United States Patent [19]

Feldstein

[11] **3,878,061**

[45] **Apr. 15, 1975**

[54] **MASTER MATRIX FOR MAKING MULTIPLE COPIES**

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[73] Assignee: **RCA Corporation,** Princeton, N.J.

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[52] **U.S. Cl.** **204/11;** 204/281

[51] **Int. Cl.** **C23b 7/00;** B01k 1/00

[58] **Field of Search** 204/3, 4, 11, 12, 281

[56] **References Cited**

UNITED STATES PATENTS

2,765,230	10/1956	Tinklenberg	204/11
2,805,986	9/1957	Law	204/11
3,703,450	11/1972	Bakewell	204/281

Primary Examiner—T. M. Tufariello

Attorney, Agent, or Firm—Glenn H. Bruestle; William S. Hill

[57] **ABSTRACT**

The matrix comprises a highly polished degenerately doped silicon single crystal substrate having a layer of an inorganic dielectric thereon and a pattern of grooves in the dielectric coating, exposing the silicon surface.

9 Claims, 8 Drawing Figures

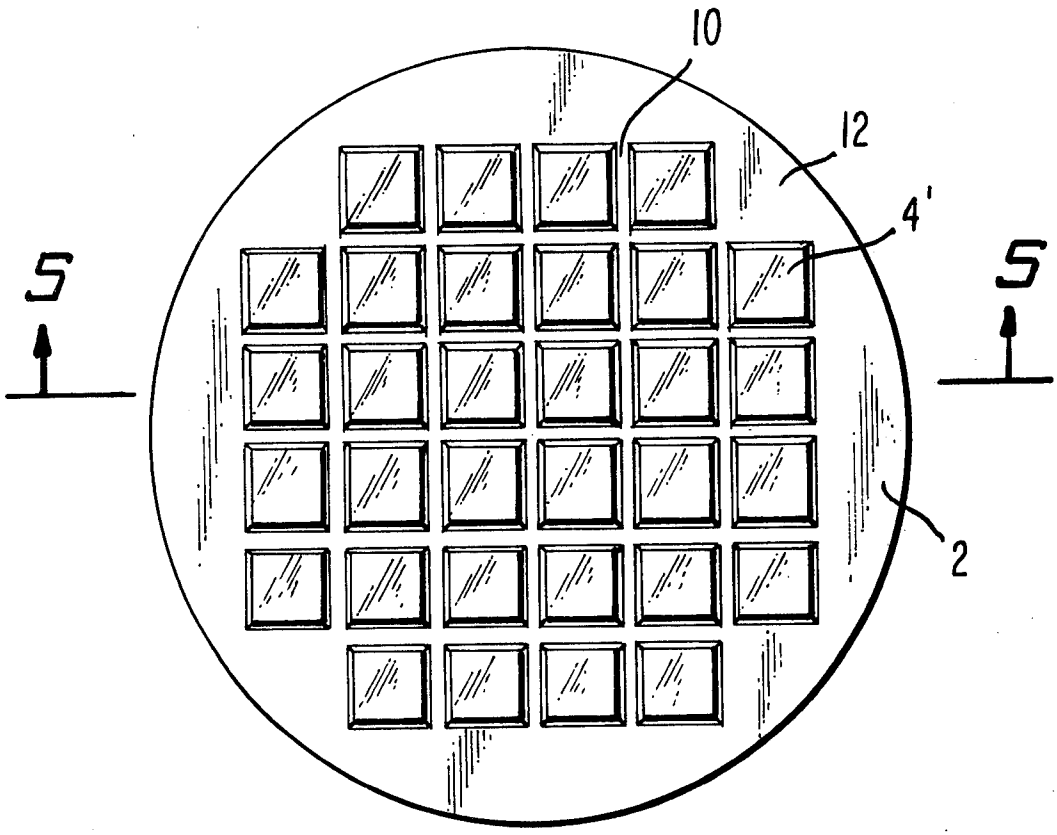
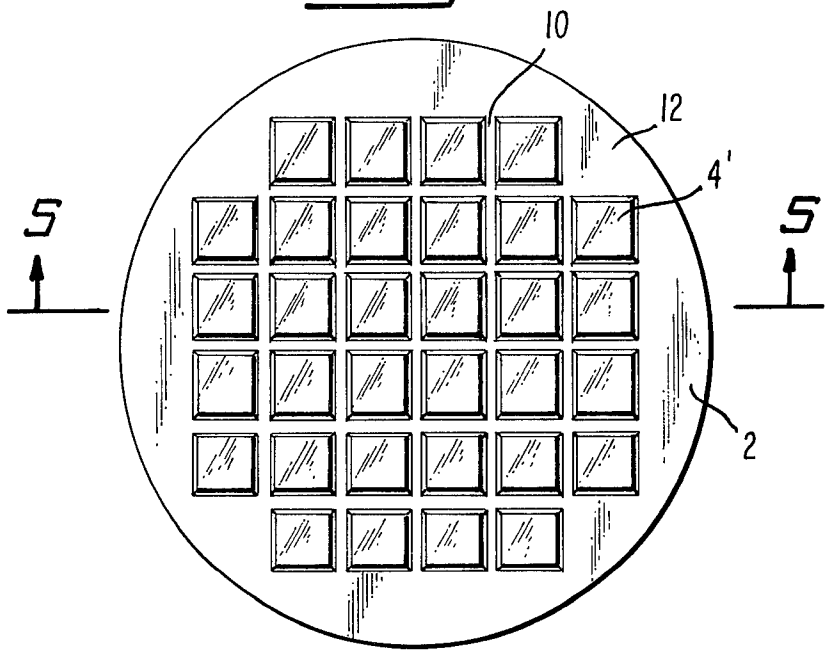


