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PATENT SPECIFICATION

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(54) ELECTRON SENSITIVE ACRYLATE RESIN

(71) We, THOMSON-CSF, a French Body Corporate, of 173, Boulevard Haussmann—75008 Paris, France, 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 resins sensitive to electrons, that is, resins capable of undergoing, under the action of an electronic irradiation to which a sufficient energy is imparted, a transformation which renders them resistant to certain chemical agents or insoluble in certain solvents. The invention also relates to a process for producing said resin.

It is known that in the production of electronic circuits, in particular in integrated microelectronics, the use of electrons permits the production of masks whose pattern is defined with a better definition than if photons were used as in conventional masking. Synthetic resins sensitive to electrons have consequently been produced. There is given hereinafter the sensitivity for electrons of 20KeV, of resins selected from among generally negative resins, which are the most sensitive known at the present time (the sensitivities being given for a quantity of 70% of resin transformed by the irradiation).

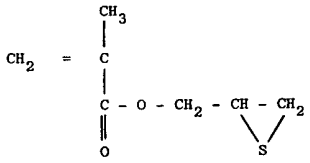
—resins having the commercial references KPR and KTFR (Kodak registered mark), sensitive to a quantity of electricity of 0.1 coulomb per square metre;

—polyvinylsiloxane: sensitivity of 0.05 C/sq.m;

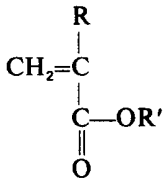
—glycidylpolymethacrylate: sensitivity of 0.01 C/sq.m.

The invention permits the obtainment of a resin which has a sensitivity about ten times higher than the best of the aforementioned resins and is easy to use as a negative resin. The new resin obtained has the required properties of adherence and resistance to the chemical agents to enable it to be used in the production of integrated circuits in microelectronics.

The resin according to the invention is a copolymer of 2.3 epithiopropylmethacrylate of the formula:



and an acrylate monomer of the general formula:



wherein R is an H radical or an alkyl group, $C_n H_{2n+1}$ with n an integer of 1 to 10, R' being an alkyl group having 1 to 5 carbon atoms.

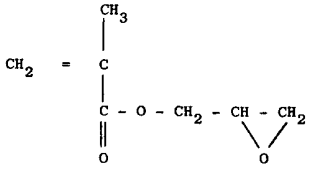
The proportion of acrylate monomers may range up to 15% to 65% by weight.

Among the acrylate monomers may be mentioned methyl methacrylate, butyl methacrylate and ethyl acrylate.

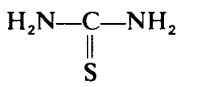
The ensuing description gives one manner of preparing the resin according to the invention, then an example of the process of utilization of this resin for obtaining a manufacturing mask.

Preparation of the Resin

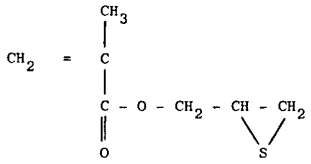
There is used as starting material glycidyl methacrylate of formula:



which is reacted at room temperature in a mixture of water and ethanol with thiourea of formula:



The reaction gives 2.3 epithiopropylmethacrylate of formula:



This compound is dissolved in ether. The solution is dried with sodium sulphate. The ether is removed under a vacuum and remaining product is distilled under a vacuum.

The epithiopropylmethacrylate obtained is mixed with an amount of vinyl monomer in a proportion of 15 to 65% by weight of the latter in a solvent such as benzene. Azobisisobutyronitrile is added which acts as a catalyst of copolymerization. The mixture is heated to 80°C under nitrogen for a period which may vary from one to several hours. After cooling, the copolymer is obtained by precipitation with methanol and then dried under a vacuum.

Process of Utilisation of the Resin

a) Principle:

The resin obtained is dissolved in a solvent such as methylethylketone. The solution is deposited on a substrate placed on a centrifuge device. Depending on the speed of rotation of the substrate there is obtained a layer of variable thickness for example from 0.2 to 0.5 micrometre. Heat treating at a temperature between 50°C and 80°C for half an hour eliminates the solvent.

The irradiation is carried out in an evacuated chamber by means of a beam of electrons the accelerator voltage of which is between 5 and 20 kilovolts for a time sufficient to absorb a charge density of between 10^{-3} and 5×10^{-3} C/sq.metre.

The resin is developed by means of a solvent such as acetone which dissolves the resin parts which are untrasformed by the irradiation (uncrosslinked).

A heat treatment of one to several tens of minutes at 120°C increases the properties of adherence of the resin for the purpose of the subsequent operations carried out by means of the mask obtained by development.

b) Example:

0.015 g of azobisisobutyronitrile is dissolved in a solution containing 7.6 g of epithiopropylmethacrylate and 2.4 g of methylmethacrylate in 30 millilitres of benzene.

The solution is heated at 80°C for an hour and a half under nitrogen. After cooling, the solution is poured into a mixture of methanol and hexane. The polymer precipitated is dried under a vacuum and then dissolved in methylethylketone to obtain a 10% solution of resin by weight.

This resin solution is deposited by centrifugation on a glass plate covered with a chromium layer: with a speed of rotation of 5000 r.p.m. a layer 0.38 micron thick is obtained. The plate is treated for half an hour at 80°C to eliminate the solvent.

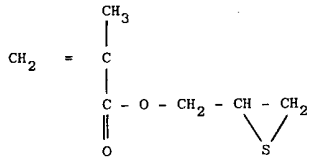
The irradiation is effected for example with a beam of 20 KeV and a charge density of 5×10^{-3} C/sq.m. The duration of the irradiation is calculated in taking into account the total quantity of charges flowing per second (current in amperes) and the useful area in square metres. The development is effected with acetone and lasts only half a minute. After annealing at 120°C for 10 minutes the plate is immersed in an alkaline solution of potassium ferricyanide for the engraving of the chromium.

The numbers of pairs of lines per millimetre which can be engraved with a mask obtained by the process employing the resin according to the invention is 500. The thickness of a line and the distance between two lines are of the order of a micron.

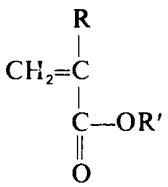
The invention is applicable to the production of masks of silica on a silicon semiconductor substrate and more generally to the engraving of a deposit of any nature on an integrated microelectronic circuit.

WHAT WE CLAIM IS:—

1. A resin sensitive to electrons which is a copolymer of 2.3 epithiopropylmethacrylate of the formula:



and an acrylate monomer of general formula:



wherein R is either an H radical or an alkyl group C_nH_{2n+1} with n an integer of 1 to 10,

R′ being an alkyl group having 1 to 5 carbon atoms.

2. A resin as claimed in claim 1, wherein R and R′ are CH_3 groups.

3. A resin as claimed in claim 1, wherein R is CH_3 and R′ is C_4H_9.

4. A resin as claimed in claim 1, wherein R is a hydrogen radical and R′ is C_2H_5.

5. A process for producing an electron sensitive resin, comprising the following steps:

a) reacting glycidyl methacrylate at room temperature in a mixture of water and ethanol with thiourea, the reaction giving 2.3 epithiopropylmethacrylate, this compound being then extracted from its solution in ether;

b) mixing 2.3 epithiopropylmethacrylate with an amount of acrylate monomer in a proportion of 15% to 65% by weight of the latter in a solvent;

c) heat treating the solution;

d) extracting the produced copolymer by precipitation with methanol, then drying it under a vacuum.

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