Electrokinetic Imaging: A New Electrostatic Printing Process for Liquid Toners

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Abstract

This paper describes a new printing/imaging technique for depositing liquid toner in which electrophoresis, in a non-aqueous medium, is used to fill the cavities of a masked substrate with functional toner. The substrate is laminated with a patterned mask that is capable of storing electrostatic charge. The mask material is similar to that used in the printed wiring board and flex circuit industries. The substrate is held in moderate proximity to a counter electrode between which an electric field will be established. The substrate/counter electrode assembly is immersed in a bath of functional liquid toner that is mechanically agitated. The substrate can be imaged in as little as 5 seconds, typically 15 to 20 seconds. The toner is a conventional liquid toner based on hydrocarbon diluents. The functional materials can be in the range of a few microns to 100 microns in diameter range.

Possible applications of Electro-kinetic imaging include any product where there is a need to build a microstructure like the ribs of a plasma display panel. Such microstructures include building of posts, spheres or cavities on electronic parts and the building of fine metal wiring structures. The process can be viewed more as a building process rather than one for printing micron thick ink layers, though it can operate in that region too.

Introduction

A grounded conductive substrate is laminated with a patterned mask that is capable of storing electrostatic charge. The mask material is similar to that used as an etch resist or solder mask in the printer wiring board (PWB) or flexible circuit industries. The trenched plate is held in moderate proximity to a counter electrode between which a voltage is established. The plate/counter electrode assembly is immersed in a bath of liquid toner that is mechanically agitated, for uniformity if necessary. The toner is a conventional liquid toner using Isopar G and industry standard charge director materials (typ. Indigo Imaging Agent). While our early work used a trenched plate, 75 microns thick; it is anticipated that conventional smooth surface plates with an image of high and low regions of electrical resistivity will also be successful.

A possible theory for the success of this process will be presented in which the bulk electrical conductivity of the Isopar plays a crucial role. Supporting data will be presented

An early commercial application of the process, the printing of solder powder toner for wafer "bumping" of silicon wafers, will be described. A finished silicon wafer (typically 200 mm or 300 mm in diameter) is laminated with a mask material that is patterned photo-lithographically. The resulting cavities in the mask are filled with solder powder, with a particle diameter 15 to 30 microns in diameter.

The toner is Type 5 or 6 conventional solder powder coated with a material that will impart an electrochemical charge to the particle, thereby allowing it to be imaged by electrical fields. The coated particles are dispersed in a linear aliphatic hydrocarbon (Isopar, TM Exxon) into which a polyelectrolyte is dissolved (the charge director material). Since the core particle is neutral to the process; virtually any material can be considered, regular 63/37 Sn/Pb, Pb free and high lead solders, other metals, glasses and ceramics, etc. Pictures of printed and reflowed bumps will be shown.

Apparently in this new imaging process the latent image is created by an external power supply (connected to the power grid), an electrostatic printing plate several orders of magnitude more insulative than the bulk resistance of the toner diluent which acts as a sophisticated charging mechanism.

Description of Electrokinetic Imaging

In this process a printing plate to be imaged consists of a conducting substrate coated with a photo polymer electrostatic printing plate (either liquid or dry film); the polymer material being patterned by exposure to actinic radiation in the region of 300 to 400 nm. In this embodiment of the process the printing plate is "trenched" by chemical development of the unexposed regions of the plate (i.e. image elements are trenches or holes in the photopolymer material). A counter electrode is held in modest proximity to the printing plate, typically a mechanical gap of 6mm across a plate/counter electrode dimension of 200mm. Between the two electrodes an electrical voltage is established to create an electric field to image the plate. The counter electrode is grounded and the substrate is driven to a positive voltage for negatively charged toners or negative voltage for positively charged toners. The printing plate/counter electrode is typically immersed in a bath liquid toner. If now a voltage of 400 volts pk-pk, triangle wave, 200 volts dc average is applied across the electrode sandwich fro 4 to 6 sec, the cavities of the printing plate are found to be filed with toner. The toner is 15 to 25 micron dia Sn/Pb powder, quite large by even dry toner standards.