Fig. 1.



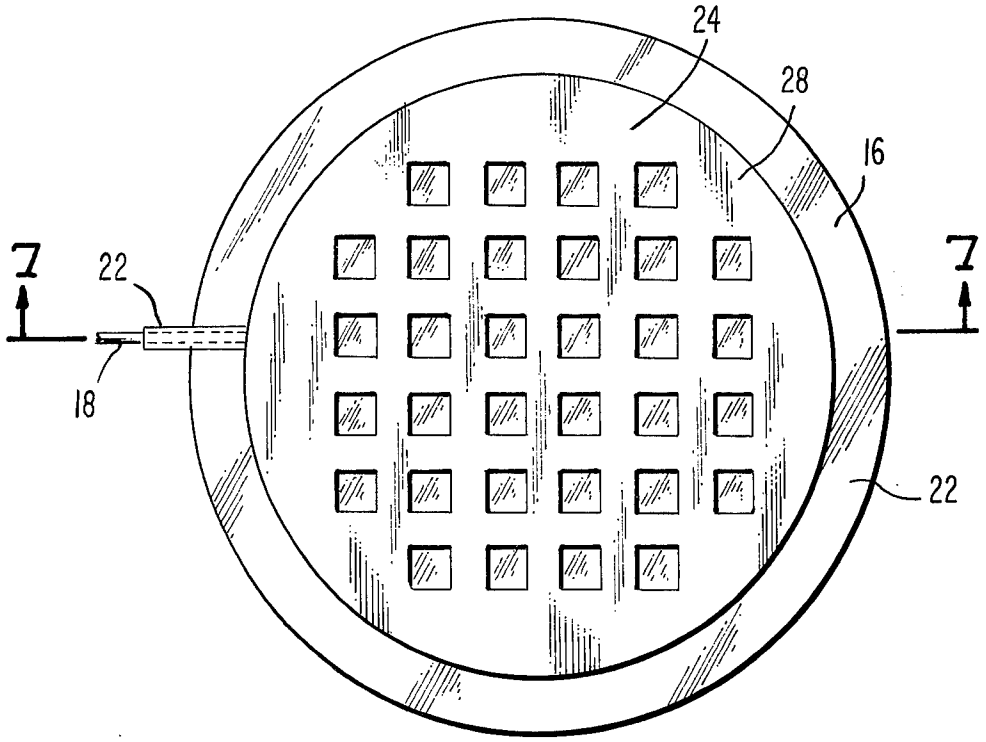


Fig. 6.

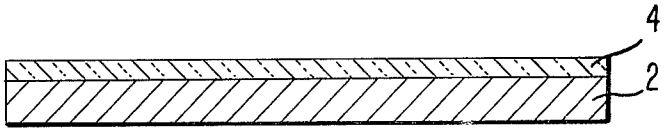


Fig. 2.

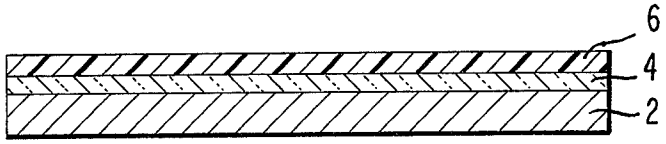


Fig. 3.

