

Sept. 9, 1969

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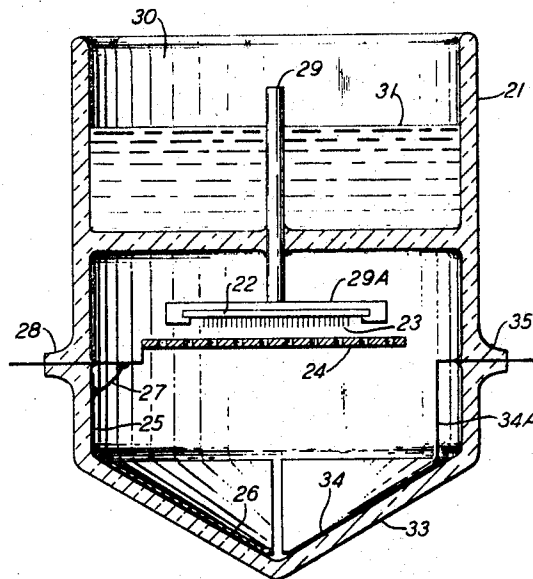
COLD CATHODE EMITTER HAVING A MOSAIC OF CLOSELY SPACED NEEDLES

Filed Sept. 21, 1967

FIG. 1



FIG. 2



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COLD CATHODE EMITTER HAVING A MOSAIC OF CLOSELY SPACED NEEDLES

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Filed Sept. 21, 1967, Ser. No. 669,534

Int. Cl. H01j 39/04

U.S. Cl. 313—95

7 Claims

ABSTRACT OF THE DISCLOSURE

Cold cathode field emitters and arrays thereof of controlled geometry may be obtained by the vapor-liquid-solid crystal growth mechanism or by the freezing of pure components to obtain a rod form eutectic.

This invention relates to field emitters. More particularly, the present invention relates to cold cathode field emitters obtained by means of crystal growth techniques.

Since its discovery more than 70 years ago, the phenomenon of field emission, in which emission occurs from a cold metal under the influence of an intense electric field, has become a sophisticated science, having resulted in a number of devices evidencing varying characteristics fulfilling diverse needs. Such devices include the field emission electron-projection microscope, the field emission flash X-ray source utilized in cineradiographic applications and so forth. Recent interest toward the practical application of field emission has been focused upon various microwave applications and the development of techniques designed to increase current, conductance and perveance levels by the operation of multiple field emission needles in parallel. However, total realization of the potential anticipated for such devices has been impeded by inherent limitations, namely, electrical instability, fabrication difficulties, and so forth. The sharp-pointed field emitters alluded to have been fabricated in a variety of ways, for example, by mechanical grinding, chemical etching, electrolytic etching, and so forth. Despite the various procedures available for the growth of field emitters, a major limitation for most materials has been the lack of uniformity in the control of emitter geometry, cone angle and tip radius. Consequently, the degree of perfection obtained has been dependent directly upon the skill of the fabricator. Furthermore, an even more significant limitation has been the inability to obtain a high emitter density in a cold cathode array.

In accordance with the present invention, cold cathode field emitters and arrays thereof of controlled geometry are obtained either by the vapor-liquid-solid crystal growth mechanism or by the freezing of pure components to obtain a rod form eutectic. Structures prepared in accordance with the described techniques comprise two-dimensional densely populated arrays of metal or semiconductor needles evidencing termination diameters less than one micron upon a selected substrate, the terminations being in parallel. More specifically, the field emitters described are required to have a minimum density of 5 needles-mm.⁻², such emitters manifesting beam currents and emission properties superior to those of the prior art. A specific embodiment of the present invention is directed to a novel photoconductor device utilizing arrays of semiconducting needles as described herein wherein densities may range as low as 1 per square millimeter.

