Curable Inks for Laser Thermal Transfer Printing

Lisa Siewierski
MARKEM Corporation
Keene, NH/USA

Abstract

The semiconductor industry has two major printing technologies: pad printing and direct laser marking. Pad printing offers highly legible marks; however, this technology is not digital and solvent-based inks are required. Direct laser etching offers digital capability with poor contrast. Our laser thermal transfer printing technology offers high contrast marks with digital capability on a variety of semiconductor materials including epoxy molding compounds, ceramic, gold, nickel and silicon.

Our laser thermal transfer printing process employs a proprietary foil ink which is transferred to an electronic component. The mark is subsequently cured with ultraviolet light or thermal energy to obtain highly durable marks. The prints on these semiconductor parts must be resistant to solvent, acid (solder flux) and abrasion.

I will present the requirements for the electronics industry and the chemical approaches that have been taken with various laser printing heads.

Introduction

In the semiconductor industry, chip makers code logos, serial numbers and dates on integrated circuit packages using techniques such as offset gravure (i.e. pad printing) or direct laser marking. Ink marking offers users a high-contrast mark at relatively affordable cost, but also requires working with volatile solvents which can be environmentally unfriendly. Consistency of print quality must be carefully monitored with constant viscosity modification and replacement or cleaning of the pads and printing plates. Offset gravure printing does not offer serialization and can be costly for small lots.

Ink markings must have very high durability to withstand the various steps of the integrated circuit assembly process which includes resistance to solvents, acids and abrasion. The durability is generally obtained by crosslinking the ink. Crosslinking can be achieved either by ultraviolet or thermal radiation. UV curing offers faster cure speeds which results in higher throughput than thermal cure. However, thermal cure can offer advantage of improved adhesion, especially to metal substrates, obtained with the slower reaction rate which minimizes stress build up within the ink.

Direct laser marking is becoming increasing popular due to reliability, speed and low maintenance. However, direct laser marking generally does not produce easily readable, high contrast prints. Poor contrast renders this method unattractive for chip makers who want highly visible company logos, human readable marks or machine readable codes on their products. Additionally, direct laser marking can potentially cause damage to component circuitry or packaging if the etch is too deep.

MARKEM has developed a laser thermal transfer printing technique which offers high contrast digital prints on a variety of semiconductor substrates and other industrial products.

Background

Semiconductor Industry Requirements

Chip makers' requirements for printing and adhesion are very demanding. Highly visible, durable and digital prints are the key requirements for most of the industry. A typical printing process for the semiconductor industry is shown in Figure 1.

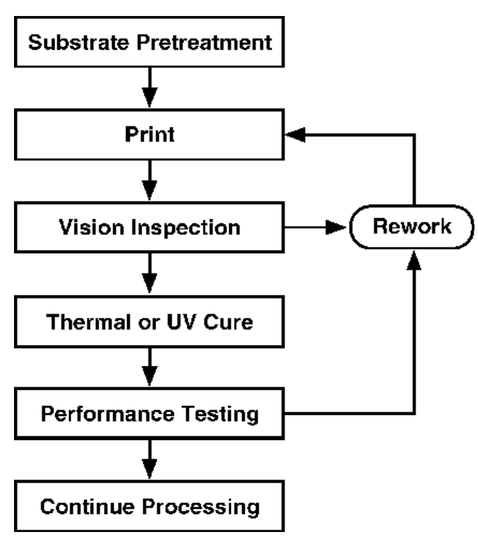

Figure 1. Block diagram of semiconductor printing process

After printing, the semiconductor components may be exposed to relatively harsh environment during processing such as solvents, cleaning detergents, solder and acidic fluxes. The ink markings must be able to withstand this exposure without becoming illegible due to missing characters or fading. The marking inks must be able to withstand abrasion, salt spray and temperature cycling. Marking ink manufacturers' must develop processes to remove crosslinked ink markings for situations when the component must be remarked. This can be particularly challenging due to the high durability requirements of the industry.

Since the semiconductor industry demands inks with high durability, chemistries used in traditional hot stamping and thermal transfer films could not be utilized and specialty formulations were developed. The durability of these specialty laser transfer foils was achieved by crosslinking the transferred ink with either UV or thermal radiation.

Semiconductor Substrates and Wetting

A variety of substrates are used in the semiconductor industry such as epoxy molding compounds, gold, nickel, silicon and ceramics. These substrates generally have low surface energy. See Table 1. These substrates and other low surface energy substrates such as Teflon® and polyolefins are often hard to wet. In any printing process, the surface energetics must be in a favorable state to obtain quality prints. In general, the surface energy of the substrate should be higher (≥ 10 dynes/cm) than the surface tension of the ink.

