Aug. 19, 1969 A. F. KASPAUL ET AL 3,462,762
ELECTRONIC BEAM RECORDING WITH VAPOR DEPOSITION DEVELOPMENT
Filed Dec. 2, 1964 6 Sheets-Sheet 1

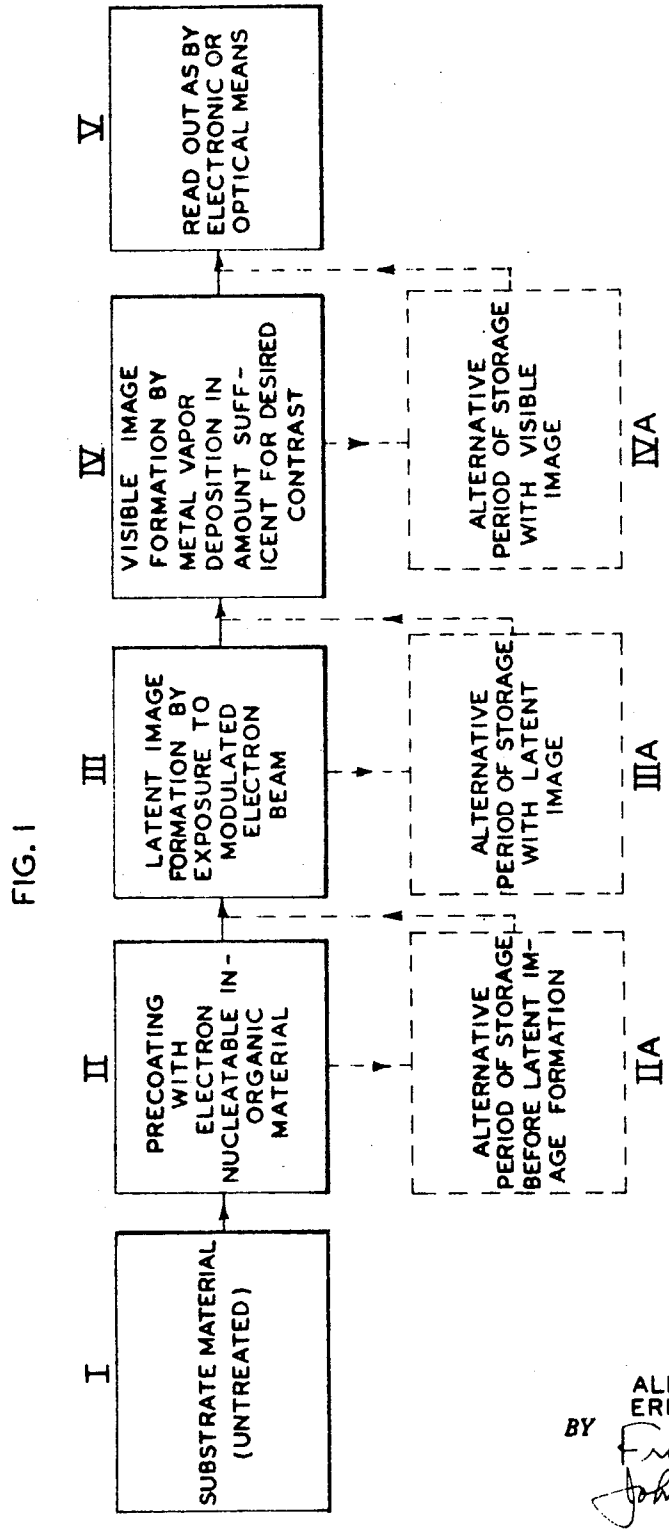
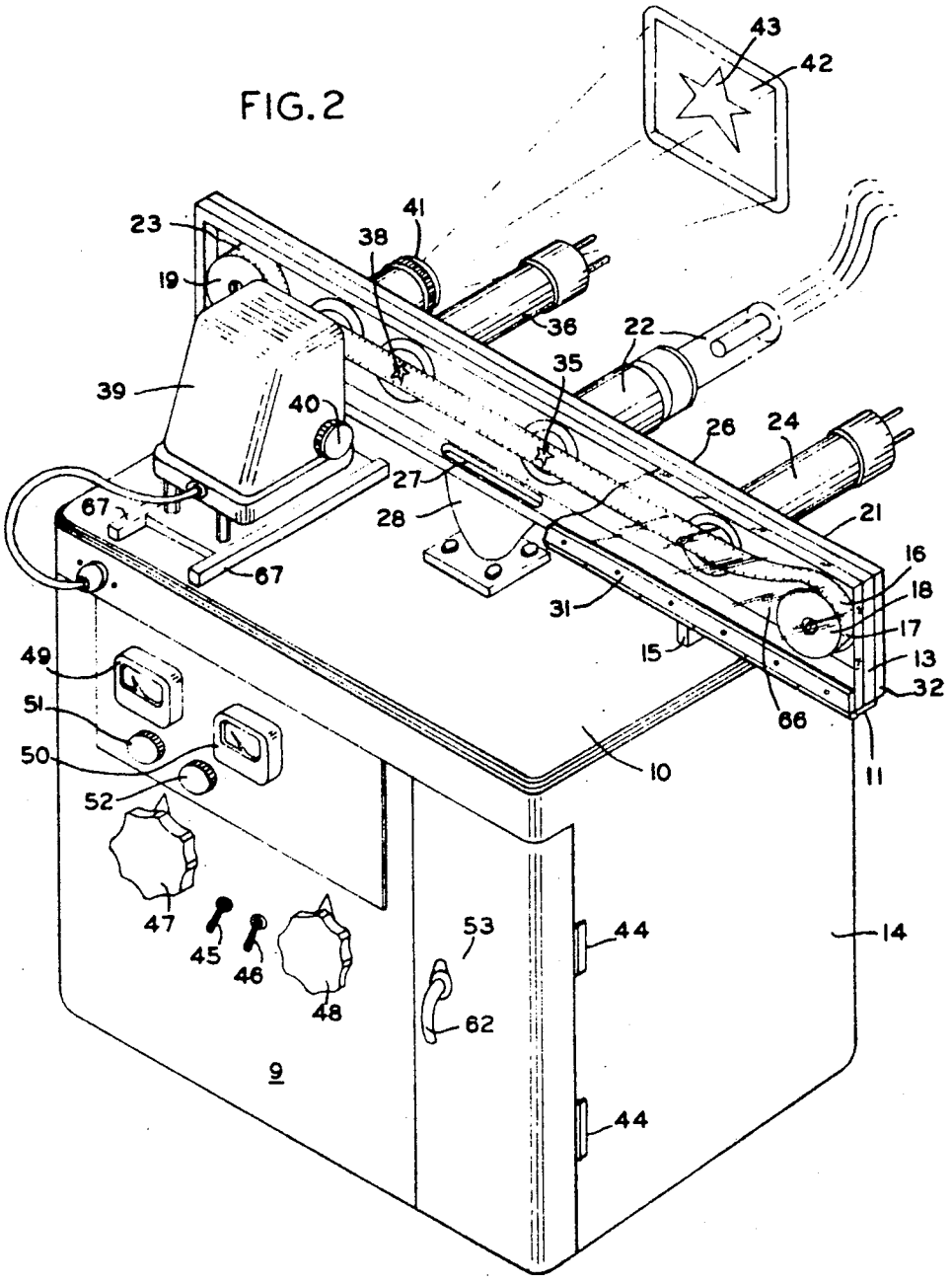


