METHOD OF MAKING LARGE AREA NANOSTRUCTURES

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ABSTRACT

Present technology appears to be limited to incremental improvements in the slow speed formation of nanostructures on small areas.

A new method is described which enables the high speed (0.1 m^2 /sec) formation of nanostructures on large area surfaces (1 m^2). The method uses a "Supersebter", an acronym for super sub-micron electron beam writer.

The Supersebter utilizes a large area multi-electrode (Spindt type emitter source) to produce multiple electron beams simultaneously scanned to form a pattern on a surface in an electron beam writer. Spindt electrodes are well known and available commercially.

Proposed is a 100,000 x 100,000 array of electron point sources, demagnified in a long electron beam writer to simultaneously produce 10 billion nanopatterns on a 1 m^2 surface by multi-electron beam impact on a 1 cm^2 surface of an insulating material. The surface is coated with a monomolecular or monoatomic layer. The monomolecular layer is altered when the electron beam impacts the surface to form a +, -, or 0 charge pattern of adjacent charges. A multiple charge pattern is thus produced on a large area. The 1 cm^2 charge pattern is then stepped over the surface to form a 1 m^2 nanopattern in 10 seconds.

Metal is deposited at atmospheric pressure and temperature onto the negatively charged pattern area from an electroless coating solution. The pattern is then rinsed dried and protected in any manner. Successful implementation of this process will result in major advances in light/electric power conversion, HDTV, lasers, computers and telecommunications.

BACKGROUND

1. Field of the Use

This describes a novel monoatomic or monomolecular resist for use with a beam writer for the production of high resolution submicron circuit patterns on an insulating substrate.

2. Description of the Prior Art

The State of the Art of "Nanometer-Scale Fabrication" has been given with an excellent bibliography, as of 1982 [1]; wherein, it is stated on p. 3:

"...electron, ion and X-ray exposure....limitations of the resist...not those of the exposure system...set the ultimate limit on...resolution", and: "The most commonly used resist for high resolution (<100 nm or 1000Å) is (PMMA) polymerthylmethacrylate. A resolution of <50 nm or 500Å may be obtained with other resists...not well studied. "; and: "exposure of PMMA with a high intensity 50 KV field-emission electron beam source with a 20 nm. beam of 10^{-7} amps...takes 1 day (86,400 sec.) to expose a dense pattern on a 4" square (100 cm^2 or 10^{-2} m^2), with additional time for stage motion and alignment."

This is a speed of about 10^{-7} m^2/sec; and a resolution of only 500Å.

The use of reactive ion etching to produce localized probes 1000 Å apart is reported [2] but this resolution is also small enough, and there is no increase in speed.

For the manufacture of Lepcon™, Elcon™ and such devices this speed is too small; and the resolution not small enough. A speed of about 0.1 m^2sec and a resolution of 10Å is required, not obtainable with these prior art devices.

A 10 Å resolution is reported [3]:

> "Using a 1/2nm (5Å) diameter beam of 100 keV electron, we have etched lines, holes and patterns in NaC1 crystals at the 2 nm. (20Å) scale size. Troughs about 1.5 nm. wide on 4.5 nm centers and 2 nm dia holes have been etched completely through NaC1 crystals more the 30 nm thick." and "The scanning transmission electron microscope (VG Microscopes, Ltd., Model HB5) in operation in the National Research and Resource Facility for Submicron Structures at Cornell University can produce up to 1 nÅ of 100 kV electron in a beam dia as small as 1/2nm (5Å). This beam current density of 1/2 x 10^6 A/cm^2 means that it takes only 10μs to deposit a dose of 5 coulombs/cm^2 in the sample." and "Two types of materials...alkali halides and aliphatic amino acids...can easily be vacuum sublimated or evaporated as uniform thin films...readily vaporized by electron beams. Using 100 kV electrons a dose of about 10^3 C/cm^2 is sufficient to etch through 30 nm of L-glycine, while a dose of 10^2C/cm^2 is needed to etch through a similar thickness of NaC1."

In the latter reference the resolution is satisfactory but the speed is too slow. Recently (1986) there has been a report on a new X-Ray lithography device [4]. This article stated:

> Submicron lithography "using storage ring XRay sources may be closer...volume production...1990'2. A compact synchroton storage ring will be mated with a vertical stepper...will produce 12Å wavelength at 630 MeV energy level. When mated to a storage ring, the XRS should have a resolution of 0.2μm (2000Å)...alignment accuracy to within 0.1μm (1000Å). The stepper will expose wafers up to 8 in. (0.2 m) dia.

A Field-Emission Scanning Transmission Microscope (STEM) has been described [5.1]. A field emitter is employed to produce an emission area having a diameter of 30-300Å. One magnetic lens with a short focal length and low spherical aberration, is used to demagnify this source to a resolution of 2 to 5Å on the specimen surface. The field emission gun and lens is mounted in an ultrahigh vacuum vessel that operates, at 10^{-8} to 10^{-7} Pa. When a short focal length lens is utilized to keep the system compact, aberration may be compensated by a "stigmator".

In these Prior Art Devices the speed is too slow for the rapid production of devices for the Lepcon™ - Elcon™ devices.

DEFINITIONS

ELCON™ A trademark for a submicron array of dipole antennae on a sheet which emits light photon power by transducing the equivalent input electrical power from a direct electric current input; thus directly converting input electric power per unit area to output light, power per unit area (watts/m^2). The light is emitted from the sheet as a parallel laser beam of a particular color or frequency. With its electric vector parallel to the long axis of the antenna. [39]

LEPCON™ A trademark for a submicron array of dipole antennae capable of receiving and transducing light photon energy $\varepsilon = hv$ into its equivalent electron energy $\varepsilon = Ve$ as direct current; thus directly converting light power per unit area (photons/sec-m^2) to electric power per unit area (watts/m^2). Randomly polarized light photons are resolved. Two orthogonal antennae arrays totally absorb and transduce the randomly oriented incident photons. In bright sunlight the electric power output is about 500 watts at 80% efficiency. [37]

SUPERSEBTER™ An acronym for Super Submicron Electron Beam Writer for the rapid fabrication of submicron arrays for LEPCON™ or ELCON™ devices, or other submicron circuits.

