Electrostatic Printing of Functional Liquid Toners for Electronic Manufacturing Applications

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Abstract

Strategies for the making functional toners are examined as well as means to convert particulate images into solid structures. Limitations on the imaging and fusing process imposed by the substrates are reviewed. Examples of electronic components printed on glass, paper, and PET film are shown.

Finally the converting of amorphous silicon layers to the polycrystalline state for high performance transistors using a catalytic toner is presented. Also the Electrophoretic Self Assembly of silicon die using toner-imaging techniques is discussed.

Introduction

The advances in performance and the lowering of costs in silicon technology has made new mass markets possible that require inexpensive electronic interconnects (now called printing wiring boards) and inexpensive assembly techniques. In particular, it is ultimately desired to print the interconnect substrates and even print the components themselves (the resistors, capacitors, inductors, transistors, etc...). And finally to achieve the desired cost goals we would want to "print" these electronic products in a roll to roll manner.

Before we proceed further in the discussion of the role of toners in electronic manufacturing, we should answer these fundamental questions:

1. Do we take a dry toner or a liquid toner approach?
2. Must I print the solid phase of a material or is a filled resin adequate (like a silver filled vinyl)?
3. How do I convert the particulate image into a useful solid structure (fusing considerations)?
4. What restraints does my substrate impose on the process?
   A. Upper working temperature limit?
   B. Is aqueous post processing available?
   C. Must I have a room temperature process for reasons of high dimensional stability.

Answers to the Fundamental Questions

The first question, dry or liquid toner, depends upon a number of factors; the material conductivity & density, particle size and availability of commercial electrostatic printing devices that can be easily converted to industrial use.

For instance a dry particle, two component developer toner for decorating ceramic table ware is:

40% resin by wt
54% glass frit powder
6% pigment (colorant)
1% charge control agent
particle size, 15 micron

This was installed in a commercial dry toner copier and imaged onto resin coated "decal" substrates. This was successful.

But if you book at Table I we see various toner particles in reference to a dry toner resin particle of 10-micron diameter. Our goal in recent years has been to print relatively large and massive particles that require as large a charge on the particle as possible. Dry toner particles have between 5&10% of charged surface "activated" due to "tribo electrofication" with their irregular surface and that of the carrier surface; intimate contact is never possible. In a liquid system all the surface area is available for generating acid/base reactions on the liquid toner particle. Also if small particles are desired, below 1 micron; liquid toners are the only available approach because of lowered van Der Waals forces. In this paper we will focus on liquid toners.

The second question, must we print the solid phase of the material; or is a resin filled alternate allowed? In some situations a filled particle toner is all that is necessary; but for mass, future applications a solid phase (ie resin free after post processing) is required. For instance Kydd discloses a resin free solver particle liquid toner that delivers 20 to 30% of the conductivity of solid silver metal.[1] And with later processing, it can be processed at 125°C, compatible with PET films.

To print useful ferroelectrics materials and ferromagnetic materials any resin "defeats" the goal of obtaining a high dielectric constant or a high permeability. One could print carbon filled resin toners for resistor elements; but their accurate repeatability seems questionable.

The answer is; in some cases when the resin coating can be "baked away" coated particles are acceptable. These applications include phosphor toners for vacuum devices like cathode ray tubes glass frit toners for building "ribs" in plasma panels and solder powder toner as described in [2].

But for many systems printing the solid phase of a material (ie resinless) is the only option. Kydd discusses the printing of solid ITO material as a controlled resistor and solid ferroelectrics for capacitors 3. Unfortunately these require high temperature post processing; in the 400°C range, acceptable for glass substrate but not for films.

The third question, converting a particle image into a useful solid structure is very important. The conductive particles must form a continuous, high conductivity trace; the dielectric particles (when re-flowed) must form a pin-hole free dielectric layer. The ferroelectric and ferromagnetic particles must be consolidated into a void free solid to achieve a high effective permeability and high dielectric constant.

At the simplest level we might be able to heat the particles to re-flow them. If the particles are a filled resin, this is a relatively low temperature operation. But Sn/Pb solder re-flows at 230C, well above the working temperature of most polymeric substrates, and its electrical conductivity is only 5 to 10% os that of pure copper. If this level of conductivity is acceptable and polyimides are cost effective, then this could be a commercial approach.