FIG. 1

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FIG. 2



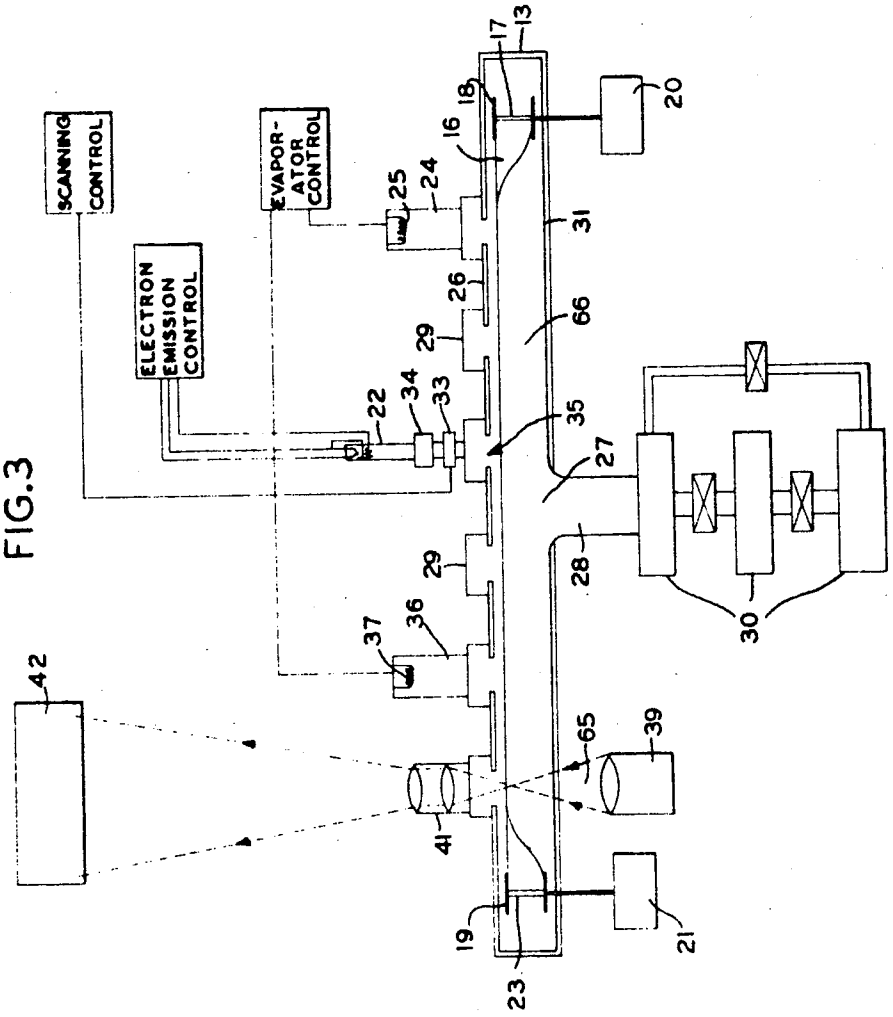
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ELECTRONIC BEAM RECORDING WITH VAPOR DEPOSITION DEVELOPMENT

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FIG. 3



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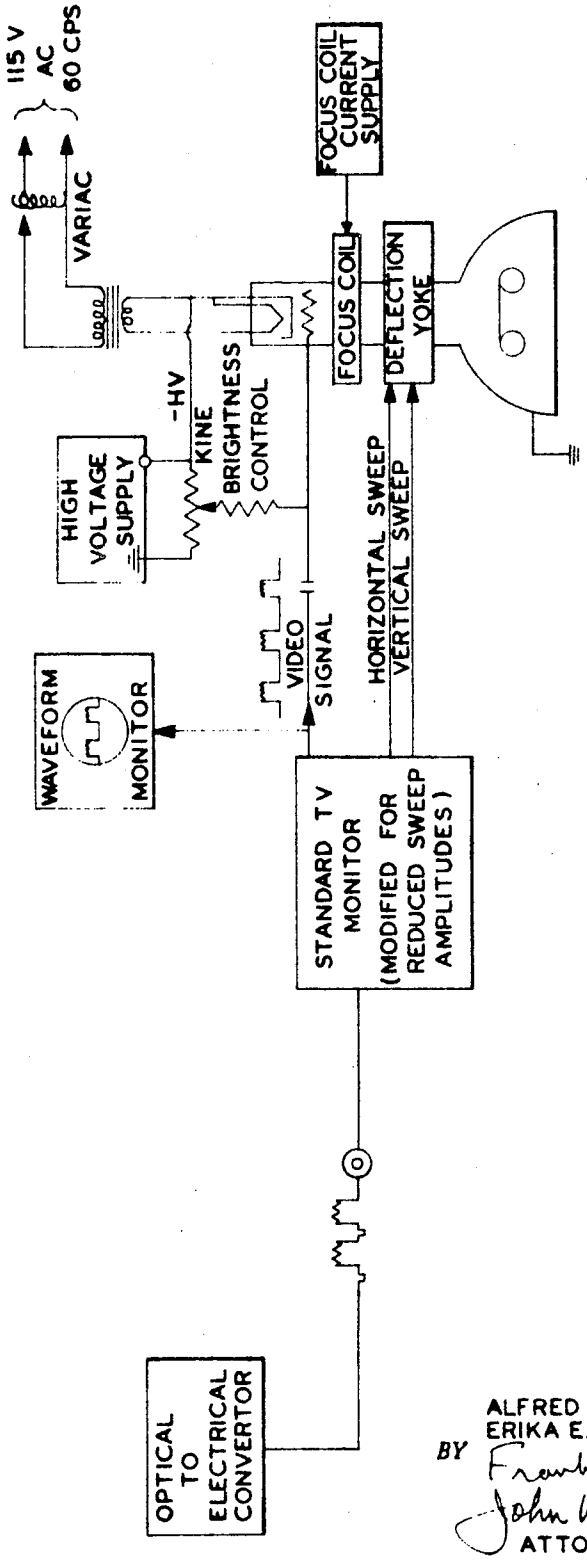