Table 1. Surface Energy of Semiconductor Substrates

Material	Uncleaned Surface Energy (dynes/cm)	Pretreated Surface Energy (dynes/cm)
Epoxy Molding Compounds	< 25	60-70
Metal (Au and Ni)	30-40	>60
Silicon	25-35	>60

Organic surface contaminants such as mold release agents, processing chemicals, finger oils and airborne hydrocarbons are known to reduce the surface energy. The low surface energy can be overcome by pretreating the substrate using methods such as hydrogen flame treatment, plasma[1] or wet chemical methods. The pretreatment methods increase the surface energy by surface oxidation and removing surface contaminates

Substrate wetting is essential for adhesion. If the ink does not spread onto the substrate, then intimate contact can not occur and minimal interactions between the ink and the substrate result in poor adhesion. Zisman[2] has extensively studied the relationships between substrate wetting and adhesion. A liquid will spontaneously spread on a substrate if the surface tension relationships are appropriate. In general, for good substrate wetting, the surface energy of the liquid must be lower than the substrate. If the surface tension of the ink/liquid is too high, the liquid forms a droplet rather than spreading onto the substrate.

In the case of laser transfer foils, it is essential that the surface energy of the substrate to be printed is higher than that of the carrier film. If the surface energy of the carrier film is higher, the ink layer will preferentially remain on the carrier film over transferring.

Adhesion Mechanisms

In addition to substrate wetting, there are many other mechanisms which contribute to ink adhesion including mechanical, chemical and diffusional. On the microscopic scale, substrate roughness can contribute to mechanical interlocking of the ink and significantly improve the adhesion compared to a smooth substrate. However, this roughness is only advantageous for adhesion if the ink penetrates into the irregularities of the substrate. If the ink does not flow into the pores of the substrate, then surface roughness is no longer advantageous since the interfacial contact is reduced. Then, water or other liquids could penetrate into the unfilled pores resulting in the ink lifting or substrate corrosion.[3]

Chemical mechanisms for adhesion include covalent bonding, hydrogen bonding, dispersion or dipole interactions. Hydrogen bonding can promote adhesion to a variety of substrates for ink formulations which incorporate resins that have hydrogen donating groups and hydrogen accepting groups.[4] Covalent bonding is the strongest bond formation (15-170 kcal/mol vs. <15 kcal/mol for hydrogen bonding) which occurs only if the substrate surface functionality is reactive with functionality in the ink formulations.

Diffusional mechanism of adhesion occurs when the substrate is polymeric. With good wetting, the polymeric segments of the ink may then be able diffuse through the interface.

System Overview

Laser Thermal Transfer Printer

Early development of laser thermal transfer printing systems included carbon dioxide, neodymium:YAG and diode lasers. All these systems were shown to work experimentally with various ink formulations; however, the carbon dioxide based laser system was chosen for commercialization based on safety, cost and power.[5]

The laser thermal transfer printing system as commercialized uses a 50W carbon dioxide laser. See Figure 2. The optical design allows for printing addressability of 500 dpi and maximum print speed of 380 mm^2/sec. Some important aspects of the system design included achieving intimate contact of the laser ink foil with the substrate and maintaining a constant time and angle for peeling. Without good intimate contact of the laser foil with the substrate, image quality was poor due to loss of resolution and non-uniform transfer. Constant peel time and angle allowed for the laser ink film formulations to be optimized for good print quality. The laser ink formulations were developed to absorb enough laser energy to melt and uniformly transfer to the substrate. This transferred ink must meet the durability requirements for the targeted industries.

Laser Transfer Foils

The laser transfer foils are prepared from a specialty pigmented liquid ink formulation. The liquid ink is applied to the carrier film using a web coating method and then dried. The dried ink layer is generally between 2-15 microns in thickness. Current commercial offerings are prepared from water-based fluids and coated onto a polypropylene carrier film. Both UV and thermal cure laser transfer foils are available in either black or white.

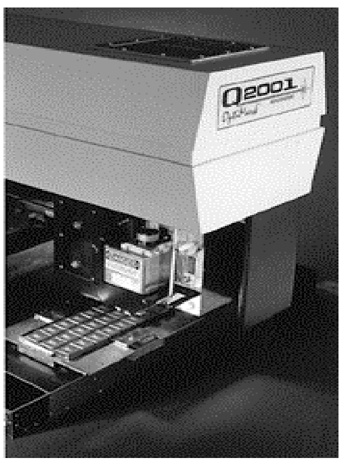

Figure 2. Laser Thermal Transfer Printer

Chemical Formulations

Cure Chemistry

In order to meet the application requirements for the semiconductor industry, marking inks must be crosslinked. Crosslinking improves the solvent resistance, abrasion, scratch and many other physical properties of inks. UV or thermal radiation can be used to start crosslinking reactions. Examples of typical UV crosslinking chemistries include: acrylates, epoxies and thiol/enes. UV curing offers the advantage of an inline cure which reduces processing times. However, adhesion to metal substrates may be slightly compromised when compared to thermal cure chemistry. Urethane, epoxy and phenolics are typical thermal radiation chemistries that offer excellent physical and mechanical properties but generally have long cure cycles. Some of the processing parameters and performance property differences between UV and thermal cure chemistries are shown in Table 2.

