(54) Title: PROCESS FOR GROWTH OF DEFECT FREE SILICON CRYSTALS OF ARBITRARILY LARGE DIAMETERS

(57) Abstract

A process for growing single crystal silicon ingots which are substantially free of agglomerated intrinsic point defects. An ingot is grown generally in accordance with the Czochralski method. No portion of the ingot cools to a temperature which is less than a temperature T_A at which agglomeration of intrinsic point defects in the ingot occurs during the time the ingot is being grown. The achievement of defect free ingots is thus substantially decoupled from process parameters, such as pull rate, and system parameters, such as axial temperature gradient in the ingot.

PROCESS FOR GROWTH OF DEFECT FREE SILICON
CRYSTALS OF ARBITRARILY LARGE DIAMETERS

BACKGROUND OF THE INVENTION

5   The present invention generally relates to the
preparation of semiconductor grade single crystal silicon
which is used in the manufacture of electronic
components. More particularly, the present invention
relates to a process for producing a single crystal
silicon ingot which is substantially devoid of
10   agglomerated intrinsic point defects over the entire
crystal radius and usable length of the ingots.

       Single crystal silicon, which is the starting
material for most processes for the fabrication of
semiconductor electronic components, is commonly prepared
15   by the so-called Czochralski ("Cz") method. In this
method, polycrystalline silicon ("polysilicon") is
charged to a crucible and melted, a seed crystal is
brought into contact with the molten silicon and a single
crystal is grown by slow extraction. After formation of
20   a neck is complete, the diameter of the crystal is
enlarged by decreasing the pulling rate and/or the melt
temperature until the desired or target diameter is
reached. The cylindrical main body of the crystal which
has an approximately constant diameter is then grown by
25   controlling the pull rate and the melt temperature while
compensating for the decreasing melt level. Near the end
of the growth process but before the crucible is emptied
of molten silicon, the crystal diameter must be reduced
gradually to form an end-cone. Typically, the end-cone
30   is formed by increasing the crystal pull rate and heat
supplied to the crucible. When the diameter becomes

small enough, the crystal is then separated from the
melt.

In recent years, it has been recognized that a
number of defects in single crystal silicon form in the
5   crystal growth chamber as the crystal cools after
solidification. Such defects arise, in part, due to the
presence of an excess (i.e., a concentration above the
solubility limit) of intrinsic point defects in the
crystal lattice, which are vacancies and self-
10   interstitials. Silicon crystals grown from a melt are
typically grown with an excess of one or the other type
of intrinsic point defect, either crystal lattice
vacancies ("V") or silicon self-interstitials ("I"). It
has been suggested that the type and initial
15   concentration of these point defects in the silicon are
determined at the time of solidification and, if these
concentrations reach a level of critical supersaturation
in the system and the mobility of the point defects is
sufficiently high, a reaction, or an agglomeration event,
20   will likely occur. Agglomerated intrinsic point defects
in silicon can severely impact the yield potential of the
material in the production of complex and highly
integrated circuits.

Vacancy-type defects are recognized to be the origin
25   of such observable crystal defects as D-defects, Flow
Pattern Defects (FPDs), Gate Oxide Integrity (GOI)
Defects, Crystal Originated Particle (COP) Defects,
crystal originated Light Point Defects (LPDs), as well as
certain classes of bulk defects observed by infrared
30   light scattering techniques such as Scanning Infrared
Microscopy and Laser Scanning Tomography. Also present
in regions of excess vacancies are defects which act as
the nuclei for ring oxidation induced stacking faults
(OISF). It is speculated that this particular defect is

a high temperature nucleated oxygen agglomerate catalyzed by the presence of excess vacancies.

Defects relating to self-interstitials are less well studied. They are generally regarded as being low densities of interstitial-type dislocation loops or networks. Such defects are not responsible for gate oxide integrity failures, an important wafer performance criterion, but they are widely recognized to be the cause of other types of device failures usually associated with current leakage problems.

The density of such vacancy and self-interstitial agglomerated defects in Czochralski silicon is conventionally within the range of about $1*10^3/cm^3$ to about $1*10^7/cm^3$. While these values are relatively low, agglomerated intrinsic point defects are of rapidly increasing importance to device manufacturers and, in fact, are now seen as yield-limiting factors in device fabrication processes.

To date, there generally exists three main approaches to dealing with the problem of agglomerated intrinsic point defects. The first approach includes methods which focus on crystal pulling techniques in order to reduce the number density of agglomerated intrinsic point defects in the ingot. This approach can be further subdivided into those methods having crystal pulling conditions which result in the formation of vacancy dominated material, and those methods having crystal pulling conditions which result in the formation of self-interstitial dominated material. For example, it has been suggested that the number density of agglomerated defects can be reduced by (i) controlling v/G_0 to grow a crystal in which crystal lattice vacancies are the dominant intrinsic point defect, and (ii) influencing the nucleation rate of the agglomerated

4

defects by altering (generally, by slowing down) the
cooling rate of the silicon ingot from about 1100°C to
about 1050°C during the crystal pulling process. While
this approach reduces the number density of agglomerated

5   defects, it does not prevent their formation. As the
requirements imposed by device manufacturers become more
and more stringent, the presence of these defects will
continue to become more of a problem.

        Others have suggested reducing the pull rate, during

10   the growth of the body of the crystal, to a value less
than about 0.4 mm/minute. This suggestion, however, is
also not satisfactory because such a slow pull rate leads
to reduced throughput for each crystal puller. More
importantly, such pull rates lead to the formation of

15   single crystal silicon having a high concentration of
self-interstitials. This high concentration, in turn,
leads to the formation of agglomerated self-interstitial
defects and all the resulting problems associated with
such defects.

20   A second approach to dealing with the problem of
agglomerated intrinsic point defects includes methods
which focus on the dissolution or annihilation of
agglomerated intrinsic point defects subsequent to their
formation. Generally, this is achieved by using high

25   temperature heat treatments of the silicon in wafer form.
For example, Fusegawa et al. propose, in European Patent
Application 503,816 A1, growing the silicon ingot at a
growth rate in excess of 0.8 mm/minute, and heat treating
the wafers which are sliced from the ingot at a

30   temperature in the range of 1150°C to 1280°C to reduce the
defect density in a thin region near the wafer surface.
The specific treatment needed will vary depending upon
the concentration and location of agglomerated intrinsic
point defects in the wafer. Different wafers cut from a

5

crystal which does not have a uniform axial concentration
of such defects may require different post-growth
processing conditions. Furthermore, such wafer heat
treatments are relatively costly, have the potential for
introducing metallic impurities into the silicon wafers,
and are not universally effective for all types of
crystal-related defects.

A third approach to dealing with the problem of
agglomerated intrinsic point defects is the epitaxial
deposition of a thin crystalline layer of silicon on the
surface of a single crystal silicon wafer. This process
provides a single crystal silicon wafer having a surface
which is substantially free of agglomerated intrinsic
point defects. Epitaxial deposition, however,
substantially increases the cost of the wafer.

In view of these developments, a need continues to
exist for a method of single crystal silicon preparation
which acts to prevent the formation of agglomerated
intrinsic point defects by suppressing the agglomeration
reactions which produce them. Rather than simply
limiting the rate at which such defects form, or
attempting to annihilate some of the defects after they
have formed, a method which acts to suppress
agglomeration reactions would yield a silicon substrate
that is free or substantially free of agglomerated
intrinsic point defects. Such a method would also afford
single crystal silicon wafers having epi-like yield
potential, in terms of the number of integrated circuits
obtained per wafer, without having the high costs
associated with an epitaxial process.