FIG. 4

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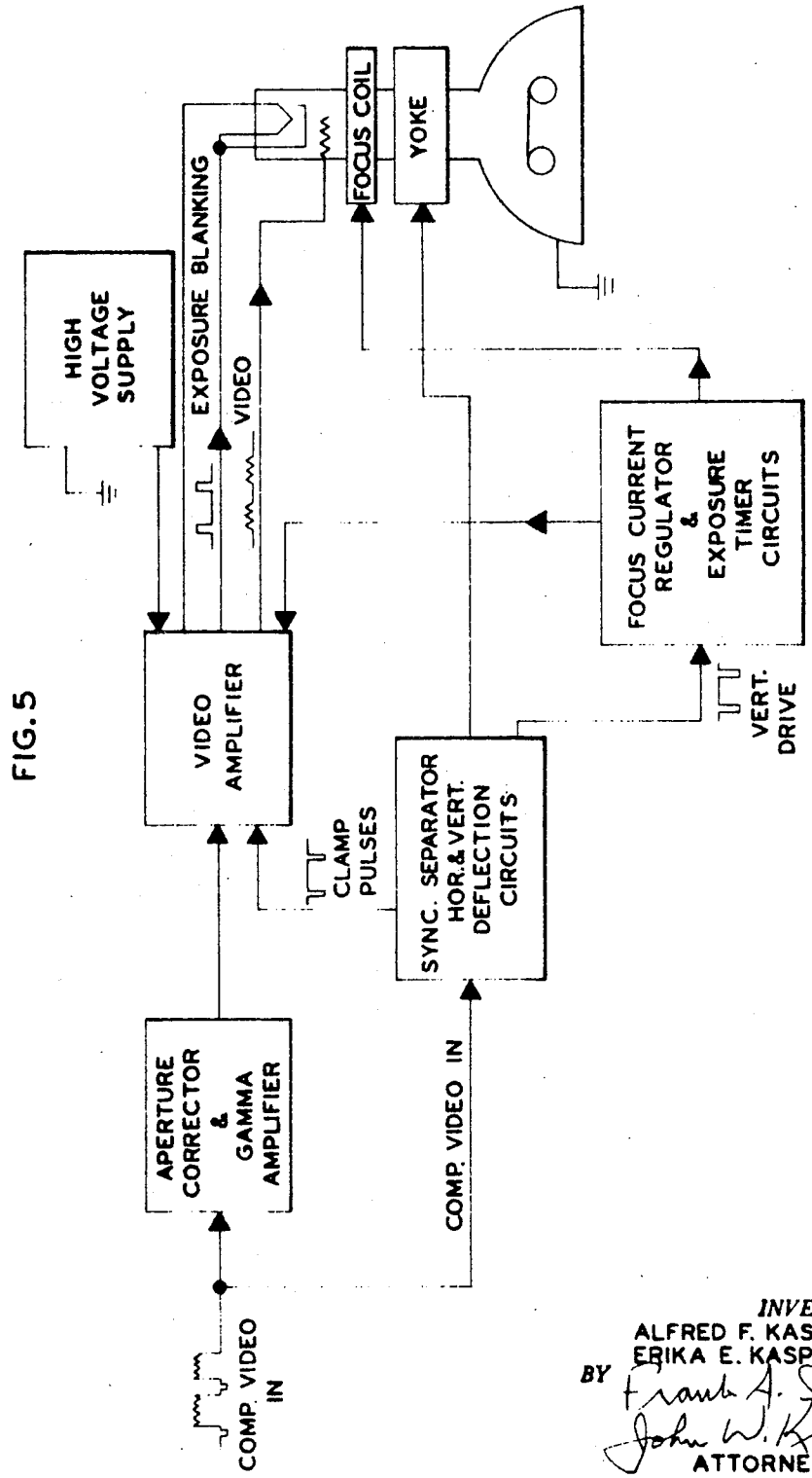


FIG. 5

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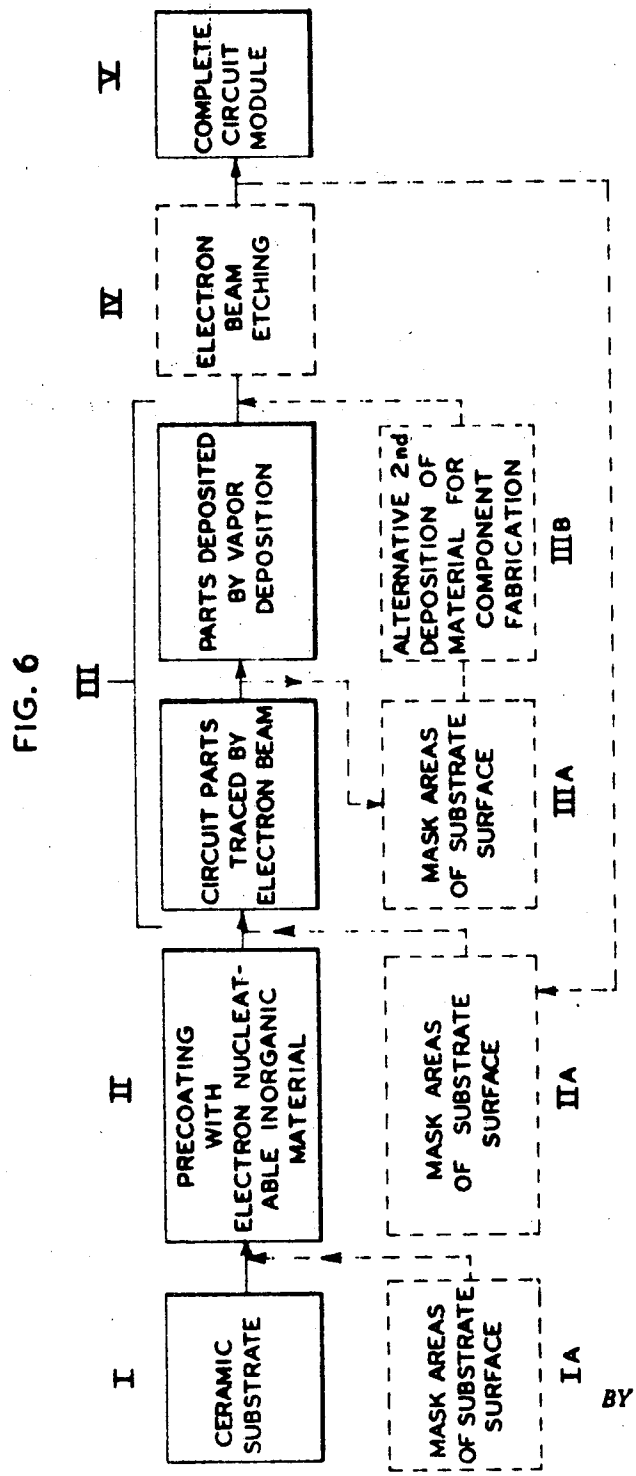