Table 2. Comparison of UV and Thermal Cure Chemistries

Property	UV Cure	Thermal Cure
Cure or Processing Speed	Fast (seconds)	Slow (minutes to hours)
Formulation Cost	High	Moderate
Shelf Life	Long (with light protection)	Variable
Adhesion	Good	Excellent
Energy Costs	Moderate	High

Formulation Considerations

There were several key aspects in developing the laser transfer foils which included film transport mechanism, choice of carrier film, ability of ink to convert laser energy to heat and final ink properties.

The film transport mechanism was fundamental to the development of the laser transfer films. Much of the early development work was in collaboration with the engineering design team. Boyer and Carter[5] have reviewed the experimental and final design. The final design offered intimate contact of the laser transfer film with the substrate and consistent time between melting the ink layer and peeling away the carrier film which aided in the optimization of chemical formulations.

There are a variety of polymeric films available for various industrial applications. For the laser transfer foil application, the carrier film has to be relatively transparent to the laser energy so it does not deform or melt during the printing or transfer process.[6] Polyolefins such as polyethylene or polypropylene are relatively transparent to laser energy of a carbon dioxide laser (10.6 microns) and will remain intact while polyester films tend to absorb the laser energy and subsequently melt. If the carrier film deforms or melts during transfer, poor print quality is obtained as in Figure 3.

Figure 3. Sample print when carrier film was deformed.

Additionally, since tension control is critical in maintaining consistency in the laser transfer printing process, the carrier film must not stretch. This is an important feature for the ink layer as well since the ink layer may not have the same elastic properties, and this differential could result in poor dry ink adherence. Lastly, the carrier film must have a low enough surface energy to permit transfer of the ink layer.

In the development of the ink layer, it is essential that laser energy be converted to heat to melt the ink layer and promote transfer of the ink layer to the substrate. For this conversion of energy, thermal convertors may be added to the carrier film, the ink layer or both. The thermal convertor may be added as a separate additive or be part of a prepolymer or resin. The particular thermal convertor was selected based upon the laser type used. In the case of carbon dioxide lasers, preferred convertors are carbon black, polyethylene glycol or talc. Several proprietary dyes are commercially available which can absorb neodymium:YAG laser radiation at 1.064 microns.

Without sufficient laser energy conversion, incomplete or no ink transfer occurs. Figure 4 shows an example of an incomplete ink transfer.

Figure 4. Sample print showing incomplete transfer due to lack of energy conversion.

The liquid ink formulations consist of at least one curable prepolymer or resin, colorant (dye or pigment), thermal convertor, catalyst or initiator, vehicle and various additives to improve coatability, print performance and durability. The liquid ink is applied to the carrier film using a web coating technique and dried to form the laser transfer foil. A generalized dry ink layer is as follows: prepolymer (25-95%), colorant (35-85%), thermal convertor (0.25-30%), initiator or catalyst (0.1-10%) and various additives (1-25%). The dry ink layer must be applied with uniform thickness on the carrier film and free of any defects such as dewets, pinholes or streaks. Defects of these types will show up in the transferred print. Since the semiconductor industry is marking identification codes, high print quality is required or the part will be rejected for mark quality resulting in costly remarking processes.

The laser transfer foils developed either had one or more layers with particular ingredients being present in any of the layers. Multilayer laser transfer foils contain a color coat which may be curable or noncurable in combination with a curable adhesion coat. These multilayer foils offer advantage in adhesion properties and improved transfer.

The laser transfer foil must be tack-free, non-blocking and resistant to cracking during manufacturing processes and customer use. Also, the laser transfer foil must be stable in regards to print performance and adhesion properties.

Figure 5 shows an example of a formulation with an acceptable print. In general, transfer requires between 15 and 22 watts of laser power with a pixel dwell time of 3.6-4.8 μsec.

Figure 5. Example of Optimized Laser Transfer Print

Conclusion

We have demonstrated that curable chemistry can be incorporated into a specialty digital printing technology. The transferable inks have high contrast and durability to a variety of solvents and abrasion. The laser thermal transfer inks have been successfully commercialized for use with our laser thermal transfer print engine.

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Biography

Lisa Siewierski is a Senior Research Chemist at Markem Corporation in Keene NH. She has a Ph.D. in Polymer Science from The University of Akron and a B. S. in Chemistry from the University of Wisconsin. Lisa has been involved in the development of UV and thermal cure inks for four years.