It is now recognized that silicon single crystal
ingots can be grown which have virtually no defects
produced by agglomeration of intrinsic point defects.
(See, e.g., PCT/US98/07356 and PCT/US98/07304.) A

6

primary mechanism for the suppression of agglomeration reactions is the radial out-diffusion of intrinsic point defects. If given sufficient time at crystal temperatures in excess of the temperature T_A at which agglomeration reactions will occur, self-interstitials and vacancies will either combine and annihilate each other or diffuse to sinks on the surface of the ingot.

Silicon self-interstitials appear to be extremely mobile at temperatures near the solidification temperature of silicon, i.e., about 1410°C. This mobility, however, decreases as the temperature of the single crystal silicon ingot decreases. Generally, the diffusion rate of self-interstitials slows such a considerable degree that they are essentially immobile for commercially practical time periods at temperatures less than about 700°C, and perhaps at temperatures as great as 800°C, 900°C, 1000°C, or even 1050°C.

It is to be noted in this regard that, although the temperature at which a self-interstitial agglomeration reaction occurs may in theory vary over a wide range of temperatures, as a practical matter this range appears to be relatively narrow for conventional, Czochralski-grown silicon. This is a consequence of the relatively narrow range of initial self-interstitial concentrations which are typically obtained in silicon grown according to the Czochralski method. In general, therefore, a self-interstitial agglomeration reaction may occur, if at all, at temperatures (T_A) within the range of about 1100°C to about 800°C, and typically at a temperature of about 1050°C.

By controlling the cooling rate of the ingot within a range of temperatures in which self-interstitials appear to be mobile, the self-interstitials may be given more time to diffuse to sinks located at the crystal

7

surface, or to vacancy dominated regions, where they may be annihilated. The concentration of such interstitials may therefore be suppressed to a level low enough so that supersaturation of self-interstitials (i.e., a

5   concentration above the solubility limit) does not occur at a temperature at which the self-interstitials are sufficiently mobile to agglomerate. The same principles apply for silicon vacancies. However, the relative immobility of the vacancies makes their outdiffusion more

10   difficult.

It would be possible to produce single crystal ingots free of agglomerated micro-defects in presently existing crystal pullers, but there are a number of contradictory conditions present in the operation of the

15   crystal puller and the ingot. Difficult compromises must be made, which materially impact the commercial practicality of the production of defect-free single crystal ingots. Growth of a single crystal silicon ingot is schematically illustrated in Fig. 1. Silicon

20   solidifies from the melt into the ingot at a temperature of about 1410° C and is thereafter continuously cooled. At some location along the length of the ingot $L(T_A)$ above the melt surface the ingot will pass through an isotherm T_A at which agglomeration reactions occur (e.g., 1050° C).

25   The ingot will pass through this point during the time it is being grown.

Essentially, growing defect-free ingots would require that temperature distribution in the hot zone be engineered to produce sufficiently long residence times

30   of the ingot at temperatures in excess of a temperature T_A (e.g., about 1050° C) at which agglomeration reactions occur to permit the out-diffusion of the intrinsic point defects. Maximizing the residence time of axial segment of the ingot above T_A requires that the pull rate be

8

slowed. However, slowing the pull rate drastically
reduces throughput for the crystal puller.

The required residence time of each axial segment of
the ingot at temperatures in excess of T_A can be reduced

5   somewhat by growing the crystal so that self-interstitial
intrinsic point defects predominate. Self-interstitial
defects are substantially more mobile than vacancy
defects. It is still necessary to minimize the initial
concentration of defects. However, to minimize the

10   number of defects, the pull rate should be maximized
within the interstitial growth conditions.

In order to produce a single crystal ingot which was
substantially free of agglomerated micro-defects over its
entire length, each axial segment along the full usable

15   length of the ingot must pass through T_A only after
residing at temperature in excess of T_A for a time
necessary to out-diffuse the intrinsic point defects.
Thus, the same relatively slow pull rate must be
maintained even while the unusable end-cone of the ingot

20   is being formed. Furthermore, the ingot must be raised
at the same slow rate even after it is formed so that the
lower end of the usable constant diameter portion of the
ingot has sufficient residence time at temperatures above
T_A.

25   The tension between pull rate and residence time
necessary for out-diffusion of intrinsic point defects
becomes more acute as the diameter of the crystal grown
increases. As the diameter of the ingot increases, the
number of defects increases and the radial distance

30   through which the defects must diffuse to the surface of
the ingot increases.

Still further, minimization of the time for out-
diffusion of self-interstitials makes it desirable to
minimize the radial variation in initial interstitial

concentration. This is achieved by minimizing the radial
variation of the axial temperature gradient $G_0(r)$. In
order to minimize the radial variation in the axial
temperature gradient, it is desirable to minimize the
average value of the axial temperature gradient G_0 at the
ingot at the surface of the silicon melt. However in
order to maximize the pull rate which will achieve
interstitial growth conditions, it is desirable to
minimize the average value of G_0.

As a practical matter, very stringent process
controls must be maintained in the operation of the
crystal puller to produce single crystal silicon ingots
which are substantially free of agglomerated intrinsic
point defects. Moreover, there is a dramatic reduction
in throughput for the crystal puller. Thus, there is
presently a need for a process to grow single crystal
ingots free of agglomerated intrinsic point defects which
decouples or substantially decouples the operation of the
crystal puller from the conditions necessary to out-
diffuse intrinsic point defects.

SUMMARY OF THE INVENTION

Among the several objects and features of the
present invention may be noted the provision of a process
of producing a single crystal silicon ingot which is
substantially free of agglomerated intrinsic point
defects over the entire usable length of the ingot; the
provision of such a process which does not substantially
diminish the throughput of the crystal puller; the
provision of such a process which substantially decouples
the operating conditions of the crystal puller from the
conditions for production of the defect-free ingot; the
provision of such a process which substantially reduces
the crystal puller from limitations on pull rate for

production of the defect-free ingot; and the provision of
such a process which substantially reduces the crystal
puller from limitations on the average axial temperature
gradient G_0.

5   Briefly, therefore, the present invention is
directed to a process for producing a single crystal
silicon ingot having a seed-cone, an end-cone and a
constant diameter portion between the seed-cone and end-
cone. The ingot is grown from a silicon melt in

10   accordance with the Czochralski method. Generally, the
process comprises growing the ingot from the silicon melt
and controlling the temperature of the ingot such that no
portion of the ingot cools to a temperature less than a
temperature T_A at which agglomeration of intrinsic point

15   defects in the ingot occurs during the time the ingot is
being grown such that at least the constant diameter
portion of the ingot is substantially free of
agglomerated intrinsic point defects.

           The present invention is further directed to a

20   process for producing a single crystal silicon ingot
having a seed-cone, an end-cone and a constant diameter
portion between the seed-cone and end-cone. The ingot is
grown in a crystal puller from a silicon melt in
accordance with the Czochralski method. The crystal

25   puller includes a lower growth chamber and an upper
pulling chamber, and the process comprises lowering a
seed crystal into contact with the silicon melt located
in the growth chamber of the crystal puller and
withdrawing the seed crystal from the melt so as to cause

30   silicon from the melt to freeze for forming the single
crystal silicon ingot. The fully formed ingot is pulled
into the pulling chamber, the pulling chamber is then
isolated from the growth chamber while the temperature in
the pulling chamber is maintained above a temperature T_A

at which agglomeration of intrinsic point defects in the ingot occurs.

