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ELECTROCRYSTALLIZER

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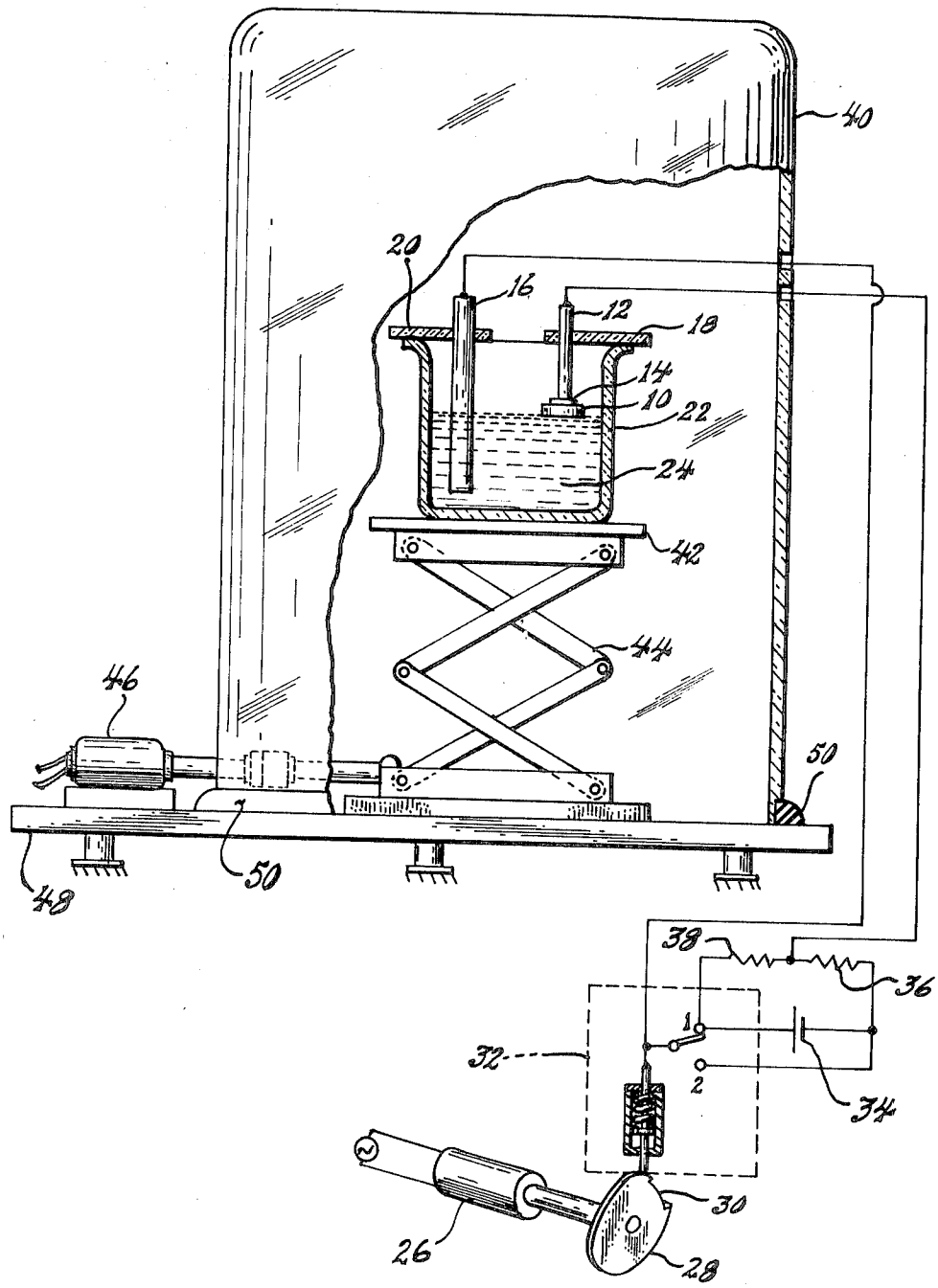

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ELECTROCRYSTALLIZER

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ABSTRACT OF THE DISCLOSURE

An apparatus and method for growing single crystals comprising an electrochemical circuit including a means for alternating in an asymmetrically timed manner the direction of current flow within the electrochemical circuit. Also included is a means to effect the vertical movement of the electrochemical circuit's electrolyte in a downward direction away from a growing crystal at a rate substantially similar to the rate of growth of the growing crystal.

