

1411600

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO
 ELECTROLUMINESCENT DISPLAY DEVICES

(71) We, WESTERN ELECTRIC COMPANY INCORPORATED of 195 Broadway, New York City, New York State, United States of America, a Corporation organised and existing under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to electroluminescent display devices.

The visibility of electroluminescent displays often is highly dependent on the contrast between the light emitting areas and the surrounding substrate.

Visibility is a subjective term generally used to indicate the degree of obviousness with which the human eye perceives an image, in this case, an electroluminescent display. Contrast ratio is the ratio of the luminance (brightness) of a display element to that of the surrounding background.

Electroluminescent display visibility is a direct function of the contrast ratio as the ambient illumination is increased and becomes strongly contrast dependent at high ambient light levels. Therefore, the background reflectivity surrounding the display element must be minimized so that reflected light does not compete successfully with the light emitting display element. Moreover, when the display element is not emitting light, the background should desirably appear similar to the light emitting regions both in hue and reflectivity in order that those portions of the light emitting region that are "off" appear invisible.

An alpha-numeric display containing light emitting diodes (LEDs) and silicon chips can be effectively fabricated on a ceramic or insulating substrate using conventional thin, or thick, film technology. The substrate which supports both the active components and the metallization used for interconnecting the light emitting diodes with the logic circuit on the silicon chip is typically a ceramic such as high density aluminium oxide. These materials are normally white or very light in colour so that although they meet the usual substrate criteria, the high optical reflectivity of the ceramic results in a low contrast ratio and less than optimum display visibility. It is also worth noting that the metallization itself is typically highly reflective, thereby reducing the display contrast, often to an extent comparable with that of the ceramic.

Various techniques are being used to improve visibility. A common technique is to provide an optical transmission filter selected to transmit only the light wavelength emitted from the display element. However, the realizable improvement in contrast is limited by the effective bandpass of the filter. If the filter transmission loss is increased to suppress ambient reflections from the ceramic, the brightness of the display suffers proportionately to the reduction in reflection.

Another approach is to blacken the ceramic, for example, by painting. This technique effectively reduces substrate reflectivity but is ineffective against reflections from the metallization applied later. In addition, the blackening process leaves the substrate surface rough and incompatible with high quality thin film processing.

The invention is intended to alleviate these difficulties. Accordingly, the invention provides an electroluminescent display device comprising a substrate having thereupon at least one electroluminescent element and having around the at least

one electroluminescent element light reflective regions in which the light reflective regions are covered with a photoresist material which is baked at a temperature sufficient to darken significantly the photoresist material so that reflection from the surface of the region(s) is inhibited.

The invention also provides a method of enhancing the contrast of an electroluminescent display device comprising a substrate having thereupon at least one electroluminescent element and having around the at least one electroluminescent element light reflective regions comprising applying to the light reflective regions a photoresist material and baking the photoresist material at a temperature sufficient to darken significantly the photoresist material so that reflection from the surface of the regions is inhibited.

The photoresist film is compatible with most of the bonding and encapsulation processes conventionally used and does not interfere with the display-observer optical link.

Conveniently, the film is a reapplication of the photoresist used for the metallization pattern, except that the mask is made such as to reveal only the bonding areas for the LEDs, the silicon chips and the interconnecting pads. With the photoresist layer in place, the substrate is heated beyond the recommended photoresist baking limit. The result is that the photoresist changes from its usual light brown colour to a deep, light-absorbing brown or black colour. At the same time, it becomes tenaciously adherent to the ceramic. This darkened photoresist layer remains in the finished device covering the regions surrounding the light-emitting regions thus enhancing the contrast of the display.

The step of heating the photoresist to darken its colour can occur at any stage in the processing. However, the process described in one embodiment includes the step of bonding the LEDs and the silicon chip to the substrate. This step includes a heating operation that is adequate to achieve darkening of the photoresist. Using this expedient, no additional heating step is required.

A specific embodiment of the invention will now be described by way of example and with reference to the accompanying drawings, in which:—

Fig. 1 is a perspective view of a metallized ceramic substrate prior to bonding of LEDs and integrated circuit components to make a finished display device; and

Figs. 2A to 2F are sectional views illustrating the processing of the ceramic substrate.

The problem of poor light contrast from conventional metallized ceramic substrates arises from the fact that the entire assembly (as shown in Fig. 1) is highly reflecting. Shown in Fig. 1 is a ceramic substrate 10, typically high density alumina, beryllia or similar stable refractory oxide or mixtures of oxides, carbides or other appropriate materials, and formed usually by compressed powder or glass forming techniques.

