



Green chemistry in the microelectronics industry

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Microelectronic devices and materials now represent one of the largest manufacturing sectors in the world. Like many large industries, growth has been accompanied by increasing concerns regarding environmental emissions and impact. One challenge for the high end of the market is the identification of alternative process technologies that are not just "greener" but provide compelling technical advantages that could foster adaptation. This review examines a few opportunities where this is possible, including the use of supercritical fluids such as carbon dioxide in advanced device fabrication. The implementation of more acceptable materials in commodity markets, including lead free solder for printed wiring boards, is also discussed.

Introduction

The microelectronics industry has advanced rapidly over the last 20 years resulting in massive increases in processor performance and reductions in the cost of computing. As a whole, it is currently the single largest industry in the world and is expected to maintain growth for the foreseeable future.¹ The desire to move towards green processing is present in all sectors of the industry, however, differences in technical constraints and manufacturing naturally lead to differences in how new technology will be integrated. For the purposes of this article we will divide the industry into two segments: the fabrication of advanced devices, such as integrated circuits using a silicon wafer platform, and the production of high volume commodity materials, such as printed wiring board and casings.

Advancement in leading-edge semiconductor components is often measured against Moore's Law, which predicts that the number of devices per unit area on a chip will double every 18 months.² This can occur by innovative component design, but has more commonly been achieved by consistent reduction in component size. The economic and technological incentive to maintain or even surpass Moore's law is enormous and compels innovation. The fabrication of advanced devices relies on the damascene process. The process involves a sequence of successive steps,

including deposition of a dielectric material, photolithography, etching of device features, cleaning, deposition of metal, metal planarization and capping that is repeated numerous times to leave a highly integrated structure. Continued reduction in feature size requires advances at each stage. However, given the complexity of wafer fabrication, evolutionary change is always preferred. New technology must therefore not only provide a clear technical advantage, but also compete on cost of ownership and overcome the perceived risk of a new process. While the same considerations apply for implementation of "greener" alternatives, there is incentive for change. The damascene process generates a large amount of waste per chip. Williams *et al.* point out that a 2 g microchip requires 1.6 kg of secondary fossil fuels, 72 g of chemicals, 32 kg of water and 0.7 kg of elemental gases.³ For high volume commodity items such as printed wiring board, the technical constraints are fewer, but cost and performance remain critical issues.

This review will discuss several examples for the microelectronics industry where 'green chemistry' is possible. The use of supercritical fluids (SCF) as process solvents, for example, offers both enhanced capability and environmental advantages and have been shown to be effective in almost every stage of device fabrication, including materials deposition and cleaning.

The implementation of 'green processing' is also evident in



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fabrication of commodity items such as printed circuit boards (PCB). Significant advances have been made in elimination of lead from solders and in the reduction of toxicity of IC packaging.⁴ These changes, which center around the removal of lead, antimony and bromine, have had a beneficial environmental impact without compromising performance. SCFs can be used as a plating medium for wiring boards and could provide a potential substitute for traditional aqueous plating baths, a major source of heavy metal waste. Finally, the industry has also given consideration to the fabrication materials and components, and the possibility of their recycling.⁵⁻⁷

Supercritical fluids in microelectronics

A supercritical fluid is a material that is heated and compressed beyond its critical temperature and pressure, see Fig. 1.⁸ In the

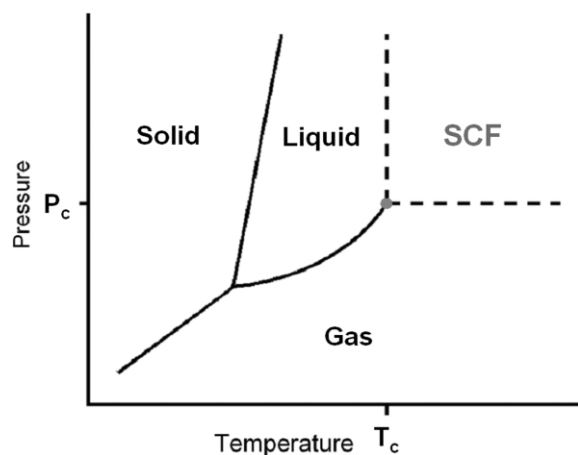


Fig. 1 Phase diagram of a pure substance. A material becomes supercritical when the critical temperature, T_c , and pressure, P_c , are exceeded. The critical point is marked with a dot.