Other objects and features of the present invention will be in part apparent and in part pointed out

5   hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view illustrating existing single crystal silicon ingot growth showing the passage of the ingot during growth through an isotherm at which

10   agglomeration reactions occur;

FIG. 2 is a graph which shows an example of how the initial concentration of self-interstitials [I] and vacancies [V] changes with the value of v/G_0, where v is the pull rate and G_0 is the average axial temperature

15   gradient;

FIG. 3 is a schematic view of a crystal puller apparatus which permits removal of a pulling chamber portion of the crystal puller and replacement with another pulling chamber;

20   FIG. 4 is a schematic view of a crystal puller apparatus which permits the ingot to be removed from the pulling chamber to a holding chamber located to the side of the pulling chamber;

FIG. 5 is a schematic view of a crystal puller

25   apparatus which permits the ingot to be removed from the pulling chamber to a holding chamber located generally above the pulling chamber;

FIG. 6A is a graph of the normalized growth rate as a function of crystal length, as described in the

30   Example;

FIG. 6B is a series of photographs of axial cuts of segments of an ingot, ranging from the shoulder to where end-cone growth begins, following copper decoration and a

12

defect-delineating etch, as described in the Example; and,

FIG. 6C is a series of photographs of axial cuts of segments of an ingot, ranging from the seed-cone to the

5   end-cone, following copper decoration and a defect-delineating etch, as described in the Example.

Corresponding reference characters indicate corresponding parts throughout the several views of the drawings.

10   DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the drawings, and in particular to Fig. 3, apparatus for carrying out a process according to the present invention is schematically shown to include a crystal puller indicated generally at 10. The crystal

15   puller includes a growth chamber 12 which houses a crucible 14 for containing a silicon melt M. The crucible 14 is mounted for rotation within the growth chamber 12 in the conventional manner. The crystal puller 10 also includes a conventional heater and

20   insulation (not shown) for heating the silicon in the crucible 14 to produce and maintain its molten state. The crystal puller 10 further comprises a pull chamber 16 located on top of the growth chamber 12 and capable of opening into the growth chamber for receiving a single

25   crystal silicon ingot I being grown from the molten silicon M. The pull chamber 16 has a winch mechanism 18 for raising and lowering a pull wire 20 having a seed crystal chuck 22 at its end. Alternatively, a pulling mechanism (not shown) which employs a shaft rather than a

30   pull wire may be used. The chuck 22 carries a seed crystal (not shown) which is used to initiate formation of the ingot I, according to the Czochralski method.

The pull chamber 16 is equipped with a valve 24 for
closing off the pull chamber from the growth chamber 12.
Similarly, the growth chamber 12 has its own valve 26 for
closing itself off from the pull chamber 16. The pull
5   chamber is releasably mounted on the growth chamber 12 so
that the entire pull chamber 16 can be removed from the
growth chamber.   The apparatus further includes another
pull chamber 16' (corresponding parts of the other pull
chamber 16' will be designated by the same reference
10   numerals as the pull chamber 16 with the addition of '
after the numeral). The other pull chamber 16' can be
mounted on the growth chamber 12 and used to grow another
ingot I'. However as illustrated in Fig. 3, one ingot I
is being grown in the pull chamber 16 while the other
15   ingot I' is held in the other pull chamber 16' at a
location spaced away from the growth chamber 12.
        A process carried out according to the principles of
the present invention will now be described with
reference to the apparatus shown in Fig. 3. As will be
20   understood, the process may be carried out by other
apparatus (some examples of which are described
hereinafter). The crystal puller 10 is initially
prepared in a conventional way, such as by placing solid
polysilicon in the crucible 14 and energizing the heater
25   to melt the silicon forming the silicon melt M. The
winch mechanism 18 is activated to let out the pull wire
20 and lower the chuck 22 so that the seed crystal
contacts the surface of the melt. The crucible 14 and
the pull wire 20 are both rotated about a vertical axis.
30   As the seed crystal begins to melt, the winch mechanism
18 is activated to slowly reel in the pull wire 20,
raising the seed crystal from the melt. Silicon from the
melt M freezes onto the seed crystal in a monocrystalline
lattice, thereby beginning to form the ingot I.

14

The ingot initially has a seed cone SC, which has a diameter which increases to the point where it equals the diameter of the ingot which is desired to be grown (typically somewhat greater than the desired diameter of semiconductor wafers ultimately formed from the ingot). A constant diameter portion CD is grown by controlling the pull rate and heating of the ingot I. An end cone EC' (shown only on the other ingot I') is formed in order to separate the ingot I from the melt M when the constant diameter CD portion has reached the length needed. This length is limited by the geometry of the crystal puller 10. The end cone EC' is also formed by controlling (i.e., generally increasing) the pull rate of the ingot and by the application of heat. After separation from the melt M, the ingot I is pulled entirely within the pull chamber 16.

According to the process of the present invention, the temperature of the ingot I is maintained above the temperature T_A at which intrinsic point defects will become supersaturated and agglomerate during the growth of the ingot. More specifically, no portion of the ingot I is allowed to cool to the temperature T_A during the time the crystal is being grown. Thus unlike the conventional Czochralski process example illustrated in Fig. 1, the ingot I never passes through the isotherm T_A while it is being grown. The restrictions on the production of single crystal silicon previously caused by the presence of the isotherm at T_A are removed by the process of the present invention. It is envisioned that control of the cooling of the ingot I may be achieved by thermal shielding, the application of heat or some combination of the two. In the illustrated embodiment, the pull chamber 16 is provided with a heater 30 (schematically shown in

15

Fig. 3) for applying heat to the ingot I as it nears and enters the pull chamber.

The ingot I is held at temperatures above T_A for a period of time selected to permit out-diffusion of
5   intrinsic point defects to a concentration within the ingot below a solubility limit necessary for agglomeration of intrinsic point defects to occur. The times (discussed more fully below) necessary for out-diffusion of intrinsic point defects are generally
10   significantly longer than the normal cycle time of the crystal puller 10. To that end, the process of the present invention further comprises removing the ingot I from the location of the crystal puller 10 within a semiconductor production facility to permit the crystal
15   puller to be recycled independently of the thermal condition of the ingot. The ingot I is maintained at temperatures above T_A during and after the time it is removed from the crystal puller 10.

In the embodiment shown in Fig. 3, removal of the
20   ingot I from the crystal puller 10 includes pulling the grown crystal entirely within the pull chamber 16. The valve 24 on the pull chamber 16 and the valve 26 on the growth chamber 12 are closed, isolating the chambers from each other and from the surrounding environment. The
25   pull chamber 16 is then detached from the growth chamber 12 and moved away, as illustrated by the position of the other pull chamber 16' in Fig. 3. The pull chamber 16 holds the ingot I at the temperature above T_A until such time as sufficient out-diffusion of intrinsic point
30   defects has occurred. The ingot I can then be cooled to ambient and removed from the pull chamber 16 for further processing into semiconductor wafers.