The ceramic is covered selectively with a metallized pattern 11. The portions designated 11a are seven bars to which the LEDs may be bonded; area 11b is a bonding area for the integrated circuit chip that provides the logic for the seven bar array, and areas denoted 11c are the bonding pads for interconnection. The metallization is typically gold but may be silicon, tungsten, molybdenum, aluminium or any other suitable conductor. Except for the regions 11a, which will be occupied by the LEDs and the region 11b that accommodate the IC chip, the remaining area, and the entire area immediately surrounding the light-emitting regions, is highly reflective.

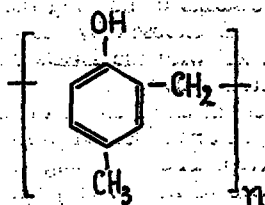
An exemplary processing sequence used to produce the substrate as it appears in Fig. 1 is schematically represented by Figs. 2A to 2C. Fig. 2C is a section of Fig. 1 at the plane indicated by line 2C—2C. Referring first to Fig. 2A, the ceramic substrate 10 is shown coated with a uniform metal layer 11. The metal layer 11 is masked with a standard photoresist mask 12, shown in Fig. 2B, and the layer 11 and mask 12 are etched so as to produce in Fig. 2C the metallized ceramic circuit board appearing in Fig. 1.

The added step, according to the embodiment of the invention, of covering the reflecting areas of the display support with a high contrast, light-absorbing coating is indicated by Figs. 2D and 2E. This step will be treated in detail because it is the point of departure from the standard process even though the photoresist technology on which it is based is also well known.

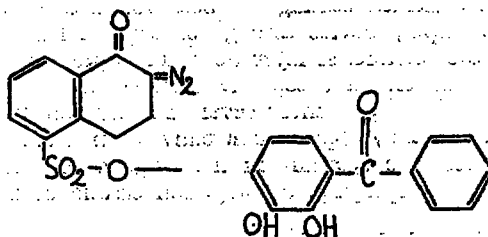
After all the photolithographic and etching steps have been completed according to standard routine and the resultant circuitry tested, the following process is applied to the entire ceramic substrate.

EXAMPLE I

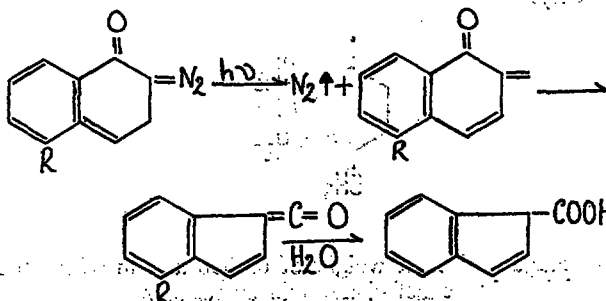
1. Immerse the entire substrate in boiling trichloroethylene for five minutes.
2. Rinse the substrate in deionized (D-I) water and ultrasonically agitate for minute.
- 5 3. While still wet from the D-I rinse, immerse the substrate in a passivation solution of 1 part ammonium persulphate to 10 parts D-I water for 5 minutes at 23°C. This treatment improves the adhesion of the metallization.
4. Rinse the D-I water (3 complete flushings) and ultrasonically agitate for 3 minutes.
- 10 5. Bake at 120°C for 30 minutes in nitrogen gas.
6. Blow clean with filtered nitrogen gas.
7. Immediately apply a photoresist film or place the substrate in a desiccator as adhesion of the photoresist film is degraded if the substrate is damp when the film is applied. The photoresist used in this example was an organic solvent solution of cresolformaldehyde resin with photodecomposable naphthoquinone diazide. The formaldehyde resin, 77% by weight, is:
- 15



The naphthoquinone diazide, 23 percent by weight, is:



- 20 The solvents are 81% ethyl glycol acetate, 10% xylene, and 9% n-butyl acetate. This is a positive photoresist that becomes soluble in aqueous alkaline developers after exposure to ultraviolet light. The change in solubility is a result of the photochemical decomposition of the diazide followed by rearrangement and hydrolysis:



- 25 8. If the substrate has been placed in the desiccator for short term storage, then the substrate is again blown clean with nitrogen before the film is applied.
9. All the photoresist should be filtered before use with a 0.8 μ membrane type filter.
- 30 10. The photoresist is applied to the substrate which is mounted on a turntable. The substrate is then spun at 600 rpm for 30 seconds in an enclosed vacuum hood.
11. The substrate with the uniform film approximately 8 μ thick is then baked

in a nitrogen ambient at 70°C for 20 minutes. The substrate then appears as in Fig. 2D with the photoresist layer shown at 13.

12. After visual inspection for cracks and poor adhesion, the film is exposed with ultraviolet light through a photomask for 4 minutes. The photomask is patterned to expose the areas where the photoresist is not wanted, i.e., the bonding regions 11a, 11b and 11c in the Figures. It may also be advantageous to leave exposed those regions between the bar segments to de-emphasize the delineation between the segments.

