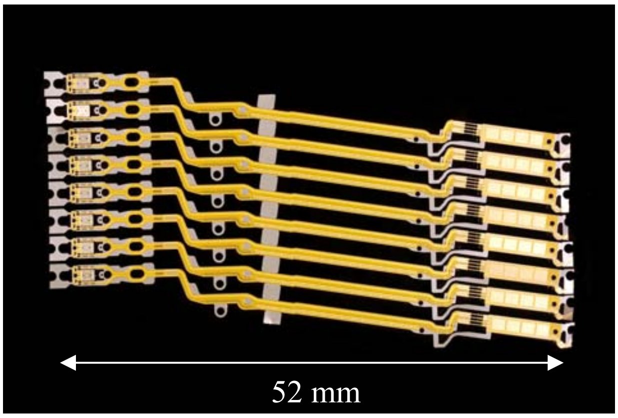

Figure 8: Etched suspension head assemblies (Courtesy of Hutchinson Technology Inc., MN, USA).

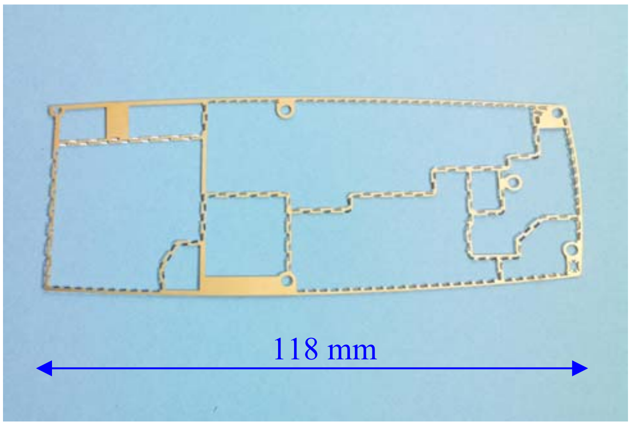

Figure 9: Etched mobile telephone gasket (Courtesy of Savcor, Copenhagen, Denmark).

to activate red, blue and green phosphors to form a colour picture pixel by pixel. The masks, formerly made of aluminium-killed steel, are now more frequently made of Invar type materials (comprising iron and approximately 36% nickel) to reduce temperature distortion of the picture.

The TV shadow mask is an example of a superb, relatively large, technical product made by an automated, continuous (24/7), conveyorised line process. Such a line was described in an anonymous 1971 paper and referred to the PCM production of shadow masks containing 400,000 apertures [14]. A schematic of the line was published in 1994 (Figure 10) and by that time the number of apertures had risen to 600,000 [15]. The process details were kept a jealously-guarded secret for many years and have only recently been discussed in the open literature [16]. By 1997, shadow masks contained as many as 2.5 million apertures, each one of which needed to be perfect as any defect would be immediately noticed by an observer of the TV screen [17]. The product is not only technically demanding because of the large number of apertures required but also because each aperture is slightly different in dimensions and geometry [17]. When a TV or computer screen is viewed, it is essential that the luminosity is constant at all parts of the screen. This cannot be achieved if all the shadow mask apertures are identical. The apertures in a shadow mask are made slightly different, the differences becoming more pronounced as the apertures are positioned further away from the screen centre. This complication in the design has been solved by the use of CAD-generated phototooling [18].

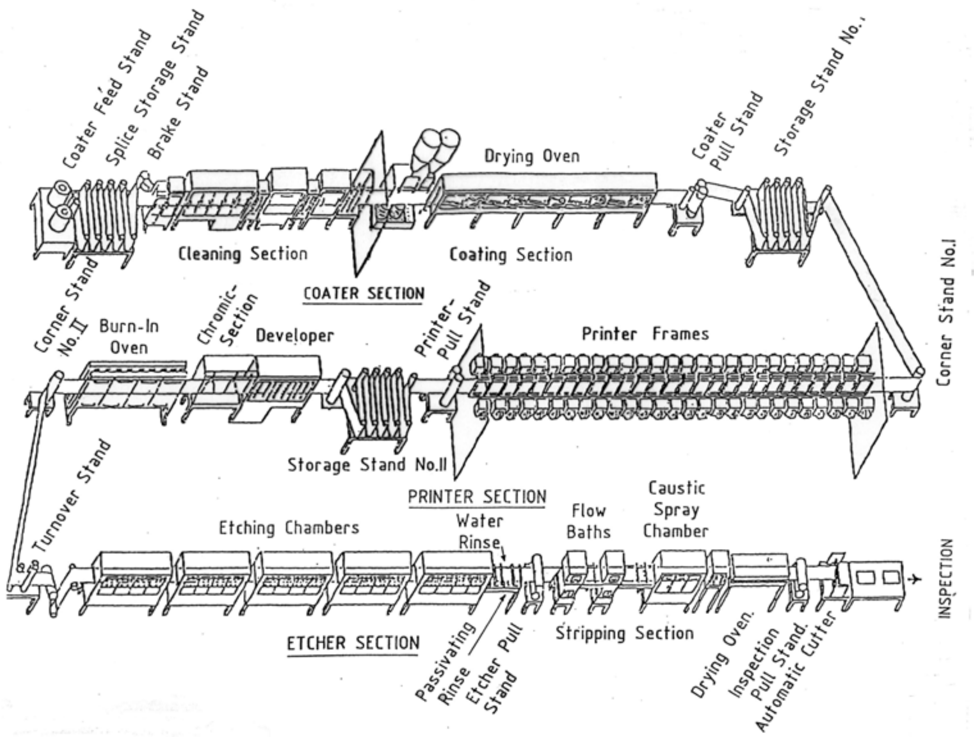

Figure 10: TV shadow aperture mask line (Courtesy of BMC, Mullheim, Germany)

Integrated circuit leadframes

In terms of the highest volume product made by PCM, the IC leadframe is the clear winner, as the JPFA has stated that Japan alone etched 14 billion leadframes in 1988 [19]. Each integrated circuit (semiconductor chip) has to be mounted onto a framework to enable electrical connections to be made from the chip to upwards of several hundred conductive metal leads or legs. The connected assembly is then fixed to the printed circuit board. As seen in Figure 7, the leadframes can be of extremely complex geometry and again the PCM process is automated to reduce process variation.