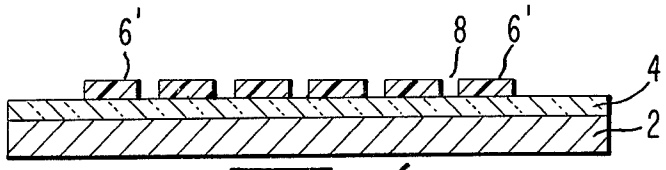


Fig. 4.

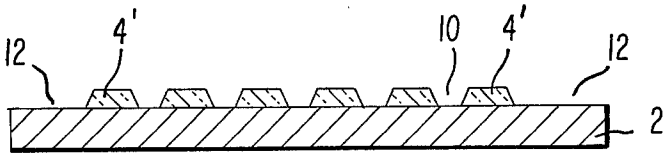


Fig. 5.

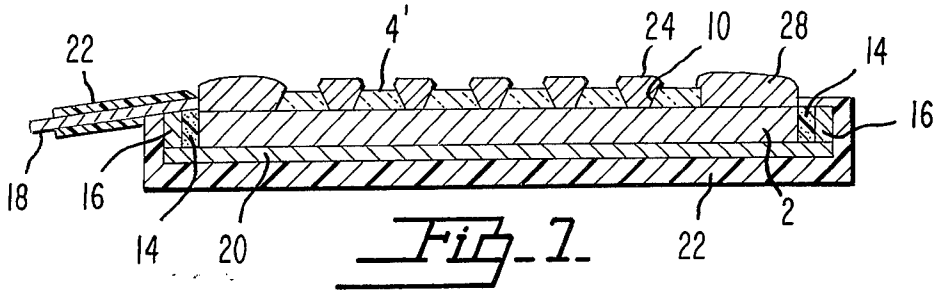


Fig. 7.

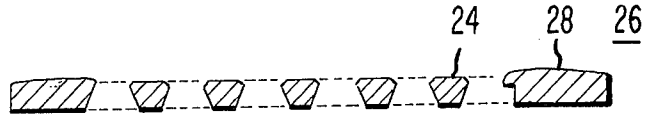


Fig. 8.

MASTER MATRIX FOR MAKING MULTIPLE COPIES

BACKGROUND OF THE INVENTION

Very fine mesh screens such as are used as the target electrodes in vidicon TV camera tubes are required to have a density of about 1,000 lines per inch. They must also have a high degree of mechanical perfection so that they will not introduce imperfections into the pictures displayed on the screens of TV receivers. The manufacture of such screens must therefore be carried out with unusual care. Also, in order to make these screens economically, it is necessary that a large number of screens be made from a single master matrix. This means that the master matrix must be durable enough to make hundreds of screen copies with little or no deterioration or change in dimensions.

Very fine mesh screens have previously been made by a number of different processes. One of these, which is described in U.S. Pat. No. 2,765,230, comprises the steps of:

1. Providing a copper plate as a substrate,
2. Nickel plating a surface of the copper plate,
3. Polishing the nickel surface to provide a good smooth finish,
4. Depositing a layer of a light-sensitive emulsion such as one comprising shellac, ammonium carbonate, ammonium dichromate and ammonium hydroxide on the polished nickel surface,
5. Exposing and developing the light-sensitive layer to form a grid pattern of grooves,
6. Depositing a very thin coating of wax over the entire surface of the grooved matrix,
7. Electrolytically depositing a metal in the grooves, and
8. Stripping the electroformed mesh from the matrix.

In this process, the matrix must be re-waxed each time after stripping the completed mesh article from the matrix. Also, the photoresist, being essentially an organic material, gradually deteriorates during each electroplating step, because of formation of hydrogen bubbles on the surface and because of the mechanical effects of peeling, and thus the lifetime of the matrix is undesirably limited.

Another process, described in U.S. Pat. No. 2,702,270, that has been used commercially for making very fine mesh screens, comprises ruling a gridwork of scratches or grooves in a glass plate substrate using a ruling machine such as used for making diffraction gratings, sputtering palladium over the entire grooved surface, removing palladium from the lands between the grooves by rubbing, electroplating a metal within the palladium-coated grooves and stripping the formed mesh from the matrix.