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The invention has been described largely in terms of the growth of needle-like tapered crystalline materials by the vapor-liquid-solid technique described in copending application Ser. No. 669,535, filed Sept. 21, 1967, by J. R. Arthur, Jr. and R. S. Wagner. However, it will be understood by those skilled in the art that the crystalline materials utilized herein may also be grown by means of the freezing of pure components and the preparation of a eutectic structure by techniques well known to those skilled in the art. Thereafter, selective etching procedures may be employed in order to expose the desired rods or filaments, choice of a specific etchant being within the skill of the artisan.

Briefly, the growth procedure utilized in the fabrication of the novel structures by means of the noted VLS process involves the control of growth parameters in the conventional vapor-liquid-solid technique so as to result in the gradual removal of the impurity agent from the liquid solution. This end may be attained by (a) utilizing a deposition temperature such that the rate of evaporation of the impurity agent is sufficient to decrease the volume of the liquid solution; (b) utilizing an agent having a distribution coefficient within the range of 10^{-2} to 10^{-1} whereby the agent is removed from the liquid by incorporation in the crystalline material being grown; (c) selectively removing the agent from solution by means of a chemical reaction whereby a volatile compound is produced; (d) gradually reducing the rate of co-deposition in those situations wherein an agent manifesting a high vapor pressure is utilized; (e) utilizing an agent which is one component of the material to be grown and introducing a vapor comprising a second component of the material to be grown into the liquid solution until the volume of the liquid solution is exhausted, and (f) selected combinations of the foregoing alternatives.

The invention will be more readily understood by reference to the following detailed description taken in conjunction with the accompanying drawing wherein:

FIG. 1 is a front elevational view of a two-dimensional cold cathode array of the invention; and

FIG. 2 is a front elevational view of a photo-conductor of the invention.

For the purposes of the present invention, the growth technique described herein will be largely in terms of the VLS procedure alluded to above. This procedure involves the growth of a crystalline body comprising a first material by a process wherein a second material comprising an "agent" is contacted with a vapor containing the first material, the agent being such that it is capable of forming a liquid solution comprising the agent and the first material, in which solution the agent is maintained at a temperature above the initial freezing temperature of the solution and from which the first material freezes out of solution at the site of the agent. Vapor-agent contact is continued for a time period sufficient to supersaturate the liquid solution with respect to the first material, so resulting in the initiation of crystal growth. At this juncture in the growth process, the temperature of the system is gradually elevated to a point sufficient to cause the evaporation of the agent, thereby decreasing the volume of the liquid solution and the diameter of the growing crystal during the deposition process, vapor agent contact being continued until the agent has completely evaporated. Crystals grown in accordance with this technique have been found to evidence a conical shape, densities of at least 1 needle per square millimeter and tip diameters less than 1 micron.

The term "agent," as applied herein, denotes a broad class of operative materials which may be employed in the practice of the VLS process. Agents may be selected from among elements, compounds, solutions, or multi-

phase mixtures, such as eutectic compositions. Further, the agent may be alloyed or admixed with one or more constituents of the desired crystalline material, or if present, with one or more constituents of a substrate material. The agent may also be or contain a minor constituent desired in the material being crystallized.

Agents employed in the practice of the invention may be required to evidence a vapor pressure over the liquid solution of sufficient magnitude to assure the continuous evaporation thereof at the operating temperatures. It will be evident from the requirements outlined that the constituent or constituents of the agent may evidence a distribution coefficient, k less than unity, k being defined as the ratio of the concentration of the constituent or constituents of the agent in the desired crystalline material to its concentration in the liquid solution from which the desired crystalline material is grown. Selection of a particular agent having desired minimum or maximum values of k is dependent upon the specific material to be grown and the vapor transport reaction selected. Thus, it may be desirable to utilize k factors of the order of 10^{-5} while the vapor pressure of the agent may be as small as 10^{-6} torr.

Still another property influencing the selection of an agent is the wetting characteristic of the liquid solution containing the agent with respect to the substrate and the desired crystalline material. Thus, in the growth of needle-like VLS crystals in accordance with the invention, it is desirable that the contact angle between the liquid solution and the substrate or crystalline body be as high as 90° or greater.