Strip: A metal electrical conductor coated or deposited on an insulating surface in the shape of a long narrow parallelpiped.

OBJECTS

Objects of this work are to provide a process and an apparatus for the manufacture of submicron circuits which have:

1. a high speed (about 0.1 m^2/s)
2. a large area (1 m^2)
3. a high resolution (less than about 5Å)
4. a low cost (less than \$250.00/m^2-1986 prices).

DISCUSSION

The present device may be employed for the rapid manufacture of submicron circuits as hereinabove set forth.

These devices comprise single crystal metal strips of Copper, Aluminum, or the like; in which, an energetic electron provided by direct conversion from photon energy travels freely in the metal for distances of about 10,000Å without collision with an impurity atom; and, hence without energy loss.

The strips may be for example 600Å long, separated by a "tunnel-junction" gap of 28-35Å, the width of the strip may be, for example, 30Å.

In the formation of this structure a single scan with a 30Å dia. electron beam may be used. The electron beam is preferably shaped with a square or rectangular section to provide a constant gap of about 30Å between successive in-line strips.

1. A small diameter image is formed from the electron emitter array by a demagnifying lens.
2. One or two long focus electron lenses of the magnetic or electrostatic type are used resulting in negligible aberration.
3. A large aperture lens may be used; to 30mm.
4. The focal length of the lens is 2.5m to 20m. compared to about 2.5cm in a standard SEM.
5. A plurality of images of the electron emitter array is simultaneously imaged onto the work surface.
6. Writing speed is increased by the simultaneous scanning with a plurality of electron beams. For example: 2 x 10^9 electron beams are scanned simultaneously to imprint the same number of identical patterns.
7. The pattern is imprinted by an electron beam impinging on a surface coated with a monoatomic or monomolecular layer, which may comprise an electric double layer. The electron beam breaks the chemical bonds, changes the chemical or electrical characteristics, or ablates the layer. Prior art masking layers were usually about 300Å thick. The layer used herein is only 1/2% to 10% of the thickness of prior art coatings. Consequently the present method is more efficient than prior art methods, requiring considerably less electron beam energy per unit area, and will accurately imprint nanostructures.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a cross section through a plate surface having no free electric surface charges.

FIG. 2 shows a cross section through a glass plate having a surface electrical double layer, with the negative charges on the outside of the layer, with no pattern impressed.

FIG. 3 shows a cross section through a glass plate having a surface electrical double layer, with the positive charges on the outside of the layer, with no pattern impressed.

FIG. 4 shows a cross section through a glass plate having a surface electrical double layer, with a pattern impressed by a reversal of the sign of the charge layer.

FIG. 5 shows a cross section through a glass plate having a surface electrical double layer, with the negative charges on the outside of the layer, a pattern being impressed by an electron beam onto adjacent areas of the surface which are thereby charged or not charged.

FIG. 6 shows a cross section through a glass plate having a surface electrical double layer, with the positive charges on the outside of the layer, a pattern being impressed by an electron beam onto adjacent areas of the surface which are thereby charged or not charged.

FIG. 7 shows a cross section through the glass plate and a back electrode, located in a Supersebter during pattern inscription with an incident electron beam.

FIG. 8 diagrammatically shows the generalized process steps of submicron pattern deposition along a production line on the OX axis of the Supersebter™, according to Process A.

FIG. 9 diagrammatically shows the generalized process of submicron metal pattern deposition along a production line on the OX axis of the Supersebter™, according to Process B.

FIG. 10 diagrammatically shows an Ion Beam Coater.

DESCRIPTION OF THE PRODUCTION PROCESS

Generalized production processes for the manufacture of submicron circuits on a plurality of substrate sheets are shown diagrammatically in FIGS.8 and 9. The main or first vacuum tube 24 of the Supersebter™ is along the OZ axis. One or more vacuum tubes 53, 54 and atmospheric pressure processing stations 51, 52 are located along the OX axis. The Production line 61, driven by the stepping motor 62 enters from the left at Station 1, and leaves at 59, Station n, to finished sheet inventory, circulating continuously. In the two production processes described herein, Process A and Process B, substrate sheets, usually glass plates, are supplied from stock 50 to a production line 61. Both Processes include the step of electron beam writing a pattern on the surface of the sheet using the Supersebter™ electron beam writer described herein.

In the generalized process, Station x refers to a processing step at position x. Referring to FIG. 8, the substrate sheet is loaded from stock 50 onto the production line 61 at Station 1. Several processes, hereinafter described, may be employed at atmospheric pressure from Stations 2 to h. The sheet enters the second tube 53 through the first air locks at Stations h + 1, h + 2, h + 3; respectively, the first low, medium and high vacuum airlocks 55. Vacuum treatment steps are located from Stations h + 4 to Station j - 1. The electron beam writer step, located at Station j, creates a pattern on the surface of the sheet. This pattern may include a gap for example 15-30Å, used for an asymmetric tunnel junction. Further treatment steps may occur at Stations j + 1 to k - 3. Stations k - 2 are second airlocks 56, which restore the sheets to atmospheric pressure. In Process B Stations k + 1 to m - 1 at 52 are at atmospheric pressure for several wet process steps such as the application of electroless metal sensitizing and metal deposition solutions, rinsing and drying.

Next, the sheets may enter airlocks 57 at m, m + 1 and m + 2. At Station m + 3 the deposited metal may be crystallized to single crystal areas. (As shown in Tables I, II, III). Then, using the ion-coating device shown in FIG. 10, the metal pattern is coated with high and low work function materials respectively at opposite faces of a gap in the deposited metal pattern. At Station m + 5 the entire pattern is coated with an insulator coating as described in Section 08.7. After passing through the fourth airlocks 58 at Stations n - 3, n - 2, n - 1, n the sheets pass from the third tube into the atmosphere and are removed from the production line to finished sheet inventory 60. The production line 61 circulates back to the start, and the process is intermittently continuous.

