

Process for Depositing Metallic Conductor Paths on a Glass
Channel Plate for Large-Screen Flat Panel Displays

The invention relates to a process for depositing metallic conductor paths on a glass channel plate for large-screen flat display panels, which has many channels extending parallel to one another, separated from one another by ridges, and provided with the conductor paths in the form of electrodes.

Modern large-screen flat display panels, so-called plasma display panels (PDPs) and plasma-addressed liquid crystal displays (PALCs) require a so-called channel plate made of glass in order to function. This plate is provided with channels formed by ridges, also referred to as barriers or separators, and has a defined number of vertically (for PDP) or horizontally (for PALC) extending conductor paths as address electrodes. These electrodes are deposited between the rib-shaped ridges, which in turn are made only after the electrodes have been formed or are formed in advance on the glass substrate. Fig. 1 shows a typical embodiment of such a channel plate.

The structure of modern flat panel displays, particularly the channel plates, is comprehensively described in the relevant literature.

Deposition of these address plates is problematic, not least of all because of the microstructuring of the channel plate - the distance between the rib-shaped ridges, i.e., the channel width, also referred to as pitch, is on the order of 100 to 600 μm .



JP 95-077892 describes a process in which the address electrodes are formed on the channel plate by the structured deposition of metalloid pastes by means of silk screen printing or other printing processes. The fundamental disadvantages of this prior art process is the inadequate resolution of the available printing processes and the high price of the metal-containing printing pastes, which prevent cost-effective manufacture of large-screen flat panel displays. Furthermore, this process is suitable only for depositing electrodes on flat glass substrates that have not yet been provided with ridges.

US-A 4,359,663 describes a process for depositing the address electrodes in the channels by sputtering the desired electrode material onto the glass substrate. A substantial disadvantage of this sputtering process is its high production cost due to high equipment investments and the relatively low substrate throughput.

The Japanese laid-open application JP-A H8-222128 describes a process for depositing electrodes on a channel plate for display applications by means of electroless and galvanic processes where the metallization is deposited non-selectively over the entire area of the display. Since the portion of the display area occupied by the electrodes ranges from 5 – 20%, the entire remaining 95 – 80% of the display area must be etched after full-area deposition in order to structure the electrodes. Thus, this process makes inadequate use of the metal content of the electroplating baths employed. As a result, metal-containing or heavy metal-containing waste is produced that has to be disposed of at high cost. Furthermore, this document concretely mentions only a single transparent conductive layer (ITO) as a base. This layer, however, can be deposited only by means of vacuum processes (sputtering or evaporating) so that the described advantages of metallization from the liquid phase partly fall away.

It is the object of the invention, based on this process, described also at the beginning of this document, to conduct the process so that it is more cost-effective, while reducing the consumption of metals being deposited, eliminating additional etching process steps and the related hazardous waste and refraining from the use of costly vacuum processes.

This object is attained according to the invention by a process for depositing metallic conductor paths on a glass channel plate for large-screen flat display panels, which has many channels extending parallel to one another, separated from one another by ridges, and provided with the conductor paths in the form of electrodes, having the steps of:

- roughening the channel plate, at least in the electrode regions of the channels to be coated with the metallic conductor paths by a combination of mechanical and chemical pretreatment;
- depositing the metallic conductor paths selectively only in the electrode regions of the channels by means of electroless and/or galvanic deposition processes, without employing laser beam technology.

The process according to the invention uses selective electroless metal deposition and galvanic metal deposition (with current applied), i.e., selective deposition from the liquid phase. Compared to vacuum processes (e.g., sputtering or vapor deposition), these processes are cost-effective since they require only low investments while offering high substrate throughputs. Furthermore, compared to high vacuum technologies, the clean room class requirements are substantially more relaxed. The process according to the invention attains these advantages, in particular, in that no full-area metallization takes place as described in the case of the above Japanese laid-open application, but that the electron paths [sic] are selectively structured on the glass substrate. This reduces the metal consumption by at least a factor of 10. Furthermore, no subsequent etching steps are required as is the case in the aforementioned process according to the Japanese laid-open application. With the elimination of these process steps, the process according to the invention also eliminates wastes containing metal or heavy metal that are very costly to dispose of.