FIG. 6

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United States Patent Office 3,462,762
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3,462,762

ELECTRONIC BEAM RECORDING WITH VAPOR DEPOSITION DEVELOPMENT

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Continuation-in-part of application Ser. No. 70,159, Nov. 18, 1960. This application Dec. 2, 1964, Ser. No. 416,963

Int. Cl. G01d 15/06

U.S. Cl. 346—74 7 Claims

ABSTRACT OF THE DISCLOSURE

A process for recording information on a solid substrate by selective deposition of metallic vapors and the like, in which the substrate is pre-treated to coat it with a layer ranging in thickness from monomolecular up to about 30 A. of an inorganic metallic compound selected from the group consisting of metal chalcogenides and metal halogenides having vapor pressure of at least about 1 mm. Hg between 500 and 1800° C. and practically no vapor pressure below about 50° C. Substrates thus coated can be subjected to the action of an electron beam modulated according to the information to be recorded, thereby producing a latent image consisting of nucleation sites on the surface. Subsequently, vapor deposition of e.g. metal causes formation of a visible image at the nucleation sites.

This application is a continuation-in-part of our earlier-filed copending application Ser. No. 70,159, filed Nov. 18, 1960, now abandoned.

This invention relates to an improved method and means for permanently recording and/or duplicating intelligence employing an electron beam.

The art appreciates that modulated electron beams can be employed to produce latent or invisible images which can be developed and read out. Thus, U.S. Patent No. 2,883,257 to H. G. Wehe describes a system for recording involving the step of exposing a solid organic dielectric surface to a modulated electron beam thereby depositing thereon an invisible charge pattern. Thereafter, the surface must be twice vapor coated, first with silver or copper, and then with zinc or cadmium, before the original beam writing becomes readable. This Wehe system suffers from several disadvantages, one of which is that it requires two separate vapor coating operations subsequent to electron beam impingement in order to develop a visible or reproducible image. Another is that it is inherently very difficult to obtain high resolution and good definition in developed latent images produced by electron charge patterns on dielectric surfaces.

We have now discovered a new and highly efficient technique for making a permanent, reproducible record of intelligence in any form which can be converted or used directly to modulate an electron beam. By our invention a substrate surface is first precoated with an inorganic potential nucleating agent. Next, the coated surface is scanned with a modulated electron beam which selectively nucleates the coated surface. The charge pattern which accompanies the impingement of the electron beam is removed. Thereafter, this selectively nucleated surface is exposed to metal vapor and metal is preferentially deposited on the nucleation sites of the coated surface, thus rendering the beam writing readable. The developed latent image is then conventionally read out by optical, electronic, or magnetic means, depending upon the nature of the image and the information involved.

An object of this invention is to provide a system for

recording by means of a cathode ray gun, which system efficiently utilizes electron beam energies and produces not merely charge differences but permanent effects on the surfaces of solid, storable recording media. Another object of this invention is to provide an improved and simplified method for producing permanent metallic records of information originating from optical, electrical, chemical, light, heat, mechanical or other physical phenomena by means of a cathode ray gun. Another object of this invention is to provide apparatus for carrying out the method of the invention. A further object of this invention is to provide a system capable of producing readable images of high resolution and good definition from electron beam writings. A still further object of this invention is to provide a means for achieving an extremely high storage density of information bits per unit of surface area on a tape or other substrate. Yet a further object of this invention is to provide a permanent metallic record which can be read out electronically, optically or even magnetically. Other objects will be apparent to those skilled in the art.

Our invention will be more fully understood from the following description, considered together with the drawings, in which:

FIGURE 1 is a block diagram of one form which the process of the invention may take;

FIGURE 2 is a diagrammatic isometric view of an embodiment of the apparatus of the invention;

FIGURE 3 is a diagrammatic cross-sectional view of the recording chamber in the apparatus of FIGURE 2 showing the sequential arrangement of the separate units employed in carrying out the process of the invention;

FIGURE 4 is a block diagram of an electronic system for photographically recording visible, optical images;

FIGURE 5 is a block diagram of an electronic system for video recording and display; and

FIGURE 6 is a block diagram of a system for producing microcircuits and microcircuit components.

Referring to FIGURE 1, the recording process of this invention begins with the solid substrate material employed as the base upon which intelligence is to be recorded. We find it convenient to have this substrate material in a tape or strip form.

Any of a very wide variety of solid materials are suitable for use as substrate materials in this invention. Preferably, the substrate surface should be substantially continuous (i.e., non-porous) in those areas over which the electron beam will pass in scanning. Also, the substrate surface is preferably one which is substantially unaffected by electron beam impact during exposure times of under about one minute (the energies of the electron beams employed in this invention are more particularly described below). Preferably too, the substrate surface has substantially no vapor pressure and is thermally stable below about 80° C. (i.e., the substrate can be subjected to ambient temperatures even under high vacuum conditions without undergoing chemical or physical changes).

We find it convenient to use a plastic, non-conductive transparent tape strip when an optical or visual read-out is contemplated. Such tapes are commercially available and chemically consist of such materials as celluloid, polystyrene, polyvinyl chloride, ethyl cellulose, cellulose acetate, cellulose acetate butyrate, methylmethacrylate and the like.

The tape strip may be a composite or layered structure, as when electronic or magnetic read out is contemplated. Thus, a base material can serve as a support for a top layer. The top layer can be a material such as mica, a ceramic, or even a semiconductor, such as germanium, silicon, cadmium sulfide, zinc oxide, barium sulfate or the like, while the base can be a metal sheet or strip, a

glass plate, paper, plastic or the like. The top layer of the tape strip can even be rare earth oxides, alkali metal halides, or single crystalline materials.

Referring again to FIGURE 1, it is seen that the solid substrate material is precoated prior to electron beam exposure (Step II). This precoating material consists of an inorganic nucleating agent. Nucleating agents we find convenient to use are inorganic metallic oxides, halides and sulfides. Other suitable nucleating agents include metal hydroxides. We prefer to use metal oxides, halides and sulfides which have vapor pressures of at least about 1 mm. of Hg at temperatures within the range of about 500 to 1800° C. and also have substantially no vapor pressure below 50° C. The term "substantially" as used in the preceding sentence has reference to the fact that the materials should have vapor pressures which are low enough not to interfere with the selective metal deposition during latent image development. Such preferred materials tend to produce the best developed images and tend to enhance the durability of any latent image during possible storage and during development. For like reasons, we also prefer to use oxides, sulfides and halides of those metals which in their free form (i.e., when the metals have a valence of zero) have vapor pressure characteristics similar to those indicated for their oxides, sulfides and halides.