Disk drive suspension head assemblies

These complex stainless steel components (Figure 8) are an essential element of current hard disk drive technology and hold the read-write heads above the disk. The 2000 global market was found to be relatively easy to analyse and it was calculated that 775 million units were made by PCM that particular year [20].

5.2 Microengineering products

PCM is now also used to fabricate components used in microsystems technology (MST) / microelectromechanical systems (MEMS), medical diagnostic equipment and biomedical engineering applications such as body implants. In the past decade there has been an interesting rise in the number of non-silicon MEMS applications. For instance, miniature wings for micro air vehicles (MAVs) have been constructed from etched Ti-6Al-4V alloy struts covered with Parylene membranes [21]. Three dimensional MEMS products are discussed in 5.4.

5.3 Aesthetic products

In addition to the above, PCM can provide parts with intrinsic aesthetic value and is much used for the production of jewellery (Figure 11), signage, commemorative plaques and Christmas decorations. Very often, the etching process is combining with electroplating, anodising, lacquering and/or painting processes to give additional colour and contrast. Whilst dimensional specifications might not be critical for decorative parts, visual appearance and surface quality is an essential characteristic requirement and great care must be exercised in production to prevent high reject levels.

In the world of model-making, model railway enthusiasts also demand great attention to technical detail, such as the precise number of rivets on an engine boiler and PCM provides this high resolution capability. Most model railway parts are etched from brass.

In addition, the luxury watch industry uses this high resolution capability of PCM to chemically engrave logos on interior 3-D parts to reduce the likelihood of counterfeiting (Figure 12). The electrophoretic photoresist coating of the 3-D part represents a state of the art development [22] that may acquire a new business niche for PCM by allowing it to expand into new applications.

5.4 Three-dimensional products

The production of 3-D products was reviewed some years ago by Allen [23]. When it is impossible to contact print a film phototool onto the photoresist (as in the case of a

Figure 11: Silver jewellery etched and filled with enamels (Courtesy of Dust Jewellery, UK).

sphere), special 3-D hard (photo)tooling is preferred. The usual way of producing a third dimension in PCM is to use the ‘origami’ approach of folding a half-etched flat metal sheet along the fold lines so produced. This technique has been used successfully in many technical applications (such as in the production of EMI screening cans) as well as in decorative applications (Figure 13).

Another technique comprises diffusion bonding a series of etched laminations to form channels utilized in fluidic and pneumatic control systems. A recent microengineering development has been the fabrication of microchannel chemical reactors, approximately 10cm in diameter, (Figure 14) from hundreds of thin AISI 316 etched stainless steel laminations [24]. Anodic bonding of silicon and glass can also be carried out to construct microchannels for bio-chip and microfluidic applications.

5.5 ‘The long and the short and the tall’ of PCM parts

Provided that the equipment used in the PCM process is capable of handling the metal substrates, there is no limit to the size range of parts made by PCM. For instance, a conveyorised etching machine can handle parts of unlimited length and has led to the development of reel-to-reel etching for mass production of parts such as IC leadframes.

Largest PCM parts

Typical products include surface etched metal interior wall decor for offices [25], elevator walls for mosques, executive aircraft panelling and elevator doors. As the width of an etching machine is the limiting factor, it has been known to convert two old identical etching machines into a ‘double width’ machine to overcome the limitation! [26].

Smallest PCM parts

Typical parts comprise

- simple 0.5 x 0.5 x 0.25mm square Kovar packing carriers (Figure 15)
- more complex products such as oval blood pressure sensor bodies (2.275 x 0.67 x 0.1mm) containing three holes and a surface-etched drainage channel connected into a half-etch recess [27].

Intricate, thin PCM parts

The resolution of etched parts depends on material thickness and thus the most intricate parts are fabricated from the thinnest materials. Such materials present handling challenges as thin foils can be easily bent and damaged during processing. One such product, produced at 3000 to 5000 parts per week, is a $10\mu m$ thick AISI 301

Figure 12: Chemically engraved Cartier watch movements for a 25mm diameter wristwatch (Courtesy of CMT Rickenbach, La Chaux-de-Fonds, Switzerland).

Figure13: 75 mm high brass Christmas decoration illustrating folding of half-etched lines to create a box-like structure (Courtesy of Chemart, RI, USA).

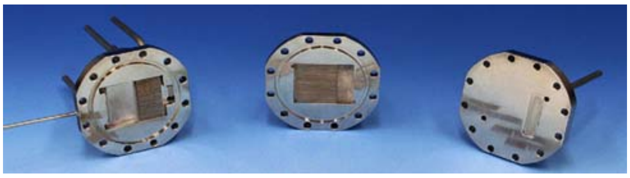

Figure 14: 100 mm diameter, laminated stainless steel microcombustor/reactor components after final machining (from left to right) reactor, combustor and top plate (Courtesy of Pacific Northwest National Laboratory, USA).

stainless steel bearing foil utilised in the reading head of a 30-60 gigabit memory capacity streamer (Figure 16). The steel has an exceptionally-high tensile strength of more than 2GPa [28]. The majority of thinner metal films are backed onto a polymeric support to aid handling and prevent *in transit* damage. Such products include chips for x-ray calibration and rate sensors for fluid flow (Figure 17).