In other technical fields, for example, when producing contact decks on flat electronic components such as LCD cells or conductor paths for microminiaturized circuits or the like, it is known per se to deposit structured metallizations on a substrate particularly by using laser beams.

Typically, large-area metallization is deposited and removed selectively by masking. However, these processes are not suitable for depositing electrodes for PDPs or PALCs since these applications require metallization of large areas with a 42 inch diagonal and more. In addition, structuring large-area substrates by a laser is not economical. Furthermore, the sides of the barrier ribs cannot be readily exposed by laser light so that it would not be possible to remove the protective layer as required. The production of PDP or PALC channel plates requires, however, that all metals along the sides of the rib-like ridges be completely removed.

EP 0 534 576 B1 furthermore describes a process for selective deposition of conductor paths on glass substrates for electronic circuits where a mask with the negative of the path structure that is to be deposited is brought into the beam path of an excimer laser. The laser beam emerging from the mask is directed onto a plane quartz glass substrate, the rear side of which is in contact with a reductive copper bath. This causes laser induced thin copper paths to be selectively deposited according to the desired structure. Since this process again requires the use of a laser, and moreover a special one, it is not suitable for large-area glass substrates such as channel plates. Furthermore, it requires expensive quartz glass to be used since only this type of glass is permeable for the light of the required excimer laser and thus permits the selective rear-side copper deposition.

In contrast to these methods, the process according to the invention advantageously uses only processes suitable for large surfaces without using vacuum technologies for the selective structuring of the address electrodes. Furthermore, the process does not require a transparent conductive layer as the base layer or quartz glass or a laser. In addition, the process according to the invention can be readily used for channel plates that are already provided with rib-like ridges or barrier ribs.

The process according to the invention is advantageous particularly for the channel structures of PDP/PALC panels since it also permits homogenous metallization of the channel walls.

Roughening of the substrate is also advantageous since it improves adhesion.

Furthermore, the invention permits the use of all metals and metal alloys that are suitable for deposition with or without application of current either as the sole material or in the form of multiple layers.

When producing printed circuit boards for electronic applications or glass substrates for electronic circuits, it is known from prior art (DE 44 38 799 A 1 and EP 0 083 458 B 1) to use selective electroless deposition to form metallic conductor paths to interconnect the components. However, these processes, known for about 10 years, are not readily suitable for the selective coating of the channels of channel plates due to the different dimensions and the different boundary conditions. Thus, they have not influenced the technology of depositing metallic conductor paths as electrodes on channel plates for large-screen flat-panel displays, which heretofore have been controlled by the principle of depositing large-area metallizations and then selectively to develop the conductor paths by means of masking techniques.

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US Patent 5,804,920 describes a channel plate for a PALC system with additional etching process steps for the selective production of metallic electrode paths, with all the disadvantages as have already been described in conjunction with the Japanese reference cited above, JP-A-H8 222128.

This reference says nothing whatever about roughening the electrode regions, nor does it provide any information about selectively depositing the metallic conductor paths by means of the claimed processes.

European Patent Disclosure EP-A 0 647 729 describes a process for depositing metallic conductor paths in the form of electrodes, and especially depositing a "black matrix" of a display device, in which the glass substrate is provided with a palladium-nucleated silane intermediate layer that is then structured using a pulsed laser, in such a way that a metal is deposited selectively electrolessly on the places not treated by the laser.

Although this known process does not require any etching or vacuum processes, still the treatment by means of a laser beam is absolutely compulsory. As already stated on page 4, paragraph 2, of the present specification, this laser process cannot be used in metallizing channel plates. This is because lasers cannot be employed economically to structure large-area substrates, which is the case for channel plates for large-screen flat display panels. Nor can the sides of the ridges be exposed readily with the laser; that is, the requisite selective removal of the silane layer from the sides of the ridges cannot be performed. Yet producing channel plates requires that the sides of the ridges be free of metal.