13. The exposed film is removed by aqueous alkaline developer and D-I water solution (1:1) by spraying and soaking for 2 minutes.

14. The substrate is then rinsed in $\approx 60^\circ\text{C}$ D-I water.

15. The substrate is dried in nitrogen gas and inspected for proper film removal.

16. The substrate is then thermally cycled in an air ambient to 350°C starting at 150°C with a slope of 50°C/5 minutes throughout the entire thermal cycle.

The resulting substrate is shown in Fig. 2E.

As a result of the thermal treatment, the photoresist layer assumes a deep brown colour, thus giving a high degree of contrast to the finished display.

The remaining processing consists of bonding the LEDs and the integrated circuit chips to the bonding pads left exposed by the darkened photoresist layer. The final assembly is shown in Fig. 2F with the LEDs denoted 14. The LEDs may be GaP, GaAsP or any other electroluminescent device.

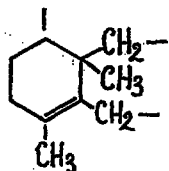
In one modification the thermal treatment is the step used for bonding the final elements of the assembly. Thus, in this modified process, the darkening of the photoresist occurs without an added step. The darkening of the photoresist has been found to occur at temperatures in excess of 200°C or preferably 300°C. The baking time to achieve optimum colour will be somewhat longer at this temperature. These temperatures are well in excess of the conventional temperatures recommended for post-baking of photoresist films. Excellent adhesion of the photoresist occurs with the change in colour. The darkened coating has been found to be scratch resistant and aids in protecting the display device through subsequent handling.

The thickness of the photoresist layer does not appear to be critical. Very thin photoresist films will take on an acceptably dark colour when heated sufficiently. Very thick films require longer, or more severe heating and are inclined to be less adherent (even though they may appear sufficiently dark) if the heat treatment is not adequate. Film thicknesses are typically in the range of 0.1 to 10 microns. Films can be applied by spinning spraying, dipping, roll casting or any other appropriate method.

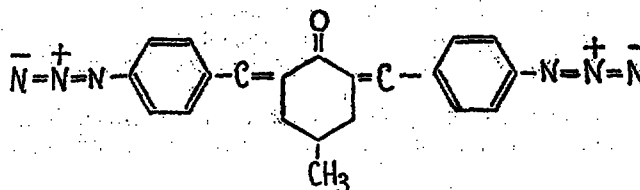
Coatings of a variety of photoresist materials were applied to ceramic substrates to demonstrate the uniform behaviour of photoresist materials when used for the purpose of the present embodiment of the invention.

EXAMPLE II

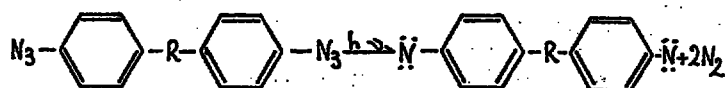
A high density alumina substrate was coated with photoresist by the technique described in Example I. The photoresist in this case was a xylene solution of the cyclized poly(isoprene):



having a number-average molecular weight of 65,000 and in which the photosensitive component is 2,6-bis(p-azidobenzal)-4-methylcyclohexanone



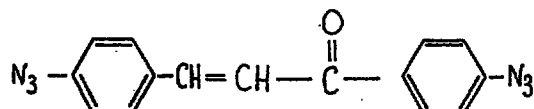
Photolysis of this azide results in the evolution of nitrogen and the formation of an active nitrene intermediate:



5 This nitrene is capable of coupling with the neighbouring poly(isoprene) either by hydrogen abstraction with addition or by an insertion reaction into either saturated or unsaturated carbon-carbon bonds. The net result therefore is classified as a negative resist. This resist is photosensitive to wavelengths between about 3500—4500 Å and can be exposed with a standard mercury arc lamp. An appropriate developer is a low boiling petroleum distillate, Stoddard Solvent and the rinse may be methanol. 10 The high temperature baking operation was the same used in the former example. The resulting darkened film was qualitatively equivalent to that obtained previously.

EXAMPLE III

15 Example II was repeated using another photoresist material, a xylene solution of poly(isobutylene) mixed with bifunctional aromatic azide compounds containing an azido-benzene group as:



20 This bifunctional agent links two of the poly(isobutylene) molecules by means of coupling reactions. This photoresist can be exposed with a mercury arc lamp and developed with Stoddard Solvent. A heat treatment at a temperature in excess of 200°C will darken the film and increase film adhesion in essentially the same fashion previously described.

25 Two other positive photoresists, consisting of solutions of cresol-formaldehyde resins with a photo-decomposable naphthoquinone diazide, were tested with the same qualitative results. While the mechanism responsible for the darkening of the photoresist film and the enhanced adhesion is not understood, the results are remarkably consistent. The several photoresist materials tested represent a cross section of the prominent photoresist materials known in the art.

