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Levinstein

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[54] **CONTROLLED EPITAXIAL GROWTH FROM SUPERCOOLED NUTRIENT-FLUX SOLUTION**

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[51] **Int. Cl.**..... **B01j 17/00,** B44c 1/18

[58] **Field of Search**..... 117/201, 113; 23/301 R; 148/1.6, 172

[56] **References Cited**

UNITED STATES PATENTS

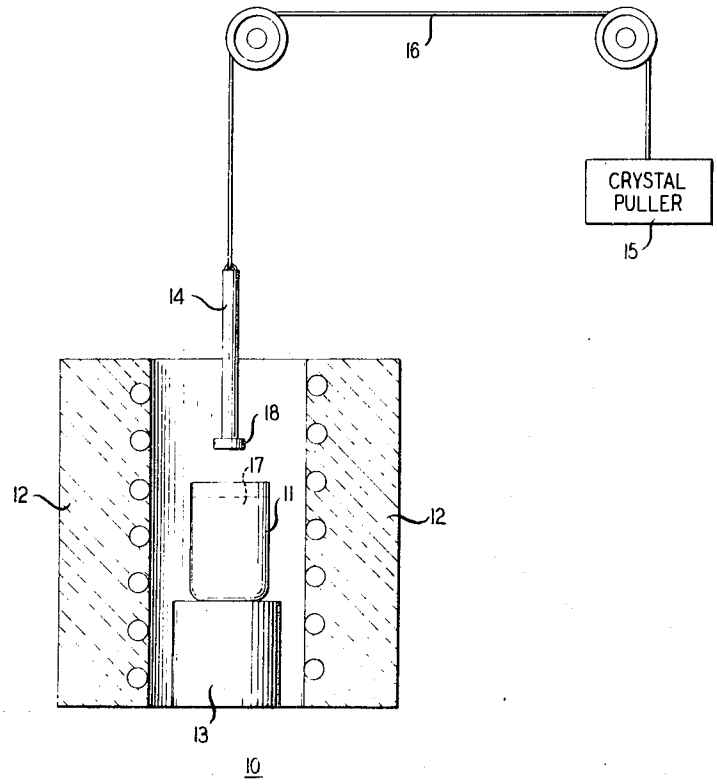
2,484,829	10/1949	Holden	23/301 R X
3,370,963	2/1968	Bonner et al.	23/52 X
3,278,342	10/1966	John et al.	148/1.6
3,394,081	7/1968	Ballman et al.	23/301 R X
3,234,135	2/1966	Ballman et al.	23/301 R X

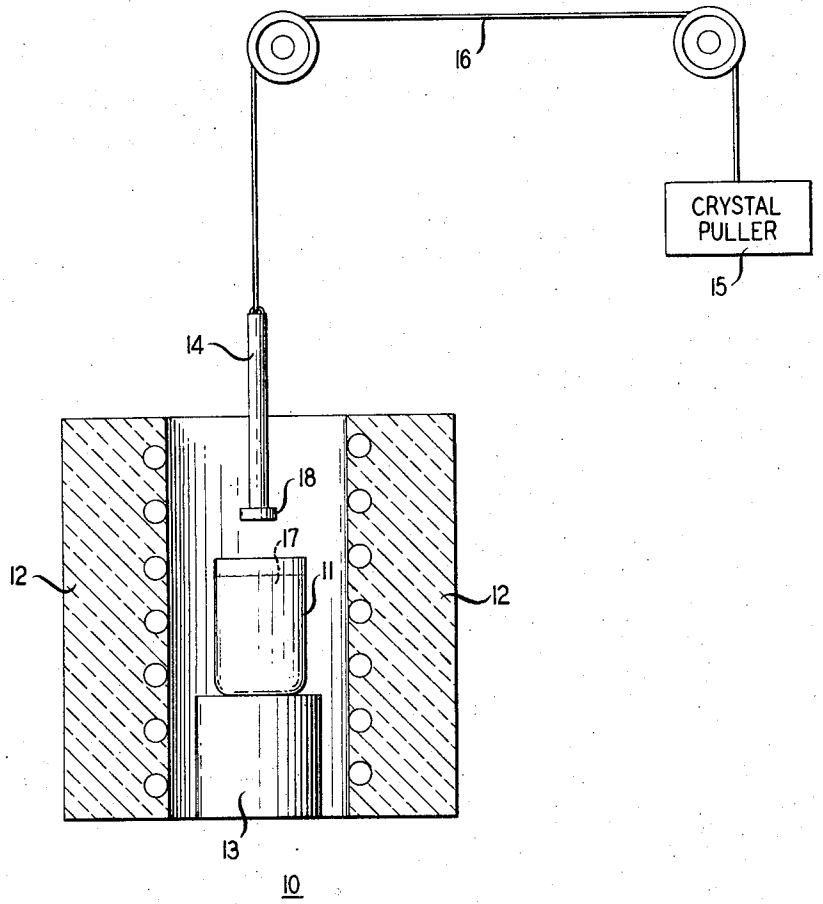
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[57] **ABSTRACT**