In the precoating operation, one coats upon the substrate surface at least about a monomolecular layer (i.e., a monolayer) of a metal chalcogenide (such as a metal oxide or sulfide) or a metal halogenide on the surface to be scanned with an electron beam. If the cross-sectional area of a beam is very small, say of the order of 10^{-5} square centimeters, then it is desirable to have a very uniform precoating. On the other hand, if the cross-sectional area of a beam is a significant fraction of a square millimeter, say of the order of 0.005 square centimeter, the precoating can be relatively irregular. Thus, depending upon the beam width to be employed and the density of recorded information, the precoating uniformity can vary widely but, in general, the precoating should be preferably at least a monolayer in thickness.

The maximum quantity and uniformity of precoating materials allowable on a given substrate is somewhat affected by the end use to which the recording material is to be placed. It is generally desirable to have precoatings of the order of 30 or more angstroms thick provided that this thickness does not cause image reversal or interfere with the quality of the projected transparencies. In general, as a practical matter, we use precoatings of such thinness as to be invisible to the unaided human eye. Excessively thick precoatings tend to cause image reversal in developed images.

We prefer to use those metal oxides, sulfides and halides which are capable of undergoing reduction to the free metal from bombardment with beams of electrons having relatively low average energy per electron. For this reason, we prefer to use metal oxides, sulfides, and halides in which the metal is in its lowest valence form.

Exactly why or how the precoating acts to record an invisible latent image is not completely certain but is believed to be as follows: The scanning electron beam is known to produce nucleation sites on or in the precoating layer. These nucleation sites are arranged in a pattern on the surface corresponding to the modulation of the scanning electron beam. Hence, the signals impressed upon the electrons issuing from the gun are accurately recorded in the latent image. The latent image formed in this way is ordinarily completely invisible to the human eye, but in some instances it may be detected visually, for example, if a very long period of exposure to the electron beam has taken place at one point on a precoated surface exceeding, say, 30 or 40 monolayers in thickness. It is theorized that the electron beam actually breaks up the bonds in the precoating compounds leaving nucleation sites having greater heats of vaporization than that of the depositing metal vapor used to develop the latent or invisible image.

As those skilled in the art will appreciate, certain metal oxides, halides and sulfides undergo rapid oxidation in air to higher oxidation states. For example, cuprous chloride, which we have found to be an excellent precoating material, undergoes oxidation to cupric chloride quickly in the presence of air. When such rapidly oxidizable metal oxides, halides and sulfides are used as precoating agents, we find it best to conduct the precoating operation under non-oxidizing conditions, say, for example, in a nitrogen atmosphere or under relatively high vacuum. We find it preferable to conduct the precoating operation with such easily oxidizable materials under vacuum conditions and then promptly scan the precoated substrate surface with a modulated electron beam to form the latent image.

Those metal oxides, sulfides and halides which do not rapidly undergo air oxidation can be precoated upon a substrate surface and then the resulting precoated substrate can be stored for a period of time in air prior to latent image formation by an electron beam. Many of these more stable inorganic precoating materials seem to require higher electron beam energies to form latent images. However, for a given electron gun with an accelerating potential of, say, several kilovolts, this means that, in general, such precoating materials require the same exposure times in order to produce latent images.

The exposure time is independent of the precoating material employed, since for the given gun, the energy of each electron is considerably greater than that energy which is required to rupture a single bond.

Examples of suitable precoating materials which can be stored in air before latent image formation includes Bi_2O_3, Cu_2O, MO_2O_3, Ag_2O, YbO and Yb_2O_3. In general, the rare earth oxides are suitable for use as storable precoating materials, provided the particular one or ones and their free metals used in a given situation have heats of vaporization higher than the metal used for subsequent selective vapor deposition.

While it appears that precoating thicknesses of the order of a monolayer may be produced by conventional methods, we find that the most favorable precoatings are obtained by employing vapor deposition under vacuum of the precoating agents. We have found that it is relatively easy to precoat using conventional evaporators under ambient pressures of less than about .01 mm. Hg. While the actual temperature in an evaporator at which vaporization of the precoating agent is obtained will, of course, be determined by the particular precoating compound employed, we found it convenient to maintain the surface of the substrate at ambient temperatures, although temperatures considerably higher or lower can be used. The evaporator is regulated in the usual manner so as to control the rate of deposition. No cooling means need be employed at the point where the substrate surface is being precoated since the amount of heat dissipated at the substrate surface during vacuum vapor deposition of precoating agent is so slight as not to significantly affect the temperature of most substrates.

The minimum vapor pressures required at various temperatures for precoating a monolayer of given precoating material is readily determined in any given instance from a consideration of the various physical quantities involved. One formula which can be used to determine the minimum vapor pressure P in terms of cm. of Hg° is:

$$(1) \qquad P = \frac{Pd'V}{C'r^2 4d \tan\theta \left(\frac{M}{T}\right)^{1/2}}$$

which can be rewritten as

$$(2) \qquad P = K'T^{1.2}$$

where

$$K' = \frac{d' V \left(\frac{1}{M}\right)^{1/2P}}{Cr^2 4d \tan \theta}$$

d=separation distance in cm.
M=mol. wt. of precoating agent
T=absolute temperature in °K.
P=density of precoating agent in gms./cc.
d'=monolayer thickness in cm.
V=substrate velocity in cm./sec.
C'=constant=1.8×10^{-5}
r=radius of source in cm.
θ=focusing angle (with respect to material being evaporated and moving substrate in degrees).

For example, if cuprous chloride is used as the precoating agent and it is assumed that the monolayer thickness is 5×10^{-8} cm., then for d=10 cm., M=99 (or 100 for convenience), T=695° K., r=1 cm., P=3.5 gms./cc., and θ=45°, then a P≅0.33 mm. Hg° vapor pressure is all that is required to deposit a monolayer of CuCl at its melting point on a target 10 cm. away moving 51 cm./sec. (or 100 ft./min.).

It should be noted that the foregoing calculations have been simplified for convenience of presentation here. Thus, Formula 1 holds provided that the mean free path is equal to or greater than the distance between source and substrate, and provided that the accommodation coefficient (i.e. the number of atoms striking the surface compared to the number sticking to the surface) is unity.

Referring again to FIGURE 1, after the precoating operation, a latent image is formed through exposure of the precoated substrate surface to a modulated scanning electron beam (Step III).

The modulated scanning electron beam is obtained using a conventional electron gun, such as that employed in an electromagnetically focused and deflected video display tube. The electron gun contains electrode structures which produce, control, focus and deflect a collimated beam of electrons. It is possible to vary the intensity of the trace (beam), as well as the beam cross-sectional area.