Two basic Processes A and B are described below:

FIG. 1

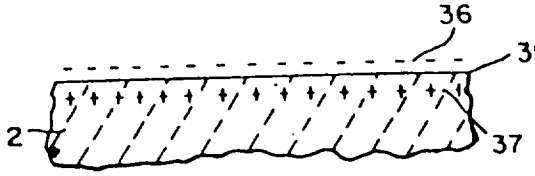


FIG. 2

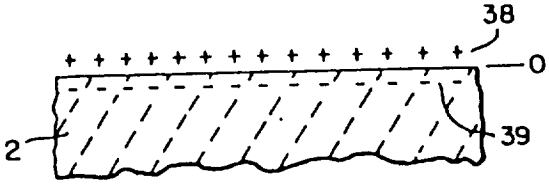


FIG. 3

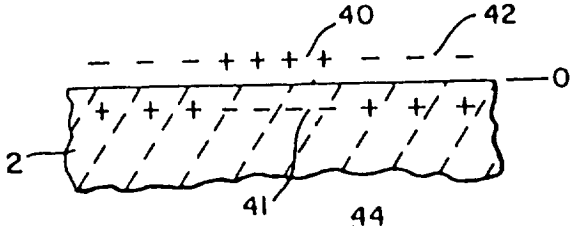


FIG. 4