Working with glass allows processing temperatures of 511 C for soda lime glass and in the 590 to 600C for the boro-silicate LCD glasses. Metal filled glass frits (i.e. hybrid circuit technology) can be made into toners and re-flowed at these temperatures. Some pure metals like zinc, which melts at 429C and has 29% of the conductivity of copper , are an interesting possibility.

Finally a new option to thermal re-flow or fusing as practiced in copy machines, are the Metallo Organic Decomposition (MOD) coatings as first disclosed by Robert W.. Vest of Purdue Uni. in the late 80's.[4] The strategy is to coat the particle with an organic compound of the "core" material, that upon heating or other chemical processing; decomposes to the core material which then sinters the particles together. This approach has been commercialized by Parelec LLC of Princeton, NJ. They offer a line of silk screenable inks of copper and silver. The silver inks can be printed on paper or PET and processed at 125C or lower; and yield 25% of the conductivity of solid silver! Note to traditional electro-photographers, like myself, fusing is no longer confined to pressure/thermal processes; a chemical dimension has been added. We will show samples of resin free silver toner printed on paper and glass; and silver ink silk screened onto the cover of a National Geographic Magazine.

The answers to the fourth question depend upon the substrate you desire to work with. Simple thermal limits are shown in Table 2. They range from 125C for PET films to about 600C for boro-silicate glass. Other considerations are important, like overlay accuracy for small feature size, multilayer structures. Finally can we employ aqueous post processing techniques like electroless or electroplating?

Table 1. Toners: Range of Size, Mass, and Materials

Material	Size (microns)	Density	Mass
Resin	1µ	1.0	.001x
Resin	5µ	"	.125x
Resin	10µ	"	1x
Metal	20µ	8.5	68x
Metal	60µ	8.5	1,800x
Silicon	400µ x 400µ x 50µ	2.42	10,000x

Table 2. Substrates

Material	Working Temp	Price
PET	125°C	$5/lb
PEN	150°C	$18/lb
PI	350°C	$80/lb
Paper	250°C	$0.5/lb
Soda Lime glass	511°C	
Borosilicate	593°C	$5/sq

A simple room temperature process is to print a catalyst seed toner,[5] then electroless plate it with whatever baths are commercially. Copper and nickel are widely used but other baths can be developed like Mo or chromium.

Finally in working with polymeric substrates, and desiring high levels of overlay accuracy (2nd layer to 1st layer, for instance), any heating of the substrate may not be tolerable. Typically heating of most films to the 100 to 125C range cause an irreversible dimensional change of 0.2% or more. That is 2mm for a 1 meter wide web! Necessarily these applications will require a room temperature process.

Conclusions

1. Liquid toners have advantages on their dry equivalents.
2. In limited instances, filled resin toner are allowed , but many applications require the solid phase of a material
3. MOD coatings that sinter at a low temperature are an alternate to thermal fusing.
4. Electroless and electroplating allow room temperature printing of high melting temperature metals.

Technical Discussion

What are some of the functional materials that are desired to be printed

a) Metals; Cu, Ag, Al, solder, Au.
b) Phosphors; EuO2, ZnS, etc.
c) Ferrites
d) Ferroelectrics, BaTiO3
e) Glass frits
f) Resins; color filters, etch resists, organic light emitters
g) Organic semi-conductors; pentecene
h) Indium Tin Oxide; resistor materials

Table 3.

Electronic Component	Feature Size Microns	Thickness Microns	Number of Layers
Metal line			
RFID	40	0.5	1
Plasma panel line	50	10	1
Printed Wiring Board	100	20	1
Resistor	50 X 500	2 –10	2
Capacitor	1 to 10 mm	10 –20	3
Inductor	2 to 20 mm	10 –20	3
Color filter	40 X 100	0.5 – 5	1
Etch resist	100	0.5 – 10	1
Plasma panel rib	100 wide, 100 high	NA	1
Organic transistor	20	0.5 – 5	4 to 5
Organic LED	40 X 100	0.1 to 10	1

Table 3 shows the typical dimensions, thickness and number of layers required in making the electronic parts typically desired.

Now, how do we make these materials into a useful liquid toner, with acidic or basic groups on their surface; to form couples with the charge director in the Isopar diluent?

For the glasses, phosphors, metals, ITO and other inorganics, we need to coat them with a disposable coating that can be removed in a post imaging step. MOD coatings can be applied to most metals(but not Al or Ti); the ferrites and ferroelectrics and ITO. The resins for color filter, etch resists, organic LED and organic semi-conductors don't need a coating to act as an effective liquid toner.