While the process has been extensive studied using the "trenched" printing plate (US 6,815,130 B2), our understanding of the process suggests that a standard printing plate and an overcoated electrostatic printing plate will work equally as well. While the process as described previously is shown in the "reversal" mode or where the low potential regions of the image are developed; it should work in the normal development of the plate (i.e. the regions around the holes).

An Analysis of the Process

To begin to understand the physical processes involved in the imaging technology, consider the electrical filed in the 6mm gap filled with a true dielectric fluid (i.e. with no electrical conductivity) 600 volts divided by 6mm (or 6000 microns) yields a field of 0.1 volt/micron, about 10% of normal development fields in electrophotography. And one would expect almost uniform development of the entire printing plate, with slightly higher deposition on the mask than in the holes. But in fact there is no or small trace amounts of toner on the mask while the holes or trenches are filled with toner. This behavior is the opposite one would expect.

Now consider the actual experimental situation. The 6mm gap between plate and counter electrode is filled with toner which consists of Isopar G with solder powder at 120 gms per liter and a charge director to yield a bulk conductivity of the diluent at 5 pico siemems per cm. Figure 1 shows an equivalent circuit of the image process. C mask & R mask represent the capacitance and leakage resistive of the mask material which R dil is the resistivity of the toner diluent.

Typical numbers for these are:

$$R \text{ diluent} = 0.6 \times 10^{11} \text{ sc/cm}^2 \quad (1)$$

$$R \text{ mask} = 10^{14} \text{ to } 10^{15} \text{ sc/cm}^2 \quad (2)$$

$$C = 1/3 \times 10^{-10} \text{ f/cm}^2 \quad (3)$$

for a square cm of surface area. One can clearly see that the mask is "ohmicaly" connected to ground through the diluent and the surface of then mask charges with negative charges from the grounded counter electrode as in Figure 2. The mask charges up to substantially all of the applied voltage with a time constant T of C mask x R diluent or T=0.6 x 10^{11} sc/cm^2 x 1/3 x 10^{-10} f/cm^2, T=2 sec. The charged mask quickly draws like charged toner particles (in this case, negative) into the holes or trenches.

We have found, empirically, that the best excitation conditions are an offset a.c. voltage, typically a triangle wave, going always positive and of frequency of 30 to 100 hz. Note, this area of the optimum excitation is still open to further investigation. It deserves extensive further study.

In support of the "ohmic" charging of the mask, consider Figure 3 in a set of experiments a bath of clear diluent was prepared (no toner particles) with increasing amounts of charge director added to monotonically raise the conductivity of the bath. The mask was inserted into the bath for ten seconds with excitation applied (+400v pk-pk, +200 v dc; 100hz), then removed and the surface voltage of the mask was measured with a Trek electrostatic type voltmeter. On can see that mask voltage increased with bath conductivity until it saturates at an electrical conductivity above 5 pico mho/cm.

A further indication of the "ohmic" charging phenomenon is shown in Figure 4a+b. In Figure 4a we show an experiment in which a metallic vessel is the counter electrode (grounded) with the printing plate free standing in the middle of the bath. Note: toner the back of the plate or it will pick up toner in a random fashion. In Figure 4b we show another experiment in which the counter electrode is facing away from the printing plate. In this situation the plate images quite well, though toner pile height will vary if the plate charging voltage is not uniform due to differences in charging path length.

An Application of Electrostatic Imaging

The first application of electrokinetic imaging is in the printing of solder powder toner for wafer "bumping". A finished silicon wafer is flash coated with Al to protect the circuits from external voltage/fields etc. Solder wiltable I/O pads (called the under Bump Metallurgy) are not covered with aluminum but will "wet" with melted solder during a reflow step. The wafer is laminated with a 75 micron thick photopolymer mask that acts as the printing plate material. This is photo pattered leaving octagonal holes which are centered on the UBM pads. The mask is treated after patterning to raise its resistivity to about 3x10 14 ohm.cm. Details of this will be discussed in the next section of the report.