Controlled growth of epitaxial layers of a variety of structures including garnet, spinel, and corundum are grown out of supercooled nutrient-flux solutions. Controlled growth, both of composition and physical characteristics, is attributed to the conditions that make the procedure primarily diffusion (rather than atomic kinetic) controlled. Such conditions include high dilution of nutrient and high viscosity of the solution.

11 Claims, 1 Drawing Figure




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CRYSTAL PULLER
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CONTROLLED EPITAXIAL GROWTH FROM SUPERCOOLED NUTRIENT-FLUX SOLUTION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention is concerned with the growth of epitaxial layers of a variety of compositions and structures, resulting layers may be homoepitaxial or heteroepitaxial and may be elemental or compound.

2. Description of the Prior Art

Continuing developments in a variety of fields have resulted in a growing interest in epitaxial devices. This interest which in many instances grows out of a desire toward miniaturization has been concerned with a variety of devices, e.g., semiconductor, optic, switching, memory, etc. A common requirement for all epitaxial devices is a high degree of perfection both from a compositional and physical standpoint. Accordingly, low energy grain boundaries, impurity inclusions, surface irregularities, thickness variations, and a number of other parameters must be kept within tolerances which in many instances have not previously been of concern. An outstanding example concerns the magnetic "bubble" device where a desire to maintain magnetic properties within sufficiently close limits to permit propagation of single wall domains of less than a mil in diameter through as many as 10^6 positions within a square centimeter film has directed attention to magnetic imperfections having coerciveness as small as one oersted.

These many demanding device requirements have resulted in an intensive and ever growing search for closely controlled growth techniques capable of producing epitaxial layers of the required degree of perfection. Most of the traditional approaches have been utilized, and, while results on many occasions have been promising, the search continues for closer and closer control. Growth procedures which have received attention include those which involve both dropping temperature and those which are isothermal. Dropping temperature techniques have been found to be limited by the degree to which temperature gradients may be maintained constant over the growth region and during the growth procedure. Not only does a variation in gradient affect growth rate but a variation in this parameter in a complex system upsets the relative effective distribution coefficients of nutrient components and so results in a changing composition of the growing layer. While very careful temperature control of substrate and solution and very careful control of the solution itself has resulted in the growth of layers, which are suitable for many devices, it is clear that such procedure is inherently limited.

A variety of procedures result in growth under "isothermal" conditions. Examples include the process in which the composition of a nutrient-flux solution is constantly controlled during growth as by flux evaporation or nutrient addition. Such procedures, again while suitably applied in certain instances, have other drawbacks. The flux evaporation procedure, for example, depends upon the use either of a single component flux or of a multicomponent flux in which the various components have the same approximate partial pressures. Implicit in such procedure also is the fact that sufficient vapor pressure may require a temperature which is not optimum from the standpoint of growth. Since evaporation is necessarily confined to the surface of the solution it also follows that there is a composition gradient through the solution.

Whereas the evaporation technique, under appropriate conditions, actually controls the growth rate so that the two may in principle be kept in balance, the nutrient-addition procedure has not such built-in control. Failure to introduce nutrient at the precise rate at which it is depleted due to growth results in a changing solution-composition and attendant difficulties in controlling both growth rate and composition.

In another form of "isothermal" growth the growing surface is maintained at a fixed temperature and reliance is had upon a temperature differential for transport of nutrient, usually from a solid source. A form of this procedure is involved in hydrothermal growth. While this process has been used successfully in the growth of a variety of materials, growth of complex compositions is complicated by the need to maintain the temperature gradient within very close tolerance.