As described above, deposition of a vaporous material is initiated at the site of the agent, a requirement being that the agent be placed at the desired site of crystalline growth in an independent manipulative step. Several techniques are available for providing the agent at the desired site of growth. For example, it may be convenient to place the agent on the growth region by manual means or to deposit films of the agent of prescribed thickness by evaporation, electroplating, and so forth. Further, masks may be employed as desired to form specific arrays and patterns. The desired crystalline material may be furnished by any of the well-known vapor transport processes, typical reactions being set forth below:

- (a) Disproportionation— $2\text{SiI}_2(\text{g}) \rightleftharpoons \text{Si}(\text{s}) + \text{SiI}_4(\text{g})$
- (b) Decomposition— $\text{CuI}_2(\text{g}) \rightleftharpoons \text{Cu}(\text{s}) + 2\text{I}(\text{g})$
- (c) Reduction— $\text{CuI}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{Cu}(\text{s}) + 2\text{HI}(\text{g})$
 $\text{SiCl}_4(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{Si}(\text{s}) + 4\text{HCl}(\text{g})$
- (d) Gaseous Cracking—
 $\text{C}_7\text{H}_8(\text{g}) + 7\text{SiCl}_4(\text{g}) + 10\text{H}_2(\text{g}) \rightarrow 7\text{SiC}(\text{s}) + 28\text{HCl}(\text{g})$
 $\text{CH}_3\text{SiCl}_3(\text{g}) \rightarrow \text{SiC}(\text{s}) + 3\text{HCl}(\text{g})$
 $\text{SiCl}_4 + \text{CCl}_4(\text{g}) + 4\text{H}_2(\text{g}) \rightarrow \text{SiC}(\text{s}) + 8\text{HCl}(\text{g})$
 $\text{SiH}_4(\text{g}) + \text{CH}_4(\text{g}) \rightarrow \text{SiC}(\text{s}) + 4\text{H}_2(\text{g})$
- (e) $\text{SiH}_4(\text{g}) \rightarrow \text{Si}(\text{s}) + 2\text{H}_2(\text{g})$
- (f) Evaporation—Condensation— $\text{Si}(\text{g}) \rightarrow \text{Si}(\text{s})$

During the course of the processing in accordance with the vapor-liquid-solid crystal growth technique the material of interest preferentially deposits at the site of the liquid droplet which eventually attains a state of supersaturation with respect to the material of interest, thereby resulting in the freezing out of solution of that material together with a small concentration of agent at the interface between the solid and the liquid alloy. As the process continues, the alloy droplet becomes displaced from the substrate crystal and rides atop the growing crystal until such time as it is desired to initiate the sharpening process. At this point, the temperature of the system is gradually elevated so as to result in the evaporation of the agent thereby decreasing the volume of the liquid solution and the diameter of the growing crystal. Evaporation is continued until a state of exhaustion of the agent is attained and the process is then terminated. The resultant structure is shown in FIG. 1.

Example I

A silicon wafer 15 mm. x 25 mm. x 1 mm. with {111} was chosen as a substrate material. The substrate was then ground flat with an abrasive paper and given a bright etch to expose undamaged crystal surfaces. The etching procedure involved treating for 3 minutes with a 1:1 solution of hydrofluoric and nitric acids followed by a 4 minute treatment with a 1:2:6 solution of hydrofluoric, acetic and nitric acids. Next, the etched substrate was washed with deionized water and dried in an oven at 110°C .

Following, gold was evaporated in the form of dots 100 microns in diameter and 1000 Å. in thickness upon the etched substrate at the desired sites of crystalline growth. Then the substrate was positioned upon a pedestal in the apparatus.

