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EPITAXIAL DIELECTRIC MgO CRYSTALS

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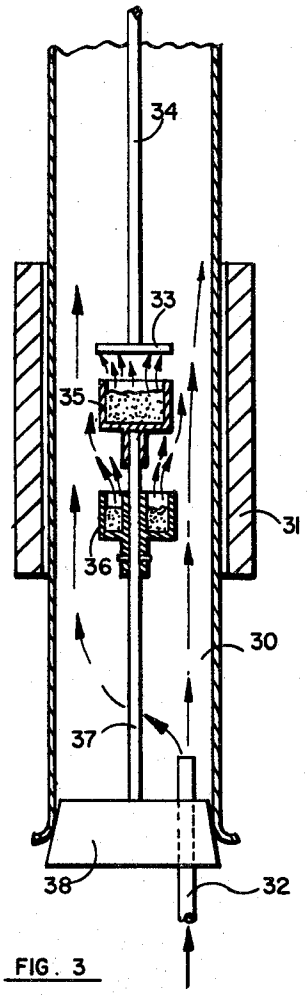


FIG. 3

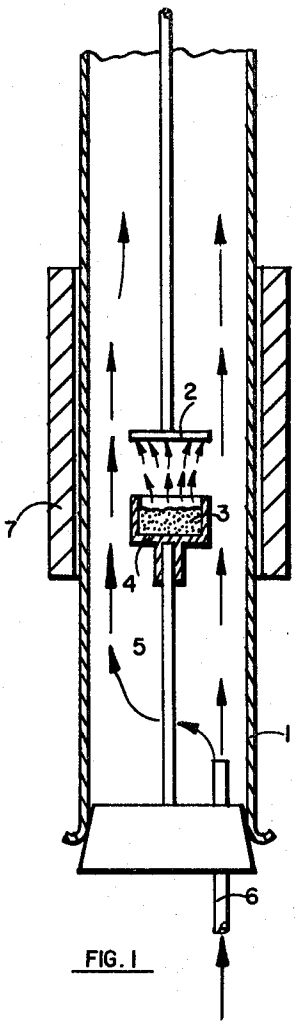


FIG. 1

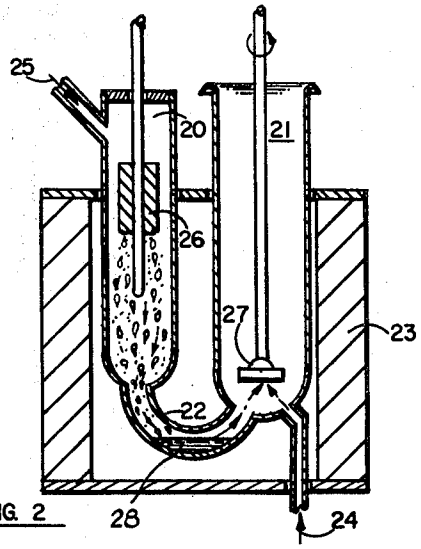


FIG. 2

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EPITAXIAL DIELECTRIC MgO CRYSTALS

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ABSTRACT OF THE DISCLOSURE

A process for epitaxially growing a single crystal of MgO. The process comprises the steps of heating a single crystal MgO substrate in a chamber in the presence of water vapor and at least one vaporized Mg halide. The vaporized halide is transported, in the presence of an inert carrier gas, toward the MgO substrate, resulting in epitaxial growth of MgO on the substrate.

This invention relates to methods for growing dielectric crystals and more particularly to a low temperature method for epitaxially growing crystalline magnesia on a single crystal magnesia substrate.

The prior art carbon arc process for producing magnesia crystals requires the use of extremely high temperatures. Such a process requires that the magnesia be melted at approximately 2825° C. and then cooled slowly to produce single crystals. The carbon arc process produces strains in the resulting crystal because of the high temperature gradients inherent in the process. These strains result in undesirable lineage in the crystal which degrade the laser operating characteristics of the dielectric crystal. Further, it is difficult to dope the crystal with an active ion in the carbon arc process because of the high volatility of the dopant oxides at the high temperature utilized in the process. Also, when the dopant material is introduced, further strains are produced because undoped melted magnesia has a composition different from the composition of the solid doped magnesia. Additionally, the most desirable oxidation state of the dopant ion cannot always be obtained because it is unstable under the growth conditions of the carbon arc process.

Accordingly, it is the principal object of this invention to provide a method for growing MgO dielectric crystals which obviates these disadvantages of the prior art process.

It is an object of this invention to epitaxially deposit magnesia on a magnesia single crystal substrate by utilizing a low temperature vapor deposition process which minimizes strains and inhomogeneities in the resulting crystal layer.

Another object of this invention is to provide an improved process for doping magnesia crystal layers with active ions.