The heaviest PCM parts

Using the diffusion-bonding process described in 5.4, printed circuit heat exchangers (PCHEs) have been used to construct heat exchangers over 109 tonnes in weight (Figure 18).

6 ECONOMIC ASPECTS

The cost of fabricating etched parts is almost directly proportional to the area that can be coated with photoresist, imaged and etched in one series of operations. A part that can be imaged 3000 times in $1m^2$ of metal surface will be substantially cheaper than one that can be imaged only a few times in the same area as the cost of processing $1m^2$ of a given metal is approximately constant if tolerances and general complexity of the parts remain unchanged [29]. The parts on the multi-imaged phototool are often ‘nested’ by CAD to ensure minimum

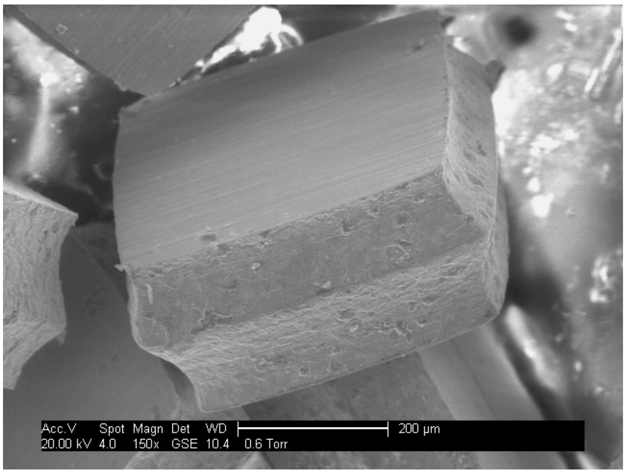

Figure 15: SEM of 0.5 x 0.5 mm Kovar packing carriers showing the characteristic profile illustrated in Figure 2(b) (Courtesy of Tecan Ltd., Weymouth, UK).

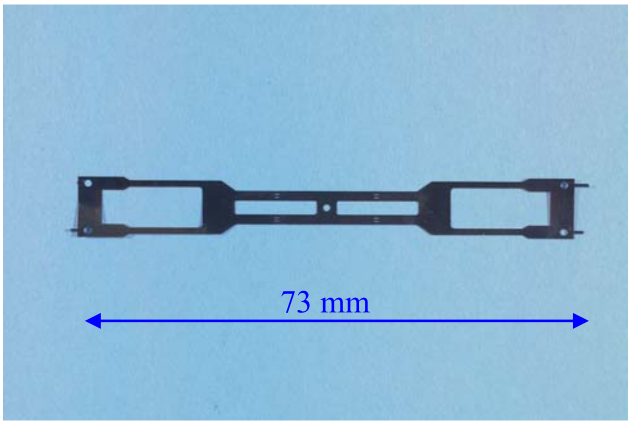

Figure 16: Stainless steel bearing foil 0.010mm thick (Courtesy of CMT Rickenbach, La Chaux-de-Fonds, Switzerland).

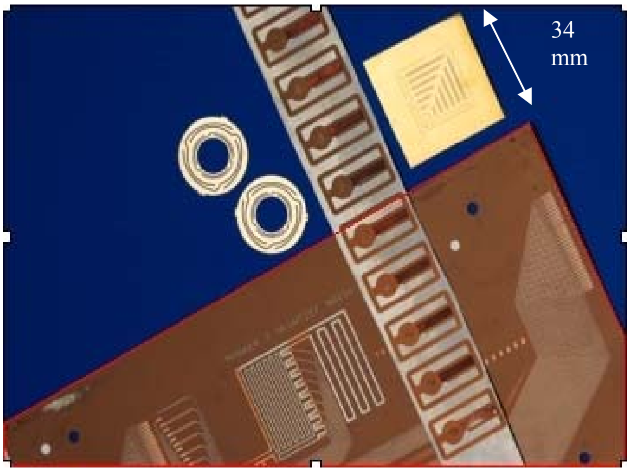

Figure 17: An x-ray calibration chip (top right) comprising a 5 µm thick copper and 3 µm gold pattern on 50 µm Kapton™ and a flow rate sensor (bottom left) comprising a 20 µm thick copper and Constantan™ pattern on 50 µm Kapton™ (Courtesy of Etchform, Hilversum, The Netherlands).