A photo of the washed plate, in this case a si wafer is shown in Fig. 5. The masked wafer is mounted in a fixture spaced 6mm from a counter electrode that is either a gold or copper coated aluminumdisc identical in diameter to si wafer, in this case 200 mm. This fixture is immersed in a tank of toner as shown in Figure 5. The counter electrode is grounded while the plate substrate is driven by a 400 v triangular ware, 200v dc average at 100 hz. Exposure time is two times 3 sec, with the wafer rotated 180 between exposures. Test results are shown in Figure 5 showing the holes in the mask completely full of toner particles and clean very low "background" particles, residual particles on the mask itself. The toner consists of type 5 solder powder (15 to 10u dia), 63/37 SnPb which is resin coated with a thin layer (approx1%by wt) of resin with strong acidi or hydroxple functionality. This material is dispersed in a diluent (typ. Isopar G) with less than 1% polyelectrolyte (the charge director) to impart an electrochemical charge to the particles. In this case an acidic resin yields a negative charge on the particles. See FM Fowkes et. al. for details of the liquid toner charging mechanism. Since solder powder has a density of 8.42 and the Isopar G a density 0.747, the solder powder quickly settles so continuous stirring or reverse rotation agitation is necessary to keep the toner particles suspended.

Conclusions

Electrokinetic Imaging is a new patterning process especially useful for printing very thick layers of toner or ink. It also allows the use of toner bath of relative high electrical conductivity and mask materials also of such low resistivity that they ordinarily would be unable to hold charge for very long.

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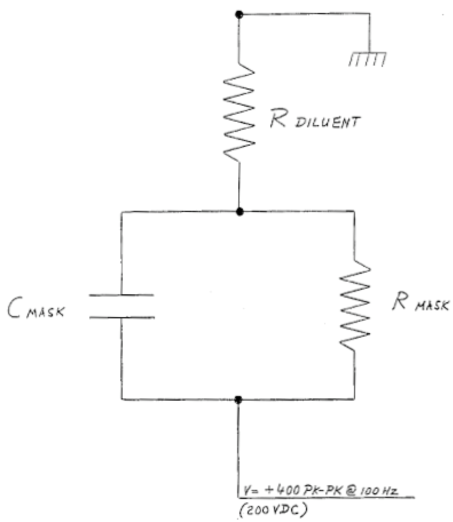