The heater in the growth chamber 12 can be deactivated so that the growth chamber may cool to

ambient. The growth chamber 12 is then opened up so that
the crucible 14 can be removed and replaced with another
crystal. Solid polysilicon held in the crucible 14 is
melted to form a new melt. At the appropriate time after

5   removal of the pull chamber 16, the other pull chamber
16' (first having had the ingot I' held therein removed)
is moved into place on the growth chamber 12. The pull
chamber 16' is attached to the growth chamber 12 and the
valves 24', 26 of the pull chamber and growth chamber are

10   opened to permit another single crystal silicon ingot I'
to be grown.
        The total time necessary to hold the ingot I above T_A
depends upon the initial concentration of intrinsic point
defects, the type of intrinsic point defects which

15   predominate in the ingot and the diameter of the ingot
being grown. Referring now to Fig. 2, the concentration
of both types of intrinsic point defects is plotted
against the ratio of the pull rate v over the average
instantaneous axial temperature gradient G_o in the ingot I

20   at the surface of the melt. At lower ratios of v/G_o,
self-interstitial intrinsic point defects [I]
predominate, and at higher ratios vacancy defects [V]
predominate. However, it may be seen that at a critical
ratio of v/G_o concentrations of both types of intrinsic

25   point defects are minimized. Presently, it is believed
that this ratio is about 2.1 X 10^{-5} cm^2/sK. It is
desirable to maintain the ratio v/G_o near the critical
value, but this is difficult to do over the course of the
entire growth process of the ingot I, particularly at the

30   seed-cone and end-cone ends. A feature of the present
invention that the growth of the ingot I is somewhat less
dependent upon the v/G_o ratio because of the out-diffusion
of intrinsic point defects permitted by the present

invention without significantly affecting the cycle time
of the crystal puller 10.

Preferably, the self-interstitial type of intrinsic
point defect will predominate in the ingot I grown
according to the process of the present invention. Self-
interstitial defects [I] are substantially more mobile
than vacancy defects [V]. Radial out-diffusion of self-
interstitials can occur about 10 times faster than out-
diffusion of vacancies. Stated another way, it takes ten
times as long to out-diffuse vacancies in a vacancy
dominated ingot as to out-diffuse interstitials of the
same concentration in an interstitial dominated ingot.
As a result, it is preferred that the ratio v/G_o be
maintained below the critical value over substantial
portions of the growth of the ingot I so that self-
interstitial defects will predominate. Of course, v/G_o
varies across the radius of the ingot I so that there
will be a radial variation of concentration and type of
defect within the ingot. However, movement into the
vacancy dominated region of v/G_o for portions of the ingot
I is permitted so long as self-interstitial defects
predominate sufficiently to recombine with the vacancies
during out-diffusion, thereby annihilating both defects
so that their concentration remains below the solubility
limit.

It is to be understood, however, that the process of
the present invention may be used for vacancy dominated
material. As a general rule, vacancy dominated material
(if present at all) will be present at the axial center
of the ingot and, depending upon crystal growth
conditions, may extend from the center to the edge of the
ingot. In those instances in which vacancy dominated
material does not extend from center to edge, a core of
vacancy dominated material will be surrounded by an

annular ring of interstitial dominated material. Due to
the slower mobility of vacancies in the silicon lattice
(as compared to silicon self-interstitial atoms), the
times involved to achieve the necessary relaxation of the

5   vacancy system (i.e., suppression of the vacancy
concentration) by out-diffusion of vacancies to the
surface can be relatively long. In one embodiment of the
present invention, therefore, the time required to
suppress the concentration of vacancies is reduced by

10   injecting silicon self-interstitial atoms into the ingot
which diffuse to and recombine with the pre-existing
vacancies and annihilate them. In this embodiment,
silicon self-interstitial atoms may be injected by
oxidizing the surface of the ingot as it is being held at

15   a temperature in excess of the temperature at which
agglomeration reactions occur. Oxidation may be
achieved, for example, by exposing the ingot to an
oxidizing atmosphere (e.g., an atmosphere comprising
oxygen or steam, preferably substantially, if not

20   entirely, oxygen or steam) during the holding period.
The oxide layer may be grown to a thickness on the order
of several microns (e.g., 3, 4, 5) or even 10 or more
microns. Because the thickness of the oxide layer
affects the rate of oxidation (which, in turn, affects

25   the rate at which silicon self-interstitial atoms are
injected), it may be advantageous in one, two or more
cycles to strip the grown oxide layer (for example, with
hydrogen or HF vapor), and then reoxidize the crystal
surface during the holding period.

30   The diameter of the ingot I being grown affects the
time needed for diffusion of intrinsic point defects,
simply because the intrinsic point defects must traverse
greater radial distances as the diameter of the ingot
increases. The necessary time for diffusion scales with

the square of the radius of the ingot I. Thus, it has
been found that where the constant diameter portion of
the ingot is about 150mm, the total time at which the
ingot resides above T_A (i.e., about 1050°C, 1000°C, or

5 even 900°C) is at least about 10 hours, preferably at
least about 12 hours, and more preferably at least about
15 hours. The total time at which a 200mm ingot resides
in a similar system at a temperature above T_A would thus
be at least about 22 hours, preferably at least about 25

10 hours, and more preferably at least about 30 hours, while
the total time at which a 300 mm ingot resides in a
similar system at a temperature above T_A would thus be at
least about 48 hours, preferably at least about 60 hours,
and more preferably at lest about 75 hours. It is to be

15 understood that the precise times for out-diffusion can
be other than described without departing from the scope
of the present invention.

          Referring now to Fig. 4, a process of a second
embodiment is illustrated. The process is the same as

20 the process of the first embodiment, except that a pull
chamber 116 of the crystal puller 110 is not removed from
a growth chamber 112. In the second embodiment, the pull
chamber 116 has been modified to open into a holding
chamber 140 next to the pull chamber. For purposes of

25 the present description of the process, the holding
chamber 140 does not form part of the crystal puller 110
even though it is physically attached to the crystal
puller. After the ingot I is fully grown and drawn up
into the pull chamber 116, a door (not shown) separating

30 the pull chamber from the holding chamber 140 is opened
and the ingot is moved into the holding chamber where it
is held at temperatures above T_A for the appropriate time.
A track 142 is shown for carrying the ingot I into the
holding chamber 140. In the illustrated embodiment, the

holding chamber 140 has a heater 144. Thereafter, the
ingot I is moved into a thermal lock (not shown) to
permit cooling and removal of the ingot from the holding
chamber 140 without compromising the thermal environment

5   of the holding chamber. In the meantime, the door
separating the pull chamber 116 from the holding chamber
140 can be closed. Another winch mechanism and pull wire
(not shown) are moved into place in the pull chamber 116
for growing another single crystal ingot (not shown).

10   A third embodiment of the process of the present
invention is shown in Fig. 5. The process is closely
similar to that illustrated in Fig. 4 because the pull
chamber 216 is not moved, but rather the ingot I is moved
to a holding chamber 240. The primary difference is that

15   holding chamber 240 is located above rather than to the
side of the pull chamber 216. Again, a separate winch
mechanism 218' and pull wire 220' would be moved into
place so that growth of another ingot I' in the crystal
puller 10 can take place without regard to the thermal

20   condition of the ingot I already grown.
          It is to be further noted that, for each of the
above-described embodiments of the present process
wherein the grown ingot is held within the pull chamber
to provide sufficient time for out-diffusion, it is

25   preferred that the pull chamber have a non-uniform
thermal profile. Stated another way, because at least a
portion of the grown ingot has cooled below temperature
at which agglomerated intrinsic point defects form (T_A),
it is not necessary that this portion be maintained at a

30   temperature in excess of T_A upon being removed or
separated from the growth chamber. In fact, it is
preferred that the temperature profile for this portion
of the crystal not exceed T_A because if the temperature is
too high (i.e., more than about 1175°C, 1200°C or more),

the concentration of intrinsic point defects could again be raised above the solubility limit, or critical concentration, as a result of diffusion. However, while the temperature of this region must not be too high, the

5 temperature of the remaining portion of the ingot must be maintained sufficiently high such that agglomerations do not occur.