WHAT WE CLAIM IS:—

30 1. An electroluminescent display device comprising a substrate having thereupon at least one electroluminescent element and having around the at least one electroluminescent element light reflective regions in which the light reflective regions are covered with a photoresist material which is baked at a temperature sufficient to darken significantly the photoresist material so that reflection from the surface of the regions is inhibited.

35 2. A device as claimed in claim 1, wherein the substrate is alumina.

3. A device as claimed in claim 1 or claim 2, wherein the light reflective regions over which the photoresist material is applied include light reflective metallic layers.

4. A device as claimed in claim 3, wherein the metal layer is gold, silicon, aluminium, tungsten or molybdenum.

40 5. A device as claimed in any one of the preceding claims, wherein the resist layer thickness is from 0.1 to 10 microns.

6. A device as claimed in any one of the preceding claims, wherein the light emitting elements are gallium phosphide light emitting diodes.

45 7. A method of enhancing the contrast of an electroluminescent display device comprising a substrate having thereupon at least one electroluminescent element and having around the at least one electroluminescent element light reflective regions comprising applying to the light reflective regions a photoresist material and baking the photoresist material at a temperature sufficient to darken significantly the photoresist material so that reflection from the surface of the regions is inhibited.

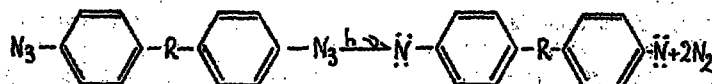
50 8. A method as claimed in claim 7, wherein the photoresist material is baked to a temperature of at least 200°C.

9. A method as claimed in claim 7, wherein the resist material is baked to at least 300°C.



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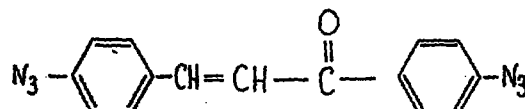
Photolysis of this azide results in the evolution of nitrogen and the formation of an active nitrene intermediate:



This nitrene is capable of coupling with the neighbouring poly(isoprene) either by hydrogen abstraction with addition or by an insertion reaction into either saturated or unsaturated carbon-carbon bonds. The net result therefore is classified as a negative resist. This resist is photosensitive to wavelengths between about 3500—4500 Å and can be exposed with a standard mercury arc lamp. An appropriate developer is a low boiling petroleum distillate, Stoddard Solvent and the rinse may be methanol. The high temperature baking operation was the same used in the former example. The resulting darkened film was qualitatively equivalent to that obtained previously.

EXAMPLE III

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Two other positive photoresists, consisting of solutions of cresol-formaldehyde resins with a photo-decomposable naphthoquinone diazide, were tested with the same qualitative results. While the mechanism responsible for the darkening of the photoresist film and the enhanced adhesion is not understood, the results are remarkably consistent. The several photoresist materials tested represent a cross section of the prominent photoresist materials known in the art.

WHAT WE CLAIM IS:—

1. An electroluminescent display device comprising a substrate having thereupon at least one electroluminescent element and having around the at least one electroluminescent element light reflective regions in which the light reflective regions are covered with a photoresist material which is baked at a temperature sufficient to darken significantly the photoresist material so that reflection from the surface of the regions is inhibited.

2. A device as claimed in claim 1, wherein the substrate is alumina.

3. A device as claimed in claim 1 or claim 2, wherein the light reflective regions over which the photoresist material is applied include light reflective metallic layers.

4. A device as claimed in claim 3, wherein the metal layer is gold, silicon, aluminium, tungsten or molybdenum.

5. A device as claimed in any one of the preceding claims, wherein the resist layer thickness is from 0.1 to 10 microns.

6. A device as claimed in any one of the preceding claims, wherein the light emitting elements are gallium phosphide light emitting diodes.

7. A method of enhancing the contrast of an electroluminescent display device comprising a substrate having thereupon at least one electroluminescent element and having around the at least one electroluminescent element light reflective regions comprising applying to the light reflective regions a photoresist material and baking the photoresist material at a temperature sufficient to darken significantly the photoresist material so that reflection from the surface of the regions is inhibited.

8. A method as claimed in claim 7, wherein the photoresist material is baked to a temperature of at least 200°C.

9. A method as claimed in claim 7, wherein the resist material is baked to at least 300°C.



10. A method as claimed in any one of claims 7—9, wherein the photoresist material is applied with a thickness of from 0.1 to 10 microns.

11. A method as claimed in any one of claims 7—10, wherein the electroluminescent device is bonded to the substrate by a bonding treatment which includes a heating step which is the same step as that of the baking of the photoresist.

12. A method of enhancing the contrast of electroluminescent display device substantially as hereinbefore described with reference to and illustrated in the accompanying drawings.

13. An electroluminescent display device substantially as hereinbefore described with reference to and illustrated in the accompanying drawings.

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