SUMMARY OF THE INVENTION

In accordance with the invention, epitaxial films, either homoepitaxial or heteroepitaxial, are grown out of supercooled nutrient-flux solutions on immersed substrates. The degree of supercooling, ordinarily at least about 20°, is sufficient to assure growth periods of sufficient duration to produce epitaxial layers a micrometer or more in thickness, sometimes repeatedly, from reasonable size solutions. Contrary to general expectation, films grown from such supercooled solution manifest a degree of physical and compositional integrity not easily achievable or perhaps not at all achievable by competing methods. This high degree of control semmingly at odds with the expected uncontrolled growth ordinarily associated with growth from supersaturated solution is attributed in the main to two factors. The first of these is concerned with nutrient-to-flux ratio by which is meant the total weight of stoichiometric nutrient material in the solution divided by the total weight of the entire nutrient-flux solution. The second factor is viscosity, it having been determined that controlled growth proceeds only out of solutions which are sufficiently viscous. While both factors are, in the main, empirical, it is apparent that both, a high degree of dilution on the one hand and a high degree of viscosity on the other, contribute to a relatively thick diffusion-controlled layer (sometimes referred to as "the σ layer") and therefore to a relatively small rate of introduction of nutrient material to the growing interface. From an experimental standpoint, it has been established, for example, that increasing temperature of initial nucleation so as to result in a less viscous system results in a film of lessening perfection from a flux-nutrient system which is otherwise identical (except for composition modification required to maintain the required degree of supercooling).

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE is a perspective view of an apparatus suitable for supercooled growth in accordance with the invention.

DETAILED DESCRIPTION

1. Process Parameters

A. Background Requirements

Certain requirements are common to growth from a flux by any procedure; certain others become some-

what more significant in the inventive procedure. The first requirement is that the flux has sufficient solubility for nutrient material so that the degree of attainable saturation may result in sufficient growth. Whereas this requirement may be met simply by increasing the size of the solution, very large solutions may complicate the procedure, e.g., may result in composition gradients. In general, fluxes found useful and in common use for conventional growth are suitable. In general, it is desirable that the flux be capable of dissolving at least about 5 per cent of its weight of total stoichiometric nutrient components. In general, this degree of solubility is sufficient to permit growth of a film of a thickness of at least a major fraction of a micrometer for the required minimal 20° supercooling out of a reasonable size solution.

It will be appreciated that the supercooled solution is intrinsically thermally unstable, and it is therefore significant that there be no predominant tendency for the flux or the nutrient or the combination to form solid compositions other than the compound which it is desired to grow epitaxially. For example, many nutrient flux solutions otherwise useful for garnet growth may result in an orthoferrite phase nucleating at a temperature higher than the initial nucleation temperature for the desired garnet. This is a well-known problem in flux growth and may generally be solved merely by adjusting the composition of the solution in order to suppress the undesired growth. In the instance of many garnet compositions, this is accomplished merely by utilizing an appreciably larger amount of iron than indicated by the desired garnet stoichiometry.

As in usual liquid phase epitaxial growth, it is required that dissolution rate of the substrate be appreciably smaller than the growth rate of the film.

B. Inventive Requirements

It has already been indicated that a minimum degree of supercooling is required if only to assure growth of reasonable film thickness. While no numerical requirement can be rigorously satisfied (increasing the size of the solution may in part overcome such inadequacy) it has been generally observed that super-cooling to the extent of about 20°C is sufficient to permit growth of films of sufficient thickness to satisfy many requirements, i.e., films of typical compositions of the order of a major fraction of a micrometer will ordinarily be grown on a substrate of a centimeter in area from a 20° supercooled solution substantially filling a 30 cc container. The maximum permitted degree of supercooling depends on other parameters, for example, viscosity should not be so great as to result in a significant lessening in growth control. Experimentally, well controlled growth has resulted out of solutions which are supercooled to the extent of 100°C.