If a non-uniform thermal profile is employed, preferably the temperature will gradually increase from

10 the seed end to the tail end, typically ranging from about 1000°C to about 1200°C and preferably ranging from about 1050°C to about 1175°C. The axial locations within the ingot having temperatures in excess of T_A will then be cooled in accordance with the present invention,

15 preferably until the temperature profile becomes uniform. The ingot may then be further cooled, as is common in the art, and removed for additional processing.

While a non-uniform temperature profile is preferred, it is to be noted that a uniform temperature

20 profile may also be employed. However, if a uniform profile is to be used, the temperature must be sufficiently above T_A to prevent agglomeration from occurring, but not so high that regions which have previously been cooled below T_A are again capable of

25 becoming critical supersaturated (as discussed above). Accordingly, therefore, the temperature will preferably range from about 1125°C to about 1200°C, and more preferably from about 1150°C to about 1175°C. Once the ingot is inside the chamber, the temperature of this

30 uniform profile will then be reduced in accordance with the present invention to cool the ingot below T_A. The ingot may then be further cooled, as is common in the art, and removed for additional processing.

The following Example illustrates the invention.

<u>Example</u>

Two 200 mm crystal ingots were grown in a crystal
puller capable of producing fully agglomerated intrinsic
5   defect-free material when the ingots are grown at the
rate depicted by the dashed line in Fig. 6A (hereinafter,
the "defect-free" growth rate curve). The two crystals
were grown at the same target growth rate, depicted in
Fig. 6A as a continuous line, with the growth rate being
10   reported as a normalized growth rate (i.e., the actual
growth rate relative to the critical growth rate,
typically expressed as a ratio of the actual growth
velocity over the critical growth velocity). As
depicted, the ingots were initially grown for a period of
15   time at a rate which was in excess of the "defect-free"
growth rate curve, then for a period of time at a rate
which was less than the "defect-free" growth rate curve,
and then again for a period of time at a rate in excess
of the "defect-free" growth rate curve. The first ingot
20   (87GEX) was allowed to cool naturally in the crystal
growth chamber upon completion of the growth of the
ingot. The second ingot (87GEW), however, was not
allowed to cool naturally in the crystal growth chamber;
instead, upon completion of the growth of the ingot, the
25   heaters in the hot zone of the crystal puller remained on
and the ingot was held for 30 hours in the pull chamber;
the temperature profile was such that regions of the
ingot more than about 400 mm from the seed end were held
at a temperature in excess of about 1,050 °C and regions
30   less than about 400 mm from the seed end were held at a
temperature less than about 1,050 °C during this period.

The ingots were sliced longitudinally along the
central axis running parallel to the direction of growth,

23

and then further divided into sections, each about 2 mm
in thickness. Using a copper decoration technique, the
sets of longitudinal sections which make-up each ingot
from seed to tail were intentionally contaminated with
5   copper and heated, the heating conditions being
appropriate to dissolve a high concentration of copper
into the sections. Following this heat treatment, the
samples were rapidly cooled, during which time the copper
either outdiffused or precipitated at sites where oxide
10   clusters or agglomerated interstitial defects were
present. After a standard defect delineating etch, the
samples were visually inspected for the presence of
precipitated impurities; those regions which were free of
such precipitated impurities corresponded to regions
15   which were free of agglomerated interstitial defects.
Photographs were then taken of the sections of each
crystal and the photographs assembled to show the results
for each crystal from seed to tail end. The set of
photographs for the first, naturally-cooled ingot (87GEX)
20   are depicted in Fig. 6B and the set of photographs for
the second, held ingot (87GEW) are depicted in Fig. 6C.
        Referring now to Figs. 6A, 6B, and 6C, it can be
seen that the naturally-cooled ingot (87GEX) contains
agglomerated vacancy defects from 0 to about 393 mm, no
25   agglomerated intrinsic point defects from about 393 mm to
about 435 mm, agglomerated intrinsic point defects from
about 435 mm to about 513 mm, no agglomerated intrinsic
point defects from about 513 mm to about 557 mm, and
agglomerated vacancy defects from 557 mm to the end of
30   the crystal. These correspond to the regions above,
within and below the defect-free growth conditions for
this hot zone. The held ingot (87GEW) contains
agglomerated vacancy defects from 0 to about 395 mm, no
agglomerated intrinsic point defects from about 395 mm to

about 584 mm, and agglomerated vacancy defects from about
584 mm to the end of the crystal. The most significant
difference between the two ingots, therefore, occurs in
the region from about 435 mm to about 513 mm in which the
naturally-cooled ingot (87GEX) contains agglomerated
intrinsic point defects whereas the held ingot (87GEW)
does not. During the holding period, the concentration
of self-interstitial silicon atoms in the held ingot
(87GEW) is suppressed by additional diffusion of the
self-interstitial atoms to the surface of the ingot and
vacancy dominated regions and thus, critical
supersaturation and the agglomeration reaction for
interstitial atoms is avoided subsequent to crystal
solidification. In the naturally cooled ingot, however,
insufficient time is allowed for additional diffusion to
the surface and vacancy dominated regions and, as a
result, the system becomes critically supersaturated in
silicon self-interstitial atoms and an agglomeration
reaction occurs.

These ingots thus illustrate that given sufficient
amounts of time and sufficiently high temperatures,
virtually any amount of silicon self-interstitial atoms
can be outdiffused to the surface.

In addition, the "defect-free" growth rate curve
depicted in Fig. 6A falls within a range of crystal
growth rates which provide fully agglomerated intrinsic
defect-free material under natural cooling conditions for
this crystal puller configuration. Even under natural
cooling conditions for this hot zone configuration, there
is a range of crystal growth rates between the growth
rate (P_v) at which agglomerated vacancy defects form and
the growth rate (P_I) at which agglomerated intrinsic point
defects form; this range is at least ±5% of the average
of P_v and P_I. When the residence time of the grown

crystal at temperatures in excess of about 1,050 °C is increased, this range is increased further with the range being, for example, at least ±7.5%, at least ±10%, or even at least ±15% of the average of P_v and P_I (for
5 example, for crystal 87GEW the residence was sufficiently great that, P_I, was not achieved and thus, P_I for this crystal was less than the lowest pull rate achieved). These results are presented in Table I, below.

TABLE I

87GEX

Transition	position mm	Normalized Pull rate, V	V_ave	Window (DV)	% variation 100(DV/Vave)
V-P	393	0.251			
P-I	435	0.213	0.232017	0.03865546	16.66
I-P	513	0.209			
P-V	557	0.249	0.22937	0.0402521	17.55

87GEW

Transition	position mm	Normalized Pull rate, V	V_ave	window (DV)	% variation 100(DV/Vave)
V-P	395	0.246			
P*	465	0.196	0.221008	0.05042017	22.81
P*	465	0.196			
P-V	584	0.271	0.233193	0.07478992	32.07

* In 87GEW where no P-I transition is observed, we take the minimum V within the window to determine the window size.