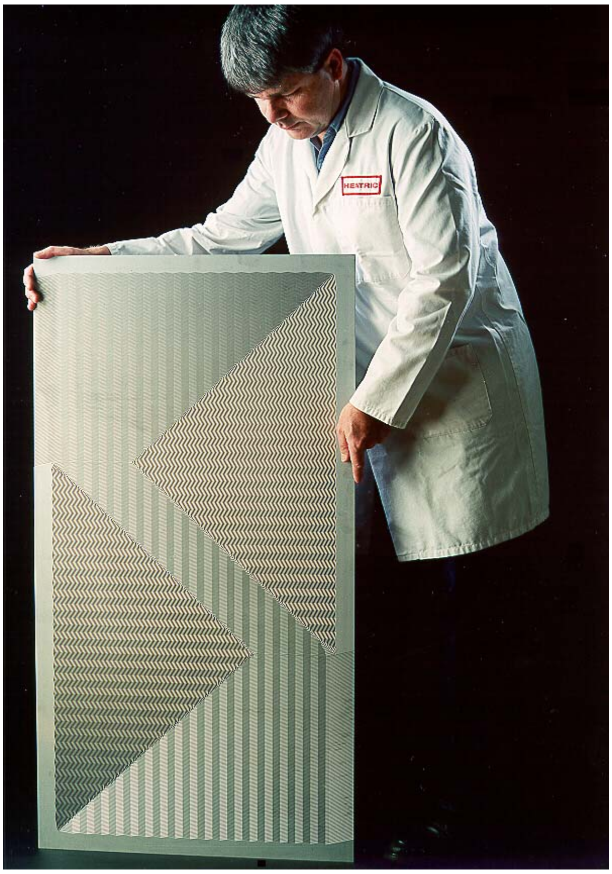

Figure 18: An etched PCHE lamination (Courtesy of Heatric Ltd, Poole, UK).

spacing between the parts, thus maximising the number of parts in the metal sheet.

To increase the rate of PCM production, a conveyorised etch line should be as long as possible.

6.1 Comparisons of PCM with stamping

In comparing the production economics of these two processes, the relative costs of the 'tools' are important factors. A phototool is relatively cheap to produce using a photographic process and contrasts with the production of a more expensive 'hard' stamping tool requiring machining by a craftsman. However the running costs of PCM are more expensive than those of stamping. Figure 19 shows the comparative costs of PCM and stamping and illustrates that stamping becomes economically viable when high volumes of product are to be produced.

Below the breakeven quantity of parts, PCM is the cheaper process and demonstrates that it is well-suited for prototype production. A simple formula for the comparison is shown below:

$$Q = \frac{D - A}{P_E - P_S} \quad (1)$$

where Q is the breakeven quantity, D is the cost for the manufacture of a punch and die, A is the cost of artwork and phototooling, P_E is the PCM part cost and P_S is the stamping part cost.

6.2 Comparisons of PCM with stamping, wire-EDM and laser machining

In selection of an economic process for making a stainless steel part that could be fabricated by PCM, Allen [4] has considered not only stamping but the more modern rival processes of wire-EDM and laser machining from both technical and financial considerations. Providing that all

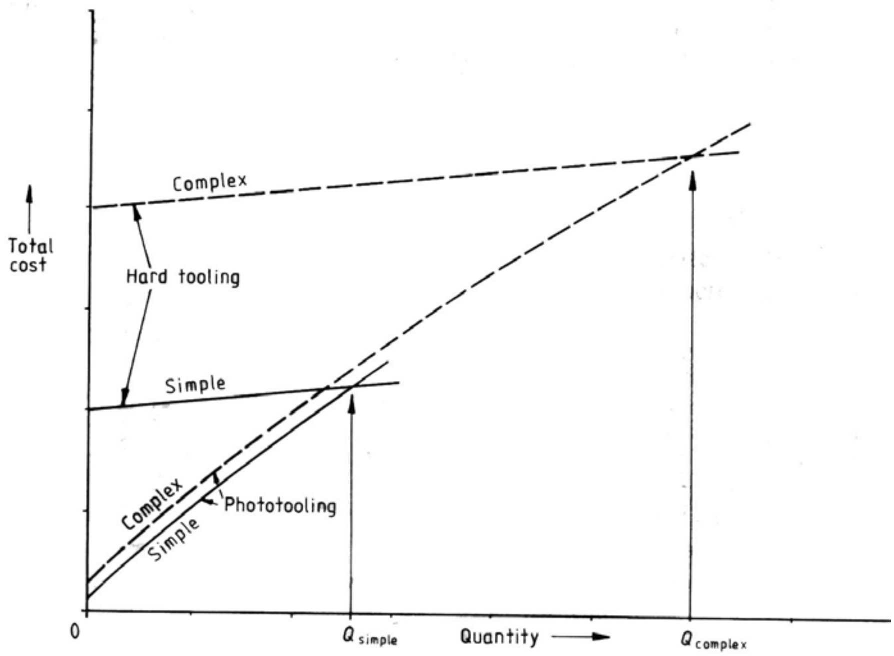

Figure 19: Typical economics of the production of simple and complex parts by PCM and stamping showing break-even quantity (Q) increasing with part complexity.

the techniques can match the technical specifications of the part, PCM was shown to be the most economic process for parts of high complexity. This is due to the fact that the etching process is not sequential and therefore it becomes possible to etch, say, 3 million holes in the same time that it takes to etch one hole.

7 THE PCM ROADMAP

Charting the development of PCM over the next decade in the form of a PCM Roadmap is a challenge. It is required to know:

- where PCM has come from
- where PCM is now
- where PCM is going.

In the technological past, information was generally suppressed due to commercial confidentiality concerns and the basic process involved manual and coordinatograph artwork generation, photographic reduction and step and repeat cameras, liquid solvent photoresists and batch processing of parts and frequent disposal of used etchants. The technological present includes more openness between companies, CAD and laser photoplotting for phototool generation, dry film and aqueous processable photoresists and a substantial amount of etchant regeneration to reduce purchase costs of etchant and the associated disposal costs.

Quantitative assessments of the PCM process are very difficult to determine and, in general, there is a considerable dearth of quantitative information and statistics available in the public forum on PCM. For instance, the size of the industry up to 2000 was unknown until very recently [20]. However, it is important that

- industry is aware of the economic benefits of PCM
- manufacturing perceives PCM as a significant industry and
- the PCM industry measures its growth over time.

No statistics were available to show which PCM market niches were increasing or decreasing and yet it is believed that PCM is a booming business with a bright future. PCM should also be regarded as a process suited to the future demands of technology, especially those of JIT manufacturing, rapid prototyping and miniaturisation (especially MST/MEMS).

