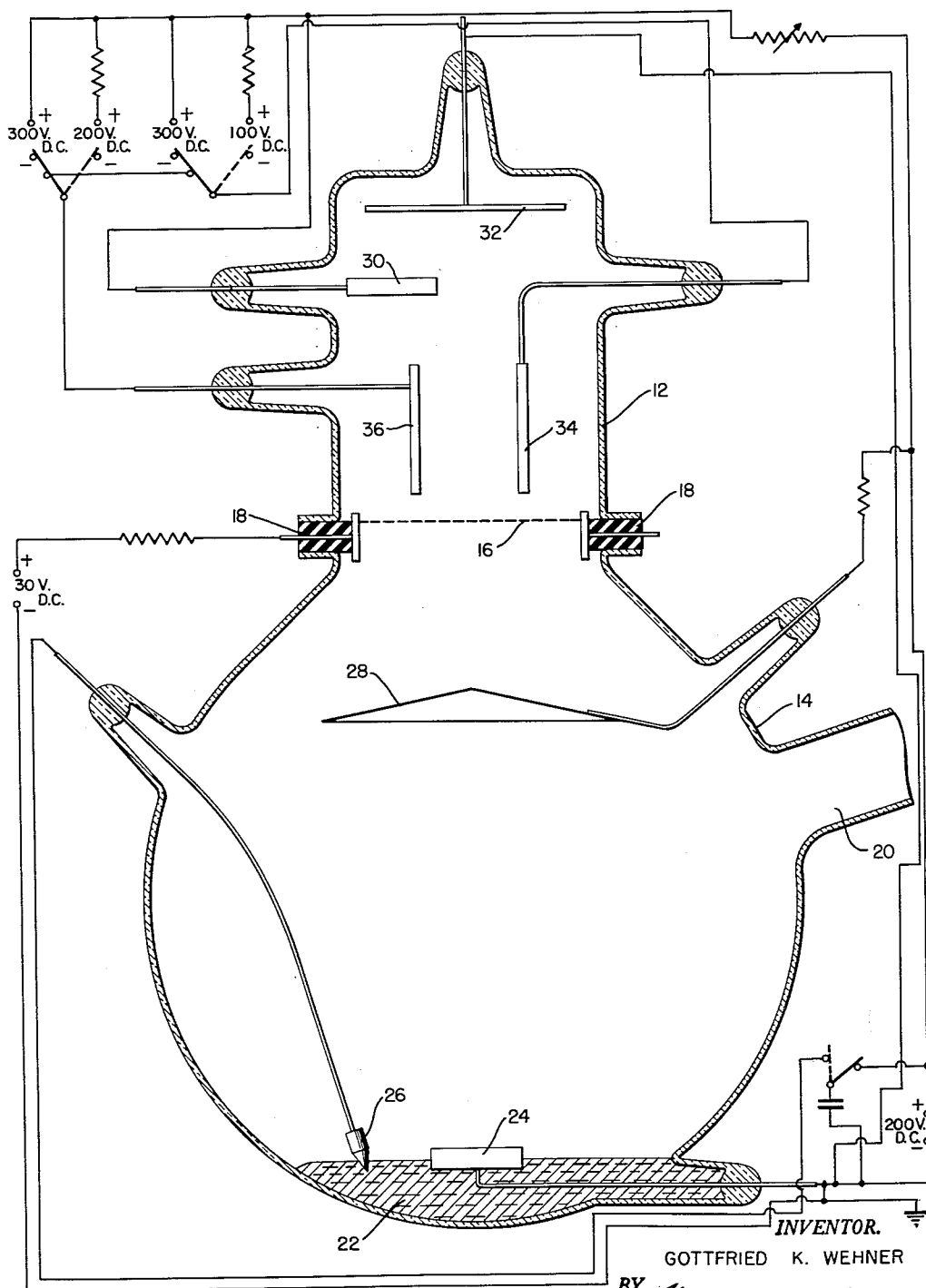


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GROWTH OF SOLID LAYERS ON SUBSTRATES WHICH ARE
KEPT UNDER ION BOMBARDMENT BEFORE
AND DURING DEPOSITION
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GROWTH OF SOLID LAYERS ON SUBSTRATES WHICH ARE KEPT UNDER ION BOMBARDMENT BEFORE AND DURING DEPOSITION
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This invention generally relates to a method for effecting the growth of solid layers on substrates with a continuance of substrate crystal orientation therein and, in particular, the growth of single crystal layers on seed crystals with a continuity of crystal orientation and improved atomic bond therebetween.