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Furthermore, this reference provides no answer to the question of adhesion of the metallic paths to the glass substrate. It can be suspected that the silane layer is also intended to perform an adhesion function. Nowhere in the reference, however, is any mention made of the claimed roughening of the channel plate in the electrode regions of the channels that are to be coated by means of a combination of mechanical and chemical pretreatment. All that the relevant prior art discloses is that an intermediate adhesion layer is applied, which is a completely different process from what is claimed. Professionals in the field have therefore taken a different course.

The claimed pretreatment is quite essential, however, for adhesion of the conductor paths, because surprisingly, by an additional chemical pretreatment along with the mechanical pretreatment, typically in the form of etching baths, better meshing of the metallic conductor path layer with the glass substrate can take place. This is surprising because conventionally, glass etching baths accomplish smoothing, instead.

The special pretreatment has the advantage that good adhesion of the electrolessly or galvanically deposited metal electrodes is attainable, since

- a purely mechanical roughening is often inadequate
- a purely chemical roughening, given the total layer thicknesses of only a few micrometers employed, is inadequate
- standard procedures for pretreatment in the printed circuit board industry cannot be used for glass substrates
- the selectively metallized glass substrates are subjected in the further course of processing to high temperatures (300 to 500°C), and extreme demands in terms of layer adhesion are thus made.

A number of methods are possible for structuring the conductor paths. Particular advantages are achieved if, according to a further development of the invention, first a thin conductor path is electrolessly deposited and is then augmented by galvanic or chemical deposition. It has proven to be advantageous if first a thin, full-area conductive layer is deposited as a starter layer, which is then selectively covered and selectively augmented galvanically and/or electrolessly on the intended surface of the electrodes. Finally, this thin full-area starter layer is removed again outside the electrode areas. Preferably, the electrode areas are selectively augmented with the help of a self-adjusting mask.

As an alternative, the process may be conducted by first depositing a thin, full-area conductive layer as starter layer, which is then structured by photolithography and subsequently augmented galvanically and/or electrolessly.

The conductive starter layer may be either a metal or a conductive oxide deposited at a maximum layer thickness of 500 nm, preferably at a layer thickness of maximum 200 nm.

A further advantageous embodiment of the process for depositing metallic conductor paths as address electrodes on a channel plate is achieved if, to prepare the selective structure of the conductor paths, the channel plate is initially structured by means of photolithography using a photo resist covering the entire channel plate and a positive mask corresponding to the conductor path structure. The photolithographically defined free paths are subsequently nucleated with palladium, the photo resist is then stripped in the other areas and finally, on the nucleated paths, the metallic conductor paths are deposited from the liquid phase

and provided with at least one protective layer. The method ensures adherent conductor paths using a relatively small quantity of metal.

Alternatively, the process may be advantageously conducted in that, to prepare the selective structure of the conductor paths, palladium nuclei are selectively deposited corresponding to the conductor path structure and subsequently the metallic conductor paths are deposited from the liquid phase onto the nucleated paths and provided with at least one protective layer.

Several options are feasible for the selective deposition of the palladium nuclei. According to one embodiment, ink jet technology is used to deposit the palladium nuclei. Alternatively, according to another embodiment of the invention, the palladium nuclei may be selectively deposited by etching or blasting the channel plate using a mechanical or photolithographically structured mask with openings corresponding to the conductor path structure. This roughens the uncovered path areas for selective nucleation from a palladium bath.

Another option of conducting the process consists in first covering the entire channel plate with palladium nuclei to prepare the selective deposition of conductor paths. Subsequently, the paths for the electrode structure are produced by selective deposition of metal in the paths by means of photolithography using a photo resist covering the entire channel plate and a mask. The photo resist with the palladium nuclei underneath it is then stripped in the other areas and the deposited conductor paths are subsequently provided with at least one protective layer. Full area palladium nucleation is not a continuous metal layer but merely a

distributed application of individual nuclei. Thus, at most a very thin full-area starter layer is needed, which is then selectively augmented as described above.

The term "photolithographic structuring" is to be understood as including the following steps: application of photo resist, exposure, development, etching of the substrate at the exposed locations and finally stripping of the photo resists (or similar processes such as lift-off).

To prevent reactions with the glass it is advantageous to apply a SiO_2 diffusion barrier over the entire area underneath the full-area palladium nucleation layer.