This invention relates to the electrodeposition of single crystals in a form which ranges from epitaxial layers to bulk crystals, depending on the time of deposition. More particularly, this invention concerns itself with an apparatus and method that utilizes a low frequency reversing current for growing single crystals by electrodepositing them from solution onto a properly oriented seed which acts as an electrode.

In general, techniques for growing single crystals either in the form of epitaxial films or as bulk crystals require the use of an elevated temperature or a high vacuum, or both. In an attempt to overcome the problems inherent in the use of high temperatures and vacuums, it has been suggested that epitaxial layers of single crystals be formed by using low frequency reversing currents to accomplish their deposition onto a substrate. The use of this method enables the production of single crystals at room temperature and ambient pressures, thereby abrogating the problems inherent in the use of high temperatures and vacuums. However, the epitaxial films so produced were not of a consistently uniform thickness throughout and, in addition, this method did not lend itself to the production of single crystals in bulk.

With the present invention, however, it has been found that epitaxial layers of single crystals can be provided which possess a consistently uniform thickness over the entire surface of the plated substrate and, in addition, single crystals in bulk form can also be produced.

The invention provides a simple and economical means for growing bulk single crystals of a uniform diameter. The use of room temperatures and ambient pressures eliminates the complex control problems encountered in high temperature and high vacuum methods.

In accordance with this invention, it has been found that the above noted deficiencies of the prior art can be abrogated by utilizing an electrolytic bath that is adapted to be moved vertically downward at a predetermined rate of speed while the single crystal is being formed. The downward movement provides a fresh surface for crystal growth with the movement timed to coincide with the rate at which the crystal grows, thereby insuring the growth of a single crystal having a constant and uniform thickness in the case of epitaxial layers; or diameter in the case of a bulk crystal.

Accordingly, it is a primary object of this invention to provide an apparatus and method for growing single crystals in a form which ranges from epitaxial layers to bulk crystals.

Another object of this invention is to provide an apparatus and method for growing microminaturized thin film components.

Still another object of this invention is to provide a method which utilizes room temperatures and pressures for the growth of single crystals from solution.

A further object of this invention is to provide an electrochemical apparatus and method for forming single crystals that utilizes a low frequency reversing current in combination with a downwardly controlled movement of the electrochemical solution in order to effect the electrodeposition of the crystal.

Still a further object of this invention is to provide a crystal growing apparatus which includes the use of a mechanical alternator for a reversing current that is timed to have a plating cycle to a deplating cycle asymmetric for the growth of single crystals.

Still a further object of this invention is to provide crystal growing apparatus which includes the use of a downwardly movable platform whose vertical velocity equals the rate of growth of the crystal in order to achieve a high degree of uniformity of growth.

Still a further object of this invention is to provide a controlled, reproducible, inexpensive apparatus and method for the growth of single crystals of metals, metal compounds or metal alloys by electrodepositing them onto a suitable substrate.

The above and still further objects, advantages and features of this invention will become more readily apparent upon consideration of the following detailed description thereof taken in connection with an illustrative embodiment shown in the accompanying drawing. The figure represents an illustration of the apparatus utilized with the method of this invention, together with a schematic electrical circuit suitable for generating the low frequency asymmetrical reversing current used with this invention.

Referring to the figure, these is shown a substrate electrode **10** on which the single crystal is to be grown. The substrate **10** may be a solid elemental metal, metal alloy or metallic compound, the choices of which are subject to the limitations imposed by the choice of the electrolytic solution as will be discussed infra. One limitation which is common to all such substrate materials is that the substrate must be a single crystal.

In the figure, the substrate **10** forms an electrode in an electrochemical circuit and is shown in the form of a cylinder of the single crystalline material. It need not be in the form of a cylinder, however, since any convenient shape may be used to provide the seed electrode upon which the single crystal is deposited, either as a film or in bulk. The substrate **10** has affixed thereto an extension rod **12**. The rod **12** is affixed by conventional means such as threads on the end of the rod **12** and a tapped hole in the substrate material **10** or by means of a silver epoxy resin **14**.

A second electrode **16** of the material or materials to be deposited as a single crystal is also provided in the form of a cylinder. Unlike the substrate electrode **10**, however, electrode **16** may be of a polycrystalline form. Each of the electrodes **10** and **16** are supported in conventional holders **18** and **20**, respectively, which, in turn, are supported by, for example, the dust box **40** or support **43** above a suitable container **22**. The container **22**, preferably a quartz beaker, holds a suitable electrolytic solution **24**. Perchlorates are preferred for the electrolytic solution since they can be refluxed to oxidize impurities in the water. Whenever impurities are present, single crystalline growth is often inhibited.