microelectronics industry, the most studied fluid is carbon dioxide, which has the advantages of being inert, non-flammable, non-toxic, cheaply available and possessing easily accessible critical parameters ($\text{CO}_2 - P_c = 73.77 \text{ bar}$, $T_c = 30.98 \text{ }^\circ\text{C}$).⁹ The real benefits of SCF processing become apparent as device dimensions fall far below 100 nm. Most traditional cleaning, resist processing and some depositions are conveniently carried out in solution. However, at length scales relevant to the smallest features, and especially for the introduction of next generation dielectric materials containing sub-5 nm pores, surface tension and transport become significant issues. In these respects, vacuum and vapor based processes offer significant advantages, but the benefits of solution based processing are lost. The use of SCFs makes it possible to retain the former without surrender of the latter. Fig. 2

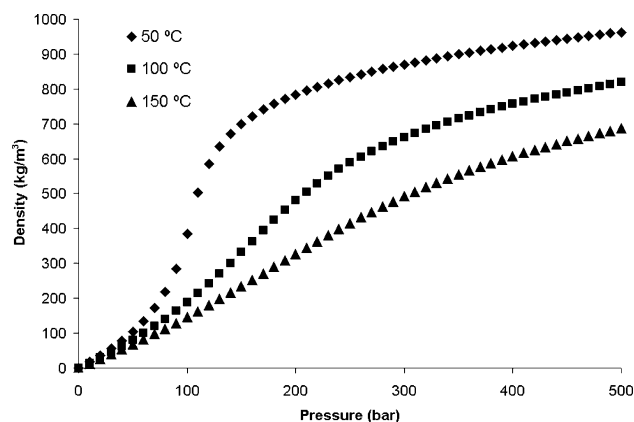


Fig. 2 Isotherms of supercritical CO_2 show tunable liquid-like densities.

shows the density of CO_2 as a function of pressure for several isotherms, 50, 100 and 150 $^\circ\text{C}$.⁹ Note that at modest temperatures

and pressures, the density of supercritical CO_2 can approach that of liquids, enabling the dissolution of many organic and organometallic species.¹² Fig. 3 shows the surface tension of liquid CO_2 ,

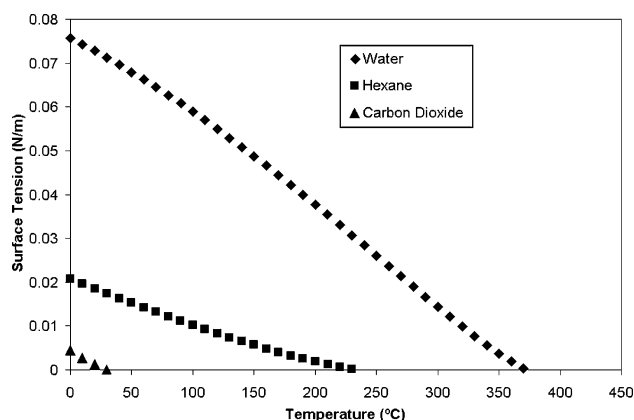


Fig. 3 Surface tension change with increasing temperature of three solvent systems. Surface tension drops to zero as the material exceeds T_c under saturated conditions. Water offers a very small window on potential operation, irrespective of corrosion concerns. Hexane possibly has some, higher temperature opportunities, while CO_2 offers zero surface tension over the whole range, making it the most attractive option.

water and hexane as a function of temperature at saturation.⁹ At temperatures above the critical point, the surface tension vanishes. The absence of surface tension combined with liquid-like densities offer the possibility of solution based processes in the highly confined geometries of microelectronic structures.