27

The increase in window size (or allowable pull rate variation for defect-free growth) is substantially limited to *slower* pull rates (i.e., to values smaller than the critical v/G for vacancy to interstitial

5   dominated material (plus some small delta to take into account interstitial annihilation of vacancies)). That is to say that the effect is strongest for interstitial dominated material, silicon self-interstitial atoms being a faster diffusing element than vacancies. In other

10   words, the window opens *more quickly* toward lower pull rates. In principle, the window for allowable pull rate variation towards faster pull rates (greater than the critical v/G value plus some small delta) into vacancy dominated material) would also open towards *faster* pull

15   rates (vacancy dominated material) with increased dwell times at temperatures greater than about 1050 °C - as *vacancies* diffuse toward the crystal surfaces - but this would require significantly longer times.

For a given crystal puller and hot zone

20   configuration, it may be assumed that the axial temperature gradient, G_0, is approximately constant over relatively short distances such as occur in the transition ranges which occur here. As a consequence, a change in the crystal growth rate leads to a proportional

25   change in v/G_0, and thus, the initial concentration of vacancies and silicon self-interstitial atoms. In general, however, the value of v/G_0 at the center ingot is the most critical value since it is the farthest distance from the surface. Thus, the results of this example

30   demonstrate that the increase in pull rate variations achieved through increased dwell times at temperatures greater than about 1000 °C implies that corresponding

28

variations in v/G_0 may occur at any point along the radius
of the crystal. In other words, radial variation of v/G_0
is irrelevant and thus, for example, may exceed (at any
radial position) 10%, 15% or more of the value of v/G_0 at
5   the center of the ingot.

        In view of the above, it will be seen that the
several objects of the invention are achieved.
            As various changes could be made in the above
compositions and processes without departing from the
10   scope of the invention, it is intended that all matter
contained in the above description be interpreted as
illustrative and not in a limiting sense.

29

WHAT IS CLAIMED IS:

1.   A process of producing a single crystal silicon
ingot having a seed-cone, and end-cone and a constant
diameter portion between the seed-cone and end-cone, the
ingot being grown from a silicon melt in accordance with
5   the Czochralski method, the process comprising growing
the ingot from the silicon melt and controlling the
temperature of the ingot such that no portion of the
ingot cools to a temperature less than a temperature T_A at
which agglomeration of intrinsic point defects in the
10   ingot occurs during the time the ingot is being grown
such that at least the constant diameter portion of the
ingot is substantially free of agglomerated intrinsic
point defects.

2.   A process as set forth in claim 1 wherein the
ingot is maintained at temperatures above T_A for a period
of time selected to permit out diffusion of intrinsic
point defects to achieve a concentration below a
5   solubility limit required for agglomeration of intrinsic
point defects to occur.

3.   A process as set forth in claim 2 wherein the
ingot is maintained at temperatures above T_A for a period
following the growth of the ingot.

4.   A process as set forth in claim 3 wherein T_A is
less than the solidification temperature of silicon and
greater than about 1050°C.

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5. A process as set forth in claim 3 wherein T_A is less than the solidification temperature of silicon and greater than about 900°C.

6. A process as set forth in claim 3 wherein the ingot is grown by controlling a growth velocity, v, and an average axial temperature gradient, G_0, so that the ingot has a predominance of self-interstitial intrinsic

5   point defects.

7. A process as set forth in claim 3 wherein the ratio of v/G_0 is controlled to be less than about 2.1 X 10^{-5} cm^2/s-K.

8. A process as set forth in claim 3 wherein the diameter of the constant diameter portion of the ingot is about 150mm and the time the ingot is held above the temperature T_A from the onset of growth of the ingot is at

5   least about 12 hours.

9. A process as set forth in claim 3 wherein the diameter of the constant diameter portion of the ingot is about 200mm and the time the ingot is held above the temperature T_A from the onset of growth of the ingot is at

5   least about 22 hours.

10. A process as set forth in claim 3 wherein the diameter of the constant diameter portion of the ingot is about 300mm and the time the ingot is held above the temperature T_A from the onset of growth of the ingot is at

5   least about 48 hours.

31

11. A process as set forth in claim 1 which is
carried out in a crystal puller at a location in a
semiconductor production facility, the process further
comprising the step of removing the ingot from the
5   location while maintaining the ingot at temperatures
above T_A to permit the crystal puller to be cooled and re-
started for growth of another single crystal silicon
ingot.

12. A process as set forth in claim 11 wherein the
crystal puller has a lower growth chamber and an upper
pulling chamber, and wherein the step of removing the
ingot comprises isolating the pulling chamber from the
5   growth chamber, detaching the pulling chamber from the
growth chamber and moving the pulling chamber away from
the growth chamber.

13. A process as set forth in claim 12 further
comprising moving another pulling chamber into position
over the growth chamber and attaching said other pulling
chamber to the growth chamber.

14. A process as set forth in claim 11 wherein the
crystal puller has a lower growth chamber and an upper
pulling chamber, and wherein the step of removing the
ingot comprises moving the ingot from the pulling chamber
5   to a holding chamber adjacent to and the pulling chamber,
the holding chamber being heated to maintain the ingot at
temperatures above T_A.

32

15.   A process as set forth in claim 1 wherein the
ingot is exposed to an oxidizing atmosphere as the ingot
is maintained at a temperature in excess of the
temperature T_A at which agglomeration of intrinsic point
5   defects in the ingot occurs.

16.   A process as set forth in claim 15 wherein the
ingot is exposed to at least one cycle as the ingot is
maintained at a temperature in excess of the temperature
T_A at which agglomeration of intrinsic point defects in
5   the ingot occurs wherein in the first phase of the cycle
the ingot is exposed to an oxidizing atmosphere and in
the second phase of the cycle the ingot is exposed to an
atmosphere which dissolves or otherwise removes silicon
dioxide from the surface of the ingot.

17.   A process of producing a single crystal silicon
ingot having a seed-cone, and end-cone and a constant
diameter portion between the seed-cone and end-cone, the
ingot being grown in a crystal puller from a silicon melt
5   in accordance with the Czochralski method, the crystal
puller including a lower growth chamber and an upper
pulling chamber, the process comprising:
       lowering a seed crystal into contact with the
silicon melt located in the growth chamber of the crystal
10   puller;
       withdrawing the seed crystal from the melt so as to
cause silicon from the melt to freeze for forming the
single crystal silicon ingot;
       pulling the fully formed ingot into the pulling
15   chamber;

33

isolating the pulling chamber from the growth chamber;

maintaining the temperature in the pulling chamber above a temperature T_A at which agglomeration of intrinsic

20   point defects in the ingot occurs.

18.   A process as set forth in claim 17 wherein the ingot is maintained at temperatures above T_A for a period of time selected to permit out diffusion of intrinsic point defects to achieve a concentration below a

5   solubility limit required for agglomeration of intrinsic point defects to occur.

19.   A process as set forth in claim 18 wherein T_A is less than the solidification temperature of silicon and greater than about 1050°C.

20.   A process as set forth in claim 18 wherein T_A is less than the solidification temperature of silicon and greater than about 900°C.

21.   A process as set forth in claim 18 wherein the ingot is grown by controlling a growth velocity, v, and an average axial temperature gradient, G_0, so that the ingot has a predominance of self-interstitial intrinsic

5   point defects.

22.   A process as set forth in claim 18 wherein the ratio of v/G_0 is controlled to be less than about 2.1 X 10^{-5} cm^2/s-K.

23. A process as set forth in claim 18 wherein the diameter of the constant diameter portion of the ingot is about 150mm and the time the ingot is held above the temperature T_A from the onset of growth of the ingot is at
5   least about 12 hours.

24. A process as set forth in claim 18 wherein the diameter of the constant diameter portion of the ingot is about 200mm and the time the ingot is held above the temperature T_A from the onset of growth of the ingot is at
5   least about 22 hours.