From an experimental standpoint, the viscosity requirement is found to be interdependent on other parameters such as the degree of supercooling. Systems which have been studied, however, have sufficient low viscosity at temperatures above about 950°C as to make control problematical. It is therefore a general requirement that the nutrient-to-flux ratio be such as to result in nucleation at temperatures no higher than 950°C. A preferred limit is about 900°C. This requirement corresponds to a minimum required viscosity of the order of 0.02 poises and a preferred limit of 0.035 poises. Since, however, the diffusion rate through a σ layer decreases with temperature, the temperature of nucleation rather than the corresponding viscosity set forth above, is considered to be the controlling parameter.

C. Miscellaneous

The relatively thick σ layer which is implicit in the inventive processes, when coupled with the other parameters set forth, gives rise to stable supercooled solutions which show little or no random nucleation. This, in turn, results in a growth pattern which while substantiating the postulated mechanism, may result in a slight lessening of the useful film area. A substantial σ layer results in an increased amount of nutrient reaching the substrate at the periphery. This results from the fact that the periphery of the sample receives nutrient material through the boundary layer from a substantially complete spherical section, i.e., 4π radians while the remainder of the substrate surface gather nutrient only from a hemisphere, that is, only 2π radians. The result is a slight thickening of the growing film at the periphery of the substrate. While such peripheral portion may simply be removed where this thickening is consequential, it is an interesting aspect of the invention that stabilizing of the supercooled solution is sufficient under the conditions noted to permit agitation of the substrate sufficient to minimize the increased peripheral growth. Such agitation which also has the effect of minimizing the effect of any undesired temperature gradient may be accomplished by rotation or vibration as through a substrate holder or may be accomplished by other agitating means, e.g., mechanical, magnetic, electromagnetic, etc.

For many purposes, it is expeditious to so arrange the flux composition as to assure rapid draining of solution on the grown film during withdrawal. This is not an absolute requirement since any such wetting layer may be of little or no device consequence, or since it may usually be easily removed by physical and or chemical means. To some extent the desire to provide adequate drainage serves as an upper limit on viscosity. From this standpoint, a preferred procedure providing for adequate drainage may utilize a solution having a viscosity no more than about 0.15 poises.

D. Substrate

General substrate requirements are also common to those for substrates found useful in other forms of epitaxial growth. For example, it is a general requirement that the substrate be sufficiently strain free to satisfy the device requirements (e.g. to result in a sufficiently imperfection-free epitaxial layer). At this time, a combination of mechanical lapping sometimes followed by a chemical or mechanical procedure is sufficient for most purposes. It is, of course, generally required that the substrate also be free of such occlusions or other defects as it will have a deleterious effect on growing film. Epitaxial growth requires a reasonable match in lattice dimensions. This requirement, too, is to some extent dependent on the nature of the device for which the film is intended. Additionally, it depends upon the growth direction. Accordingly a somewhat poorer match between substrate and growing film is permitted where growth is on one of the natural growth facets which occur in bulk growth. Where growth is to proceed in a direction which ordinarily caps a closer match is ordinarily required. In general, a match of ± 0.5 per cent is adequate for growth in such high free energy direction. A preferred match is about 0.1 per cent for growth in such natural direction. Growth in the natural

direction may be achieved with a match in lattice parameter of the order of 1.0 per cent although it is preferred that the match be within 0.5 per cent for such natural direction.

2. Flux Composition

Many of the experiments upon which the inventive concept is based were carried out in boron oxide-lead oxide or in bismuth oxide-vanadium oxide fluxes. Such fluxes may be characterized as a $(B_2O_3)_y(PbO)_y$ where x=from 0.9 to 0.6 and y=from 0.1 to 0.4 and $(Bi_2O_3)_a(V_2O_5)_b$ where a=from 0.9 to 0.65 and b=from 0.1 to 0.35. Such limits are not rigidly imposed but have been empirically found to define systems with sufficient solubility and other characteristics to be expedient. These systems show the requisite characteristics for growth in accordance with the invention as well as with earlier growth methods and, while by no means unique, are suitably incorporated for growth of a large variety of compositions. Compositions which have been successfully grown out of such fluxes include substantially all of the yttrium and rare earth garnets, both those which are primarily iron-containing and those in which iron has been partially or totally replaced by gallium or aluminum or other elements; substantially all of the rare earth orthferrites; various compositions of the magnetoplumbite structure; corundum; a variety of spinel ferrites and yttrium rare earth orthoaluminates, and lead niobates.