Supercritical fluid deposition

Controlled metal deposition is a vital part of the generation of IC components. Systems are built in many steps in which metal and insulator layers are added sequentially to a semiconductor substrate, interspersed with etching, to generate a 3D lattice of components on a very small scale, Fig. 4. Metal deposition is also

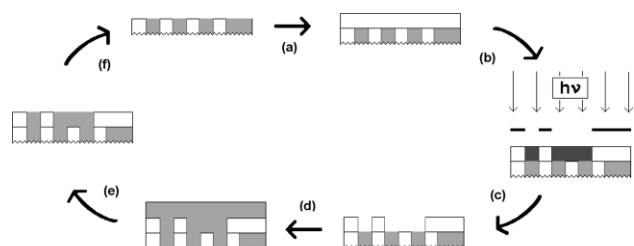


Fig. 4 Creating a metal interconnect structure is carried out in layers. Deposition of each layer requires a number of separate stages. (a) An interconnect structure is coated with a photoresist. (b) The sample is exposed to UV light through a mask. In the diagram the mask is 1 : 1, however in an industrial arrangement a $4\times$ larger mask is used and the light passing through it is focused by lenses underneath. The UV light initiates a chemical reaction in selective regions of the photoresist. (c) In this example of a positive resist system the exposure to UV light has made regions of the photoresist more soluble and these are removed with cleaning solutions to leave the desired resist structure. (d) The wafer is then coated in copper to create the electrical contact. (e) Excess copper is removed by chemical mechanical planarization (CMP). (f) The cycle is complete and the process can begin again one layer higher.

required for many other products, including printed wiring boards. These depositions are traditionally carried out by chemical vapor deposition (CVD), aqueous electrolytic or electroless plating techniques or sputtering.¹⁰ Each of these techniques has its own distinct advantages and disadvantages.

Electroless methods involve the plating of surfaces using electrochemical baths containing the desired metals. This process can occur at low temperatures and be carried out using inexpensive precursors, however it is limited by slow mass transport and capillary forces that can damage finely etched structures. Also, due

to the insolubility of gas reductants in water, more toxic liquid systems must be used, such as sodium hypophosphite and formaldehyde. Electroless deposition also requires the use of several plating and rinsing baths and as such generates large volumes of waste water, which then require remediation.

Cu interconnect structures, in advanced integrated circuits, are presently fabricated using electrolytic plating. The process involves the sequential deposition of a continuous Cu seed layer by sputtering followed by aqueous plating. The seed layer serves as the cathode for the plating process and thus must be continuous. Plating in narrow features is enabled through a combination of additives that promote bottom-up filling and the use of surfactants to reduce surface tension. While limitations to plating from solution will exist at successively smaller dimensions, the first limitation involves the preparation of conformal seed layers in high aspect ratio features. SCFs offer the possibility of eliminating both constraints by void-free filling in < 100 nm topographies and by the ability to deposit continuous seed layers. These features could be applied simultaneously, followed by a simple electroplating step which would fill very small structures and prepare other larger structures for electroplating, see Fig. 5.

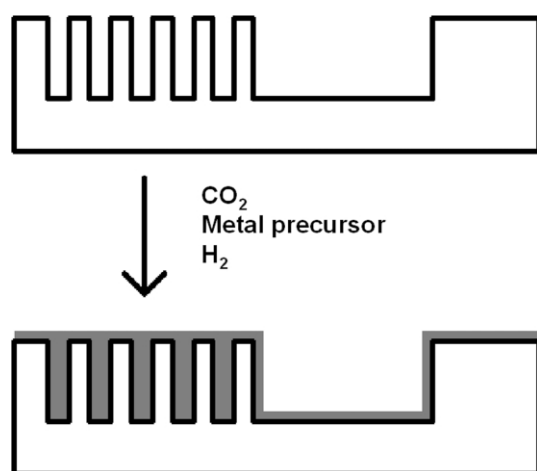


Fig. 5 SCF deposition allows the possibility of completely filling small structures, while simultaneously adding a seed layer to larger topographies for later conventional aqueous electrolytic plating.

