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2,958,636

METHOD OF THE APPLICATION OF LIQUIDS TO SOLIDS

Filed Sept. 10, 1956

2 Sheets-Sheet 1

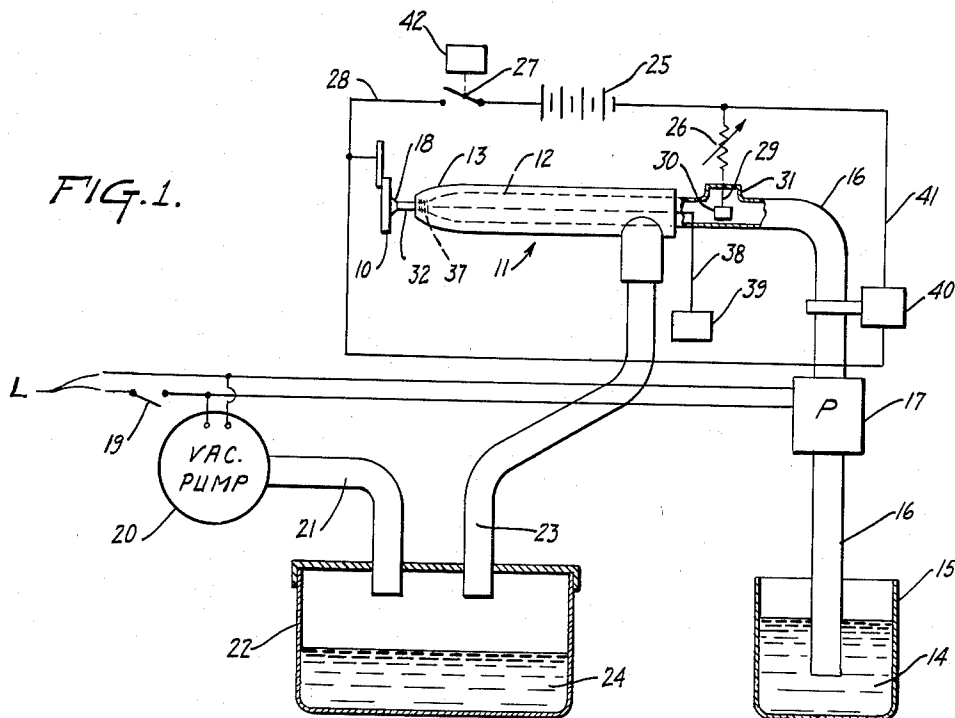
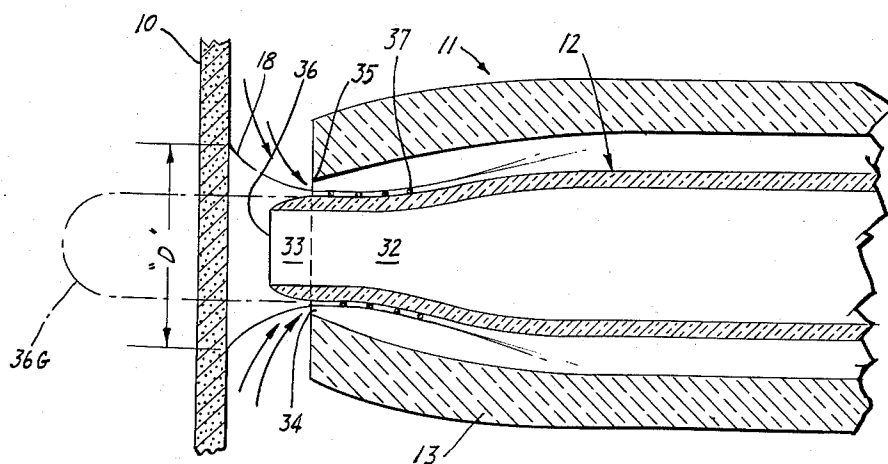


FIG. 2.