The deposition of solids on substrates with true atomic bond therebetween and with a continuance of substrate crystal orientation in the deposited material has heretofore been attempted by utilization of vacuum evaporation, sputtering decomposition of gaseous compounds and electrolytic deposition from solutions. In each of the above mentioned methods the critical parameters are the substrate temperature and the corresponding rate of deposition. The temperature apparently determines, among other things, the rate of surface migration of the arriving atoms of the deposited material and, as such, the activation energy in the form of heat necessary to transport the deposited atoms to the location of the lowest free energy, i.e. their right lattice positions. These attempts, except for certain special and simple cases involving layers of preferred orientation or very thin single crystal layers, have generally been unsuccessful due to the difficulty of removal of oxide or other chemically adsorbed layers from the substrate surface, which interfacial obstruction serves to block the growth and continuation of the substrate crystal structure.

This invention may be briefly described as a method of effecting the growth of solid layers on substrates which includes, in its broader aspects, the step of maintaining the substrate surface under controlled condition ionic bombardment before and during deposition. In more particularity, the herein described invention includes utilization of ionic bombardment of such energy and current density as to provide the activation energy necessary to move the deposited atoms to their right lattice positions and to effect sufficient sputtering of the substrate surface as to effectively remove contaminant surface layers therefrom prior to deposition and to materially contribute to the maintaining of an atomically clean substrate surface during deposition.

Among the advantages of the herein described invention is a wide increase in the number of permitted combinations of deposit and substrate materials determinable, at least in part, by congruity of crystal configuration and similarity of lattice constants, the removal of foreign atoms, stacking faults and dislocations from the substrate surface and consequent permitted increase in the degree of bond perfection and the permitted utilization of polycrystalline materials as one of the solid components. The invention described herein, due at least in part to the advantages set forth above, is possessed of marked utility in most, if not all, fields wherein metal, semi-conductor or insulating layers are desirably atomically bonded to a substrate surface such as in, for example, the fabrication of semi-conductors, the preparation of surfaces for electrical contacts, for the preparation of corrosion resistant surfaces or for covering surfaces with heat-resistant material, such as tungsten.

The principal object of the invention is the provision of an improved method for effecting the deposition of materials on substrates.

Another and further object of this invention is the pro-

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vision of an improved method for effecting the growth of solid layers on substrates with an improved atomic bond therebetween and with a continuance of substrate crystal orientation in the deposited material.

Other objects and advantages of the invention will be pointed out in the following specification and claims and illustrated in the accompanying drawings which depict one type of apparatus suitable for practical realization of the advantages attendant practice of the herein disclosed methods.

Referring to the drawings:

FIGURE 1 is a schematic representation of the essentials of one type of apparatus by which practice of the herein disclosed invention may be effected.

In its broad aspects the invention herein disclosed includes the step of subjecting a substrate surface to ionic bombardment to effect the removal of contaminant material therefrom and to otherwise prepare the same for the receipt of the material to be deposited prior to deposition thereof and the step of maintaining said substrate surface under controlled ionic bombardment during deposition so as to effect at said substrate surface the ratio of the material deposited thereon to the material sputtered away therefrom and to maintain the overall rate of deposition below a predetermined critical value.

In more particularity, desirable growth conditions in the practice of the herein described invention may be conveniently achieved by immersing, in face to face relationship, the substrate and the source for material to be deposited as separate electrodes in a low pressure high density gas discharge plasma with low background impurity pressure, such as a D.C. mercury vacuum arc plasma of the type created at about 1 micron mercury gas pressure between a pool type cathode and an anode. With the material to be deposited and the substrate so disposed, both are subjected to preliminary ionic bombardment to effect the removal of contaminant surface layers therefrom and otherwise prepare the substrate surface for receipt of the material to be deposited. After a predetermined cleaning period, the potentials on the material to be deposited and the substrate are modified to effect selective and controlled condition ionic bombardment thereof so as to effect the arrival at the substrate surface of more of the material that is to be deposited than is being sputtered away therefrom and to control the overall rate of deposition so as to maintain the same below a predetermined value.

The above mentioned initial ionic bombardment effects a sputtering of both the surfaces of the substrate and the material to be deposited and in the removal of oxide or other chemically adsorbed contaminant layers therefrom as well as possibly correcting possible stacking faults and dislocation from the substrate surface. Under the selective and controlled condition ionic bombardment sputtering of the surface of the material to be deposited continues as does the sputtering of the substrate surface. However, if the operational conditions are controlled so that a greater quantity of the material to be deposited arrives at the substrate surface than is being continually sputtered away therefrom and if the overall rate of deposition upon the substrate surface is maintained below certain critical values, which apparently vary with the substances involved, growth is effected characterized by a close approach to, if not actual attainment of, a true atomic bond and a continuance of substrate crystal orientation in the deposited material. If the critical rate of deposition is exceeded, the deposit will not usually grow as a single crystal but will usually show only a preferred orientation of very small crystallites. As such the deposition rate is probably one of the major determinants of the perfectness of the deposited crystal.