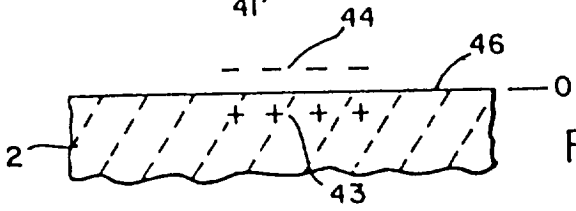


FIG. 5

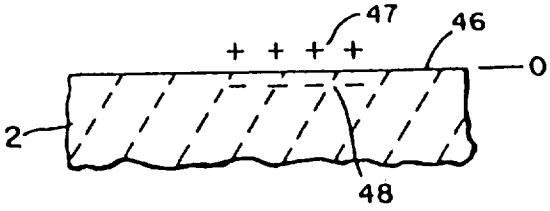


FIG. 6

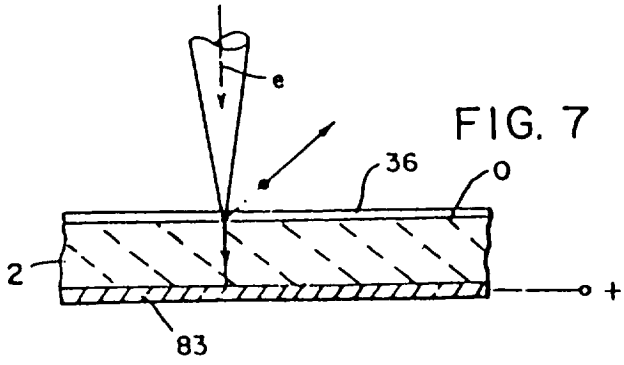
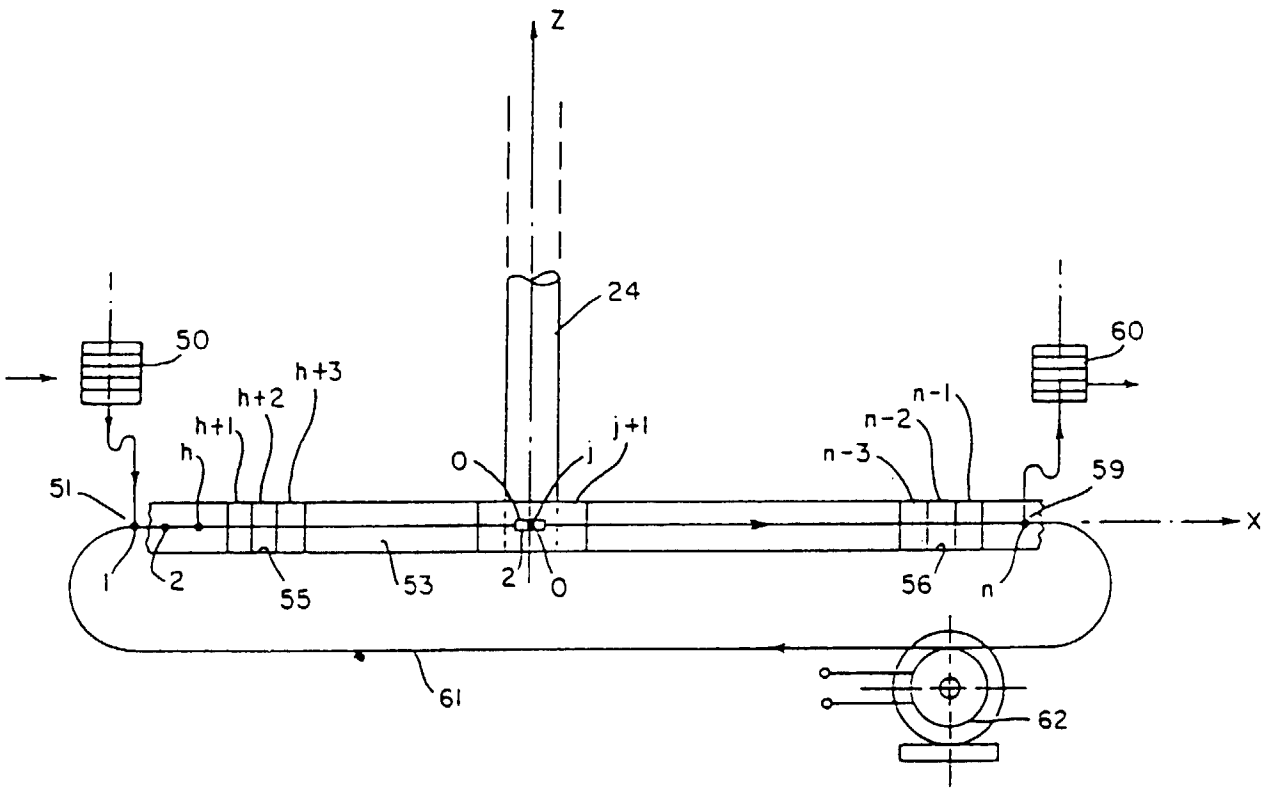
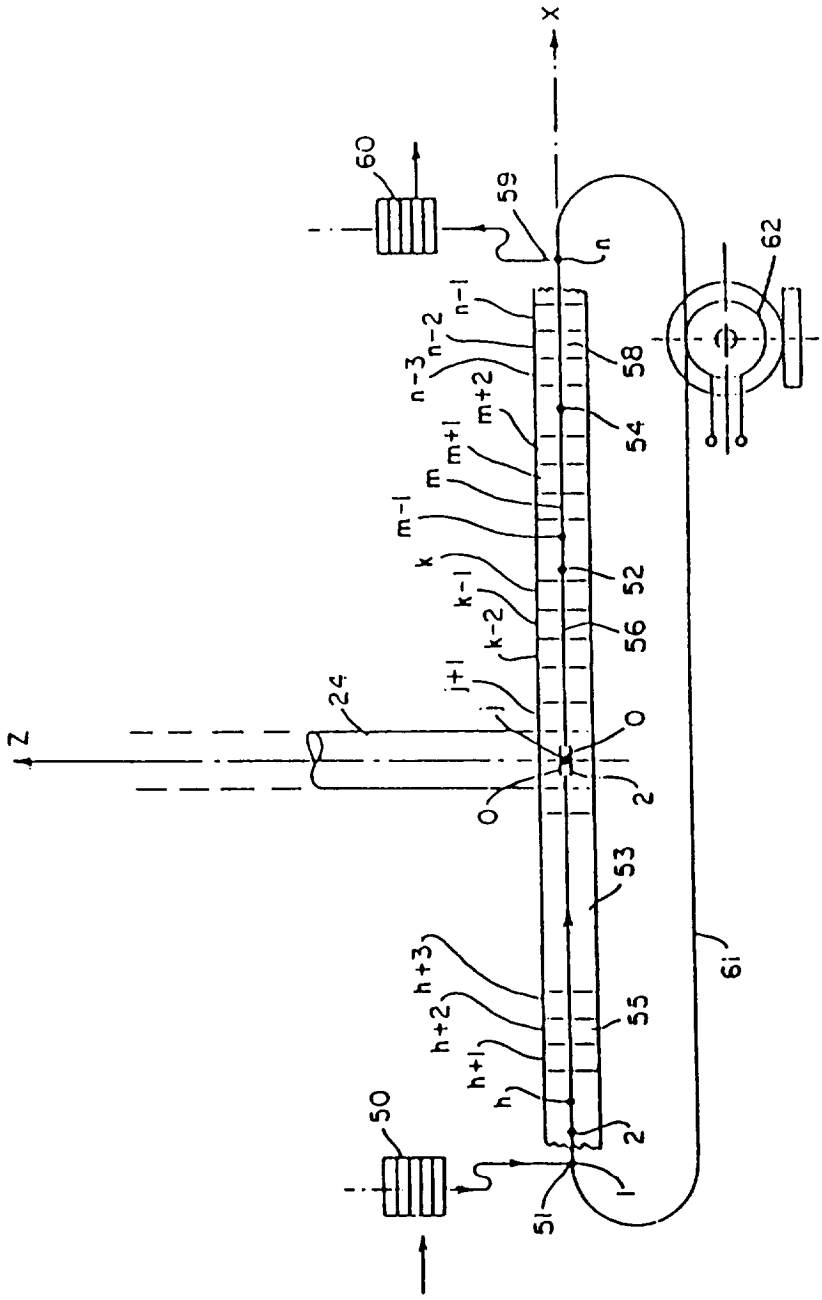