CVD relies on the deposition of metals from the vapor of a suitable metal precursor compound.^{11–13} The process can yield high purity metal films, however it is limited by a number of factors. The metal precursors often do not exhibit sufficient vapor pressure to yield high concentrations in the CVD atmosphere. Low precursor concentration can lead to mass transfer limitations, which prevent conformal coverage in narrow features.¹⁴ CVD can also require high temperatures due to precursor volatility constraints, reduction chemistry and/or desorption of ligand fragments from the nascent film surface. For IC fabrication, the deposition temperatures must be kept below 400 °C to avoid thermal damage. Significant advances have been made using metal–organic precursors (MOCVD) to increase vapor pressure and allow deposition at lower temperatures. This commonly means the use of fluorinated ligands or toxic carbonyl compounds which generate their own contamination, performance and emission issues. In particular, the presence of fluorine adversely impacts adhesion.

The use of supercritical fluids as a deposition medium circumvents many of the problems mentioned above by allowing an amalgamation of liquid and vapor phase techniques. scCO_2 provides an inert solvent for the dissolution of metal precursors. This allows orders of magnitude greater concentrations of precursor to be present in the deposition system. At the same time the overall deposition temperature can be lowered to the temperature required to reduce or oxidize the precursor species (typically 200–300 °C). Moreover, precursor vapor pressure is no longer an issue, therefore the fluorination of precursors is not needed, and hydrocarbon based

ligand systems can often be used. Low surface tension of the SCF allows facile transport within finely etched surfaces and can lead to very good filling in high aspect ratios. scCO_2 is miscible with H_2 and O_2 , so these simple species are able to provide clean deposition agents. For high volume plating operations in particular, the potential elimination of aqueous waste streams represents a significant advantage.^{15–17} Finally, plating in CO_2 involves a less severe deposition step and does not necessarily destroy the precursor ligand, instead merely liberating it, allowing it to dissolve into the CO_2 . Therefore it may be possible to recycle ligands when the deposition is complete.

The first use of supercritical fluids connected with CVD was carried out by Sievers *et al.*, where CO_2 was used to dissolve a mixture of precursor and a deposition promoting agent^{18,19} This mixture was then sprayed onto a surface by the rapid expansion of a supercritical solvent (RESS), which allowed mixing on a very small scale. The process generated a very fine precursor aerosol. The sprayed surface could then be annealed (500–800 °C) under atmospheric pressure to generate an even film. The process was given the name supercritical fluid transport and chemical deposition (SFT-CD). Films of Al, Ag, Cr, Cu, In, Ni, Pd, Y and Zr have been successfully grown using this technique. The process has been modified to generate metal oxide films by expansion from solutions in N_2O into high energy plasma. Under these circumstances, N_2O was the oxidizing agent and surface temperatures of only around 100 °C were required. This technique has allowed the generation of Al_2O_3 , Cr_2O_3 , CuO , SiO_2 and B and P doped SiO_2 . Sievers research enabled the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}$ by spraying quantities of components in supercritical propane, followed by annealing.¹⁹ Novel fluid systems were also used by Popov *et al.* who synthesized films of InP by a similar method, though the previous name was abbreviated to supercritical fluid chemical deposition (SFCD).²⁰ This was carried out by the expansion of a CO_2 , C_2F_6 or Xe solution of triphenyl phosphine and tris(*o*-dimethylaminomethyl-phenyl) indium(III). InP was then generated by heating in a vacuum after deposition. This technique improved consistency of mixed components and was able to support IC architecture of the time, however as size decreased the spraying of solids has become less useful. It is important to note that, in each of these processes, the actual deposition does not occur in a SCF medium and likely will not yield conformal coverage in confined geometries.

More recently SCFs have successfully been used to allow direct chemical deposition onto a surface by chemical fluid deposition (CFD). This has allowed generation of high quality, conformal films of metal using CO_2 as solvent.^{21–30} A typical experiment involves the placement of a substrate wafer on a heated stage in a cold wall, high pressure reactor. The vessel is loaded with a quantity of precursor and the system is purged with N_2 . The vessel is then pressurized with SCF and a quantity of reducing agent (H_2 or alcohol). The substrate wafer is brought to temperature by heating the pedestal stage it is mounted on. The deposition is believed to occur rapidly and a film generated. A number of precursor systems have been investigated using this technique including 2,2,6,6-tetramethyl-3,5-dionate, 1,5-cyclooctadienyl, cyclopentadienyl, 2-butyne, vinyltrimethylsilane, 2-methyl-1-hexene-3-yne, methyl allyl and allyl ligands. Using these systems films of Au, Co, Cu, Ni and Pd have been grown. This system circumvents some of the problems associated with CVD and aqueous plating and permits access to a sub 100 nm chip architecture in a cold-wall reactor. Use of the cold-wall reactor confines deposition to the heated substrate. Mixed precursor systems can be used to produce alloys or to catalyze the deposition of metals such as Ni and Cu by the presence of easily reduced precursors such as Pd, Pt and other metals.²¹

