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EPITAXIAL DEPOSITION ON THE SURFACE OF A FRESHLY GROWN DENDRITE

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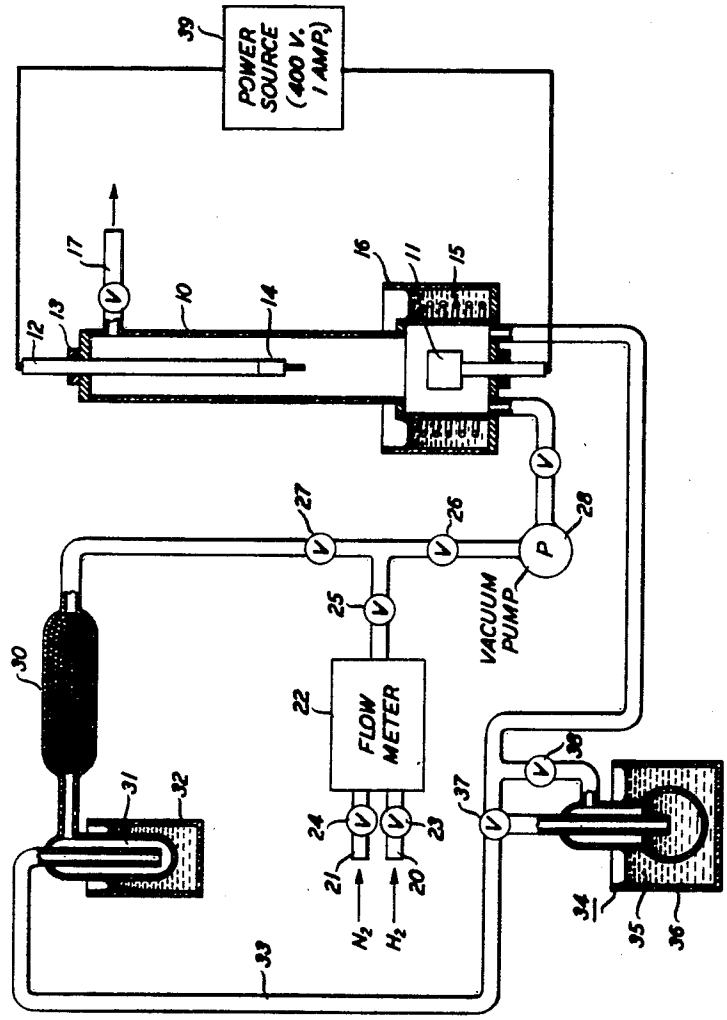

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EPITAXIAL DEPOSITION ON THE SURFACE OF A FRESHLY GROWN DENDRITE

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This invention concerns epitaxial deposition of semiconductors and, more particularly, epitaxial growth on semiconductor substrates prepared by dendritic growth.

Typical prior art techniques for the growth of epitaxial films on semiconductor substrates include elaborate and costly techniques for surface preparation preparatory to deposition. The usual slice cut from crystal ingot prepared in the ordinary fashion, such as by zone refining, possesses a surface which is unfit for epitaxial growth. The surface must first be lapped to remove the large surface discontinuities resulting from the cutting operation. This step may involve electromechanical or electrolytic polishing with or without mechanical abrading, the latter often involving a stepwise operation with abrasives of diminishing size. The surface is then washed, dried, and etched to remove strains introduced into the crystal surface during the abrading step. Another rinse follows with a final drying of the surface. All of these operations are time consuming and costly with the added danger of fracturing the crystal during abrading, or of incomplete or imperfect surface preparation ultimately resulting in a defective device unit.

These difficulties are overcome by the teachings of this invention. The invention consists essentially of preparing a semiconductor crystal by the technique of dendritic growth and, as a successive step in the same operation, depositing an epitaxial film on the freshly grown substrate.

A more thorough understanding of the invention may be obtained with the following detailed embodiment taken in conjunction with the drawing in which the figure is a schematic representation of an appropriate apparatus useful in carrying forth the principal operation of this invention.

The apparatus of the figure consists basically of a reaction chamber fitted for the introduction of the necessary gaseous components for the process and provided with appropriate heating means. The reaction vessel itself is a long vertical quartz tube **10** having approximate dimensions of 4 inches (diameter) by 3 feet (length). The tube contains a graphite crucible **11**, filled with charge material for the melt from which the dendrite is pulled. Depending from the top of the tube is an electrically conductive pulling shaft **12**, sealed with O-ring seal **13**. The shaft terminates in a graphite tip **14** which serves as the seed holder. Surrounding the base portion of the quartz tube is an R.F. heating coil **15** contained in a container **16**, for water-cooling the coil. An exhaust tube **17** is provided as shown.

The gas system here provides a means for evacuating the reaction chamber, flushing it with nitrogen and introducing a hydrogen atmosphere for pulling the crystal. Provision is made to alternatively direct the hydrogen through a source of semiconductor for the epitaxial deposition. In the system shown in the figure purified hydrogen and nitrogen are introduced at inlets **20** and **21** and into a flow meter **22**. Valves **23** and **24** control the entry of the desired gas into the chamber. The single line **25** leaving the flow meter is divided into two separate paths the choice of which may be controlled by valves **26** and **27**. The direct line leads into the reaction vessel through vacuum pump **28**. The alternate portion of the

system is designed to provide a source material for epitaxial growth. The first stage of the epitaxy so system is a purifying operation which consists of pas the H_2 gas through tube **30** containing palladin Alundum. The gas is then directed through a li nitrogen trap **31** which includes container **32** for liquid coolant. The purified gas leaving the trap is rected through the line **33** into the saturator **34** w the hydrogen is saturated with a semiconductor v compound. In this particular case the growth layer i be germanium so that $GeCl_4$ is chosen as the source m rial contained in the saturator. The saturator is pended in a cold bath **35** contained in beaker **36**. cold bath is appropriately ethylene glycol and Dry which maintains the $GeCl_4$ at $-40°$ C. The inlet outlet to the saturator are controlled by valves **37** **38**. The outlet leads into the reaction vessel.