7.1 Market Assessments

One of the few PCM market niche surveys has been published recently by Cane who examined the 1999 global market for surface mount technology (SMT) stencils [30]. He determined that the PCM market share was valued at approximately US $64 million at that time.

To calculate the total world PCM market value is challenging, as few statistics exist from which to build any model of the market. At the start of the new millennium a market analysis of four PCM sectors, namely;

- suspension head assemblies
- shadow masks
- integrated circuit (IC) leadframes and
- independent PCM job-shops

was carried out with currency exchange rates calculated using http://www.oanda.com/ [20].

7.2 Suspension head assemblies

These components are an essential element of current hard disk drive technology and hold the read-write heads above the disk. The 2000 market was found to be relatively easy to analyse based on data published in company annual reports of two of the world's major suppliers; Hutchinson (USA) and KR Precision (Thailand). The results are shown in Table 3.

This particular product line has developed considerably in the past decade from etched stainless structures to etched stainless steel parts backed onto polyimide film that acts as the insulator backing for integrated electrical copper wiring. This development has simplified the assembly of suspension heads. Etching is, of course, used to fabricate the circuits in a similar manner to that used in the well-established flexible circuit production industry. An example of an integrated suspension head assembly is illustrated in

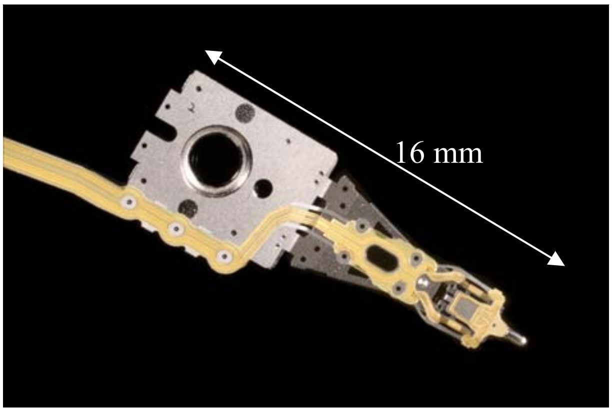

Figure 20: An example of a wiring-integrated suspension head assembly (Courtesy of Hutchinson Technology Inc, MN, USA)

Figure 20.

7.3 TV shadow aperture masks

Japanese shadow mask production by PCM was well documented by the JPFA between the years 1980 and 1988 but since that time the statistics have not been openly available. In Japan in 1998, 37 million shadow masks were made comprising 26 million CPTs and 11 million CDTs. Some information exists on the quantities of shadow masks made in the past decade but the $ value is more difficult to calculate as price varies according to size, material, place of manufacture and application [low resolution (LR) or high resolution (HR)]. An estimation of the sales value of the shadow mask market is shown in Table 4.

These two values are somewhat contradictory and need rationalisation. Taking into account the facts that:

- USA and European prices are higher than those from the Far East
- the Far East prices have not included those of HRTV masks and
- approximately twice as many Far East masks are made in comparison to USA/European masks, it has been estimated that the total global market value is approximately $ (1/3 x 4.123 + 2/3 x 1.736) billion i.e. $2.531 billion.

7.4 Integrated circuit leadframes

Semiconductor market sales have grown at a compound annual rate of approximately 15.3% between 1980 and 1999, reaching $ 149.4 billion in 1999. However in 1996 and 1998 the industry experienced downturns which were reflected in lower sales of IC leadframes.

The PCM leadframe market is extremely difficult to analyse as

- leadframes may be etched or stamped
- numbers manufactured are vast
- leadframes are etched both in-house and by job-shops.

An insight into leadframe production has been obtained by scanning the web-sites and literature of leadframe manufacturers, trade associations and companies specialising in industrial market intelligence. In summary, over the past decade, the average world market for both stamped and etched leadframes is $2.31 billion and the stamped market is $0.34 billion, leaving **the world market for etched leadframes as $1.97 billion.**

7.5 Job-shop PCM

The sales figures for PCMI member companies over the years 1996-1999 have been analysed from annual returns to PCMI. Roughly, over a period of 4 years, 132 companies generated sales of $778.2 million. However, it is not known if all these companies are job-shops. If they are, **and if there are 200 job shops worldwide**, then the total world job-shop sales are $1.179 billion per year.

To check this figure an alternative approach was also taken. An analysis of annual sales of 11 UK job-shops over the period 1996-1999 was undertaken and amounted to $34.3 million. By analysing the **job shop members of PCMI**, remembering not to count those companies solely involved in manufacturing leadframes, and assuming a direct comparison with UK sales, world job-shop sales were estimated (see Table 5) as $426.3 million.

It is surprising to estimate that only 9 (6x11/7) 'rest of the world' job-shops exist when the sales of Japan's job-shops are estimated to be approximately $150 million. This is due to the high number of Japanese job-shops involved in the etching of leadframes so that the sales may have already been accounted for. If the additional $150 million is put into the world sales figures, the total world sales amount to $576.3 million.

7.6 Global overview

Table 6 shows the cumulative world PCM sales based on the analyses of the various market sectors discussed above.

8 STATE OF THE ART TECHNOLOGY

8.1 Automation

It is very obvious from the large volumes of products referred to above that automation of the PCM process is essential to keep up with the demand for high quality components.

Few papers have been written on the subject in general [31] or have referred to automated PCM of specific products [14, 15, 32]. The secret of automated PCM is bound up with maintaining control of etchant composition such that it becomes 'constant'.