In general, the electron guns most useful in this invention are those which are capable of producing a beam which can be focused on a surface to a cross-sectional area not greater than about 10^{-4} square centimeters and preferably about 10^{-5} sq. cm. Also, the electron guns useful in this invention are those which are capable of producing current densities of at least about 0.5 amp per sq. centimeter. The voltage associated with such electron guns can vary within wide limits, at least about 5 kilovolts and preferably at least about 15 kilovolts being used.

The minimum amount of energy which must be supplied to a given unit of precoated substrate surface in order to create a nucleation site varies with a number of different factors, especially with the precoating material and with the number of electrons supplied to a given point per unit of time. We prefer to use more than the minimum amount of energy required because we find that better developed images with significant differences in optical density result from the subsequent vapor coating development step. Because of the complexities involved it is not possible simply to give a single minimum energy value applicable to all guns and all precoated substrates.

However, reference to a specific system is a useful guide. Conventional video display electron guns (which type of cathode ray gun is entirely useful for this invention) have the following characteristics:

(1) Spot duration per single picture element is about 2.1×10^{-8} seconds, the number of picture elements per second is about 1.1×10^{7} elements/second.

(2) Beam spot area is approximately 1 sq. mil or 625 sq. microns; and
(3) Number of electrons per picture element at 5 amps/cm.^{2} is about 1.77×10^{7} electrons/picture element.

Hence, the energy per picture element in ergs or calories for a voltage of 15 kilovolts is equal to (1.77×10^{3}) (1.59×10^{-19}) (1.5×10^{4}) or 0.422 erg, which is equivalent to about 10^{-8} calories per picture element.

Electron beam writing according to this invention is carried out under reduced pressure of the order of about 10^{-2} to 10^{-6} millimeters of mercury, and preferably about 10^{-3} to 10^{-5} mm. Hg.

Referring once more to FIGURE 1, it will be observed that after latent image formation by exposure to the modulated electron beam, the scanned, precoated substrate surface is ready for development (Step IV). The latent image can be stored for an interval of time before development. Storage is possible in this invention because the electron beam has actually chemically changed the precoated substrate surface. The nucleation sites comprising the latent image on the precoated substrate surface are more or less permanent, depending on the particular precoatings and storage conditions involved. We have found it most convenient when recording information to promptly vapor coat so as to develop the latent image, because the latent image is already under the low pressure required for vapor deposition of metals.

Conventional metal evaporation techniques for the vacuum deposition of a thin metal layer upon a substrate are employed for "development" or visualization of the latent image. The selective or preferential condensation of the metal vapor on the scanned precoated substrate substrate surface bearing the latent image forms the visible (readable) image. We find it best to use pressures of not more than about 10^{-2} mm. Hg when carrying out the selective metal vapor deposition.

The metal preferentially deposits upon those sites where there is nucleation as a result of the electron beam exposure. Sufficient metal is deposited until the latent image becomes visible. By the term "visible" is meant that the image can be "read-out" by some conventional or known optical electronic or magnetic technique. Usually only very small quantities of metal need to be deposited in order to develop the latent image. Deposits of the order of about 100 A. units thick usually produce images of excellent optical contrast. Only about 10^{17} atoms of metal per sq. cm., or about 100 monolayers thick, is needed to produce optical densities of about 1.

The density of the metal deposit at a given point depends upon the number of renucleating sites which are present at that point on the surface. When transparent substrate material is used, the image formed can be diapositive or dianegative and the resulting record is adapted for projection by optical means. Thus positives and negatives in continuous tone, half-tone and line images can be produced.

The image may, however, also be read out electronically and therefore is useful for storage of images to be employed for video recording and playback. Similarly, information can be stored for use with computers, in which electronic or magnetic readout is employed.

The metals which are employed for deposition upon the latent image produced by the impingement of the electron beam upon the substrate are those metals which have a lower heat of vaporization than either the precoating metal oxide, sulfide or halide or the free metal itself when the precoated, nucleated substrate surface is maintained at a temperature below about 100° C.

Useful metals for the purpose include zinc, cadmium and magnesium. The ΔH (heat of vaporization expressed in Kcal./mole) for zinc is 27.6; for cadmium is 26.6; and for magnesium is 30.7. These metals are used because they produce the best selective deposition upon the nucleation sites at a temperature below about 100° C. The lowest useful temperatures for this invention seem to be

determined more by substrate and apparatus limitations than by substrate surface temperatures but it is preferred that the substrate temperature be above 10° C.

Metals other than zinc, cadmium or magnesium can, of course, be used to develop the latent image, but many of these have higher heats of vaporization. For example, the ΔH for silver is 60.9; for silcon, 105; for aluminum 70.2; for barium, 36.1; for beryllium, 70.4; bismuth, 36.2; cerium, 75.0; cobalt, 91.4; germanium, 79.9; iridium, 135.0; iron, 83.9; manganese, 52.5; molybdenum, 142.0; osmium, 150.0; tin, 69.4; tungsten, 191.0; and zirconium, 139.0. For metals such as these, we have found that selective deposition of vapor of such metals is possible by heating the substrate bearing the latent image to temperatures in excess of 100° C.

The temperature at which maximum selective deposition occurs, that is, the substrate temperature at which the best definition and greatest clarity of developed image is produced, varies with a number of different factors, such as type of substrate, type of nucleation sites in the latent image, material being used to develop the latent image, etc., so that it is not possible to give the optimum substrate temperature for every combination of variables. There is, however, for every given combination of pressure, substrate and nucleation sites, a rough correlation between the ΔH of the developing material and the particular accommodation coefficient (see col. 5).

Indeed, we have found that the latent images can be veloped by any of a very wide variety of non-metallic materials, including Sb_2S_3, BiO_3, CdS, CdSe, CdTe, PbS.

The rate of condensation of atoms onto a substrate unit area depends upon

(a) the time each individual atom can spend in two dimensional motions in the surface-energy field before it will either re-evaporate or be captured due to energy loss in nonelastic collisions with other atoms.
(b) the substrate temperature (T) and
(c) the surface energy (ϕ_{ad}) or energy of adsorption therefore Equation 3 can be written as follows:

$$\log \frac{\dot{N}_i}{N_{ad}} = \log A - 0.434 \frac{\phi_{ad}}{k \cdot T} \qquad (3)$$

in which

$\dot{N}_i$ is the rate at which atoms are incident upon unit surface area
N_{ad} is the rate at which atoms condense upon unit surface area
ϕ_{ad} is the energy of adsorption of a single atom $\sim \frac{1}{6}$ of ΔH_{298}
log A is a value characteristic of a given metal and relatively insensitive to temperature, usual values being between about 13 and 15.