The process may be conducted particularly cost-effectively by using metals or metal alloys for electroless or galvanic deposition, which perform the function of transporting the current as well as the function of corrosion protection and sputter protection. According to a first embodiment of the invention, it is advantageous if the electrode material comprises nickel and/or copper in conjunction with a metallic corrosion protection, whereby the corrosion protective metal is one that can be electrolessly deposited, preferably nickel, palladium or gold. Alternatively, it is advantageous if the electrode material comprises nickel and/or a precious metal in conjunction with a metallic corrosion protection. In this case, the precious metal is a metal that can be electrolessly or galvanically deposited such as, for example, palladium, silver or gold and the corrosion protection metal is one that can be electrolessly deposited, preferably nickel, palladium or gold. With electroless deposition, the metals are present in a reductive bath. For example, if

copper is to be deposited, a reductive copper bath is provided, also referred to as “chemical copper,” which permits autocatalytic deposition of the metals.

The examples described below further explain the sequence of the process according to the invention and concretely illustrate its advantages.

Example 1 (Fig. 2)

A plane AF 45 glass substrate (100 x 100 x 3 mm³) is coated on one side with a positive resist (photo resist), e.g., (Shipley 1818) to a thickness of 2 µm and selectively exposed via a mask corresponding to the desired electrode structure (Step 1). After development, the substrate is dipped into an aqueous ammonium hydrogenfluoride solution for three minutes. This causes a slight chemical roughening of the glass surface to provide better adhesion of the metal on the glass. The glass substrate is mounted in a frame such that only one glass side is exposed to the liquid. The glass substrate is then dipped into a 5% hydrochloric acid tin(II)chloride solution, then rinsed for 30 seconds with distilled water and then dipped for one minute into a 0.05% hydrochloric acid palladium(II)chloride solution to initiate palladium nucleation (Step 2). The glass substrate is then rinsed under running distilled water for one minute. The photo resist is subsequently stripped by dipping into acetone. This leaves only palladium nuclei on the glass, which are required for further structuring of the electrode (Step 3).

The glass thus treated is dipped for one minute into a chemical nickel bath (Ni content 4.5 g/l, hypophosphite content 22 g/l, pH value 4.5) at a temperature of 70° C. This causes nickel paths to be selectively deposited at a thickness of 150 nm and a width defined by photolithography (Step 4). These conductor paths are dried at 200° C to achieve better adhesion. The glass thus selectively nickel-plated

is now dipped for 45 minutes into a chemical copper bath (Cu content 2.5 g/l, formalin concentration 37% 8 ml/l, pH value 8.2) at 40° C, which causes the deposition of 2.5 µm copper on the nickel (Step 5). The copper paths are now nickel-plated for corrosion protection. The substrate is dipped for 30 seconds into a 5% hydrochloric acid tin(II)chloride solution, then rinsed for 15 seconds with distilled water and subsequently dipped for 30 seconds into an activator (Pd content 50 mg/l, pH value 2). After rinsing with distilled water, the glass substrate is again dipped into the above chemical nickel solution for 5 minutes at 65° C, which causes a 1 µm thick nickel-phosphorous layer to form which serves as corrosion protection (Step 6).

Example 2 (still Fig. 2)

A glass substrate is again selectively provided with palladium nuclei as in Example 1, except that ink jet technology is used to deposit the palladium nuclei directly in a structured manner. The glass thus treated is then dipped for one minute into the previously described chemical nickel bath at a temperature of 70° C which causes the selective deposition of 150 nm thick nickel paths with the width defined by the printing technique (Step 4). After the printing process, the layers are thermally fixed at 200° C. The glass thus selectively nickel-plated is dipped for 45 minutes into the previously described copper bath at 40° C, which causes 2.5 µm thick copper layer to be deposited on the nickel (Step 5). The copper paths are now nickel-plated for corrosion protection. The substrate is dipped for 30 seconds into a 5% hydrochloric acid tin(II)chloride solution, then rinsed for 15 seconds with distilled water and subsequently dipped for 30 seconds into the activator mentioned in Example 1. After rinsing with distilled water, the glass substrate is again dipped for five minutes at 65° C into the described chemical nickel solution. This causes a 1 µm thick nickel phosphorus layer to

form which serves as corrosion protection (Step 6).