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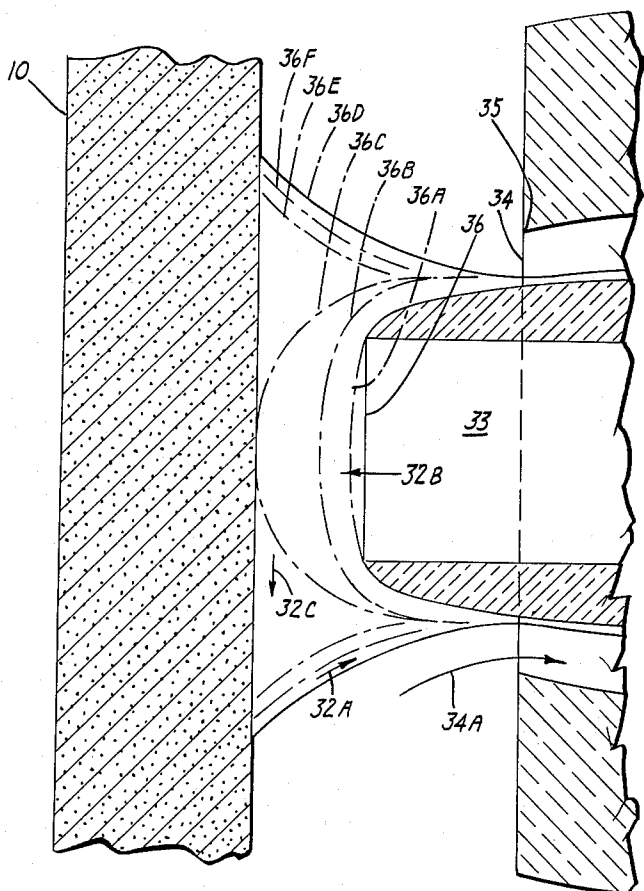
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2 Sheets-Sheet 2

FIG. 3.



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METHOD OF THE APPLICATION OF LIQUIDS
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2 Claims. (Cl. 204—143)

The invention hereinafter described has to do with the application of a liquid, such as an etching solution, to a solid, such as a semiconductive body. While the invention has much broader applicability it will be described as applied to the electrolytic etching and plating of a wafer of germanium in the formation of a so-called collector or emitter and of the area for the same.

In operations of this kind it is generally important to produce certain configurations of the solid body with extreme accuracy and also with considerable speed. In some instances it is possible to further these objectives by confining the liquid between walls, for instance in a so-called etching cup; but more often such confinement is either insufficient, for instance because of leakage, or objectionable, for instance because of scratching of the solid body which in turn leads to trouble in conjunction with the etching treatment.

Greater success has been achieved by treating a semiconductor with a solution in the form of a jet flow electrode, as described for example in the copending applications of Tiley and Williams, entitled "Semiconductive Devices and Methods for the Fabrication Thereof," Serial No. 472,824, filed December 3, 1954, and of Williams, entitled "Method for Electrolytic Etching," Serial No. 477,034, filed December 22, 1954, now Patent No. 2,799,637. A jet flow method of measuring and controlling the thickness of the etched body has been disclosed in the copending application of Bradley and Roschen, entitled "Electro-chemical Method and Apparatus," Serial No. 575,159, filed March 30, 1956. In addition, means for and methods of so treating and measuring semiconductors have been disclosed by the present applicant in an application entitled "Method and Apparatus for Etching," Serial No. 550,722, filed December 2, 1955, now abandoned, of which this is a continuation-in-part. The applications mentioned are assigned to the assignee of the present invention.

The present method, in one aspect thereof, is an improvement over or modification of the methods of the copending applications referred to. It allows complete elimination of the use of a "jet" stream; or at least it eliminates problems caused by forcible impingement or wide spreading of a jet stream. It uses, advantageously, a small liquid electrode body under operative conditions such as to enforce a substantially viscous and almost solid rod-like behavior of said liquid body and mainly of the core thereof, although the liquid material may be quite mobile. Such a liquid body will contact a solid body with much less friction than a jet stream does, although exposed surface portions of said liquid body may be subject to very rapid movement. The new arrangement of the liquid body or liquid electrode provides greatly improved control over the configuration of the solid body to be liquid-treated; the control being improved both as to the peripheral configuration and as to the cross-sectional profile of the solid body, pursuant to etching or other treatment. The new arrangement also

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facilitates accurate application of the aforementioned measuring and controlling method.

Apparatus for producing and using the novel, viscous electrode may include a re-entrant system of outflow and inflow nozzles, generally of minute dimensions and minutely spaced from the solid body under treatment. As to the specific arrangement of such nozzles it is preferred, as in the earlier application of this applicant, to arrange the discharge nozzle coaxially within and slightly in front of the return suction nozzle; and certain electrode means may be used in each nozzle.