Examples of crystalline materials and flux compositions from which they have been grown together with literature references are set forth in the following table.

Crystal Composition	Flux	Reference
$Tb_3Al_5O_{12}$	$PbO—PbF_2—B_2O$	48 J.Amer.Ceram.Soc. p.105 (1965)
$REFeO_3$	PbO	78 Jr.Amer.Chem. Soc. p.4259 (1956)
$Sm_{0.5}RE_{0.5}FeO_3$	$PbO—PbF_2—B_2O_3$	25A Physics Letters 297 (1967)
$PbFe_{12}O_{19}$	$PbO—PbF_2$	5 Phys.Chem.Solids 202 (1958)
$Ba(Al,Fe)_{12}O_{19}$	$PbO—PbF_2—B_2O_3$	
$Sr(Al,FE)_{12}O_{19}$	$PbO—PbF_2—B_2O_3$	
$Y_3Fe_5O_{12}$(film)	$PbO—B_2O_3$	3,4 Jr.Cryst.Growth 443 (1968)
$O_{12}(Bi,Ca)_3(Fe,V)_5$	Bi_2O_3	35 Jr.Appl.Phys. 2551 (1964)
$Pb_3(Mg,Zn)Nb_2O_9$	$PbO-B_2O_3$	3 Growth of Crystals 309 (1962)
Al_2O_3	$PbO—B_2O_3$	35 Jr.Appl.Phys. 522 (1964)
Al_2O	$BiO_2O_3—PbF_2$	Jr.Metals p.33 (1964)
Al_2O_3	PbF_2	37 Jr.Appl.Phys. 832 (1966)
$ZnAl_2O_4$	PbF_2	47 Am.Ceram.Soc. 388 (1964)
$ZnAl_2O_4$	$PbO—PbF_2—B_2O_3$	U.S. Patent 3,370,963
$MgAl_2O_4$	PbF_2	3,4 Jr.Cryst.Growth: 485 (1968)
$ZnRh_2O_4$	PbO	51 Jr.Am.Ceram.Soc. 292 (1968)
$ZnGa_2O_4$	$Bi_2O_3—PbF_2$	50 Jr.Am.Ceram.Soc. 325 (1967)
Ga_2O_3	$Bi_2O_3—PbF_2$	50 Jr.Am.Ceram.Soc. 325 (1967)
$YA10_3$	$PbO—(B_2O_3)$	78 Jr.Am.Chem.Soc. 4259 (1956)
In_2O_3	$PbO—B_2O_3$ (or $+PbF_2$)	35 Jr.Appl.Phys. 2803 (1964)
$RECrO_3$	$PbF_2—B_2O_3$	49 Jr.Am.Ceram.Soc. 576 (1966)
$REMn_2O_5$	$PbF_2—B_2O_3$	49 Jr.Am.Ceram.Soc 576 (1966)
$REMnO_3$	$PbF_2—B_2O_3$	49 Jr.Am.Ceram.Soc. 576 (1966)
ThO_2, HfO_2	$PbF_2—B_2O_3$	49 Jr.Am.Ceram.Soc. 576 (1966)
ZrO_2, ThO_2	PbF_2	50 Jr.Am.Ceram.Soc. 325 (1967)
ZnO		
$REPO_4$	$Pb_2P_2O_7$	47 Jr.Am.Ceram.Soc. 257 (1964)
$REAsO_4$	$Pb_2As_2O_7$	50 Jr.Am.Ceram.Soc. 433 (1967)
$REVO_4$	$Pb_2V_2O_7$	51 Jr.Am.Ceram.Soc. 538 (1968)
NaF(Gd)	$PbO—PbF_2$(Gd)	2 Solid State Comm. 261 (1961)
$CaMgSi_2O_6$	PbO	46 Jr.Am.Ceram.Soc. 356 (1963)
$SrTiO_3$	SiO_2	2 Jr.Cryst.Growth 402 (1968)
$BaTiO_3$	TiO_2	178 Lab for Ins.Res.MIT 44 (1963)
$Bi_4Ti_3O_{12}$	Bi_2O_3	32 Jr.Appl.Phys. 959 (1961)
$GaFeO_3$	$B_2O_3—Bi_2O_3$	31 Jr. Appl. Phys. 263S (1960)
$RECrO_3$	Bi_2O_3	78 Jr.Am.Chem.Soc. 4259 (1956)
$(Bu,Ca)_3(Fe,V)_5O_{12}$	$Bi_2O_3—V_2O_5$	35 Jr.Appl.Phys. 2551 (1964)