Example 3 (Fig. 3)

A plane D 263 glass substrate (100 x 100 x 3 mm³) is dipped for five minutes into an aqueous ammonium hydrogenfluoride solution for a slight chemical roughening of the glass surface to improve adhesion of the metal on the glass. The glass substrate is mounted in a frame in such a way that only one glass side is exposed to the liquid. The glass substrate is then dipped into a 5% hydrochloric acid tin(II)chloride solution, then rinsed for 30 seconds with distilled water and subsequently dipped for one minute into a 0.05% hydrochloric acid palladium(II)chloride solution to initiate palladium nucleation (Step 1). The glass substrate is then rinsed for one minute with running distilled water. Subsequently, the negative photo resist (3 μ m) is applied to the chemically treated glass side and structured with a corresponding mask (Step 2). The glass thus treated is then dipped for one minute into the previously described nickel bath at a temperature of 60° C. This causes the selective deposition of nickel paths with a thickness of 100 nm and a photolithographically defined width (Step 3). The glass thus selectively nickel-plated is dipped for 45 minutes into the previously described copper bath at 40° C, which causes 2.5 μ m of copper to be deposited on the nickel (Step 4). The photo resist and the palladium nuclei underneath it are now stripped by dipping into an aqueous alkaline solution (10% sodium hydroxide solution) that contains the complexing agent ethylenediamine tetraacetic acid (EDTA) at a concentration of 100 g/l (Step 5). The copper paths are then nickel-plated for corrosion protection, whereby the substrate is dipped for 30 seconds into a 5% hydrochloric acid tin(II)chloride solution, then rinsed for 15 seconds with distilled water and subsequently dipped for 30 seconds into the aforementioned activator. After rinsing with distilled water, the glass substrate is again dipped for five

minutes into the chemical nickel solution. This causes a 1 μm thick nickel-phosphorous layer to form which serves as corrosion protection (Step 6).

Example 4 (Fig. 4)

A plane AF 45 glass substrate (200 x 150 x 3 mm³) is coated by silk-screening with a mechanical resist (Step 1). The glass substrate thus structured is now subjected to a blasting process using aluminum oxide grains (Step 2). After blasting, the resist is stripped which leaves only the roughened structures produced by blasting on the glass substrate (Step 3). This produces channels with a depth of ca 5 μm . On the channel floor, the peak-to-valley height is 0.5 μm . The roughened glass substrate thus defined is dipped into a 5% hydrochloric acid tin(II)chloride solution, then rinsed for 30 seconds with distilled water and dipped for one minute into a 0.05% hydrochloric acid palladium(II) chloride solution to initiate palladium nucleation (Step 4). The glass substrate is then rinsed for five minutes with distilled water by means of a directed spray. This removes the nuclei from the non-roughened parts of the glass, while leaving sufficient nuclei in the roughened channel areas (Step 5). The glass thus treated is then dipped for one minute into the described nickel bath at a temperature of 60° C which deposits nickel paths with a thickness of 100 nm and the defined width (Step 6). The glass thus selectively nickel-plated is now dipped for 45 minutes into the aforementioned copper bath at 40° C which deposits 2.5 μm copper on the nickel (Step 7). The copper paths are now gold-plated for corrosion protection. The substrate is dipped for 15 minutes into a gold bath (gold content 3 g/l, pH value 4.6) at a temperature of 85° C. This causes selective deposition of a 100 nm thick gold layer on the copper (Step 8).

These examples show that the invention permits cost-effective deposition of the address electrodes onto the channel plates for flat panel displays and thus provides a process that is economical both in itself as well as based on the significantly reduced metal consumption due to the selective deposition of the metallic conductor paths.