***Figure 1**. Equivalent Circuit of the Process*

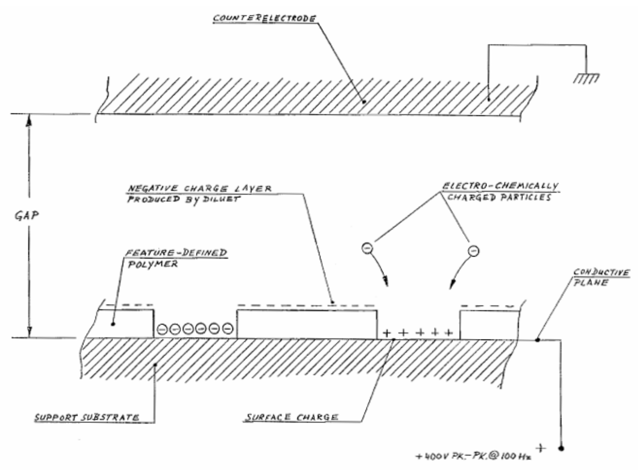

***Figure 2**. Schematic with Details of the Charging Mechanisme.*

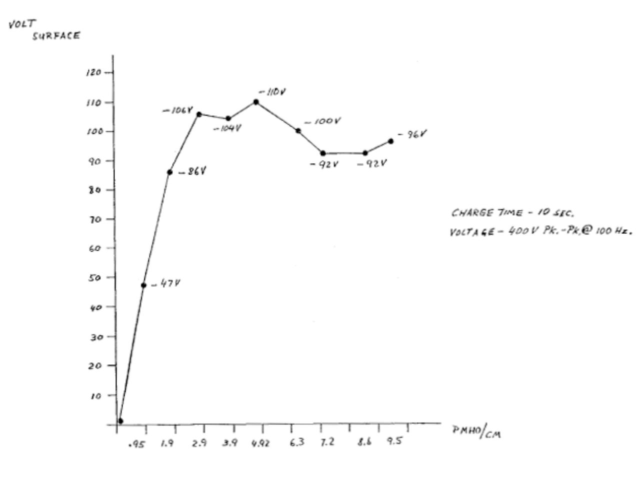

***Figure 3**. Test Showing the Charging of the Mask by the Toner Diluent*

References

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Author Biography

Robert H. Detig founded Electrox Corporation in 1992 to apply electrographic imaging technology as a manufacturing tool for various industries. He holds some of the fundamental patents on the photo-polymer electrostatic printing plates and functional liquid toners.

He was awarded a PhD in Electrical Engineering by Carnegie-Mellon University in Pittsburgh, Penna.

Dietmar C. Eberlein is Chief Engineer and a principal of the Electrox Corp. He has broad experience in all aspects of electrophotography, with extensive practical experience with liquid toners at Savin/Ricoh. He also worked at Olivetti USA and Minox Camera in Germany,. He holds a BS in Mechanical Engineering.

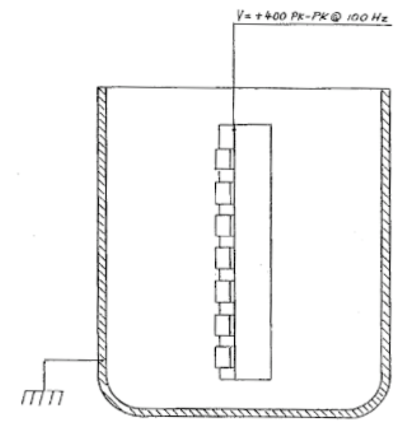

***Figure 4a** Test where Metallic Beakers is the Counter Electrode*

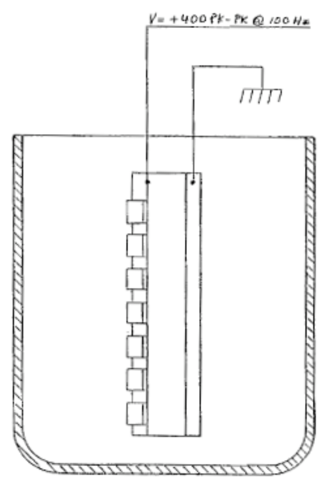

***Figure 4b**. Test where Counter Electrode faces "AWAY" from Masked Wafer*

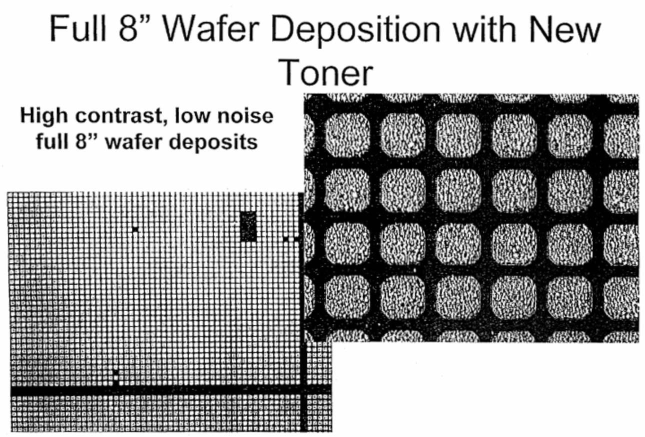

Figure 5. *Masked wafer with Cavities filled with Solder Powder Toner.*