It is believed that under the deposition conditions de-

scribed herein that the bombarding ions provide the necessary activation energy for the movement of the deposited atoms into their right lattice positions.

By way of general example, growth conditions of the type herein described may conveniently be obtained through utilization of apparatus of general character schematically illustrated in FIGURE 1 and as also generally shown and described by the inventor hereof in conjunction with certain published studies at pages 690-704 in vol. 102, No. 3 of The Physical Review and, for example, a German article cited therein beginning on page 501 of Annalen Der Physik 5 Folge Bd 71 Heft 7 u. 8 (1942). As depicted in FIGURE 1, suitable apparatus may include a demountable tube having upper and lower sections 12 and 14, respectively, with a properly designed fine mesh graphite grid 16 which separates the tube anode space from the cathode space thereof. The upper and the lower sections of the tube are suitably sealed together by rubber gaskets 18. The graphite grid 16, which may be about 0.4 mm. thick having about thirty-six holes per cm.² of 1.3 mm. diameter as explained in the above identified publication, permits a considerable increase in plasma density within the anode space in the upper tube section 12 without utilization of undesirably high discharge currents and also permits an appreciable, yet simple, control of the velocity of accelerated beam electrons by variations on the grid potential.

The lower tube section 14 preferably contains a suitable exhaust pump conduit 20, a mercury pool cathode 22 having a cathode spot anchor 24 and an igniter 26. The upper portion of the lower tube section 14 contains an axially disposed auxiliary anode 28.

The upper tube section 12 contains an anode 30 preferably disposed outside of the path of the beam electrons and an associated repeller 32. The anode 30 and repeller 32 are preferably positioned so as to effect a reflection of the beam electrons back into the plasma and thereby produce a further increase in plasma density within the anode space of the tube. If desired, a still further increase in plasma density may be readily effected by application of suitable magnetic fields. Immersed within the area of high plasma density within the anode space is the substrate or seed crystal 34. Facing the substrate surface and disposed in closely spaced relationship therewith is the source of the material to be deposited, conveniently termed the depositor 36.

Circuitry for the operation of the low pressure plasma discharge liquid mercury pool tube of FIGURE 1 is well known in the art. For example, a circuit such as illustrated on page 507 of the previously noted article beginning on page 501 of Annalen Der Physik 5 Folge Bd 41 Heft 7 u. 8 (1942) would be adequate to establish the necessary plasma density in the upper tube section 12. The biases on the substrate 34 and the depositor 36 mentioned below can be obtained, as is well known in the art, by the use of a battery with appropriate dropping resistors and switches.

By way of specific example of the practice of the herein disclosed method with employment of the above described tube, germanium crystal, prepared to have a polished and chemically etched plane (100) surface, was immersed in the region of high plasma density as the substrate. Also immersed in the region of high plasma density and spaced about 2 to 3 cm. away from the above described substrate, was the source of material to be deposited, specifically a piece of very pure polycrystalline germanium. The substrate and depositor surfaces were then subjected to cleaning by ionic bombardment for about 15 minutes under conditions approximating 300 volts ion energy and 5 ma./cm.² ion current density. After the ionic bombardment cleaning period and without interruption the potential of the germanium crystal substrate was changed to minus 100 volts with respect to the anode, and that of the depositor to minus 200 volts with respect to the anode. Under these conditions and at roughly 5 ma./cm.² ion cur-

rent density approximately eight germanium monolayers were sputtered from the depositor per second. The sputtering rate from the germanium substrate was, at about 100 e.v. ion energy, approximately one monolayer per second. Under such conditions the deposited germanium grows on the germanium substrate as a single crystal with a continuance of substrate crystal orientation at the rate of roughly 0.5 μ per hour.

If the overall rate of growth is too rapid, as for example, as would be obtained by application of minus 300 volts to the depositor (with respect to the anode) instead of the minus 200 volts as set forth in the above example, the deposited germanium does not grow as a single crystal but shows only a preferred orientation of very small crystallites.

In order to effect proper growth on the substrate it is necessary to prevent surface contamination thereof by external contaminants such as the gas contained within the tube. In the above described example contamination of the substrate surface by condensation of mercury atoms thereon may be effectively prevented by maintaining the substrate at a temperature of at least 250° C. In the described example and under the conditions of operation described, the target automatically assumed a temperature of about 300° C. under the intense ion bombardment which was well above any temperature at which undesired contamination could be effected by condensation of mercury atoms.