Claims

1. Process for depositing metallic conductor paths on a glass channel plate for large-screen flat display panels, which has many channels extending parallel to one another, separated from one another by ridges, and provided with the conductor paths in the form of electrodes, having the steps of:
 - roughening the channel plate, at least in the electrode regions of the channels to be coated with the metallic conductor paths by a combination of mechanical and chemical pretreatment;
 - depositing the metallic conductor paths selectively only in the electrode regions of the channels by means of electroless and/or galvanic deposition processes, without employing laser beam technology.
2. Process according to Claim 1, characterized in that first a thin conductor path is electrolessly deposited which is then augmented by galvanic or chemical deposition.
3. Process according to Claim 2, characterized in that first a thin full-area conductive layer is deposited as a starter layer which is then selectively covered and subsequently augmented galvanically and/or electrolessly in the intended areas of the electrodes and finally the thin full-area starter layer outside the electrode areas is removed again.
4. Process according to Claim 3, characterized in that the electrode areas are selectively augmented by means of a self-adjusting mask.
5. Process according to Claim 2, characterized in that first a thin full-area conductive layer is deposited as a starter layer which is then photolithographically structured and subsequently galvanically and/or electrolessly augmented.

6. Process according to Claim 2, characterized in that first a thin conductive layer is selectively structured as a starter layer, preferably by ink jet technology and preferably by spraying metal-containing solutions, suspensions or pastes that are subsequently galvanically and/or electrolessly augmented.
7. Process according to one of Claims 3 through 6, characterized in that a metal with a maximum layer thickness of 550 nm is applied as the conductive starter layer.
8. Process according to Claim 7, characterized in that the layer thickness is 200 nm maximum.
9. Process according to Claim 3 or 4 or 5, characterized in that a conductive oxide with a maximum layer thickness of 500 nm is applied as the conductive starter layer.
10. Process according to Claim 9, characterized in that the layer thickness is 200 nm maximum.
11. Process according to Claim 1 or 2, characterized in that, to prepare the selective structuring of the conductor paths, the channel plate is first structured according to the conductor path structure by means of photolithography using a photo resist and positive mask covering the entire channel plate, then the photolithographically defined free paths are covered with palladium nuclei, subsequently the photo resist is stripped in the other areas and finally the metallic conductor paths are deposited from the liquid phase on the nucleated paths and provided with at least one protective layer.

12. Process according to Claim 1 or 2, characterized in that, to prepare the selective structure of the conductor paths, palladium nuclei are selectively deposited according to the conductor path structure and finally the metallic conductor paths are deposited from the liquid phase on the nucleated paths and provided with at least one protective layer.
13. Process according to Claim 12, characterized in that the palladium nuclei are deposited by means of ink jet technology.
14. Process according to Claim 12, characterized in that the palladium nuclei are selectively deposited by etching or blasting the channel plate via a mechanical or photolithographically structured mask with openings corresponding to the conductor path structures to roughen the non-covered path areas for selective nucleation from a palladium bath.
15. Process according to Claim 1 or 2, characterized in that, to prepare the selective deposition of the conductor paths, the entire channel plate is first covered with palladium nuclei, the paths for the electrode structure are subsequently produced by the selective deposition of metals in the paths by means of photolithography using a photo resist covering the entire channel plate and a mask, the photo resist together with the palladium nuclei underneath it is then stripped and the deposited conductor paths are subsequently provided with at least one protective layer.

16. Process according to Claim 1 through 15, characterized in that preferably an SiO_2 diffusion barrier is deposited over the full area of the channel plate, preferably underneath the full-area palladium nucleation layer.
17. Process according to Claim 1 through 16, characterized in that, for the electroless or galvanic deposition, metals or metal alloys are used which perform both the function of current transport and the function of corrosion protection and sputter protection.
18. Process according to Claim 17, characterized in that the electrode material comprises nickel and/or copper in conjunction with a metallic corrosion protection, whereby the corrosion protection metal comprises an electrolessly depositable corrosion protective metal, preferably nickel, palladium or gold.
19. Process according to Claim 17, characterized in that the electrode material comprises nickel and/or precious metal in conjunction with a metallic corrosion protection, whereby the precious metal comprises an electrolessly or galvanically depositable metal such as, for example, palladium, silver or gold and the corrosion protection metal comprises an electrolessly depositable corrosion protective metal, preferably nickel, palladium, chromium or gold.
20. Process according one of Claims 1 through 19, characterized in that the layers forming the electrodes are made as multilayered layers.

21. Process according to Claim 20, characterized in that the multilayered layers each comprise an adhesion promoting layer, an electrically conductive layer and at least one protective layer.