Solutions other than perchlorates also may be employed as the electrolyte provided ultra-pure materials

are utilized in combination with a dust-free atmosphere. When proper control conditions are maintained, the electrolytic solution **24** may comprise most acids such as nitric, sulphuric and hydrochloric.

In the event a perchlorate electrolyte is utilized with a single crystal of metal, the substrate material is chosen from elements on the electromotive series more noble than hydrogen, except for those materials which are less noble, and have a hydrogen overvoltage condition which does not allow for the formation of hydrogen at the electrodes. All metal elements and compounds capable of single crystal formation may be utilized by the appropriate choice of an electrolyte. The cation concentration of the constitutents of the solution and the making of complexes in the solution allow for the proper crystal growth. Thus, the EMF of compounds is adjusted for the elements.

This invention has also proven to be capable of utilizing dissimilar materials, for example, copper may be grown on a single crystal of nickel by using a copper sulfate electrolyte. The parameters of the lattice of the substance to be deposited, however, must be within 20% of the lattice parameters of the substrate.

In obtaining the growth of single crystals in bulk form or as epitaxial layers at room temperatures and pressures, it has been found that the apparatus and method of this invention requires the utilization of a low frequency asymmetrically timed reversing current. As described in the figure, the means for producing the reversing current utilized in this invention is electrically connected to the electrodes **10** and **16** and comprises a motor driven mechanical alternator having a constant speed motor **26** which controls the frequency of the reversing current. Attached to the motor **26** is a circular cam **28** from which a section has been cut, as shown at **30**, such that the ratio of the circumferential length of the cutout section to the remaining circumference of the cam determines the ratio of the duration of the plating portion of the cycle to the deplating portion of the cycle. A single pole double throw mircoswitch **32** is arranged to ride on the cam surface in order to reverse the flow of current coming from the 6 volt battery **34** through 620 ohm resistors **36** and **38**. These resistors are connected respectively to the electrodes **10** and **16**. By means of the mechanical alternator, an asymmetrically time square wave is generated in order to accomplish the desired crystal deposit.

The apparatus also comprises a Lucite dust box **40** to prevent contamination during the growth of the single crystal and a platform **42** adapated to move the beaker **22** vertically downward in a controlled manner by means of a scissors jack arrangement **44** which, in turn, is driven by a geared down motor **46**. The entire apparatus rests on a conventional support as indicated at **48**.

The apparatus will be described relative to the operation of the system utilizing copper as the substrate **10** on which an epitaxial deposit is to be grown. The substrate **10** is formed from a single crystal copper cylinder which was spark cut to result in a half-inch length of half-inch diameter which was attached to the extension **12**. The copper substrate **10** was treated to remove residual or organic impurities by immersing it in a concentrated hydrochloric solution overnight. The electrolytic solution **24** was prepared in an all quartz refluxing apparatus which had been previously cleaned with a sulphuric acid-chromic acid cleaning solution followed by thorough washing with distilled water. Eight grams of spectrographically pure copper oxide and 24 cc. of perchloric acid, doubly distilled in Vycor, were mixed with distilled water to a volume of 100 cc. and refluxed for two hours in the all quartz system with a loose-fitting cover. The conductance of the distilled water is the same as that obtained by having 0.1 part per million of sodium chloride in absolutely pure water.

The electrolytic cell was provided by a 100 cc. quartz beaker **22** which had previously been cleaned as above. Each run was made in the Lucite dust-box **40** to prevent contamination of the electrolytic solution. Prior to utilization of the copper substrate **10**, both it and the polycrystalline copper electrode **16** were etched with concentrated nitric acid and hydrochloric acid followed by a thorough washing with distilled water. The current density generated at the cathode in a typical run is 5 milliamperes per square centimeter with the ratio of plating to deplating cycles of 4.7 to one with a frequency of 30 cycles per minute.