A new adaptation of this technique was applied by Ye *et al.* who used HF as a reacting agent to facilitate deposition on Si and Ge surfaces by the fluorination of semiconductor surfaces initiating reduction of the precursor.³¹ This has allowed growth of films of Ag, Cu and Pd.

Supercritical drying

For sub-50 nm structures, removal of liquid solvents by evaporation can be problematic as the liquid–vapor interface can exert damaging capillary forces on a surface. This is particularly important in next generation ICs where high aspect ratio resist patterns are used and simple evaporation of a solvent can lead to the collapse of etched structures.^{32–34} Feature collapse becomes increasingly important as porosity is introduced into advanced dielectrics. Supercritical drying avoids these difficulties by eliminating the liquid vapor interface. Fluids above the mixture critical point do not exhibit surface tension, so removal of solvents in this state does not lead to feature collapse. In one approach, aqueous solutions are exchanged for solvents such as alcohols that are miscible with CO₂. In other approaches miscible solvents are removed directly by dissolution in CO₂. Co-solvents can also be added to CO₂ without initiating phase changes and act to promote water solubility in the fluid.³⁵ Alternatively, the addition of surfactants can be used to remove water more effectively.³²

In one study, Goldfarb *et al.* demonstrated the use of a CO₂–hexane–surfactant system.^{36–38} Structural integrity was maintained during the drying of resist lines 140 nm thick, with a spacing of 370 nm, aspect ratio of 6.8 and length of 8 μm.³⁸ To emphasize the point these samples were then rewetted with water and hexane and allowed to dry conventionally. The resist structures all collapsed under these conditions. Namatsu was later able to show that it is possible to dry features as small as 7 nm in width with an aspect ratio of 10.³⁹

Photolithography

Photolithography is the selective exposure of specific regions of a photoresist with radiation of a defined wavelength to initiate a chemical change in the resist structure. This change is often promoted by chemical amplification, usually through the presence of a photoacid generator (PAG) that catalyzes the desired transformation. Exposure can lead to cleavage of a chemical bond to deprotect a functional group, induce chain scission to reduce the molecular weight of the resist, or crosslink the resist. These structural transformations alter the solubility of the exposed regions through polarity and/or molecular weight changes. For example, reduction of the molecular weight of a polymer to make it soluble in a rinsing solution creates a positive resist pattern. Alternatively, cleavage of a protecting group on the polymer chain that renders the exposed region insoluble in the rinsing solution yields a negative resist pattern. In either case the soluble region would be traditionally removed by conventional solvent, which in turn could be dried by CO₂ as above. Ober *et al.* showed the possibility of eliminating solvents from the rinsing step by using silicon and fluorinated resist systems that could be developed directly in supercritical CO₂.^{40,41} Hoggan *et al.* produced similar results also using a fluorinated polymer system.⁴² The North Carolina group also developed a technique analogous to conventional spin coating using scCO₂ as solvent.⁴³