FIG. 7



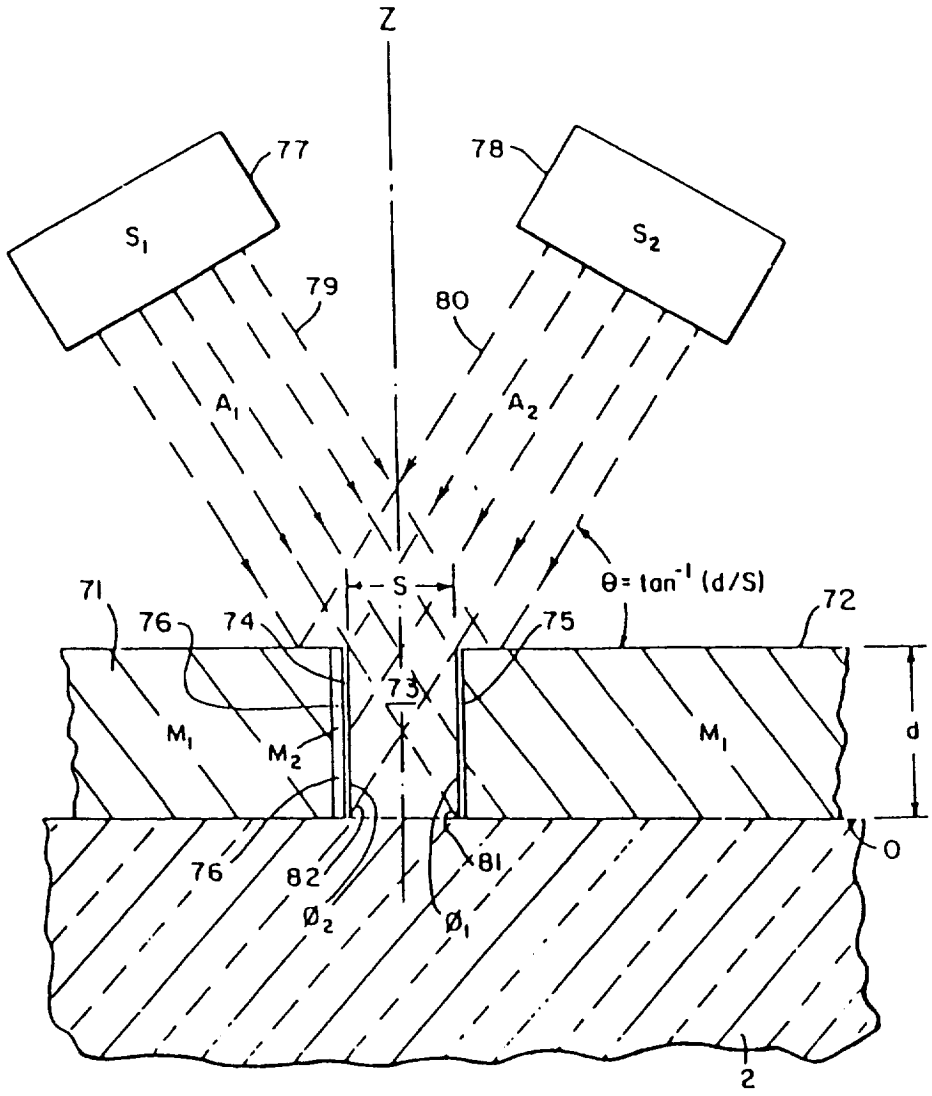
PROCESS A

FIG. 8



PROCESS B
FIG. 9

FIG. 10
ION COATER



PROCESS A

FIG. 8 shows a device employing Process A: the first vacuum tube 24 of the electron beam writer joins the production-line second vacuum tube 52 in a T section. Process A takes place entirely within the second vacuum tube 53. The substrate sheets enter at Station 2, being processed before and after the electron beam writing step at Station j, and leaving at Station n as finished sheets. An example of the processing steps which may occur at the various Stations follows:

1. The sheets enter the airlocks at stations h + 1 to h - 3.
2. At Station h + 4 the sheets are heated to 700° C. and Argon-plasma cleaned to de-gas their surface.
3. The surface chemistry may be changed by ions implanted into the surface by known means.
4. At Station j the pattern is imprinted onto the surface of the glass panel by the electron beam. The electron beam "sensitizes" the surface atoms by directly altering their electrical and/or chemical properties.
5. The sensitized surface is exposed to positive ions such as Sn^{++}, Pd^{++}. The positively charged ions are attracted to negatively charged pattern areas where they deposit on and, adhere to the surface; but are repelled by positively charged areas. The positive ions do not adhere to surface areas having no charge, but may reflect elastically.
6. Tile surface is exposed to a metal vapor such as Cu or A1 which may comprise positive ions of these metals. These ions are attracted to the previously metallized areas by an induced negative image charge. The thickness of the metal deposit is controlled by the metal vapor concentration and exposure time.
7. The patterns are formed with a gap S = 15-30Å at locations where an asymmetric tunnel junction is to be placed. The pattern includes gaps 73, 15 - 30Å wide in the metal deposit.
8. The deposited metal is crystallized to single crystal by locally heating with an electron beam or laser, and then cooling to ambient temperature.
9. At station m + 3 the gaps 73 in the metal pattern are ion coated in an ion coating device such as shown in FIG. 10. This provides the facing surfaces 81 and 82 of the gap 73 with two materials having different work functions ϕ_1/ε and ϕ_2/ε.
10. The entire surface is then coated with an insulator layer; for example, silicon dioxide, titanium dioxide, silicon nitride, and the like. The insulating material is chosen from one having a dielectric constants, such that the effective work functions are ϕ_1/ε and ϕ_2/ε. Conventional vapor coating techniques and apparatus may be used.
11. The sheet is again removed to atmospheric pressure through the airlocks 58, exiting at 56, Station n, as a finished product.

PROCESS B

FIG. 9 shows a device utilizing Process B. Process B takes place in two vacuum chambers 53 and 54, with a space 55 between them for stations for process steps at atmospheric pressure.

1. The process steps are the same as in Process A, to and including the electron beam writing step at Station j.
2. The sheet is removed from the second vacuum tube 53 into the atmosphere through the airlocks 56, and wet-processed with solutions which provide an electroless deposit of metal on the sensitized pattern areas [8].1].
3. The sheet is then dried, and passed into a third vacuum tube 54 through the airlocks at Stations m to m + 2.
4. From Stations m + 2 to n - 1, the steps are the same as in Process A, from 0.18 to 0.21 inclusive.

SURFACE CHEMISTRY OF GLASS

There is an electric double layer surface charge naturally existing on the surface of glass, which varies with glass composition [14-17]. The silica network is the most important in determining the surface charge. Most silicas have a population of silanol SiOH groups on the surfaces which may disassociate:

$$(\equiv SiOH) + OH \; <- - -> \; (\equiv Si - O^-) + H_2O$$

This forms negatively charged $\equiv Si - O^-$ groups in water, the greater the pH, the greater the number of $\equiv Si - O^-$ groups formed. The pH for which $\zeta = O$ is similar to that for other forms of silica pH = 2 to 2.5).

The charge on the surface of the glass depends on the physical and chemical treatments to which it is subjected, as discussed in connection with the following examples:

.1 At Station 2 the glass surface is polished with Cerium Oxide.
.2 At station 3 the surface is rinsed with distilled water.
.3 At station 4 the sheet is dried at about 60° C. for about 10 minutes.

This process results in hydroxyl groups (–OH) attached to the glass surface (=Si–OH) making the surface electronegative, and capable of reacting with positive ions in the vapor or liquid phases; such as Sn^{++}.

An alternate method is:

.4 Expose the surface of glass to fuming sulphuric acid H_2SO_4 for a few minutes [25, 26].

This process attaches a sulphonic group (SO_3=) to the glass forming an electronegative surface charge on the surface (=Si=$S0_3$–).

In a similar manner the glass surface may be made electropositive:

.5 At Station 4 the glass surface is exposed to a solution or vapor containing bifunctional electropositive groups such as:($-NH_2^+$) which results in a glass surface with a positive charge having the composition ≡Si–O–NH_2^+.

A positive surface charge tends to repel positively charged ions and attract negatively charged ions from the vapor or solution. A third method is to render the glass surface charge neutral by utilizing reactive monofunctional atoms; such as a halogen, fluorine –F.