The details will be more fully understood from consideration of the following description, taken together with the accompanying drawings wherein:

Figure 1 is an enlarged, schematic presentation of a system in accordance with the invention;

Figure 2 is a more enlarged, fragmentary, sectional view of a preferred nozzle structure; and

Figure 3 is a still more enlarged, fragmentary, sectional view of an important detail of said structure.

Figure 1 shows a germanium wafer 10 under fabrication for the production of a semiconductor diode. This wafer is held in front of a nozzle structure 11, which as shown comprises two closely associated, particularly coaxial nozzles, identified as outflow nozzle 12 and inflow nozzle 13. An electrolytic solution or etchant 14 from reservoir 15 is fed through a suitable conduit 16 into the suction zone of a feed pump 17, which maintains a gradual movement of this liquid into and through the outflow nozzle 12 and toward the germanium blank 10, where the liquid forms a seemingly motionless but actually mobile drop 18. In order to return the liquid into the inflow nozzle 13, there is provided a power line L—from which the feed pump 17 is also energized—a switch 19 and a vacuum pump 20. The latter pump creates reduced air pressure in a conduit 21, a closed reservoir 22 a further conduit 23 and the suction nozzle 13, these elements being connected with one another in series. Thus there is created an area of low pressure around the outflow nozzle 12, to draw large quantities of air into the suction nozzle and thereby to entrain a return flow of spent etching solution over the exposed surface of the drop 18. This return or reentrant flow passes into the reservoir 22, wherein the spent etchant 24 may be accumulated while the air is exhausted by the vacuum pump.

Preferably all portions of the apparatus which come into contact with the etchant are made of materials which are electrically non-conductive and electrolytically non-reactive with the etchant. This etchant may comprise, for instance, an aqueous solution of sodium nitrate, sodium chloride, potassium nitrate, sodium sulphate, nitric acid, or the like.

An electrolytic circuit is established, comprising a potential source 25, a current regulating resistor 26, a switch 27 and conductors 28 and 29; the first of these conductors being connected to the germanium wafer 10 and the second to an electrode 30 within the electrolyte supply conduit 16. This electrode 30 is desirably arranged so as to avoid contamination and disturbance of the electrolyte flow, which might be caused by decomposition of electrode material and by dissociation of the electrolyte itself. Accordingly, the electrode is desirably made of a material substantially non-reactive with the electrolyte, for instance, sometimes of stainless steel. Any gas which may be liberated by the electrolytic current is desirably intercepted in a trap 31, in order to avoid interference of gas bubbles with the electrolyte application. This application will now be described in greater detail.

Referring to Figure 2, the liquid outflow nozzle 12 forming part of nozzle unit 11 comprises a central tubular element 32, having an outlet end portion 33 which

extends a slight distance out of the inlet end 34 of the inflow nozzle 13; this outlet end portion 33 having an outer diameter which is slightly smaller than the diameter of the inner edge 35 of the inlet 34 and having an outlet opening 36 of still smaller diameter.

In a preferred form of the nozzle unit 11 there is provided a sensing electrode 37 which may have the form of a short coil of very thin wire, wound upon and secured to the outflow nozzle portion 33, a short distance from the restricting zone defined by the edge 35. This electrode, as shown in Figure 1, is connected by conductor 38 with an electronic circuit unit 39, for instance in the manner in which a similar electrode 182 is connected by a conductor 194 with an electronic circuit or process controller and associated apparatus in accordance with the Bradley-Roschen disclosure, mentioned above.

In operation, a low pressure is created in the inflow nozzle 13 by the vacuum pump 20, thereby maintaining, as indicated by the curved arrows in Figure 2, a rapid inflow of air. This inflow can be maintained even in the absence of an outflow of liquid, but normally the feed pump 17 keeps the discharge nozzle 12 full of electrolyte liquid and causes such liquid to issue from the nozzle, whereupon it is entrained by the inward air flow and enters the inflow nozzle 13 (Figure 1).