Supercritical cleaning

Cleaning of IC systems using CO₂ is a process that has received much attention.^{44,45} The ability to remove solid waste material from lithographic processes effectively, yet gently enough not to damage device structures, offers significant advantages over existing techniques that rely on chemical washes. The most common wash systems are H₂SO₄–H₂O₂, HF–H₂O, NH₄OH–H₂O₂–H₂O and HCl–H₂O₂–H₂O. All systems are then rinsed with ultra-pure H₂O.⁴⁶ The key reason behind the harsh solvent use is the ability to remove tenaciously deposited residues of metals, photoresists and anti-reflection coatings. However, this becomes increasingly difficult as the trench dimensions are reduced due to surface tension and damage. Moreover, continuous reduction in device dimensions requires the introduction of dielectric materials containing sub-5 nm pore structures. It is imperative that contamination or damage to

the dielectric structure be avoided during lithography, etching and cleaning. The use of carbon dioxide to clean these structures eliminates concerns over residual solvent and pore collapse due to capillary forces and has been shown to be highly effective.^{47,48}

In some processes, CO₂ is used in its solid form sprayed through a nozzle as fine solid particles. These particles physically remove material from the surface while not leaving any residue behind. The concept has been improved recently in the SCORR system developed at the National Laboratories in Los Alamos, in conjunction with SC Fluids Inc.⁴⁹ Here CO₂ bombardment is carried out under a CO₂ atmosphere containing modifier molecules. The pressure of the system is pulsed from 7.5–11 MPa to remove debris then rinsed with a purge of CO₂. The waste materials are not believed to be solubilized by the fluid system, yet sufficient mobility is afforded to the surface debris to remove it from the wafer.⁵⁰ This has allowed highly efficient cleaning of narrow wafer patterns. The commercialization of this process won a 2002 Presidential Green Chemistry Challenge award.⁵¹

Synthesis

SCF has long been used as a solvent for synthesis of various materials.⁵² In this review two classes are of interest, porous low *k* dielectrics and nanoparticles and wires.

Low *k* dielectrics are currently a major issue for the microelectronics industry as current techniques are unlikely to be extended below a dielectric constant around 2.5. It is necessary to continue the reduction in *k*, however the only perceived way to do this requires a porous material. As porosity is introduced into a structure, however, the system is physically weakened, making it less able to survive chemical mechanical planarization (CMP), to remove excess material, or the final IC packaging process. Synthesis of mesoporous silicas in scCO₂ offers an elegant solution to both problems. Block co-polymer surfactants have been shown to successfully self assemble, producing highly ordered arrays over a large area.⁵³ This structure can be rapidly penetrated by silica precursors, such as tetraethoxysilane (TEOS), dissolved in scCO₂, which condense to form a silicates network.⁵⁴ A key to the process is the containment of the precursor reaction to one phase domain of the template by partitioning a catalyst to a specific region. Moreover, while CO₂ facilitates transport of the precursor into the template, the presence of the solvent does not disrupt order. Removal of the template then yields a robust, highly ordered mesoporous film that survives CMP. The process occurs rapidly relative to conventional sol–gel synthesis and per wafer process times in the order of minutes are accessible.

Supercritical fluids have also been useful in the generation of nanoparticles and nanowires of conducting and semiconducting materials. These materials are believed to be increasingly important in the future of microelectronics.⁵⁵ The topic has been recently reviewed by Ye and Wai¹⁵ and Holmes *et al.*⁵⁶ Several routes have been suggested to generate nano-systems including RESS, antisolvent precipitation and direct synthesis in a SCF. Each of these systems have produced interesting results, however they also have their own inherent difficulties: RESS relies on solubility in the SCF, antisolvent precipitation is only viable for high value added products and direct synthesis has tended to require a SCF with high T_c and P_c, such as water or hexane.⁵⁷ Recent research in the field has been conducted on water in CO₂ microemulsions, which use surfactants to yield ultra-fine suspensions of water in scCO₂.⁵⁸ These regions of water are then capable of dissolving ionic species, allowing a reaction to occur and precipitating nanoparticulate materials when the CO₂ pressure is released. Using this system nanoparticles of several materials have been generated, including Ag, CdS, Cu, TiO₂, ZnS.^{59–63}

Other non-SCF based synthetic routes have been suggested for the generation of nanomaterials. For example Peng uses the principles of green chemistry to examine more environmentally friendly methods to generate CdSe and CdTe.⁶⁴ Similarly a

synthetic route to CdS has been suggested by Bayer *et al.* for generation of thin films for photovoltaic cells.⁶⁵

Toxic chemical reduction

The second aspect of this review, dealing with the replacement of toxic chemicals in device manufacture.