An H atom in 0.3 above may be removed by an electron beam to form patterns on the glass surface, as shown in FIGS. 5 and 6, forming positively and negatively charged patterned areas. FIG. 3 shows a uniformly charged positive layer 38, and a negatively charged lower layer 39, on the glass surface. FIG. 4 shows the same surface after a pattern has been created by the electron beam. The pattern appears as adjacent areas of charge reversal, 40 and 42; with the charges reversed at 41, 43 in the lower layer.

The surface chemistry of glass may be altered by for example heating.

Glass surfaces prepared in contact with water as in 0.1 to 0.3 above have Silanol groups; ≡ SiOH.

Such surfaces heated to >400° C. give off water, adjacent group forming siloxane groups:

≡ SiOH

Such surfaces heated to >400° C. give off water adjacent group forming siloxane groups:

$$2(\equiv Si - OH) \; <- - -> \; (\equiv Si - O - Si \equiv) + H_2O$$

At 800° C. only a few silanol groups remain. At 1200° C. no silanol groups remain. On cooling surface rehydration is slow. Aging in water restores the hydrated state.

An initial heating stage at Station 3 in which the temperature is maintained for a time at sufficiently high temperature may be utilized to fully dehydrate the surface.

METAL PATTERN DEPOSITION

The pattern is inscribed by an electron beam writer such as a Supersebter. Metal is deposited on the pattern using Process A or Process B described above.

In Process A, metal pattern deposition occurs from the ionic vapor in a vacuum onto charged surface areas that attract the metal ions and cause them to deposit. For example, as shown in FIG. 5, the electronegative portions of the pattern attract Sn^{++} ions which sensitize only those areas. These ions may be produced by known methods [29-31 include.]. A second ion source deposits Copper, for example, Cu^{++} from an ionic vapor, onto the sensitized areas of the pattern.

In Process B, metal pattern deposition occurs at atmospheric pressure from solution, for example by electroless coating of Copper or other metals using known methods [18-24].

SINGLE CRYSTAL METAL GROWTH

The pattern may comprise a deposit of long, narrow thin metal strips, for example having dimensions 1000Å x 100Å x 50Å. The metal is preferably Copper, Aluminum or other metal having a long mean free path for energetic electrons in a single crystal of the metal. A single metal crystal is essential to the best functioning of the device. At these dimensions metal particles may form single crystals spontaneously; but especially when heated and cooled. An electron beam may be employed to locally heat a plurality of the metal strips to induce their conversion to single crystals [27].

ION DEPOSITION

An Ion Beam Device for producing an asymmetric Tunnel Junction is shown in FIG. 10. The cross section of an asymmetric tunnel junction on a substrate surface O is magnified to a scale of 10,000,000 to 1. Thus, in the drawing, the gap S = 20Å measures 2 cm.

The asymmetric tunnel junction comprises a pattern of deposited metal layers 71, 72 of a metal M_1 of substrate surface O. There is a gap 72 between adjacent faces 74, 75 of the metal layers; for example, 20 to 100Å. Two or more ion sources 77 and 78 are provided to coat the gap faces with various materials 76, 81, 82 having different work functions ϕ_1 to ϕ_2. One of the metal faces of 71 may first be coated by the ion source 78 with a thin metal layer 76 of a second metal M_2 a few atoms thick; then coated with said materials.

INSULATOR COATINGS

As a last step in the vacuum tube at Station n - 1, insulator coatings are applied to the sheet, utilizing standard vapor coating or sputtering techniques and apparatus.

The insulator coating material is selected for its dielectric constant, ε, to produce effective work functions ϕ_1/ε, and ϕ_2/ε, as described in the following section entitled Work Function.

At station n, electric connections may be made and the surface of the sheet further protected by lamination to a second sheet of glass using known methods.

FIGS. 1 to 3 show various continuous surface layers of noncharge and electric charge on which the pattern may be inscribed by the electron beam writer.

FIG. 1 shows a noncharged surface 35 comprising, for example, siloxane groups with no exposed reactive chemical radical. Such condition may be reached by heating the glass.

FIG. 2 shows a glass surface having an electronegative charge layer 36 over an electropositive layer 37, forming a monomolecular electric double layer. The layer 36 may comprise, for example, sulphonic radicals, previously described herein.

FIG. 3 shows a glass surface with an electropositive surface layer 38, over an electronegative layer 39, forming a monomolecular electric double layer on the surfaced. The electropositive radical may be, for example an amino radical, previously described herein.

FIG. 4 shows a charge pattern inscribed by the electron beam, for example, in the charge structures shown in FIG. 3. In this case, the electron beam neutralizes an electropositive area and adds negative charge to reverse the charge pattern.

FIG. 5 shows a pattern inscribed by the electron beam which comprises adjacent negative charge - noncharge areas 44, 45 respectively, produced, for example by the electron beam breaking chemical bonds of the noncharged siloxane chains on the glass surface, exposing the negative free bond of an oxygen atom.

FIG. 6 shows a noncharge - positive pattern 46, 67 respectively, produced by an electron beam on the electropositive surface layer 38 of FIG. 2. In this case the amino radicals, are neutralized or ablated and free oxygen bonds and form noncharged surface areas of siloxane.

FIG. 7 shows a cross section through a substrate sheet O mounted on a base electrode 83 in an electron beam writer of this invention. The base electrode 83 may be connected to a positive voltage source to attract and discharge electrons driven through the sheet by the high velocity electrons in the beam.

Reverse current through the junction is constant, being limited by the junction structure and electric voltage. The forward current in the quantum regime is limited only by the input rate of energy quanta. Hence the forward/reverse current ratio of the Femto Diode may be very large. [37]

The tunnel junction used in the Femto Diode of this invention comprises an asymmetric Metal 1 - Insulator - Metal - 2 configuration. The first metal and its insulating interface has a work function ϕ_1 in the range of 1.1 to 1.9 eV; and the second metal and its insulating interface has a work function ϕ_2 in a range from 1.8 to 3.2 eV; A result of the analysis is that a maximum forward/reverse current occurs when $\phi_1/\phi_2 \approx 0.6$. The insulating barrier has a thickness which depends on the selected current density; for example from 28 to 38Å for a current density in the range 0.1 to 10 amps/cm^2. The dimensions of the facing metal surfaces are submicron, $< 100Å \times 100Å$.