Table – Continued

Crystal Composition	Flux	Reference
$REVO_4$	$V_2O_5(Na)$	36 Jr.Chem.Phys. 702 (1962)
$Be_3Al_2(SiO_4)_3$	V_2O_5	33 Jr.Appl.Phys. 3209 (1962)
$ZrSiO_4$	V_2O_5	44 Jr.Am.Ceram.Soc. 128 (1961)
$BaTa_2O_6$	$BaO—B_2O_3$	2 Mat.Res.Bull. 533 (1967)
$KNbO_3$	K_2CO_3	29 Jr.Appl.Phys. 233 (1958)
$KTaO_3$	K_2CO_3	Jr.Phys.Chem.Sol. p. 437 (1967)
$K(Nb—Ta)O_3$	K_2CO_3	114 Phys.Rev. 63 (1959) 44 Am.Ceram.Soc.Bull. 9 (1965)
$K_6Li_4Nb_{10}O_{15}$	K_2CO_3	1 Jr.Cryst.Growth 318 (1967)
LiO_2	$Na_2B_4O_7$	Los Alamos Reports No. LA 2076-OTS (1957)
$BaFe_{12}O_{19}$	$NaFeO_2$	47 Jr.Am.Ceram.Soc. 13 (1964)
$Ba_2Me_2Fe_{12}O_{22}$	$NaFeO_2$	47 Jr.Am.Ceram.Soc. 13 (1964)
$Ba_2Me_2Fe_{18}O_{27}$	$NaFeO_2$	47 Jr.Am.Ceram.Soc. 13 (1964)
$BA_3Me_2Fe_{24}O_{41}$	$NaFeO_2$	47 Jr.Am.Ceram.Soc. 13 (1964)
$Ba_2Me_2Fe_{28}O_{46}$	$NaFeO_2$	47 Jr.Am.Ceram.Soc. 13 (1964)
$Ba_4Me_2Fe_{36}O_{60}$	$NaFeO_2$	47 Jr.Am.Ceram.Soc. 13 (1964)
$CaWO_4$	$Na_2W_2O_7$	31 Jr.Appl.Phys. 328 (1960)
$NaRE(WO_4)_2$	$Na_2W_2O_7$	31 Jr.Appl.Phys. 328 (1960)
$REAl_3B_4O_{12}$	$K_2Mo_2O_7$	47 Am.Min. 1380 (1962)
$Be_3Al_2Si_6O_{18}$	$Li_2O—MoO_3$	33 Jr.Appl.Phys. 3209 (1962) 46 Jr.Am.Ceram.Soc. 6 (1963)
Be_2SiO_4	$Li_2O—MoO_3$	33 Jr.Appl.Phys. 3209 (1962) 46 Jr.Am.Ceram.Soc. 6 (1963)
$BeAl_2O_4$	$Li_2O—MoO_3$	33 Jr.Appl.Phys. 3209 (1962) 46 Jr.Am.Ceram.Soc. 6 (1963)
BeO	$Li_2O—MoO_3$	47 Jr.Am.Ceram.Soc. 274 (1964) 50 Am.Min. 44 (1965)
$ZrSiO_4$	$Li_2O—MoO_3$	48 Jr.Am.Ceram.Soc. 130 (1965)
ThO_2	$Li_2W_2O_7$	36 Jr.Appl.Phys. 2143 (1965)

3. Film Composition

There are no inherent requirements on the process other than those stated above. Use of the prototype flux systems set forth in the preceding paragraphs or of variations or modified fluxes based on such prototypes (e.g., PbO or PbF_2 containing compositions), however, is suitable for growth of many film compositions. Since technological interest in many types of epitaxial devices is now centered on oxidic materials and since suitable fluxes are readily available for growth of such oxidic materials, such compositions constitute a preferred embodiment of the invention.