8.2 Monitoring etchant compositions

The etching process, invariably carried out with aqueous ferric chloride solution, is difficult to control because, as etching proceeds, the ferric ion is consumed and the ferrous ion concentration increases according to the equation:

$$nFe^{3+} + M \rightarrow nFe^{2+} + M^{n+} \quad (2)$$

where M is a metal of valency 'n' and consequently the etch rate slows. In an automated, conveyorised etching machine, the resultant slower etch rate necessitates a slowing of the conveyor for the product to comply with its dimensional specifications. This lower production rate results in increased costs. What is required in PCM automation is a 'constant etch pool' analogous to a 'sharp cutting tool' in conventional CNC machining.

Chemical monitoring of a fresh ferric chloride etchant is relatively simple [6] but becomes more complex with

1. the addition of hydrochloric acid to maintain byproduct solubility and prevent hydrolysis and subsequent precipitation.
2. the dissolution of different metal ions into the etchant depending on the chemical composition of the dissolved material.

It has been found that interactions between the chemical species in solution make accurate monitoring of free acid difficult to achieve by chemical analysis but manageable by physical probes. Research into the accurate monitoring of etchant compositions **on-line** is underway and involves

Company	No. of units	% of world market	Value ($)
Hutchinson	488 million	63	460 million
KR Precision	62 million	8	28 million
Others	225 million	29	102-212 million
World total	775 million	100	**590-700 million**

Table 3: Calculation of world market sales for suspension head assemblies.

Estimate from source material of	**140 million CPTs @ $6-00**	**112 million CDTs @ $8-00**	**99% LR @ $14 plus 1% HR @ $250**	**Global market value ($)**
Japan	$ 840 million	$ 896 million	(HR ignored)	1.736 billion
USA	-	-	$ 4.123 billion	4.123 billion

Table 4: Estimated sales of shadow masks

the measurements of:

- pH and conductivity for free hydrochloric acid [33]
- Oxidation-reduction potential (ORP) for ferric ion concentration and [33]
- microphotospectrometry for analysis of nickel, chromium and copper content [34, 35].

8.3 Etchant recycling

The disposal of waste ferric chloride based etchants has received considerable attention over the past two decades. Ferric chloride can be regenerated by chemical oxidation from the waste ferrous chloride byproduct as shown below:

$$FeCl_2 + [O] \rightarrow FeCl_3 \quad (3)$$

and a recent analysis has shown that companies that regenerate ferric chloride etchant are almost seven times more efficient in etchant usage than companies that do not regenerate [36].

The most commonly-used methods for regeneration of ferric chloride from the ferrous chloride byproducts are

- Sodium chlorate and hydrochloric acid (used mainly in Europe and Japan) [37]
- Electrolytic regeneration (favoured in Europe) [37]
- Ozone and hydrochloric acid (rare but seen in USA) [37]
- Chlorine gas regeneration (favoured in USA) [38]

and they have all been studied from both technical and economic viewpoints. The most economic process depends on the quantity of metal etched per unit time. For higher throughputs (>1.6 tonnes metal dissolved per annum), chlorine regeneration is the most economic of the regeneration processes [38].

As chlorine and ozone are toxic, the use of oxygen has been investigated for ferric chloride regeneration with some success [39]. The oxidation reaction is slow and a static mixer has been employed to ensure sufficient dwell-time of the oxygen in the hot acidified etchant [40].

8.4 Processing of stainless steels

As stainless steel is the most commonly etched material in job shops and, in particular, is the material of choice for suspension head assemblies, PCHEs and SMT screens, much research has been carried out on the determination of the best etching parameters to achieve high quality products from stainless steel. Variables include the etchant concentration [1, 41, 42], spray pressures [42], temperatures [1, 41, 42] and photoresist characteristics [1, 42].

The removal from the used etchant of dissolved alloying elements, such as nickel that adversely affects the etch rate and quality of surface finish, has also received considerable attention over the past decade [43] utilising such techniques as electro-dialysis [44] and cementation by iron [45]. The latest research has demonstrated that nickel can be removed efficiently (to a level < 70 ppm) by extractive precipitation [46] and this technological advance will now benefit industrial spent ferric chloride recycling.

Domain	Number of job-shops	Sales ($ million)
UK	7	34.3
Continental Europe/ Middle East	17	83.3
USA	57	279.3
Rest of the World	6	29.4
PCMI job-shop total	87	426.3
Total job-shops (87x11/7)	137	426.3

Table 5: PCM sales based on PCMI regional membership

Market niche	**Maximum ($ millions)**	**Estimate for 2000 ($ millions)**	**Minimum ($ millions)**
Suspension head assemblies	700	687	590
Shadow masks	4,123	2,531	1,250
IC leadframes	2,330	1,970	1,680
200 Job-shops?	*1,179*	-	*622*
137 Job-shops?	-	*576*	*426*
Combined market	8,332	**5,764**	3,946

Table 6: World PCM sales

Failure to control the etching conditions can also produce insoluble surface products, known as 'smut' [47], poor surface quality, slow etching and silicon oxide deposits within the etching machine [48]. The primary cause of smutting is now known to be due to aerial oxidation at the diffusion boundary layer [49, 50].

8.5 Lowering environmental impact

Over the past decade much effort has been put into lowering the environmental impact of PCM. The problem of solvent usage in metal cleaning has been resolved by using aqueous cleaning solutions. If possible, liquid photoresist is now coated from aqueous solution rather than organic solvents and both liquid and dry film photoresists are now developed in aqueous solutions. The disposal of waste etchant has been tackled with great success by implementing on-site etchant regeneration processes. Consequently, as the financial burden of environmental compliance has been reduced, this has enabled PCM to remain an economically viable process in comparison to wire-EDM and LBM (that also have a significant environmental impact) and stamping.