Even organic dyestuffs, such as the phthalocyanine dyes, can be selectively deposited from their vapor upon a substrate bearing latent images. In general any material may be selectively deposited upon such substrates provided that it is vaporizable and has a heat of vaporization below that of the substrate and latent image nucleation sites. Since most of these materials have rather high heats of vaporization (i.e., above that for magnesium), best developed images are produced by raising substrate temperatures above about 100° C., the optimum temperature for a given system being determined for a given system by simple experiment.

While reference is made to the heat of vaporization, since this is a useful and convenient criterion for selection of the metals to be used, it will be apparent that surface energies are involved. The substrate surface temperature and its surface absorption energies affect the choice of metals to be used for vapor coating. In general, the metal used should have a heat of vaporization which is not greater than that of either the substrate surface or the nucleation sites on this surface. Thus, it is only necessary that the metal to be used for vapor deposition not have such a high ΔH that the temperature involved will destroy or otherwise impair the latent image. The amount of metal to be deposited selectively will of course vary widely, depending upon a number of more or less subjective variables, so that it is not possible to state exactly the amount needed for every latent image. However, in general, sufficient vapor is deposited to produce an image which can be read out electronically, optically or magnetically.

Optical read out is accomplished by simply passing a focused beam of light through a transparent film and projecting an image upon a screen in a conventional way; or by reflected light if an opaque substrate is used.

Electronic and magnetic read out can also be accomplished using known techniques.

Turning now to FIGURES 2 and 3 there is shown an apparatus for carrying out the processes of the invention. In this apparatus, the precoating, electron beam writing, and vapor development are accomplished in a single vacuum chamber as a continuous operation.

Tape strip **16** is initially gathered in roll **17**. Roll **17** is set on mandrel **18**, from which it is continuously or discontinuously fed over a series of rolls and guides (not shown) to a final winding mandrel **19**. For continuous feed, a conventional mechanical tape drive means can be employed for uniformly drawing the tape across the various recording stages. For discontinuous feed, mandrel rotation can be controlled by electric motors at **20** and **21** which can be synchronized with the cathode ray gun **22** so as to move tape strip **16** in coordination with electron beam movement (i.e., for frame scanning). Suitable tape guides and supports (not shown) are provided to maintain the position and orientation of the tape. At the end of the recording operation, the record bearing substrate tape is gathered in a roll **23** on mandrel **19**.

The entire recording operation is conducted in a vacuum chamber **66** in which strip **16** and its attendant mandrels **18** and **19** are entirely contained. Upon the rear wall **26** of vacuum chamber **66** are mounted various units employed in carrying out the recording operation (explained below). Chamber **66** is evacuated through orifice **27** which connects with duct **28**. In turn, duct **28** leads to the vacuum pump system **30**. Note that face **31** of vacuum chamber **66** is transparent and is so mounted as to be pivotable upon an axis running horizontally through the base portion of face **31** upon hinge **11**.

The tape strip **16** is first precoated with a potential nucleating agent such as copper chloride, as explained. Such precoating is accomplished through vapor deposition from a conventional evaporator **24**, here depicted as having an electrically heated filament **25** which serves to heat the inorganic precoating material to vaporization. By controlling the temperature of evaporator filament **25**, the amount of precoating material deposited on the surface of film strip **16** can be controlled for a given strip speed; hence, the amount of material precoated can be carefully controlled.

After precoating by the evaporator **24**, tape strip **16** is moved along until it is positioned in front of electron beam gun **22**. An electrically conductive backing plate (not shown) supports the film in a plane perpendicular to the beam axis. At this position **35**, film strip **16** is scanned by cathode ray gun **22**. Deflection yoke **33** and focus coil **34** control the modulation of the electron beam (not shown). The modulated electron beam projected upon the precoated surface of tape **16** traces out a latent or invisible image on the precoated surface. When a continuous tape movement is employed, a line scanning technique is best; when however, tape movement is so arranged as to be discontinuous a frame scanning technique can be employed. The latent image produced is shown schematically at position **35** in FIGURE 2.

Any charge pattern produced by the impingement of the electron beam is then removed. Grounding of the backing plate is sufficient if the tape is conductive. When

not conductive, the application of an AC field (5 kv., 60 cycles) suffices to remove the charge. In this instance, the tape is passed between suitable electrodes to which the AC source is connected. A corona discharge may be present. Similarly ionization of the air near the tape, as by use of a radioactive source, is useful for the purpose, but depends on the presence of significant amounts of gas in the chamber. The latent image 35 which is believed to be formed of nucleation sites by chemical change in the precoated layer, persists after the static charge is removed. Removal of such parasitic electrostatic charges is important because their presence is detrimental to the definition of the vapor-deposited metallic images.

After formation, latent image 35 is moved along until it is in position 38 in front of evaporator 36. Evaporator 36, like evaporator 24, is of conventional design and equipped with a coil 37 which serves as the heat source for evaporating metal vapor such as cadmium vapor. The metal vapor is deposited upon the nucleated surface of the film strip 16 preferentially upon latent image 35. The rate of metal vapor deposition upon tape strip 16 is controlled by the temperature of the coil 37 for a given tape strip speed. Sufficient metal is deposited upon film strip 16 to develop latent image 35 into the visible or readable image at position 38. The developed visible image continues to move with the tape 16 towards mandrel 19.

In FIGURES 2 and 3, the developed visible image is shown being read out optically by focusing a beam of light 65 from projector 39 (on cabinet top 10) upon film strip 16 so as to form an enlarged image 43 on screen 42. Adjusting knob 40 provides means for adjusting the position of projector 39 on tracks 67 so that light passing through film strip 16 can be focused at the exact point where the sharpest image results upon screen 42.

Shown in FIGURE 2 upon the front panel 9 of the cabinet 14 (upon which the entire recording operation is carried out) are various control means for handling the mechanical aspects of the recording operation. In cabinet 14 is contained the vacuum pump system 30. Entry to the chamber is obtained by pivoting handle 62 and swinging outward door 53 upon its hinges 44. Switches 45 and 46, respectively, control energization of the heating coils 37 and 25 of evaporators 36 and 24. Knobs 47 and 48 control rheostats which adjust the temperature of coils 37 and 25, respectively. Meters 49 and 50 record the temperature of the coils 37 and 25, respectively. Knobs 51 and 52 control reference needles (not shown) in meters 49 and 50, respectively.

Note than in FIGURE 3 windows 29 are provided which permit observation of the tape strip 16 as it progresses through the recording apparatus.

FIGURES 4 and 5 each show block diagrams of electronic systems utilizing the teachings of this invention for recording and storing different types of information. These figures are believed to be self-explanatory to those of ordinary skill in the art.