There are a number of disadvantages in using this process. The ruling must be done with great care. It therefore takes considerable time. A single imperfection may cause the entire master to be discarded. Hence the yield of good masters is quite low. Also no two masters are ever exactly the same since the ruling process is never identical from one substrate to another. Also, the palladium sputtering process must be done in vacuum and the master must be re-sputtered after every replica is made since the palladium adheres to the metal mesh when the screen is stripped from the substrate. A still further disadvantage is that the palladium on the lands between the grooves must be removed by hand, using a rubbing operation. This step requires a highly trained operator.

The present invention is an improved master matrix for making fine mesh screens comprising a substrate of highly polished single crystal degenerately doped silicon having on one surface a durable, adherent layer of silicon dioxide or other suitable inorganic dielectric, and a gridwork of grooves in the dielectric. A mesh screen is made from this matrix by electrodepositing metal, such as nickel, in the grooves and stripping the completed mesh from the matrix. Several hundred mesh copies can readily be made from a single master matrix.

THE DRAWINGS

FIG. **1** is a plan view of a completed master,

FIG. **2** is a section view taken anywhere through a matrix at an early stage in its manufacture,

FIGS. **3, 4** and **5** are similar section views illustrating successive steps in manufacturing a matrix, FIG. **5** being taken along the line **5—5** of FIG. **1.**

FIG. **6** is a plan view of the matrix of FIGS. **1** and **5** with metal deposited in the grooves to form a mesh screen,

FIG. **7** is a section view taken along the line **7—7** of FIG. **6,** and

FIG. **8** is a section view of a completed screen after it has been stripped from the matrix.

DESCRIPTION OF PREFERRED EMBODIMENTS

An example of a master matrix of the present invention (FIGS. **1** and **5**) comprises a disc-shaped substrate **2** of degenerately doped silicon and a gridwork of grooves **10** defined by isolated areas **4'** of an inorganic dielectric such as silicon dioxide. An annular region **12** around the periphery of the disc **2** is free of oxide.

The substrate **2** is a slice taken through a single-crystal boule of highly doped silicon having a resistivity of the order of about 0.01 ohm-cm. Silicon of this degree of resistivity is known as "degenerate" and is a relatively good electrical conductor. The material is readily available commercially in a form having a high degree of crystalline perfection. Thus the material is capable of taking a high mirror finish, which is one of the principal advantages of using this material in the invention. The diameter of the slice **2** is not critical and conveniently may be from 1.5 to 3 inches, for example. Thickness of the slice also is not critical but, for convenience in handling, it may be about one-eighth inch.

A polished surface of the silicon substrate **2** is provided with a layer **4** (FIG. **2**) of (as a preferred example) silicon dioxide having a thickness of about 1 μm. The layer **4** may be grown by oxidation of the silicon substrate in steam at 1,100° C for 4 hours. Thermally-grown silicon dioxide layers are dense, adherent and durable. They are also uniform in thickness and are of a high degree of perfection in terms of freedom from pinholes and thin spots. These properties are all advantageous in connection with the present invention. Somewhat less desirably, the silicon dioxide layer may be deposited by other well known methods such as evaporation or pyrolytic decomposition of a silicon compound. Other suitable inorganic dielectric materials are aluminum oxide and silicon nitride.

Next, a coating of photoresist **6** (FIG. **3**) is deposited over the entire surface of the silicon dioxide layer **4.**

Then, by conventional exposing and developing techniques, a gridwork of grooves **8** (FIG. **4**) is formed in the photoresist coating **6**, leaving isolated lands **6'** of photoresist. The photoresist layer **6** may be exposed using a photo-master (not shown) comprising a thin glass plate having a gridwork pattern of optically opaque chromium lines on one of its surfaces. The lines may have a width of 3μ. The grooves **8**, which are formed in the photoresist layer **6** also have a width of 3μ.

The masked layer of silicon dioxide **4** is then etched (FIG. **5**) using buffered hydrofluoric acid until the silicon dioxide beneath the grooves **8** is removed down to the surface of the silicon substrate **2**. Since the etching process normally results in forming tapered grooves, as shown in the drawing, stripping of the subsequently formed mesh is facilitated. After removal of the areas of photoresist **6'**, the substrate **2** is left with a gridwork of grooves **10** and isolated silicon dioxide lands **4'**. The silicon dioxide is also removed from an annular region **12** around the periphery of the silicon disc **2** and from the back surface of the disc. This is now a completed master.