The heating circuit shown was used to provide the l necessary for the epitaxial deposition. It is connecte that the current flow is through the dendrite after dendrite is pulled. For this purpose it is necessary the dendrite not be withdrawn from the melt after p ing. The current flow from source **39** is adjusted so the Joule heat in the dendrite maintains the proper t perature for the epitaxial deposition. The conduc crucible **11** and seed holder **14** are included for this p pose.

Other heating arrangements such as a tunnel furn are, of course, suitable. The latter has the advantag simple adaptability to continuous growth.

A specific operation using this apparatus is describe follows:

The system was flushed with nitrogen and a hydrc atmosphere was introduced for the growth operat The crucible **11** was charged with 60 grams of high pu zone-refined germanium doped with arsenic to a resisti of 1.3 ohm-cm. The seed crystal, the form of wl dictates whether the growth is polyhedral (slow) dendritic (fast), necessarily contains at least two t planes, for dendritic growth. The presence of a cohe twin plane presents a groove at the twin boundary al which nucleation and growth proceed rapidly. If one twin plane is present the rapid growth is soon te nated because the ridges of the hexagonal platelet gro the expense of the grooves until the crystal is boun wholly by ridges. Growth along a ridge is slow sinc relies on surface nucleation and thus grows by polyhe or slow growth. Two twin planes present a continuo available groove for continuous fast growth.

In this embodiment the seed crystal contained twin planes parallel to (111) having external faces pa lel to (111). The vertical direction (toward the m was $[1\bar{2}1]$. The temperature of the melt, which is ne sarily supercooled to a practical operating value by least 3° C., was adjusted to give a stationary solid-lic interface and then reduced about 10° C. as measured a thermocouple ½ cm. below the surface. The cry was then withdrawn at a rate of 0.5 cm./sec. The de of supercooling bears a linear relation to the growth so that highly supercooled melts are preferred from standpoint. A practical maximum in the degree of su cooling useful for this invention is 20° C.

The seed crystal may, of course, itself be a dend or it may be cut from a polyhedrally grown crystal. either case it must contain two twin planes. The of the seed was approximately 5 cm. x 3 mm. x .1 n

During the dendrite growth an atmosphere of hydro was maintained. The crystal was pulled to a length about 20". The melt was allowed to solidify with dendrite immersed. The heating circuit was turned and the current through the dendrite was adjusted approximately 80 v. at 1 amp. The initial volt

ıust be substantially higher due to the difference in re-
istivity encountered as the crystal heats. This power
:vel was found to produce the desired deposition tem-
erature, 835° C., as measured on an optical pyrometer.
he hydrogen flow was diverted through the $GeCl_4$
aturating system and adjusted to enter the chamber at
00 cc./min. The epitaxial deposition continued for ten
ıinutes after which the heating circuit was disconnected
nd the gas flow returned to pure hydrogen. The dendrite
as separated from the melt by using the R.F. heater to
ıelt off the lower end. The system was flushed with
itrogen and the sample was removed.

The dendrite substrate has its long dimension in
ıe (111) plane. The crystal was n-type as expected and
ıd a resistivity of approximately 1.3 ohm-cm. The film
ɔtained in the second or epitaxial growth step was
:amined by angle lapping and etching. It was found to
: epitaxial in nature with a thickness of 8 microns.
ıe film in this embodiment was also n-type. However,
proper doping p-type films can also be obtained
ing the procedures of this invention.

As will be appreciated to those skilled in the art this
vention is directed to epitaxial growth on a freshly
epared dendritically grown surface. Since this concept
more or less physical in nature it is obvious that it is
plicable to any semiconductor material. While silicon
d germanium are currently of primary practical in-
est, the III–V compounds are of increasing importance
semiconductor device development. III–V compounds
particular interest are GaAs, GaP and InSb. Epitaxial
ns on dissimilar semiconducting substrates and par-
ularly heterojunctions may also be grown according to
: techniques of this invention. The conditions for
: epitaxial depositions according to this invention may
the same as those known in the art for deposition on
linary polyhedrally grown semiconductor substrates.
While the principles of dendritic growth are known
the art, the term is defined here as simply rapid crystal

growth, i.e., at least 0.01 cm./sec. from a supercooled melt on a seed crystal containing at least two parallel coherent twin planes. The growth occurs along a (111) crystal plane and may be of unlimited length. The latter fact suggests a continuous processing operation according to the present invention.

Various other modifications and extensions of this invention will become apparent to those skilled in the art. All such variations and deviations which basically rely on the teachings through which this invention has advanced the art are properly considered within the spirit and scope of this invention.

What is claimed is:

1. A method for growing an epitaxial semiconductor film on a semiconductor substrate which comprises suspending a seed crystal in a melt of the semiconductor desired as the substrate, said melt being supercooled at least 3° C., the seed crystal having at least two parallel twin planes, pulling the seed crystal from the melt at a rate of at least 0.01 cm./sec. in a direction parallel to the twin planes to form a dendrite and, as a successive step in the same process and in the same apparatus vapor-depositing an epitaxially grown semiconductor film on the surface of the freshly formed dendrite.

2. The method of claim 1 wherein the seed crystal has a diamond cubic crystal structure.

3. The method of claim 1 wherein the seed crystal has a zinc blende crystal structure.

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