Compound systems other than oxidic have been grown from flux solutions. Supercooled solution growth in accordance with the invention for all such systems, and, in fact, any others for which suitable fluxes may be formed, is suggested. Such systems include: Fluorides such as YF_3 from BeF_2 flux and sulfides such as ZnS from a ZnF flux. Certain of these may require additional precautions, as for example, to suppress loss of constituents through evaporation to avoid undesired balance change, etc. All of such precautions are identical to those now taken in the growth of such materials by conventional flux growth techniques.

4. Processing

The process has been described in terms of supercooling in degrees centigrade. Such limits have been found to adequately describe necessary growth conditions. The basis for this prescription concerns desired maximum film thickness as well as growth rate. Both desiderata may be prescribed in terms of percentage supersaturation rate than degrees of supercooling. For many systems the prescribed minimum of 10° C corresponds with a supersaturation of approximately 5 weight per cent. In many other systems, depending on the solubility curve, such minimum may be obtained for a lesser degree of supercooling. The minimal condition for adequate growth is more generally expressed, therefore, as 5 weight per cent of supersaturation, with this figure representing the excess amount of stoichiometric nutrient component in solution above the value required for saturation expressed as a fraction of the total solution.

Growth in accordance with the invention proceeds upon an immersed substrate. For convenience, the substrate is generally suspended within the liquid and the suspending means is generally used for withdrawing the substrate together with the grown layer at the termina-

tion of the process. Other arrangements may be expeditious under other certain circumstances, e.g., flux may be poured or spun off at termination of growth, etc.

Nutrient-flux solution is prepared in the usual manner, generally from powdered ingredients which are capable of yielding or are identical to the final flux and nutrient components. Powdered mixes are homogenized to the degree required and as is well known this may necessitate a sequence of one or more millings interspersed with firings.

Liquification is carried out at a temperature at least corresponding to that of the saturated solution. Generally it is expeditious to prepare at a somewhat higher temperature, for example, at a 100°C or more above this temperature. Following liquification, the solution is reduced in temperature to produce the desired degree of supersaturation (generally to a temperature of from 20°C to 100°C below that corresponding with saturation).

Following preparation of the solution it is usually desirable to bring the substrate to the temperature of the liquified solution. This may be achieved simply by suspending the substrate over the surface of the solution for a short period. Following this "equilibration" step, the substrate is immersed in the supercooled solution and is kept immersed for the period required to produce sufficient film thickness. Protective atmospheres, stirring, use of over pressures of particularly volatile ingredients and any other precautions required for the particular system being grown may be incorporated.

After withdrawal, substrate and film are permitted to cool at a rate sufficiently slow to avoid substantial thermal stress. For systems for which protective atmospheres or over pressures are required during growth it may be necessary to maintain such protection during at least the initial portion of the cooling cycle. All such considerations are conventional and are well known to those versed in this art.

5. The FIGURE

The apparatus of the FIGURE resembles Czochralski pulling apparatus and includes a platinum crucible **11** heated by a resistance furnace **12.** Crucible **11** is supported by pedestal **13** so as to position the flux in a region of low thermal gradients. The remainder of the apparatus consists of a substrate holder **14,** pulling means **15,** and some interconnecting means **16.** The FIGURE also shows a flux solution **17** and a garnet substrate **18.**

6. Examples

EXAMPLE 1

A layer of $Er_2Eu_1Fe_{4.3}Ga_{0.7}O_{12}$ of a thickness of approximately 10 micrometers was grown in a period of 10 minutes on a substrate of $Gd_3Ga_5O_{12}$ of an area of approximately 1 square centimeter in a vessel as depicted in the FIGURE. The flux solution was produced from a powdered mixture consisting of

0.63 grams Eu_2O_3
1.356 grams Er_2O_3
10.00 grams Fe_2O_3
0.70 gram Ga_2O_3
140 grams PbO
2.8 grams B_2O_3

(In common with other procedures in which lead oxide-containing fluxes are used, this composition represents a degree of iron enrichment. As is well known, iron enrichment is necessary to produce garnet and to suppress orthoferrite growth.) Temperature was maintained at 920°C during growth (representing supercooling of 30°C).

EXAMPLE 2

The procedure of Example 1 was followed, however, to grow a layer of $Gd_3Ga_5O_{12}$ of a thickness of 3μ on a substrate of $Gd_3Ga_5O_{12}$. Nutrient-flux solution was fluxed from a powdered mixture of

4.72 grams Gd_2O_3
5.62 grams Ga_2O_3
150 grams PbO
10 grams B_2O_3

Temperature was maintained at 910°C during growth (representing supercooling of 30°C).

EXAMPLE 3

The procedure of Example 1 was repeated to grow a layer of the same composition there set forth on a substrate of the same composition, however, utilizing a $Bi_2O_3-V_2O_5$ flux. The flux solution was produced from a powdered mixture consisting of

5.26 grams Er_2O_3
2.46 grams Eu_2O_3
6.50 grams Fe_2O_3
0.40 gram Ga_2O_3
120 grams V_2O_3
12 grams V_2O_5

Temperature was maintained at 930°C during growth (representing supercooling of 20°C).

EXAMPLE 4

The procedure of Example 1 was followed, however, to grow a layer of chromium doped Al_2O_3 on Al_2O_3. The composition of the flux nutrient mixture employed

7 grams Al_2O_3
0.2 grams Cr_2O_3
150 grams PbO
6 grams B_2O_3

Temperature was maintained at 850°C during growth (representing supercooling of 60°C).

EXAMPLE 5

The procedure of Example 1 was followed, however, to grow $CoFe_2O_4$ on an MgO substrate. The composition of the flux nutrient mixture employed

2 grams Co_2O_5
6 grams Fe_2O_3
100 grams PbO
2 grams B_2O_3

Temperature was maintained at 930°C during growth (representing supercooling of 20°C).

What is claimed is:

1. Method for the epitaxial growth of a first composition on a substrate of a second composition the lattice parameters of the said compositions being matched within ± 1.0 percent comprising immersing the said substrate into a liquid body of nutrient-flux composition and permitting growth to occur on the said substrate while immersed characterized in that said nutrient-flux composition is supercooled by an amount of at least 10°C, in that the total concentration of nutrient expressed in terms of the equivalent stoichiometric composition is a maximum of 10 percent by weight of the entire nutrient-flux composition and in that initial nucleation occurs at a temperature of less than 950°C.

2. Method of claim **1** in which the said epitaxial growth is homoepitaxial and in which the said first

composition and second composition are substantially identical.

3. Method of claim 1 in which the said epitaxial growth is heteroepitaxial and in which the said first composition and second composition differ.

4. Method of claim 3 in which the lattice parameters are matched within ± 0.5 per cent.

5. Method of claim 1 in which growth is on a substrate a major face of which defines a plane corresponding with a natural facet evidenced in a bulk-grown crystal of the said first composition.

6. Method of claim 1 in which the degree of supercooling is a minimum of at least 20°C during at least a portion of the growth period.

7. Method of claim 1 in which the said first composition is an oxidic material.

8. Method of claim 7 in which the flux independent of nutrient ingredients comprises lead oxide.

9. Method of claim 8 in which such flux consists essentially of a mixture of lead oxide and boron oxide, the relative amounts of such flux constituents being indicated by the formula $(PbO)_x$ $(B_2O_3)_y$ where x is from 0.9 to 0.6 and y is from 0.1 to 0.4.

10. Method of claim 7 in which the flux independent of nutrient ingredients consists essentially of a mixture represented by the formula $(Bi_2O_3)_a(V_2O_5)b$ where a is from 0.9 to 0.65 and b is from 0.1 to 0.35.

11. Method of claim 7 in which the oxidic material evidences a structure selected from a group consisting of garnet, spinel, ferrite, orthoferrite, and corundum.

* * * * *

PRINTER'S TRIM LINE

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,790,405 Dated February 5, 1974

Inventor(s) Hyman J. Levinstein

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 6, change "not" to --no--; and
line 33, change "semmingly" to --seemingly--.

Column 5, line 9, change "$(B_2O_3)_y(PbO)_y$" to
--$(B_2O_3)_y(PbO)_x$--.

Column 6, the 11th line under the heading "Flux", change "BiO_2O_3-PbF_2" to --Bi_2O_3-PbF_2--.

Column 10, line 26, change "120 grams V_2O_3" to
--120 grams Bi_2O_3--.

Signed and sealed this 5th day of November 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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