The master is used to make mesh copies or replicas as follows. The disc **2** is prepared for an electroplating step by sandblasting the rim and back surface. The rim is then coated with a conductive layer **14** of silver-filled epoxy resin. A stainless steel ribbon **16** which is 10 mils thick is then pressed tightly over the conductive resin layer **14** and a tab **18** is provided to make an electrical connection to a plating cathode. The epoxy resin is cured at room temperature. The back surface of the disc **2** may then be coated with a layer of nickel **20**, for example by electroplating from a sulfamate type bath, to make better electrical contact to the disc and this coating is extended over the edge of the conductive epoxy rim layer **14** and the edge of the stainless steel ribbon **16**. All of the conductive surfaces except the bottoms of grooves **10** are then masked with a non-conductive epoxy resin layer **22**.

The grooves **10** are then filled with metal **24** by suspending the assembly in an electrolytic nickel plating bath and passing a current through the bath until the desired amount of metal has been deposited. Almost any conventional nickel-depositing bath may be used. A suitable bath for low-stress films may be prepared by mixing together 108 g of boric acid, 94 g of $NiCl_2.6H_2O$, and 4.4 liters of a nickel sulfamate concentrate containing about 140 g/liter of nickel metal, and this is then diluted to a total volume of 7.5 liters with water.

The bath is operated at 50° C and an initial current density of 30 amps/sq. ft. for about 4 minutes or until the light transmission through the mesh drops to 50%.

The metal **24** fills the grooves **10** to their tops (FIG. **7**) and then starts to spread over the tops of the isolated areas **4'**. Plating is discontinued when the metal has closed off the openings to the desired extent. The extent to which the metal is allowed to spread depends upon the requirements of the particular article being made.

Finally, the completed screen **26** is stripped from the matrix (FIG. **8**). A rim of metal **28** is left around the periphery of the screen for handling and mounting purposes. Optionally, a dilute ammonium bifluoride solution or a nickel etchant such as aqua regia or ferric chloride may be occasionally used to briefly treat the master after stripping the mesh.

The master can be re-used hundreds of times by rinsing it in water after each use, and then re-plating with nickel.

A particular advantage of the present invention in addition to those already mentioned (compared to the grooved glass method) is that during the electroplating step, current distribution is uniform over the area of the mesh being formed. In the older method, the sputtered lines of palladium offered considerable resistance to current flow, resulting in appreciable IR (voltage) drop. This causes non-uniformity of metal deposition.

A particular advantage of highly polished silicon compared to polished nickel, as described in U.S. Pat. No. 2,765,230, previously referred to, is that silicon passivates itself by rapidly forming a very thin oxide film on its surface on exposure to air. Thus, the electrodeposited nickel is stripped from the passivated surface with ease. When polished nickel was used as the substrate, a thin film of wax or other passivating substance had to be deposited before each electrodeposition so that the electrodeposited nickel could subsequently be stripped from the surface.

The present method has the capability of producing screens having 1,000 lines per inch or higher. Metals other than nickel (copper for example) can be utilized as the metal for making the screen.

Although the invention has been described as a master matrix for making fine mesh screens, it can take other forms and is especially advantageous where the article being duplicated includes very fine detail structure.

I claim:

1. A master matrix for making multiple copies of an article by electroplating metal in the grooves of a groove-patterned base substrate and stripping the formed article therefrom, comprising:

a substrate consisting essentially of a degenerately doped silicon body having a highly polished flat surface, said surface having a thin oxide film thereon,

an adherent layer of an inorganic dielectric material on said surface, and

a pattern of grooves in said dielectric layer such that said polished silicon oxide surface is exposed at the bottoms of said grooves.

2. A matrix according to claim **1** in which said dielectric is SiO_2.

3. A matrix according to claim **2** in which said SiO_2 is thermally grown.

4. A matrix according to claim **1** in which said article is a fine mesh screen and said grooves are in a gridwork pattern.

5. A matrix according to claim **4** in which said grooves are of the order of 3μ wide.

6. In a method of making a plurality of fine mesh screens as replicas from a single matrix, whereby

a metal is electroplated in a grid pattern of grooves in a dielectric layer on a base substrate of a master matrix to form a mesh screen,

said screen is stripped from said matrix, and

the electroplating and stripping steps are repeated,

the improvement comprising a matrix consisting essentially of a substrate of single crystal degenerately doped silicon having a highly polished surface, said surface having a thin oxide film thereon, a layer of an inorganic dielectric material on said

surface and a grid pattern of grooves in said dielectric layer exposing said silicon oxide surface.

7. A method according to claim 6 in which said metal is nickel.

8. A method according to claim 6 in which said metal is copper.

9. A method according to claim 6 in which said screen has at least 1,000 lines per inch.

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