At the start of operation the outflow nozzle 12 may be filled by liquid the surface of which may have the configuration of a meniscus, indicated in Figure 3 by the broken line 36A which curves very slightly beyond the opening 36 of the outflow nozzle. If neither feed pump 17 nor mainly vacuum pump 20 were operated, a larger drop might hang from the nozzle opening. Actually, because of the inward pressure and velocity of the air stream entering the nozzle, the drop is flattened into the form shown at 36A. If the feed pump 17 also operates, constantly supplying liquid to this drop, the contour 36B may be established, which is slightly more advanced beyond the opening 36. The added liquid is immediately and constantly carried away by the rapid air stream, so that the contour 36B tends to remain, forming a seemingly motionless, actually mobile, globular liquid cap over the opening 36, so long as inflow and outflow velocities are suitably balanced.

In order to change from this condition, characterizing the start of the operation, to the normal operating condition of the system, the blank 10 of germanium is inserted in front of the cap-shaped liquid drop 36B; there being a very short distance, such as a few thousandths of an inch, spacing the liquid cap from the blank. Thereafter, momentarily, the forward projection of the drop is enlarged to establish contact between the drop and the blank. This can be done by various means and procedures, for instance by temporarily speeding up the operation of the pump 17 by suitable control means, not shown; it is, however, most readily achieved by simply utilizing a flexible supply duct 16 (Figure 1), together with a device 40 in a relay-controlled circuit 41 for momentarily pinching this flexible duct, whereby the liquid cap 36B is slightly enlarged so that it has a surface 36C in contact with the blank 10 (Figure 3).

As soon as this liquid-solid contact is established the liquid drop tends to spread over the solid blank, if and as the liquid and solid materials are so selected as to provide a force of adhesion or so-called wetting tendency between the two materials; and in some instances this force of adhesion may even be slightly enhanced, by adding a suitable wetting agent to the etchant. However, the spreading of the liquid is kept within definitely limited confines, by the surface tension of the small liquid body; and in accordance with this invention the spreading is not to be significantly enhanced by any application of dynamic or fluid flow forces.

On the contrary, the condition of the liquid body may and should remain viscous and almost like that of a solid body. More particularly, when the contacting and limited spreading of the liquid drop has taken effect, the pinching

of conduit 16 (Figure 1) can be terminated; the exposed body of liquid has meanwhile lost the former shape of a globular cap and it now advantageously has and keeps the approximate form of a cone-shaped drop or cap, covering the inflow nozzle and also contacting the germanium blank, as shown by lines 36D (Figure 3). The liquid of this cone-shaped cap forms a viscous body which tends to adhere to the blank 10 and which is subject to a force tending to pull it away from this blank and into the inflow nozzle. Actual pulling away occurs as to surface portions 32A of the liquid body, by the friction of air rushing into the nozzle. The continuing central supply 32B of liquid electrolyte, in the core of the liquid body, replaces the liquid removed by the entrainment of surface portions.

As a result of these conditions there can be maintained a type of solid-contacting, liquid flow 32C of very advantageous nature for the etching process; that is, the particles of liquid, contacting an area of the germanium body, move in a laminar or viscous flow, wherein the liquid friction is extremely low, being proportional only to the velocity of the flow and inversely proportional to the square of the width of the flowing body. This condition is in sharp contrast with that established by an ordinary jet stream or the like, which involves turbulent flow of liquid particles at least in and adjacent the area of impingement, with liquid friction proportional to the square of the velocity of this flow and inversely proportional to the width thereof. In other words, the viscous liquid electrode of the present invention exposes the germanium blank only to a minor and insignificant part of the friction that is caused by an ordinary jet electrode of equal dimensions.

When the present flow condition has been established, the switch 27 can be closed and it should then be kept closed for a suitable period of time, for instance, in many cases about ten or twenty seconds. A suitable electrolytic etching potential is maintained, by proper adjustment of the resistor 26. Accordingly, the electrolyte body, contacting the germanium blank, now acts as an etching agent. The etching process, which may be promoted further by application of light or the like, causes the formation of certain oxides and/or other products of electrolytic treatment on the surface of the blank. These products go into solution and are carried off by the viscous flow of liquid which has been mentioned; that is, they are removed from the solid surface with extremely little friction and with no eddying whatsoever. This condition, in turn, insures the formation of an etched recess with a peripheral outline and cross-sectional contour very similar to those of a true cylinder of diameter D, recessed into the blank and having a flat bottom; a recess which is generally quite superior to the flat crater, formed by the jet processes of the prior art.