A particularly interesting feature of this invention is the latent images formed by electron beam scanning as described above. These latent images although invisible to the unaided human eye are nevertheless a real, existing physical phenomena as is demonstrated by the fact that these latent images can be developed by vacuum vapor deposition techniques, as indicated. They are not electrostatic charge images, such as those utilized heretofore by the prior art. Instead, these latent images or recordings comprise the described substrate bearing upon its surface a latent image composed of nucleation sites produced by exposing the coated substrate surface to the described scanning electron beam, whereby the coating material is converted to a different substance having nucleating properties.

FIGURE 6 illustrates by means of a block diagram a particularly interesting application of this invention to the field of microcircuitry. Using the technique of latent image formation by electron beam writing, as taught by this invention, one can form very small-sized circuit components and even whole circuits. Then, by a subsequent series of steps, such as that illustrated in FIGURE 6, one can "develop" the "latent" circuitry into the "readable" or finished and completed circuit possessing the desired characteristics needed for a particular situation. Note that in Step III of this embodiment of the invention an electron beam is used not to etch or remove extraneous material but to build or cement additional superstrate material upon a base substrate. In this way, conductors, resistors and the like circuit elements can be produced.

What is claimed is:

1. In a method for recording information upon a solid substrate by selective vapor deposition of image-forming solid material thereupon at pressures of less than about .01 mm. Hg, the steps of (1) coating a solid substrate surface while maintaining a substrate temperature below about 100° C. with from at least a monomolecular layer up to about 30 A. in thickness of an inorganic metallic compound selected from the group consisting of metal chalcogenides and metal halogenides, said metallic compounds being further characterized by having vapor pressures of at least about 1 mm. Hg between about 500 and 1800° C. yet having substantially no vapor pressure below about 50° C., said solid substrate surface being substantially continuous; (2) contacting said coated substrate surface with an electron beam modulated according to information to be recorded to produce a latent image consisting of nucleation sites on said surface; (3) removing residual parasitic electrostatic charges from the said substrate and (4) vapor-depositing a solid image-developing material having vapor pressure lower than that of said inorganic metallic compound upon said nucleation sites until a visible image corresponding to said latent image is produced.

2. The method for recording information upon a solid substrate by selective vapor deposition of metal thereupon at pressures of less than about .01 mm. Hg which comprises the steps of (1) vapor coating a solid substrate surface while maintaining a substrate temperature below about 100° C. with from at least a monomolecular layer up to about 30 A. in thickness of an inorganic metallic compound selected from the group consisting of metal chalcogenides and metal halogenides, said metallic compounds being further characterized by having vapor pressures of at least about 1 mm. Hg between about 500 and 1800° C. yet having substantially no vapor pressure below about 50° C., said solid substrate surface being substantially continuous; (2) contacting said coated substrate surface with an electron beam modulated according to information to be recorded to produce a latent image consisting of nucleation sites on said surface; (3) removing residual parasitic electrostatic charges from the said substrate and (4) subjecting the surface bearing the said latent image to vapors of a metal having vapor pressure lower than that of said inorganic metallic compound under conditions of reduced pressure to render said latent image visible.

3. In a method for recording information upon a solid substrate by selective vapor deposition of metal thereupon at pressures of less than about .01 mm. Hg, the steps of (1) vapor coating a solid substrate surface while maintaining a substrate temperature below about 100° C. with from at least a monolayer up to about 30 A. in thickness of cuprous chloride, said solid substrate surface being substantially continuous; (2) contacting said coated substrate surface with an electron beam modulated according to information to be recorded to produce a latent image consisting of nucleation sites on said surface; (3) removing residual parasitic electrostatic charges from the said substrate and (4) subjecting the surface bearing the said latent image to vapors of metal having vapor pressure lower than that of cuprous chloride under conditions of reduced pressure to render said latent image visible.

4. The method for recording information upon a solid substrate by selective vapor deposition of metal thereupon at pressures of less than about .01 mm. Hg which comprises the steps of (1) vapor coating a solid substrate surface while maintaining a substrate temperature below about 100° C. with from at least a monolayer up to about 30 A. in thickness of an inorganic metallic compound selected from the group consisting of metal chalcogenides and metal halogenides, said metallic compounds being further characterized by having vapor pressures of at least about 1 mm. Hg between about 500 and 1800° C. yet having substantially no vapor pressure below about 50° C., said solid substrate surface being substantially continuous; (2) contacting said coated substrate surface with an electron beam modulated according to information to be recorded to produce a latent image consisting of nucleation sites on said surface; (3) removing residual parasitic electrostatic charges from the said substrate and (4) subjecting the surface bearing the said latent image to vapors of a metal of Group II-B of the Periodic Table under conditions of reduced pressure to render said latent image visible.

5. In a method for producing microcircuitry upon a dielectric substrate by selective vapor deposition of metal thereupon at pressures of less than about .01 mm. Hg, the steps of (1) vapor coating a dielectric substrate surface with from at least a monolayer up to about 30 A. in thickness of an inorganic metallic compound selected from the group consisting of metal chalcogenides and metal halogenides, said metallic compounds being further characterized by having vapor pressures of at least about 1 mm. Hg between about 500 and 1800° C. yet having substantially no vapor pressure below about 50° C.; (2) contacting said coated dielectric substrate surface with an electron beam modulated in accordance with the location of circuit elements to produce a latent image consisting of nucleation sites; (3) removing residual parasitic electrostatic charges from said substrate and (4) subjecting the surface bearing the said latent image to vapors of a metal having vapor pressure lower than that of said inorganic compound under conditions of reduced pressure to convert said latent image to circuit elements.

6. In a method for producing microcircuitry upon a dielectric substrate by selective vapor deposition of metal thereupon at pressures of less than about .01 mm. Hg, the steps of (1) vapor coating a solid substrate surface with from at least a monolayer up to about 30 A. in thickness of an inorganic metallic compound selected from the group consisting of metal chalcogenides and metal halogenides, said metallic compounds being further characterized by having vapor pressures of at least about 1 mm. Hg between about 500 and 1800° C. yet having substantially no vapor pressure below about 50° C.; (2) contacting said coated dielectric substrate surface with an electron beam modulated in accordance with the location of circuit elements to produce a latent image consisting of nucleation sites; (3) removing residual parasitic electrostatic charges from said substrate and (4) subjecting the surface bearing the said latent image to vapors of zinc, cadmium or magnesium under conditions of reduced pressure to convert said latent image to circuit elements.

7. An apparatus for making a metallic record of phenomena comprising, in combination, a substrate material in sheet form; means for precoating such substrate material with a potentially nucleatable inorganic metal compound; means for scanning such precoated substrate surface with a modulated electron beam to create a latent image; means for vapor coating such scanned substrate surface with metal in an amount sufficient to render the latent image readable; means for maintaining pressures not above .01 mm. Hg in the total space surrounding said substrate material, said means for scanning, said means for vapor coating and said means for precoating; and means for moving said substrate material successively past said means for precoating, said means for scanning and said means for vapor coating, respectively.

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