9 MODELLING PCM

9.1 The ferric chloride etching process

As ferric chloride serves as a relatively cheap, safe and versatile industrial etchant, modelling of ferric chloride etching mechanisms has been carried out by both industrial users and university research groups. The mechanism of etching has been shown to be complicated by changes in etchant composition caused by the formation of complexes of ferric ions with the chloride ions present in solution. The addition of free hydrochloric acid to ferric chloride is necessary to prevent hydrolysis and precipitation of byproducts.

To effect chemical attack on a metal surface a reactive, solvated ionic species must be transported through the Helmholtz layers to the metal where it must then oxidise it (and consequently be reduced itself). The ionic reaction products must then be solvated and transported away from the metal surface back into the bulk solution so that other reactive ions can be transported to the surface. The rate of etching will therefore be controlled according to which of the three reactions (transport of the reactant; chemical reaction; transport of the reaction product) is the slowest.

Investigations of the kinetics by Maynard's group, intent on controlling the PCM of shadow masks, started with the reaction kinetics of the ferric hexaaquo ion (found in aqueous ferric perchlorate solution – an etchant not used commercially) [51] . The reaction rate was found to be limited by the rate of encounter of ferric hexaaquo ions with a steel surface. The rate of disappearance of ferric hexaaquo ions is dependent upon the first-order ferric hexaaquo ion concentration and the steel surface area and is inversely dependent upon solution volume and viscosity. This indicates diffusion controlled kinetics and the enthalpy of activation, $\Delta H = 2.8$ kcal mol^{-1}, is in the range for diffusion of small molecules in solvents of low viscosity.

Mathematically, diffusion controlled reactions are described by the equation:

$$-\frac{d[M]}{dt} = \frac{ADC}{S} \qquad (4)$$

where:

$-d[M]/dt$ is the rate of dissolution of metal (mmol s^{-1}), A is the surface area of metal exposed to the etchant (cm^2), D is the diffusion coefficient (cm^2 s^{-1}), C is the concentration of etchant (mol l^{-1}) and S is the diffusion layer thickness (cm).

The mechanism is more difficult to resolve when using ferric chloride solutions because of the complexation discussed earlier. Complexed water molecules are displaced by chloride ions as the concentration of the solution or chloride ion is increased. The principal species in solution appear to be $FeCl_2(H_2O)_4^+$ (predominant in dilute solution), $FeCl_3(H_2O)_3$ and $FeCl_4^-$ (predominant in concentrated solution).

At higher etchant concentrations the rate of etching is reduced and it has been suggested [52] that this phenomenon results from the slower rate of absorption of $FeCl_4^-$ onto the metal so that surface-limited kinetics predominate. Measurement of the enthalpy of activation, $\Delta H = 10.9$ kcal mol^{-1}, also supports the hypothesis as this value is too high for a diffusion-limited reaction.

At high etchant concentrations the viscosity of ferric chloride increases considerably thus reducing the rate of diffusion of the etchant species to the metal surface. This characteristic also reduces the rate of diffusion of dissolved aerial oxygen to the etched surface thereby reducing the chance of metal oxidation and smut formation. By raising the etchant temperature and hence lowering the viscosity, the rate of diffusion is increased and accounts for the recent observation of increased smut formation on stainless steel at higher temperatures [53].

Although no external current is supplied to the reaction site, cathodic and anodic sites are present on the metal surface and the current flowing as a result of metal oxidation must be balanced by the current flowing due to reduction of the etchant species. Applying Faraday's Laws of Electrochemistry to the reaction, this allows the maximum theoretical rate of etching ($R_{maximum}$) to be calculated as

$$R_{maximum} = 0.00618\ (M/nd)i\ (\mu m\ min^{-1})$$ where:

M = atomic weight of metal (g), n = valency change, d = density of metal (g cm^{-3}) and i = current density (mA cm^{-2}) [1].

9.2 Cost modelling

For a multi-stage fabrication process such as PCM, it is not a trivial task to develop a cost model for the complete process. A prototype model has recently been developed that can be customised by industrial companies to keep control of the costs of the various operations within a PCM plant [54].

10 THE FUTURE – CRITICAL TIMES AHEAD

10.1 Technology trends

PCM faces many changes in the future. The incorporation of both rival and complementary processes to PCM is predicted to continue. It should be remembered that the customer is primarily concerned with the quality and price of the desired product and, providing the technical specifications are met, **not** the method that is used to fabricate it.

The range of products made by PCM will continue to expand. Although some products will become obsolescent, new products will continue to evolve. The number of shadow masks etched is still increasing year by year (see Figure 21) despite predictions that flat screen TVs will eventually corner the market. Vast untapped markets still exist in China and India for TVs and electronic products. It is therefore not a coincidence that major facilities for the production of TV shadow aperture masks and IC leadframes are being transferred into China at this time to