In a typical run, the electrode **16** was immersed into the solution **24** and the substrate **10** was placed in contact with the surface of the freshly prepared perchlorate solution **24** and connected to the appropriate electrical leads and electro-etched for seven minutes using a reversing current with a deplating to plating ratio of 4.7 to 1. In this manner, the substrate becomes anodic longer than it is cathodic and oxide layers are removed electrochemically. After this pretreatment, the leads to the electrodes are reversed and the run is continued for about two hours for a 10 micron deposit, or overnight for a 140 micron deposit. After the run the substrate and deposit were weighed to calculate the apparent thickness. Laue back reflection X-ray methods were used to determine the degree of crystallinity using 13 kv. copper X-rays at 20 milliamperes. The X-ray patterns of a typical run in which 100 microns of copper were deposited showed sharp well defined dots indicating good single crystallinity.

In a further illustration of the use of the apparatus of this invention, a single crystal of copper in bulk form may be grown on on a copper seed. The apparatus is cleaned as was discussed heretofore with an appropriate cleaning solution. The electrolyte comprises a solution of copper perchlorate prepared from eight grams of copper oxide and twenty-six cc. of perchloric acid, doubly distilled in Vycor. The quartz beaker **22** rests on a platform **42** which is adapted to move vertically downward in a controlled manner by reason of the scissors jack arrangement **44** and geared down motor **46**. The rate of travel of the platform is determined from the rate of crystal growth and can be calculated in the following manner. If the radius of the single crystal seed equals 0.635 with a current of 0.01 amperes, then the rate of growth of the crystal equals:

$$\frac{(0.01)(31.75)}{(96.500)(8.92)(3.14)(0.635)^2}=2.9\times10^{-7}\text{ cm./sec.}$$

or

$$2.9\times10^{-3}\text{ microns per second}$$

This velocity is attained by bearing down a 60 cycle, 115 volts, 3 watt, 1/15 r.p.m. synchronous motor. The beaker, electrodes, platform and scissors jack arrangement are maintained in a dust-free manner by covering them with either a glass or Lucite dome. The loss of electrolytic solution through evaporation is minimized through the use of a rubber gasket or silicone grease sealing means **50**.

In a typical run, the electrodes **10** and **16** are carefully immersed in a freshly prepared perchlorate solution **24** so that only the surface of the solution **24** touches the bottom of electrode **10**. The electrodes are then connected to the appropriate electrical leads. The glass cover **40** is assembled on its support **48**. After a seven-minute electroetch, similar in manner to that described heretofore, the single crystal copper seed **10** is made cathodic and the run begun. The run is continued depending on the size of the bulk crystal desired. Single crystal deposits of a constant and uniform diameter, confirmed by X-ray Laure patterns, have been obtained.

From a consideration of the foregoing, it becomes apparent that this invention provides a method and appara-

tus for obtaining the growth of single crystals in the form of epitaxial layers or as bulk crystals. The technique employed in this invention is not limited by the difficulties encountered in obtaining and controlling the high temperatures and high vacuums required by methods employed heretofore. The operation of the apparatus is not critical with respect to the plating or deplating cycle; however, the plating portion should be greater than 50% to result in crystal growth. Likewise, the frequency should be limited to allow the travel of ions from the solution. The invention also allows for the growth of single crystals whose crystallinity can be controlled by the current, whose size can be controlled by time, and whose purity can be controlled by voltage.

The crystalline products of this invention can be deposited with barrier functions, as metal layers for contact purposes, as alloy layers with magnetic characteristics, or as oxide layers for insulation in electronic circuitry. The unique feature of utilizing a movable support for lowering the electrolyte bath at the same rate at which the crystal grows ensures the growth of a constant diameter crystal or an epitaxial layer of uniform thickness making the product of this invention especially useful.

Although the invention has been described with reference to particular embodiments, it will be understood by those skilled in the art that the invention is capable of a variety of alternative embodiments within the spirit and the scope of the appended claims. For example, elements proven usable with a perchlorate electrolyte are copper, silver and lead, as well as the alloy brass and the compound indium antinomide. Gold crystals have been shown capable of formation by the process when a chloride electrolyte is used and copper on a nickel substrate has also been demonstrated to be practical.

What is claimed is:

1. An apparatus for the growth of metallic single crystals comprising:

an electrolytic cell adapted to contain an electrolyte,

a pair of electrodes supported to extend in said cell with one of said electrodes being a monocrystal of a metal,

a means for effecting the vertical movement of said cell in a downward manner at a precontrolled rate of descent, and

electrical means connected with said electrodes for providing a low frequency, asymmetrically times, square wave current which produces between said electrodes a current flow reversing between positive and negative polarities.

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