Another example illustrative of the practice of the herein disclosed invention with employment of the above described tube included the utilization of a piece of optical grade silicon as the depositor disposed about 2 centimeters away from the substrate in the region of the high plasma density. The particular substrate again was a germanium crystal having a polished and chemically etched plane (100) surface. With the depositor and substrate so positioned, they were both subjected to cleaning by ionic bombardment for about 15 minutes under conditions approximating 300 volts ion energy and 5 ma./cm.² ion current density. After the cleaning period, and without interruption, the potential of the germanium crystal substrate was changed to minus 100 volts with respect to the anode and that of the silicon depositor, which has a lower sputtering rate, to minus 500 volts with respect to the anode. Under these conditions and at roughly 5 ma./cm.² ion current density approximately six silicon monolayers are sputtered from the depositor per second with the sputtering rate from the germanium crystal substrate again being roughly 1 monolayer per second. Under such conditions the deposited silicon grows on the germanium substrate at a rate of about 0.3 μ per hour. Here again, if the overall rate growth is too rapid, the deposit does not grow as a single crystal but shows only a preferred orientation of very small crystallites.

The above examples are intended only to be illustrative of the practice of the method herein disclosed. The values set forth may not be, and probably are not, the optimal growth values and will change with materials employed, geometric arrangements and other variables that would be attendant any given operation. The overall considerations, however, which apparently determine the actual values to be desirably employed include, at least that more depositor material arrives at the substrate surface than is being sputtered away therefrom and that the overall rate of deposition of the depositor material on the substrate surface remain below a certain value, since this latter is probably a major factor or determinant of the perfectness of the deposited crystal.

Although the above described examples relate to operations effected by means of the illustrated apparatus wherein release of the depositor material was effected by sputtering under ion bombardment, the invention is not so limited. For example, the depositor material could equally as well have been released by evaporation. In

such case, the depositor could be made an anode and be heated up to the necessary temperatures by electron bombardment or by inclusion of a separate heating element as is well known in the art. As will also be apparent to those skilled in the art, the illustrated positional arrangement between the depositor and substrate can readily be modified without departure from the principles of the herein described invention as for example, having the depositor concentrically, or even spherically, enclose the substrate so as to minimize loss of depositor material. Moreover, the discharge plasma may as well be created by other means than a D.C. discharge, as for example by high-frequency ionization of a low pressure gas. Likewise practice of the invention is not confined to a mercury plasma, other noble gases like He, Ne, Ar, Kr and Xe may be used just as well for the ion bombardment. In addition, the herein described method is not intended to be limited to single crystal growth but may well find utility in the more general covering of polycrystalline materials with other materials with improved bond therebetween.

Having thus described my invention, what I claim is:

1. In the growing of solid layers on substrates the steps of immersing the substrate and the material to be deposited thereon as separate electrodes in a low pressure supported gas discharge plasma of high density established between two other electrodes, subjecting said substrate and said material to ionic bombardment to effect the removal of contaminant material therefrom, then lowering the potential of said substrate and said material so the potential of said material is more negative than the potential of said substrate, and subsequently subjecting said substrate and said material to selective ionic bombardment such that atoms of said material are sputtered from said material to said substrate and from said substrate in a manner such that the rate of said atoms arriving at said substrate is higher than the rate of said atoms leaving said substrate.

2. In the growing of solid layers on substrates the steps of immersing the substrate and the surface of the material to be deposited as separate electrodes facing each other

in a low pressure supported gas discharge plasma of high density established between two other electrodes, subjecting said substrate surface and said material surface to ionic bombardment with positive rare gas ions to effect the removal of contaminant material therefrom, then and without interruption lowering the potential of said substrate and said material surface so the potential of said material surface is more negative than the potential of said substrate, then subjecting said substrate and said material surface to an ion current density such that atoms of said material surface are sputtered from said surface to said substrate, said current density being such that the rate of atoms arriving at said substrate surface is higher than the rate of atoms sputtered away therefrom.

3. In the growing of solid layers on substrates the steps of immersing the substrate and the surface of the material to be deposited as separate electrodes facing each other in a low pressure supported gas discharge plasma of high density established between two other electrodes, subjecting said substrate surface and said material surface to ionic bombardment with Hg-ions to effect the removal of contaminant material therefrom, then and without interruption lowering the potential of said substrate and said material surface so the potential of said material surface is more negative than the potential of said substrate, then subjecting said substrate and said material surface to an ion current density such that atoms of said material surface are sputtered from said surface to said substrate, said current density being such that the rate of atoms arriving at said substrate surface is higher than the rate of atoms sputtered away therefrom.

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