The tunnel junction used in the Femto Diode facilitates the tunneling transmission of an electron in the forward direction through the insulating barrier; and impedes the tunneling transmission of an electron through the insulating barrier in the reverse direction. The total absorption of a light photon accelerates a single electron to velocity determined by the energy of the photon.

The tunnel junction is based upon particular values of the work functions ϕ_1 and ϕ_2 of metal 1 and 2, and their insulator interfaces, respectively; the barrier thickness s; and the cross-section A, for which the forward and reverse tunnel currents have a maximum ratio of about 14; and in which forward average current through the diode area of 50Å x 50Å is about 2.2×10^{-13} amps; and for which the average forward current density is about 0.88 amps/cm^2.

The Femto Diode has an efficiency of about 80%, and is useful for many applications, particularly in light/electric power converters.

WORK FUNCTION

The work function of a metal is defined as the difference between the electric potential of an electron outside the surface (-eV) and the electron potential of an electron inside the same metal.

$$\phi = -eV - \mu$$

The work function ϕ is also the energy difference separating the top of the valence band (the Fermi energy) from the bottom of the conduction band at the surface of the metal.

The work function of a metal can be changed by the adsorption of one or more monolayers of positive or negative ions at the metal surface to change the electric potential distribution. The change in the work function $\Delta\phi$ depends upon the crystal orientation of the metal surface, the chemical structure of the adsorbate ions, and the number of monolayers. The work function can increase or decrease depending on the nature of the adsorbate. The change in the work function also depends on the order in which the interface ions are deposited.

The dielectric constant ε of the insulator layer changes the work functions ϕ_1 and ϕ_2 on the adjacent metal faces to (ϕ_1/ε) and (ϕ_2/ε), respectively; whereby, the work function (ϕ_2/ε) is adjusted to be approximately equal to the electron and photon energy; that is:

$$(\phi_2/\varepsilon) \approx eV$$

electron energy = hv photon energy enabling electron tunneling and conversion of photon energy to electrical energy to occur at the corresponding wave-length.

Table I shows experimental data for the decrease in work function ϕ on various metal substrates for various absorbates.

TABLE I

Decrease of Work Functions for Metals on Adsorbates

Experimental Data

METAL	SYMBOL	CRYSTAL FACE	WORK FUNCTION	ADSORBATE		RESULTING WORK FUNCTION	DECREASE IN WORK FUNCTION
			Φ eV	Material	Formula/ Order of Deposition	Φ_1 eV	$-\Delta\Phi$ eV
Aluminum	Al		4.28	Aluminum Oxide	Al_2O_3 on Al	1.64	2.64
	Al		4.28		Al on Al_2O_3	2.40	1.88
Iridium	Ir		5.27	Barium Oxide	BaO on Ir	1.4	3.87
Nickel	Ni	100	5.15	Sodium	Na on Ni	2.15	3.00
Nickel	Ni	112	5.15	Oxygen	O_2 on Ni	4.15	1.0

For specific wavelength μ, expressed eV, the work function $e\phi_2 = eV$; or $\phi_2 = V$. A peak ratio of (j_2/j_1) occurs across the junction when $\phi_1/\phi_2 = 0.6$. Table II illustrates this relationship for 3 wavelengths.

TABLE II

Wavelength versus work function $\Phi_1\Phi_2$

COLOR	WAVELENGTH Å	$V = \Phi_2$ eV	Φ_1 $0.6\Phi_2$
RED	7000	1.77	1.06
GREEN	6300	1.97	1.18
BLUE	4000	3.10	1.86

The following Table III illustrates the method of selecting metals to match the work functions listed in Table III for specific wavelengths.

TABLE III

METHOD OF SELECTING INTERFACE MATERIALS

2-1 Work Functions Required $\phi_1 = 1.06$			
ADSORBATE/ METAL	$-\Delta\Phi$ OBSERVED	REQUIRED WORK FUNCTION OF METAL $\Delta\Phi - \Phi_1 = \Phi_{M1}$	METAL SELECTED FROM TABLE OF WORK FUNCTIONS F_{M1}
BaO/Ir	3.87	4.93	Mo(111),Be,Co,Ni(110)
Na/Ni	3.00	4.06	Al(110),Hf,In,Mn,Z
Al_2O_3/Al	2.64	3.70	Mg,U
Al/Al_2O_3	1.88	2.94	Tb,Y,Li,Gd
2-1 Work Functions Required $\phi_2 = 1.77$			
ADSORBATE/ METAL	$-\Delta\Phi$ OBSERVED	REQUIRED WORK FUNCTION OF METAL $\Delta\Phi - \Phi_2 = \Phi_{M2}$	METAL SELECTED FROM TABLE OF WORK FUNCTIONS F_{M2}
BaO/Ir	3.8~	5.64	Pt
Na/Ni	3.00	4.77	Ag(111),Fe(111),M
Al_2O_3/Al	2.64	4.41	Sn,Ta,W,Zr
Al/Al_2O_3	1.88	65	Sc,Mg

Tables I, II and III illustrate selection principles which may be utilized to obtain the required values of ϕ_2 and ϕ_1 for a tunnel junction matched to a particular energy $eV = \phi_2$.

(1) Metals, absorbates, and the observed change in work function $\Delta\phi$ are listed in Table I.

(2) The work function of the metal surface is added to the decrease in work function $\Delta\phi$ produced by the adsorbate/interface to obtain the work function required for the metal.

(3) From the Table of Work Functions of the Elements, Candidate metals are selected which have a work function close to the required work function calculated in Table II.

(4) The order of deposition must be taken into account; for example: Ni/BaO or NaO/Ni For example: In Table (III) line 1, the metal selected Mo, Be, Co, Ni is tested with the adsorbate BaO such as BaO/Ni; BaO/Co; etc.

The selection of materials for a junction suited to each wavelength range has been illustrated with examples. Other combinations of materials may be employed for the metal surface alloys, surfaces with ion implantation, semimetals such as bismuth and the like, and various crystal orientations.