MOD Technology, Printing Pure Metal on Low Temperature Substrates

Kydd[1] disclosed a small silver particle coated with an organo-metallic of silver (silver neo decconaoate) where the organo-metallic acts as the charge control agent and imparts a negative charge on the particle. This was imaged and easily transfer to metal and dielectric surfaces (PET, glass, paper etc). Initially these toners required heating to 230C to chemically sinter them; though subsequent work has brought this down to 125C which is a useful working temperature for PET. Kydd (2) has also disclosed similar MOD coatings for ITO (a resister material) and BaTiO3 (a capacitor material) though in ink form but there is no reason to prevent the manufacture of useful toner of these materials.

Room Temperature Printing of High Melt Point Metals (1000c and Above)

To direct print useful, metals like copper, silver, gold, whose melt points are the order of 1000c, the only approach is to print a catalyst toner (typically palladium) and then electroless or electroplate it. Copper and Nickel are commercially available as electroless systems but Mo, Co and Cr should be easily produced. The steps in the printing process are utterly simple.

1. Print catalyst toner
2. Fix toner (mostly resin) in place
3. Electrolessly plate(or electroplate) to the desired thickness.

Electroless processes are typically slow and unable to produce thick layers (above 10 microns) of metal, of good quality. There are “brush” techniques for electroplating free standing, isolated conductive structures and we will show samples of such structures.

Printing Electronic Components

Referring to Table 3, electronic components; R,L&C and transistors are 2 to 5 layers devices. Liquid toners are uniquely suited for this task as then can be electrostatically transferred across a finite mechanical gap. We will show samples of such components.

Special Topics

Converting Amorphous Silicon to Poly Crystalline Silicon

Refer to Table 4 which shows the carrier mobility of various semi-conducting materials. The organic material pentecene, and amorphous Si have a mobility of 1 to 2.5 cm2/volt sec. Single crystal silicon has a mobility of 1000 and is considered useful for clock rates to 2 gigahertz. Polycrystalline Si has a mobility of 100 to 300 so the conversion of amorphous to ploy Si is immensely important. Fortunately there is a toner solution. If we print a palladium seed toner on an amorphous Si layer on glass, then heat to 500c for 30min the amorphous Si crystallized to the poly form. To date this remains a high temperature process but two major markets can benefit from it, liquid crystal panels (LCD's) which use borosilicate glass (to 600 C) and plasma panels (to 511 C). See Ref. 5.

Special Topics 2: Electrophoretic Self Assembly

RFID, radio frequency identification devices require the placement of very small silicon chips (400 micron x 400 micron x 50 micron thick) accurately on a web at high speed. Conventional pick and place technology (a vacuum probe on an x-y table) yields costs of 1 cent per chip, unacceptable for RFID.

Our approach is to take the finished RFID chip, coat it on one or both sides with a photo-imagable polymer that will act as a charge control agent. This chip now becomes a toner particle which can be placed in x, y, and Theta, and orientation; (obverse or reverse) on a substrate. While the technology is in its early stages, calculations show that electrostatic forces are 50x those of gravity, so possibilities of success are exciting. See Ref. 6.

Table 4. Semi-conducting Materials

Mobility: velocity/field,	cm^2/volt. sec
Silicon, single crystal	1.000
“ polycrystalline	100-300
“ amorphous	1
Cd Selenide. Crystalline	400
Organics	
Pentecene	2.5
P3HT	0.1
Other organics	.001-.03

Typical electronic part, critical dimensions and number of layers

References

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3. Detig, Kydd, & Richard; “Electrostatic Printing of Microstructures…” Proc NIP 15, 1999, pg 293-6.
4. Teng & Vest, “Liquid Ink Jet Printing with MOD Inks …”IEEE Trans, Components, Hybrids & Manufacturing Tech., Vol. CHMT – 12,#4, Dec. 87, pg.545-9
5. Fonash, Kalkin & Detig, US Pat 6,171,740 & 6,361,912.
6. Detig, PCT/US02/06279

Biography

Robert H. Detig founded Electrox Corporation in 1992 to apply electrographic imaging to technology as a manufacturing tool for various industries. He has some of the basic patents relating to the polymeric electrostatic printing plate. He has extensive experience in all aspects of the electrographic imaging process going back to his early years at Xerox. He has pioneered the concept of functional toners made of high density materials like metals and glasses; to be used in a manufacturing process.

He was awarded a PhD in Electrical Engineering from Carnegie Mellon University in Pittsburgh, Pennsylvania.