When this etching process has been continued for the predetermined period of time, for instance, twenty seconds, it may become desirable to measure the remaining, usually minute thickness of the blank. While such measurement can be effected by infrared light or the like, I prefer to effect it by electrolytic application of an electronic "punch-through" technique. In the Bradley and Roschen application, this technique is described as being used in conjunction with an ordinary liquid jet or pair of jets. Such measurement can similarly be effected by one or two viscous liquid electrodes 18 (Figures 1, 2). It requires no change in the form of the liquid cone established at 36D (Figure 3). The liquid electrode, which does not wet even a fringe portion of the germanium blank outside the blank area to be etched, provides a most satisfactory precision mechanism for the application of the "punch-through" measurement; more so than the various jets and similar processes so far employed, which involved the use of liquid electrodes of significantly irregular and unstable form. Of course, care must be taken to avoid irregularities which might

be caused by such factors as accumulation of insulating oxides in a liquid electrode area.

The measurement may be followed by renewed application of the electrolytic treatment; and after another suitable period, there may follow another measurement. It is further possible to perform such alternating processes automatically.

The etching and measuring cycle can be terminated when the predetermined electronic "punch-through" condition has been established by the sensing electrode 37 and its circuit unit 39. It is possible, for instance, at this moment to automatically or manually open switches 19 and 27. The mere termination of an outflow caused by the feed pump 17 would tend to reduce the diameter of the remaining liquid cone, establishing some contour such as that shown at 36E. The simultaneous cessation of suction caused by the vacuum pump 20 leads to the establishment of some contour such as that shown at 36F, which occupies an intermediate position between 36D and 36E. Neither the mere cessation of liquid feed nor the simultaneous termination of liquid feed and air suction causes any complete or even significant disruption of the liquid body 18. There is only a minor change of configuration of this body. The liquid continues to bridge the space between the germanium blank 10 and the nozzle 11, by virtue of its adhesion to those devices and of its own cohesion and surface tension.

It is therefore possible to proceed immediately to an electroplating operation for the formation of permanent, solid transistor electrodes, as soon as the etching and measuring cycle has been completed. The same electrolytic body 18 can be used; it is only necessary to reverse the direction of the former electrolytic current and of the migration of ions, in order to provide for an electroplating condition.

The liquid bridge is finally destroyed when the finished transistor body 10 is removed from the position shown. Thereupon the liquid body collapses to its original form 36A. A new blank can then be inserted and the process repeated.

In a modified form of the process, as suggested in Figure 2 at 36G, the pressure and velocity generated by the liquid feed pump 17 is increased so that it tends to maintain the liquid in the form of a substantially elongated drop, projecting from the outflow nozzle. The blank 10 can be inserted across this elongated drop-shaped body. In this case the diameter of the resulting liquid body becomes larger than D, unless the spacing between the blank and the nozzle is increased; and no pinching of the tube 16 or similar operation is required to start the establishment of the bridging liquid body. However, the previously described operation, starting with the condition shown at 36A and then establishing a liquid cone 36D, is generally preferred. It avoids initial wetting of germanium areas which are not to be etched, and it thereby and otherwise facilitates maintenance of the most desirable form of the liquid electrode.

This maintenance of proper form of the electrode may be further explained as follows. In the interest of precise etching, it is generally desirable to make the diameter D as small as possible and also to keep the circular area thereof as sharply and steadily outlined as possible. Because of the liquid adhesion mentioned above, this area is generally somewhat larger than the outflow aperture 36; the latter of course being made just as small as is practically possible in conjunction with the other requirements of the invention. At first glance it may appear to be a mere matter of choice whether a liquid contact area of diameter D is established in the position shown in Figure 2 in full lines, or in a corresponding, leftwardly displaced position of the blank 10, adjacent the end of a longer liquid column 36G. However, in the latter case, the inrush of air, described above, would tend to cause relatively significant lateral motion or even lateral whipping or vibration of the liquid column, thereby tending

to cause the etching of a recess of relatively irregular outline and profile, which in most of the applications presently considered is undesirable.