Other materials may be employed for the adsorbate metal oxides, alkali metals, the number of monolayers may be varied; and mixtures of absorbates may be used. The order of deposition may be varied to change $\Delta\phi$.

The selection of materials for tunnel junctions having the requisite work functions ϕ_2 and ϕ_1 for each wavelength range may be made to meet these requirements using the available materials and techniques described above; or modifications.

The device is simple and inexpensive. It utilizes a readily available amorphous substrate such as glass, although it is not limited thereto. It does however require precision fabrication. In a submicron facility Electron beams may be employed to produce the extremely small structures required, using Process A or Process B described above. Ion beams or molecular beam epitaxy may be used to lay down the appropriate metal and insulating areas in producing submicron electron devices. The insulating layer may be silicon dioxide, aluminum oxide, or other insulating layers. The metal strip may be a single crystal which may form spontaneously in such small dimensions or which may be induced to crystallize by suitably heating and cooling the coating, and/or by the momentary application of electric or magnetic fields, and/or by epitaxial growth on a crystalline substrate. The metal strip may have any cross-section but is preferably a square or rectangular high purity single crystal having a long mean free time, such as tungsten, for which $\tau = 1.6 \times 10^{-13}$ sec.

The laws of physics which apply to large-scale electrical circuits in the macro regime are different from the quantum electrodynamic laws of physics in the quantum regime. Because of the small current and time intervals concerned, individual electrons are utilized one at a time. In a Femto Diode, a single electron approaches the barrier traveling over submicron distances - with an energy $\varepsilon = hv = Ve$.

The penetration of a barrier by an electron possessing an energy eV slightly less than the barrier potential $e\phi_2$ occurs according to quantum mechanics by an effect known as "electron tunneling through a barrier". According to the quantum theory of tunneling, an electron moving in a metal approaching an insulating barrier, either passes through the barrier to the metal on the other side by "tunneling"; or is totally repelled by the electric field potential at the barrier/metal interface, and reverses its direction of motion. The waves are transmission/reflection probability waves, not actual particles.

According to the well-established theory, the effect occurs because an electron has a probability wave function which extends a considerable distance and penetrates a thin barrier ($s \approx 30$Å). The probability of transmission of an electron passing through the barrier depends on various parameters, which are defined in mathematical equations derived from fundamental considerations.

The passage of the electron through the barrier occurs because the location of an electron in space is indeterminate, expressed as a probability wave function of the electron being in a given position. This wave function extends over a distance of at least 100Å which is greater than the thickness s of the insulating barrier; usually 28 to 38Å for a Femto Diode.

The electron penetrates the insulating barrier because its position along the axis normal to the plane of the barrier is described by a probability law derived from the Schrodinger equation, from which the Tunnel Transmittance Equation was derived.

The electron may penetrate the barrier and appear on the other side, with its kinetic energy now converted to an equal quantity of potential energy; or, the electron may be reflected, and reverse its direction without loss of energy. A single electron oscillates back and forth in the well without loss of energy until it passes through the barrier.

These phenomena occur without loss because there are no electron collisions, and in the reversal of direction, the initial and final velocities of the electron are equal and opposite.

In this region the effective mass m* of an electron may be about 0.01 m_e the rest mass of an electron. Hence, in a metal, the electron velocity increase from a given quanta of energy is greater than that of an electron in free space.

As an example, the current through a Femto Diode may be about 1.6×10^{-13} amps; for which the number of single electrons/sec is: $N = 10^6$ electron/sec; or 1 electron per μ sec. These are single electron events.

RECENT WORK

Our early work on the manufacture of nanostructures was to enable the large scale rapid manufacture of photovoltaic sheets which are 80% efficient, and low cost, <50 cents/watt. Now, however, many other uses are foreseen; efficient, high definition (1 pixel/μm_2) 2D and 3D HD TV [37], low cost laser polarized lighting sources for general illumination [39], and ultraminiaturized nanometer computer circuits of high density at low cost, all on glass surfaces. The produce and processes describe herein obviate the present high cost of semiconductor crystal substrates.

The Super Submicron Electron Beam Writer, or "Supersebter" [38, 40] is the device used in the method of making large area nanostructures. A key component of the supersebter is a large area field emitter array. Such arrays with packing densities of 1.5×10^7 tips/cm^2 have been fabricated for flat displays and other uses [46]. These emitter arrasy are commercially available and will facilitate the construction of a Supersebter.

A recent paper [41] describes the desorption of NH_3 from a TiO_2 surface using a 400 eV electron beam and 2.5×10^{15} electrons/cm^2; that is, an incidence of about one electron onto an area of 4Å^2. Thus one 400 eV electron is able to desorb one NH_3 positive ion from a surface. Consequently, a low voltage, low current electron beam should be capable of writing a charge pattern on a surface.

Recent work [42-45] has shown that a submicron antenna-diode structure will polarize incident visible light, and convert incident light power to electric power at a load. Thus, large area photovoltaic panels using a submicron antenna-diode structure was shown to be feasible, and further work recommended.

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[43] Letter dated October 31, 1994 from John O'M Bockris, Distinguished Professor of Chemistry at Texas A&M University, to U.S. Gov't. Project Officer states:

"I must support Dr. Lin's contention that a significant contribution has been made here. It seems to me that a new principal has been proved: one can indeed create electricity from antenna absorption of solar light.

What the efficiency of this electricty is will eventually be is difficult to say at the moment because we have some way to go in understanding rectification. On the other hand, there are certain features which would seem to make the eventual development of such a device more efficient than those of photovoltaics.

But of course, we must always remember that the basic idease from Alvin Marks, and I believe that he should be given some kind of award - along. perhaps, with Dr. Lin - for the verification of this remarkable suggestion."

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"1. Enclosed please find final report summarizing the work accomplished at Cornell University... over the last year in regards to assessing the feasibility of the collection of solar energy with antenna structures (idea based on your patent #4,445, 050).

2. We judged the effort a success, but there are still many unknowns that would effect the overall efficiency of such a device. Based on the funding availability, we plan to pursue the concept further..."

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