Still another object of this invention is to epitaxially produce a magnesia crystal layer having high crystalline perfection and improved dielectric and laser characteristics.

In accordance with the process of the present invention, a single crystal magnesia substrate is heated in a chamber and a magnesia layer is epitaxially deposited thereon. It is a preferred feature of the process of the present invention that the deposited magnesia layer is formed on the substrate by reacting at relatively low temperatures at least one halide of Mg and water vapor to epitaxially deposit the magnesia layer in a preselected crystallographic form. In one embodiment of the present invention, selected halides of dopant elements are included with the magnesium halide and also reacted with water vapor to produce an epitaxial magnesia layer containing a preselected dopant.

Other objects and features of the invention will become

apparent in the following description taken together with the drawings in which:

FIG. 1 is a representation of a simple vertical reactor;

FIG. 2 is a representation of a long-run vertical reactor;

FIG. 3 is a representation of a vertical codeposition reactor.

Referring now to FIG. 1, there is shown schematically a simplified reaction chamber **1** in which a single crystal substate **2** is appropriately suspended. A source material supply **3** is provided in container **4** which is supported by rod **5** directly under the substrate **2**. The crystal **2** and the source material **3** are both heated by furnace **7** positioned to surround the reaction chamber **1** adjacent the crystal **2** and supply **3**.

Inert gas and a controlled amount of water vapor are admitted into the chamber through tube means **6**. As described in detail hereinafter, MgO is epitaxially deposited on the MgO single crystal substrate by the hydrolysis of the anhydrous halide vapors of magnesium which may include a dopant halide near the crystal in accordance with the reaction

$$MgX_2 + H_2O \xrightarrow[\Delta]{\text{inert gas}} MgO + 2HX$$

where X is a designation for F, Cl, Br or I, the chloride, bromide, and iodide being preferred.

The water vapor admitted into system **1** by tube means **6** may be produced by bubbling an inert carrier gas, preferably helium, through water in a container (not shown) maintained at room temperature, or by other means well-known in the art.

FIG. 2 is a schematic diagram of modified apparatus useful in carrying out the method of the present invention which permits longer growth or deposition cycles and thicker deposits than provided by the apparatus of FIG. 1. As shown in FIG. 2, the reactor system is comprised of chambers **20** and **21** having their lower ends connected by conduit **22**. Furnace **23**, which surrounds both chambers, provides means for heating the two chambers **20** and **21** and conduit **22** in a controlled manner. Rod **26** of solid magnesium halide is supported by any conventional means in chamber **20**. An MgO substrate crystal **27** is rotatably supported in chamber **21** near the base of the chamber so that it is located adjacent the opening of conduit **22**. Chamber **21** has a tube means **24** through which inert gases and water vapor are injected at a point adjacent the position of crystal **27**. The water vapor may be supplied from a source as indicated above in connection with FIG. 1. Chamber **20** has an inlet means **25** through which an inert gas is injected above the rod **26** so that the magnesium halide vapors will be carried through conduit **22** into the chamber **21**. In this manner the magnesium halide vapors will react adjacent crystal **27** with the water vapor to epitaxially deposit MgO on the MgO single crystal substrate.

Another reactor system in which the process of the present invention may be utilized is illustrated in FIG. 3 and comprises a reactor tube of quartz or other heat resistant material which forms chamber **30** in which a single crystal substrate **33** and other elements are appropriately supported within the effective area of the furnace **31** by rod means **34**. A pair of container means **35** and **36** is supported by rod **37** so that the source materials contained therein are also within the effective area of furnace **31**. Means **35** and **36** contain source materials, e.g., anhydrous halides of magnesium and a selected dopant material. The lower end of chamber **30** is closed by base portion **38** which may consist of any inert material through which tube means **32** may be inserted and by which rod means **37** may be held.

The substrate on which the epitaxial MgO crystal is

deposited or grown is comprised of single crystal MgO having an exposed crystal face whose structure is similar to that of the MgO layer to be deposited. For the purposes of describing the invention the substrate material is single crystal MgO of a few millimeters thickness.

The substrate may be prepared by cleaving optical grade MgO along a {100} cleavage plane or by cutting the MgO into plates of desired configuration along its other crystal faces. The plates are ground flat to produce a plate having a selected size and then chemically polished in an acid etch solution.

The source materials for producing the epitaxially deposited MgO layer on the substrate may be anhydrous magnesium halide for undoped layer deposition, where the halide is preferably the bromide, chloride and iodide. Where the epitaxially deposited MgO layer is to be selectively doped an additional source of a hydrolyzable anhydrous metal halide may be utilized. Suitable metal halides are selected from the fluorides, chlorides, bromides and iodides of Fe, Ni, Cr, Mn, Co and V.