Lead free soldering

Lead exists as finish on printed circuit boards and the component leads as well as solder for establishing electrical contacts. Europe and Japan have put forth much effort in the pursuit of lead free solders for manufacturing. By 2003 70–80% of the Japanese electronics industry had established lead free technologies.⁶⁶ By 2005 all are expected to have made the transition to lead free alternatives; a legislative deadline currently exists for lead removal by 2006. An overview of the Japanese approach to lead free manufacture is given by Fukuda *et al.*⁶⁶ A similar approach to the issue is taken in Europe with the Waste Electrical and Electronic Equipment directive from the EU set to mandate the removal of Pb, Cd, Hg, hexavalent chromium, polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers from electronic equipment by 1st July 2006.⁶⁷ The efforts have produced new soldering systems that provide safer alternatives without compromise on conventional Sn–Pb mixtures.⁶⁸ In Japan the release of products labeled ‘lead free’ were greeted by a 20% market share increase of sales by Sony and 4.7–15% by Matsushita.⁶⁶

The solder itself must physically and electrically link materials with very different thermal expansion coefficients. Mechanical stress will rise as the connection points decrease in line with miniaturization. The materials challenges are significant. The solder must have adequate wetting properties to connect components when fluid and enough mechanical strength to hold the contact in place when solid. Melting also must occur at temperatures close to that of Pb–Sn solder (183–230 °C) to allow use of current soldering manufacturing. The system is also complicated by the fact that two types of soldering joint exist: Level 1, which connects a microchip to a substrate, with many precise linkages; and Level 2, which connects conventional components, such as resistors and capacitors, to a printed circuit board (PCB).⁴ Traditionally Pb–Sn solder has been used in a near eutectic mixture for both applications. Investigation of replacement materials permits tailoring of the novel compound to one process or the other.⁶⁸ The review by Abtew *et al.* details the precise features and compositions of the many possible lead free solders available in 2000, with a detailed description of the physical properties and how they are measured.⁴ Properties of traditional and novel solders have also been studied by Plumbridge, who compared Pb–Sn with two lead free systems.⁶⁹

Specific companies are developing their own replacement technology, however most center around Sn blended with one or two of the following: Al, Ag, Bi, Cu, In, Pd or Zn.⁶⁶ The presence of Ag, In or Pd in the solder will increase the raw materials costs. This has led to Pb free solders typically costing 2–3 times that of traditional solder. Sn–Cu solders only cost 1.3 times that of the conventional material and have therefore found favor in some applications.⁷⁰ Since European and Japanese legislation mandates the change there is little room to maneuver. The small quantities used in each device, coupled with the high value of IC products, suggest that the cost change has not had a large impact on production. A cursory search reveals more than 50 US patents in this area.

Lower toxicity IC packaging

Following a similar trend in the elimination of lead from manufacture, the examination of ‘green’ casings attempts to remove Sb and Br from the compounds used to seal microchips. This follows from safety concerns over toxicity of waste products in a similar manner to the removal of lead. As mentioned above, the

removal of the Br based compounds is scheduled for mid 2006 in Europe.⁶⁷ These compounds are used as flame retardants and alternative materials must be found to replace them. These compounds must be able to seal the chip from contamination, particularly moisture, yet be resistant to thermal damage during soldering. Lin *et al.* describe possible alternatives to the conventional system and point out that incorporating a lead free soldering environment means that the casing system must exhibit stability to a greater temperature than for leaded solder. This is due to the higher melting point of the most commonly used lead free alternatives to conventional Sn–Pb solder.^{71,72} As with Pb free solder, there are too many patented systems to list here. Unfortunately, relatively few papers on the subject exist in the open literature.

Conclusion

Technologies that offer distinct technical advantages and also minimize reactant toxicity and waste inherent in conventional syntheses are the most likely to be adapted in demanding fabrication schemes for integrated device manufacturing. Supercritical fluids may provide both of these advantages. Changes in packaging materials and commodity items such as printed wiring board are more accessible and are currently under way. Environmental concerns and increasing legislation will likely hasten development in all areas.

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