Next, hydrogen was passed through the system. Then an RF furnace was turned on and the reaction chamber heated to 1050°C . for a period of 10 minutes, so resulting in the formation of a mosaic of molten alloy droplets containing silicon and gold. Thereafter, hydrogen was passed through a saturator where silicon tetrachloride, obtained from commercial sources, was picked up and carried to the chamber. Silicon was permitted to deposit at the sites of the alloy droplets for a period of $1\frac{1}{2}$ hours, the flow of hydrogen through the system being maintained at approximately 350 cm^3 per minute, and the molar ratio of silicon tetrachloride to hydrogen being maintained at approximately 1–100 by means of cold bath 24. At this point in the process, the temperature of the system was gradually elevated to 1150°C . and maintained at this temperature for one hour with a hydrogen flow of 450 cm^3 per minute, so resulting in the evaporation of the agent and a decrease in the volume of the liquid solution with a concomitant decrease of the diameter of the growing crystal until the agent was totally exhausted. The resultant needle-like crystals were found to be highly perfect in nature. A linear array of five VLS grown silicon whisker emitters, approximately 1 mm. in length, grown upon a silicon substrate crystal were mounted approximately 3 mm. from a fluorescent screen anode placed perpendicular to the whisker axes. The substrate crystal containing the whiskers and the anode assembly was mounted in a glass ultra-high vacuum chamber which was baked at 300°C . for 12 hours in order to obtain a background gas pressure of 5×10^{-9} torr. After cooling the substrate crystal to 77°Kelvin with liquid nitrogen, current-voltage data were obtained, the data indicating that the current was due to field emission. The pattern on the fluorescent screen consisted of randomly arrayed spots with a spread of approximately 2.5 mm. perpendicular to the line of emitters, and 5 mm. along the line of emitters, indicating that more than one whisker in the array was emitting since the maximum possible spread of emission from one whisker could not have extended more than 3 mm. due to the small emitter-anode separation.

It has long been recognized by workers in the art that a semiconducting field emission cathode of proper doping would function effectively as a photodetector were it not for the microscopic photosensitive region of a single emitter and the low photogenerated emission current of 10^{-9} – 10^{-6} amperes available from a single emitter.

The limitations may be effectively obviated by the use of two-dimensional arrays described herein, thereby resulting in an image intensifier. Accordingly, if an image is focused upon the inventive array, electrons are emitted by the illuminated emitters, and electromagnetic focusing of the emitted current, as, for example, by an axial magnetic field, results in the preservation of the image which may conveniently be displayed by directing the beam against a phosphor screen.

Example II

This example describes the preparation of a cold cathode field emitter in accordance with the invention by the growth of a rod form eutectic.

An ingot, approximately one-half inch in diameter and approximately eight inches in length was produced by inductively melting zone refined aluminum and high purity nickel rods in recrystallized alumina crucibles (99.7 percent Al_2O_3) under a dynamic argon atmosphere. The melt was held at 900°C . for 1 hour to insure complete mixing, allowed to cool to room temperature and examined for uniformity. Each of the resultant castings was then cut into smaller specimen blanks which were then remelted under argon in a carbon crucible and unidirectionally solidified to produce an ingot having the approximate composition Al_3Ni . The ingot was then cut into pieces about one-half inch in length by cross-sectional cuts, the pieces then being subjected to metallographic polishing. Following, the polished faces were etched for approximately four minutes in a 5 percent aqueous sodium hydroxide solution in order to expose rods or filaments of Al_3Ni having rounded tip diameters less than 1 micron and uniform lengths equal to about 3 diameters.

A sample prepared as described was mounted on a negative metal clamp in a vacuum apparatus with the filaments projecting about 2 millimeters from a molybdenum anode internally cooled by means of liquid nitrogen. Thereafter, the apparatus was pumped to a pressure of the order of 10^{-7} millimeters of mercury and a difference of potential ranging from 7 to 13 kilovolts impressed between the cathode and anode, so resulting in current emission ranging from 10^{-9} to 10^{-6} amperes. A logarithmic plot of current against the reciprocal of voltage was linear over the indicated current range, thereby verifying the observance of true field emission.