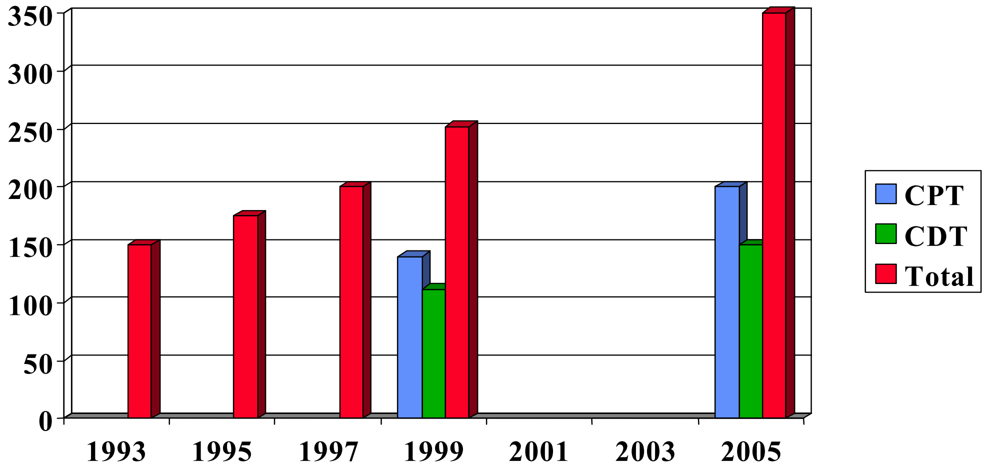

Figure 21: Number of shadow masks (etched and predicted) in millions.

be close to that captive market. This trend has recently been blamed for the planned closure of the Buckbee-Mears, Cortland, N.Y., USA shadow mask plant by June 2004 [55]. This marks the end of an era for one of the most famous American PCM companies that has been involved in shadow mask manufacture since the 1950s

10.2 Environmental pressures

More consideration will need to be given to lowering of environmental impact and the overall process may be modified to that shown in Figure 22 [56].

The 'greening' of PCM will encourage more use of:

- aqueous, natural product and electrophoretic resists,
- laser direct imaging (LDI) of photoresists, thereby eliminating photographic processing,
- high resolution ink jet printing of resists, again eliminating photographic processing,
- environment-friendly etchant regeneration (the extraction of dissolved metal ions with simultaneous conversion of the waste ferrous chloride byproduct back to ferric chloride etchant) and
- monitoring and automation of the etching process to increase process efficiency [31].

10.3 Economic pressures and entrepreneurial activity

In terms of personnel requirements to implement PCM, it should be noted that many of the entrepreneurs who started PCM companies in the 1960s and 1970s are approaching retirement. Some companies will be handed down to family members to continue the family business, but in all cases PCM companies are keen to acquire and train new staff, especially those with knowledge of chemistry.

As the result of a difficult economic climate in the past few years, acquisitions and mergers of PCM companies have been prominent in PCM in 2003. For example, LK Engineering (Denmark) was acquired by Savcor whilst, in the UK, Microponent Ltd and Micrometallic Ltd have merged to form Precision Micro, one of the largest independent (job-shop) companies in Europe, if not the world.

10.4 Education and personnel

The opportunities to carry out PCM research and to train technical personnel for PCM have become severely restricted. Since the closure of PCM facilities at the University of Bremen (Germany), Cranfield University is now believed to be the only European university specialising in the field of PCM. Consequently, Cranfield

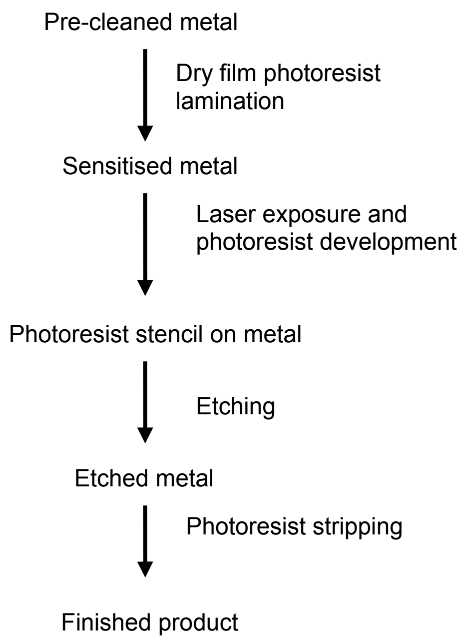

Figure 22: An idealised PCM process of the future.

has started two new annual Continuing Professional Development Short Courses in 'Understanding PCM from a Practical Viewpoint' [57] and 'Advanced PCM' [58].

11 CONCLUSIONS AND SUMMARY

11.1 Economic

The best estimate for PCM sales at the end of the 20th century appears to be approximately US $5.8 billion. The maximum of US $8.3 billion and minimum of US $3.9 billion (giving an average of US $6.1 billion) indicate that the best estimate may be somewhat conservative and lower than the true figure. The calculated size of the PCM industry has surprised those involved in it, being much larger than anticipated. It will be informative to monitor how the PCM sales over the next few decades compare to this estimated 2000 benchmark. The significance of the sales figures would be greatly enhanced by more accurate statistics supplied from more PCM companies.

11.2 Technical niche markets

There appear to be many opportunities for PCM in the future. The technique has the following attributes that should ensure a prosperous future.

- With its ability for rapid production (e.g. prototype part production within 24 hours), it is compatible with agile manufacturing and JIT philosophy.
- Miniaturisation and part complexity favour PCM for economic part production [4]. As the etching process is not sequential, it allows the etching of millions of high resolution apertures or features in a single operation.
- As product sophistication increases, a trend to the use of more exotic materials in products has been detected. These materials are often difficult-to-machine conventionally, often corrosion-resistant, usually costly to purchase and consequently may require a hybrid electrochemical/photochemical machining process to attain an acceptable rate of metal dissolution [59].

11.3 Aesthetic niche markets

Fine arts students and practitioners are beginning to discover the benefits of PCM. The technique is now used in architectural art and model-making, film set constructions (e.g. the Eiffel Tower in *Superman II*), sculptures, jewellery, clock- and watch-making, signage, recognition awards and luxury decorative goods such as Christmas decorations.

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