25. A process as set forth in claim 18 wherein the diameter of the constant diameter portion of the ingot is about 300mm and the time the ingot is held above the temperature T_A from the onset of growth of the ingot is at
5   least about 48 hours.

26. A process as set forth in claim 17 wherein the crystal puller is disposed at a location in a semiconductor production facility, the process further comprising the step of removing the ingot from the
5   location while maintaining the ingot at temperatures above T_A to permit the crystal puller to be cooled and re-started for growth of another single crystal silicon ingot.

27. A process as set forth in claim 26 wherein the step of removing the ingot comprises detaching the pulling chamber from the growth chamber and moving the pulling chamber away from the growth chamber.

35

28.   A process as set forth in claim 27 further comprising moving another pulling chamber into position over the growth chamber and attaching said other pulling chamber to the growth chamber.

29.   A process as set forth in claim 26 wherein the step of removing the ingot comprises moving the ingot from the pulling chamber to a holding chamber adjacent to and the pulling chamber, the holding chamber being heated
5   to maintain the ingot at temperatures above T_A.

30.   A process as set forth in claim 17 wherein the ingot is exposed to an oxidizing atmosphere as the ingot is maintained at a temperature in excess of the temperature T_A at which agglomeration of intrinsic point
5   defects in the ingot occurs.