By contrast, highly favorable conditions are established by close proximity between outflow area 36 and blank 10; and the preferred distance between these parts is therefore even smaller than the diameter of the outflow area 36. On the other hand, the intake aperture 34 is relatively widely spaced from blank 10 in order to give substantial and gradually increasing effect to the friction of the air, entraining surface portions of the liquid. By means of these combined arrangements a mobile, generally non-viscous electrolyte material can pass over the germanium area to be treated as a viscous, practically frictionless flow, and can yet very positively entrain the etching waste products, by gradual transition to a turbulent condition of the liquid particles in the exposed surface of the liquid body. The liquid is centrally supplied as a flow or stream which generally is viscous although a turbulent condition thereof would be allowable, and is peripherally removed as a layer gradually accelerated to a very considerable speed by the friction of the inrushing air, the maximum force of which is applied in the restricted intake aperture 34. Thus, the process avoids violent action of liquid on the solid material even in the most minute portion of the area under treatment. The solid germanium particles to be removed are successively dissolved, without any forcible erosion applied to such particles.

Many of the arrangements, proportions and dimensions described can be varied, at least within certain limits. This applies, for instance, to the area of contact, indicated at D, which is determined by the magnitude of the force of adhesion between the liquid and the solid surface, the liquid surface tension in the electrolyte body, the velocity and pressure of electrolyte flow through the outflow nozzle, the velocity and geometry of the air flow, the distance between the nozzle and the body being etched, the applied electrolytic current and other features as will be understood in the light of this disclosure. Either one or several or all of these factors may be changed to certain extents.

As a specific example, the diameter of the aperture 36 may be of the order of .010 inch, while the width of the annular inflow space 34 may be approximately .002 inch to .003 inch; the wall thickness of the outflow nozzle being of approximately the latter magnitude. Excellent results may then be obtained if the outflow nozzle 12 extends beyond the inflow nozzle 13 a distance which may amount to about .005 inch and if the transistor blank is spaced by an equal distance of about .005 inch from the outflow aperture 36.

In the practical, continued use of the present apparatus the pumps 17 and 20 can run continuously and uniformly, thereby tending to maintain the etchant surface shown at 36D. A blank 10, secured to a suitable holder, may be inserted and accurately registered relative to the nozzle 11, by well known guiding equipment, not shown. This insertion may automatically cause closure of the electrolytic current switch 27, thereby also energizing the circuit 41 of the pinching device 40 for the momentary establishment of the extended drop condition 36C. A suitable program timing system, diagrammatically shown at 42, may after predetermined periods open and close the switch 27; and by means of well known circuitry, not shown, these and connected operations may be repeated, until a "punch-through" response is obtained in the measuring system 39. This may be evidenced by a suitable signal and thereupon the plating process may be started, by suitable circuit means, not shown. When this has deposited a suitable solid electrode, the germanium blank and holder may be removed, manually or automatically, causing the electrolyte body to collapse to the original form 36A; and the entire process can then be repeated upon the insertion of a new blank. It will be recognized by persons skilled in the art that this cycle

of operations eliminates several auxiliary steps and sources of delay, involved in the procedures so far employed, and that it accordingly accelerates the production of semiconductor devices, as well as it improves their quality by the improved etching and sensing procedures.

While only certain preferred forms of apparatus and method have been described, it will be understood that the details thereof are not to be construed as limitative of the invention, except insofar as set forth in the following claims.

I claim:

1. In electrolytic treatment of a semiconductor solid: providing a small, coherent, generally stationary liquid body which consists of electrolyte liquid tending to adhere to a surface of said solid; keeping one end of said liquid body adherent to a surface portion of the solid, while subjecting the exposed surfaces of said liquid body to an atmosphere; maintaining an electrical current which passes through the liquid and the solid in series; maintaining a stream of said liquid into the interior of said liquid body, in a direction toward said surface portion; and counteracting progressive adhesion of the liquid across said surface portion by maintaining a stream of gas in said atmosphere, adjacent said liquid body, and flowing countercurrently to said flow of liquid, thereby propelling liquid portions of said liquid body along said exposed surfaces in counterflow relation to said flow of liquid and away from said surface portion of the solid.

2. In the treatment of a semiconductor solid: holding a small drop of electrolyte liquid, with one drop surface exposed, with another drop surface contacting a surface of the solid, and with an electrical potential maintained between the liquid and the solid; feeding a small stream of liquid into the inner portion of the drop in a direction toward said surface of the solid; and propelling the liquid of the exposed drop surface away from the surface of the solid and in counterflow relation to said small stream of liquid by maintaining a current of gas along the entire exposed surface of the drop, flowing countercurrently to said stream of liquid.

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