Example III

A photosensitive image forming array was prepared as follows:

An array composed of eight whiskers of undoped high resistivity silicon grown as described in Example I was placed in a glass envelope with a fluorescent screen anode about 3 mm. from the substrate crystal. The envelope was pumped on an all-glass ultra-high vacuum pump to a background pressure of 5×10^{-9} torr. After cooling the crystal to 77°K by thermal contact with a liquid nitrogen reservoir, anode voltages from 2.5–8.1 kilovolts produced emission currents from 7.5×10^{-9} amperes to 1.2×10^{-5} amperes in the dark. The light from a zircon arc lamp was then focused and collimated to produce a spot approximately 10^{-2} cm. in diameter. The lens assembly and lamp were mounted on a carriage having a micrometer adjustment in horizontal and vertical planes, so permitting the light to be swept across the emitter array. Four distinct positions were located which produced an increase in emitter current and each position produced a different pattern on the fluorescent screen anode, thereby establishing that at least four of the eight whiskers were emitting and that the magnitude of the current from each whisker could be controlled by the light. The total current increased from 5–30 percent when the light beam struck an emitter, the specific variation being dependent upon anode voltage and choice of whisker.

Example IV

The procedure of Example III was repeated with the exception that an array of 4 whiskers of undoped high resistivity silicon was utilized, one of the whiskers having a significantly smaller diameter than the others and dominating the emission. The total current increased by three orders of magnitude by exposure to room light.

With further reference now to FIG. 2, there is shown in front elevational view a field emission photo-detector in accordance with the invention. Shown in the figure is a

cylindrical container 21 having disposed therein a substrate crystal 22 having an array of closely spaced whiskers 23 and an anode grid 24 of high optical transparency below the termination plane of the whiskers, one-half of the lower portion of container 21 being coated with a transparent electrically conductive coating 25 having a fluorescent screen 26 thereupon, coating 25 and grid 24 being connected by means of lead 27 to anode contact 28. The device also includes cathode rod member 29, mounting bracket 29A, and independent chamber 30, containing a coolant 31. Cylindrical container 21 also includes an image window 33 coated with a transparent conductive coating 34, coating 34A being connected by means of lead 34 with repeller contact 35.

In the operation of the device, a pattern of light is focused upon the emitter array through the image window 33, a difference of potential being applied between the anode grid 24 and the emitter array 23, so resulting in the production of field emission current which is enhanced by those emitters which are illuminated. The initial current passes through anode grid 24, is deflected by a potential applied to repeller lead 35, and strikes the fluorescent screen 26 to produce an intensified image of the light pattern. A suitable coolant, such as liquid nitrogen, may conveniently be placed in the upper chamber or reservoir 30 to magnify the sensitivity of the structure.

What is claimed is:

1. Cold cathode field emitter comprising a crystalline body including a substrate member having a mosaic of closely-spaced needles manifesting maximum tip diameters of 1 micron thereon perpendicular to said substrate, said needles having a minimum density of 5 mm.^{-2} , the said substrate member and needles being a part of the said crystalline body.
2. Emitter in accordance with claim 1 wherein said substrate member and said needles comprise silicon.
3. Emitter in accordance with claim 1 comprising a rod form eutectic structure.
4. Emitter in accordance with claim 3 comprising Al_3Ni .
5. Photodetector including a cold cathode field emitter comprising a crystalline body including a substrate member having a mosaic of closely-spaced semiconducting needles manifesting maximum tip diameters of 1 micron thereon perpendicular to said substrate, said needles having a minimum density of 1 mm.^{-2} , the said substrate member and needles being a part of the said crystalline body.
6. Device in accordance with claim 5 wherein said emitter comprises a silicon substrate having a mosaic of silicon needles thereon.
7. Device in accordance with claim 5 including a vacuum chamber, an anode member, a cathode member, means for evacuating said vacuum chamber and means for impressing a difference of potential between said anode and said cathode members.

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U.S. Cl. X.R.

313—96, 309, 329, 351