31.   A process as set forth in claim 30 wherein the ingot is exposed to at least one cycle as the ingot is maintained at a temperature in excess of the temperature T_A at which agglomeration of intrinsic point defects in
5   the ingot occurs wherein in the first phase of the cycle the ingot is exposed to an oxidizing atmosphere and in the second phase of the cycle the ingot is exposed to an atmosphere which dissolves or otherwise removes silicon dioxide from the surface of the ingot.
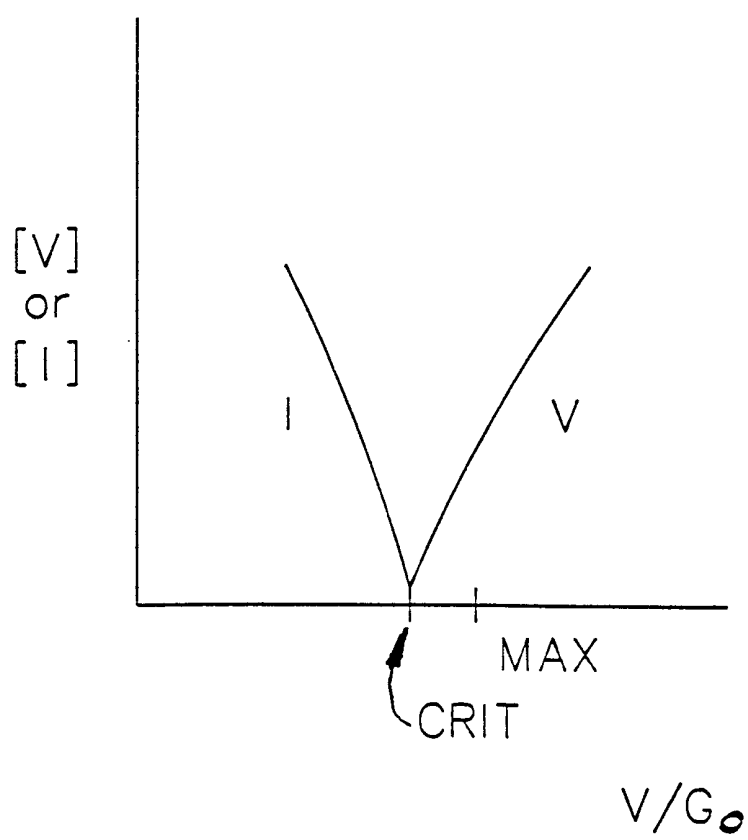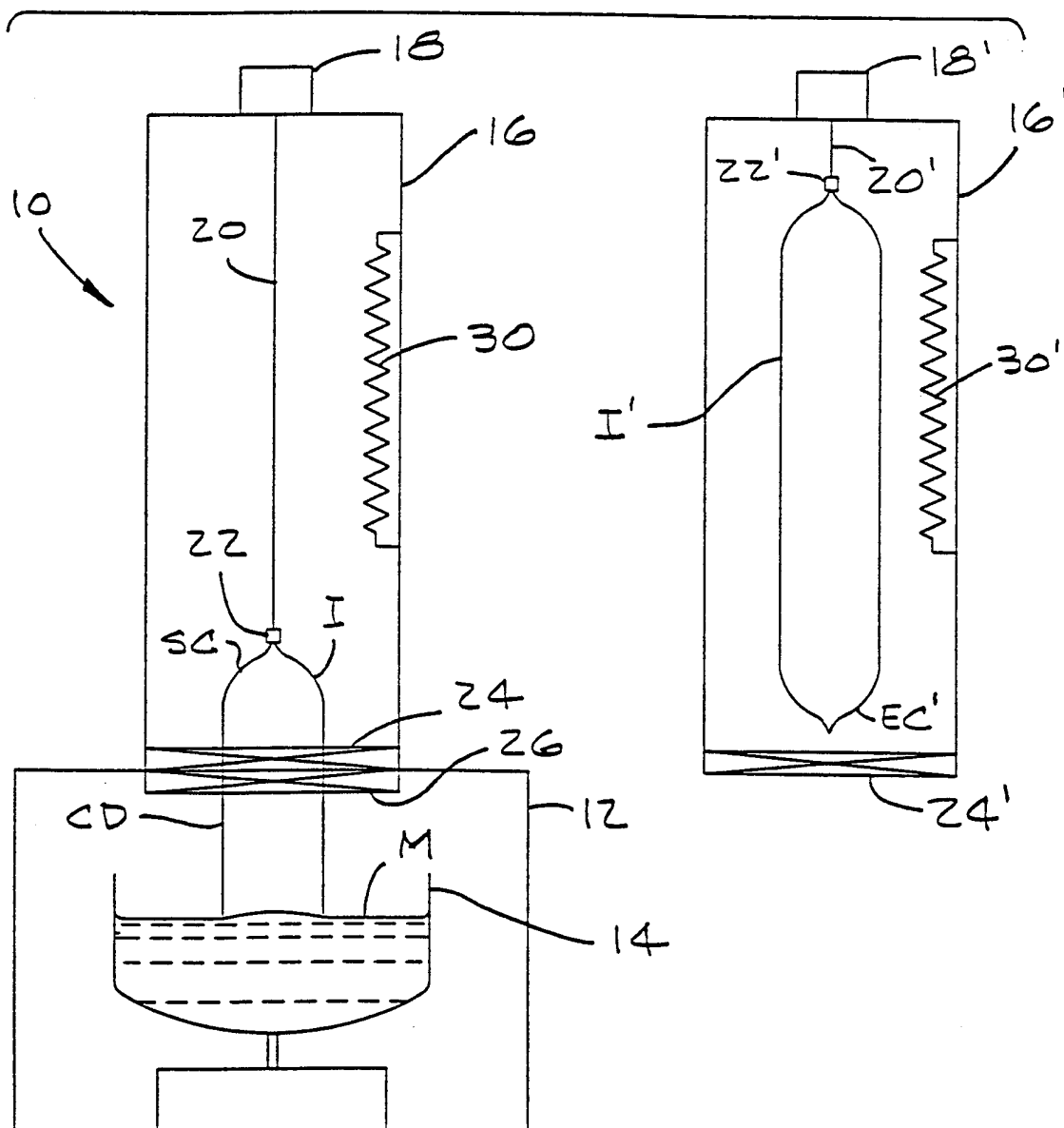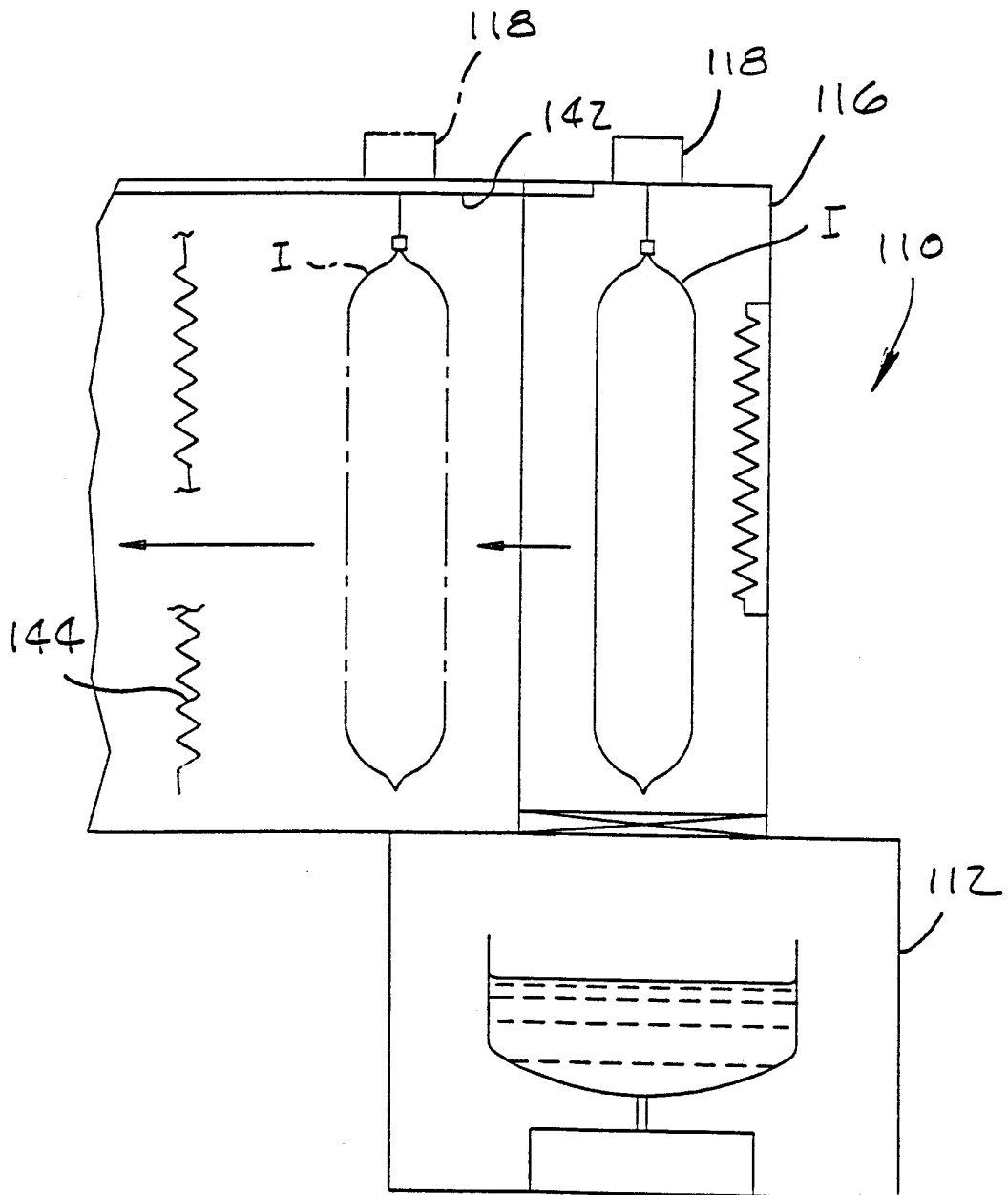
FIG. 1
PRIOR ART
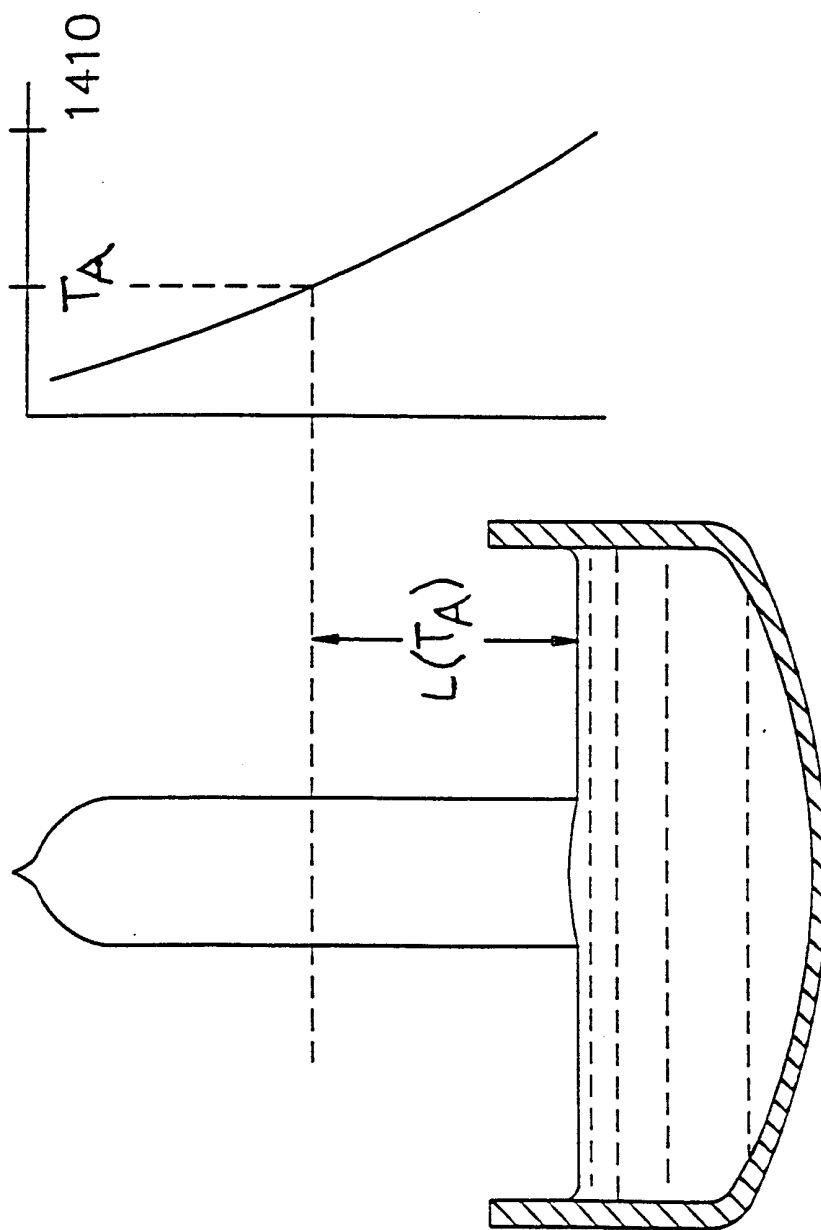
FIG. 2

FIG. 3

FIG. 4

FIG. 5

Fig.6A

Normalized growth rate vs. L

Fig.6C

87GEW

Fig.6B

87GEX