Essentially the same hydrolysis reaction takes place at the surface of the substrate as occurs with the anhydrous magnesium halide, with the additional codeposition of the active impurity ion in the crystal lattice of the MgO layer. Generally, the chlorides, bromides and iodides are preferred because of their lower melting points and ready availability.

The method of producing epitaxial layers on substrate materials by utilization of the vapor deposition process of the present invention is described more fully with reference to the following examples.

EXAMPLE I

A freshly cleaved {100} MgO substrate crystal of approximately 2 millimeters thickness is fastened to a fused silica (Vycor) rod by platinum wire and lowered into a Vycor reaction chamber as shown in FIG. 1. The corners of the substrate may be chemically rounded and the substrate is preferably rotated during the deposition process to prevent spurious formation of polycrystalites on the edges. Anhydrous $MgBr_2$ is placed in a Vycor container **4** and supported by a Vycor rod **5** in the reaction chamber so that the top surface of the $MgBr_2$ is supported one inch below the MgO substrate crystal. The reaction chamber is sealed at the bottom by a convenient closure. A Nichrome wound cylindrical furnace **7** is positioned around the reaction chamber adjacent the crystal **2** and container **4**.

The reaction chamber **1** is thoroughly flushed with dry inert gas, and the furnace **7** activated so that the temperature of the MgO crystal and the $MgBr_2$ source material is raised to and maintained at about 950° C. Water vapor is then introduced into the reaction chamber through tube **6** by bubbling the inert gas, e.g., helium, through water immediately before the gas enters the chamber. The water vapor reacts with the $MgBr_2$ vapor to deposit a layer of MgO epitaxially on the MgO substrate. Deposits of an MgO layer on an MgO substrate in the range of 100 microns thickness are produced in one-half hour on a substrate approximately 2 centimeters square. Microscopic examination and X-ray Laue patterns show the overgrowth to be single crystal in nature.

EXAMPLE II

The process as described in Example I was repeated using a source material of $MgCl_2$ rather than $MgBr_2$ and a temperature of about 1100° C.

The MgO layer deposited on fresh cleaved {100} MgO substrate and chemically polished {100} MgO substrate were both single crystal deposits.

EXAMPLE III

The process as described in Example I was also used to grow discontinuous but epitaxial MgO layers on the {111} face of an MgO substrate. The only process change was

the use of MgI_2 in place of $MgCl_2$ as a source material and the use of a reduced temperature, i.e., about 680° C.

EXAMPLE IV

The process utilizing the system illustrated in FIG. 2 was carried out to grow single crystal layers of MgO in a manner similar to Example I. An MgO substrate crystal is appropriately placed in the device and heated to approximately 1100° C. An $MgCl_2$ rod **26** is supported in chamber **20** so that a molten pool **28** of $MgCl_2$ is maintained at 1100° C. in the conduit **22**. The $MgCl_2$ vapors are carried to the substrate crystal by an inert carrier gas injected into the system through inlet **25**. Water vapor is carried to the substrate crystal by bubbling argon carrier gas through water (not shown) maintained at room temperature and injecting it into chamber **21** through tube **24**. Single crystal layers of MgO of about one millimeter thickness were epitaxially deposited on MgO in sixteen hours.

EXAMPLE V

The system shown in FIG. 3 was utilized to epitaxially deposit a single crystal layer of Co^{+2} doped MgO on an MgO substrate. The MgO substrate crystal is heated to approximately 950° C. and is positioned approximately one inch above an $MgBr_2$ source which is also maintained at 950° C. The second source material, $CoBr_2$, is positioned approximately four inches below the $MgBr_2$ source and is maintained at a temperature of approximately 800° C. Water vapor is injected into chamber **30** as described above. The $CoBr_2$ and $MgBr_2$ vapors are hydrolyzed by the water vapors to produce Co^{+2} doped MgO on the MgO substrate crystal. The deposited layer was found to be single crystal in nature and had an approximate thickness of 100 microns.

EXAMPLE VI

The process of Example I was repeated utilizing the apparatus of FIG. 1 and a source material consisting of a solution of $CoBr_2$ and $MgBr_2$ in place of the pure $MgBr_2$ used in Example I. One (1) percent by weight of the solution was $CoBr_2$.

The solution was produced by heating a mixture of $CoBr_2$ and $MgBr_2$ until the $MgBr_2$ melted and dissolved the $CoBr_2$. The molten solution gave off vapors which consisted of both $CoBr_2$ and $MgBr_2$. The vapor composition was controlled by controlling the temperature and composition of just the molten solution, rather than by controlling the temperature of the two, separate source materials as in Example V. The $CoBr_2$ and $MgBr_2$ vapors were more intimately mixed because of the complete mixing of the $CoBr_2$ in the molten $MgBr_2$, resulting in a more uniform doping of the resultant MgO with the Co^{+2} ions. The temperature of the source material and MgO substrate was maintained at 935° C. A single crystal layer of Co^{+2} doped MgO was epitaxially deposited on the MgO substrate.

EXAMPLE VII

The process of Example VI was repeated utilizing the apparatus of FIG. 2 and a source material consisting of a solution of $CrCl_3$ in $MgCl_2$. As in Example VI, the solution was produced by heating a mixture of $CrCl_3$ and $MgCl_2$ until the $MgCl_2$ melted and dissolved the $CrCl_3$. The temperature of the substrate and source material was maintained at about 1100° C. A single crystal layer of Cr^{+3} doped MgO was epitaxially deposited on the MgO substrate.

In Examples IV and VII utilizing the apparatus of FIG. 2 deposits of about 0.9 gram (1 mm. thick) were achieved on a 2 cm. square MgO substrate. Other deposits were formed as thick as 2.0 mm., but over smaller areas, for example, 0.5 cm. by 0.5 cm.

In the other unitary source material examples, depositions within the range of one to two millimeters in thickness are attainable by controlling crystal preparation,

growth rates and temperatures. The epitaxial layer thickness desired may be obtained by selective variations in these parameters. Thus, temperatures of at least about 1075, 950 and 680° C. for the Mg halides of Cl, Br and I, respectively, are preferably utilized if optimal epitaxial deposits are to be obtained.

Crystal quality, as indicated by the dislocation etch counts, shows that epitaxial MgO deposited by the low temperature chemical vapor deposition process of the present invention is at least equivalent if not improved over the MgO deposited by the carbon arc process. Thus, dislocation counts of 10^5/cm.^{2} with some areas as low as 5×10^4/cm.^{2} have been achieved by the process of the present invention while the carbon arc process achieved counts of the order of 10^5/cm.^{2}. Further, the number of subgrain deposits is lower by the process of the present invention.

In a typical case, a dislocation etch pattern of an MgO epitaxial deposit on an MgO substrate exhibited two subgrain boundaries in the substrate crystal which were not continued into the epitaxial MgO deposit. On one such crystal 17 subgrain boundaries were in the crystal and only four were continued into the epitaxial MgO deposit. No subgrain boundaries were observed in the deposit which were not initially present in the substrate. Thus, the 300 subgrains/cm.^{2} of the substrate may be reduced to as few as 70/cm.^{2} in the epitaxial MgO deposited in accordance with the present invention. This reduction in subgrains results in less axis wander or lineage within the crystal, which is of particular significance in providing laser crystals of improved efficiency.

Although particular embodiments of the present invention have been described, various modifications will be apparent to those skilled in the art without departing from the scope of the invention. Therefore, the present invention is not limited to the specific embodiments disclosed but only by the appended claims.

We claim:

1. A process for epitaxially growing MgO dielectric crystals comprising, heating a single crystal MgO substrate to at least 680° C. in the presence of water vapor and at least one vaporized anhydrous Mg halide to epitaxially deposit MgO on said substrate.

2. The process as described in claim 1 wherein said metal halide is at least one selected from the class consisting of $MgBr_2$, $MgCl_2$ and MgI_2.

3. The process as described in claim 1 wherein said metal halide is at least one selected from the class consisting of $MgBr_2$, $MgCl_2$ and HgI_2 and wherein a second halide of a dopant selected from the halides of Fe, Ni, Cr, Mn, Co and V is hydrolyzed at the same time as said first halide to form an epitaxial codeposit with said MgO.

4. The process as recited in claim 1 wherein said Mg halide is $MgBr_2$.

5. A process for epitaxially depositing MgO dielectric crystals comprising, heating a single crystal MgO substrate of preselected crystallographic orientation in the presence of an inert carrier gas and water vapor and at least one vaporizable anhydrous Mg halide, said water vapor and halide being at a temperature sufficient to vaporize and hydrolyze said halide to epitaxially deposit MgO on said substrate.

6. A process for epitaxially growing doped MgO dielectric crystals comprising the steps of, providing an MgO single crystal substrate, providing a solution of a dopant metal halide selected from the class consisting of the halides of Cr, Co and V in an Mg halide, heating said solution and said MgO crystal in proximate relation at a temperature sufficient to vaporize said solution, and introducing water vapor into said solution vapor to hydrolyze said halides so that an oxide of Mg is epitaxially deposited on said substrate together with the dopant metal ion.

7. The process of claim 6 where said halide is $MgBr_2$ and said dopant halide is $CoBr_2$.

8. The process of claim 6 wherein said halide is $MgCl_2$ and said dopant halide is $CrCl_3$.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,386,852 June 4, 1968

Jack E. Mee et al.

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

Column 6, line 2, "HgI_2" should read -- MgI_2 --.

Signed and sealed this 2nd day of December 1969.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents