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[54] CHEMICAL VAPOR DEPOSITION OF DIELECTRIC THIN FILMS OF RUTILE

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[58] **Field of Search** .....117/106, 107, 107.1, 107.2 R; 23/202

[56] **References Cited**

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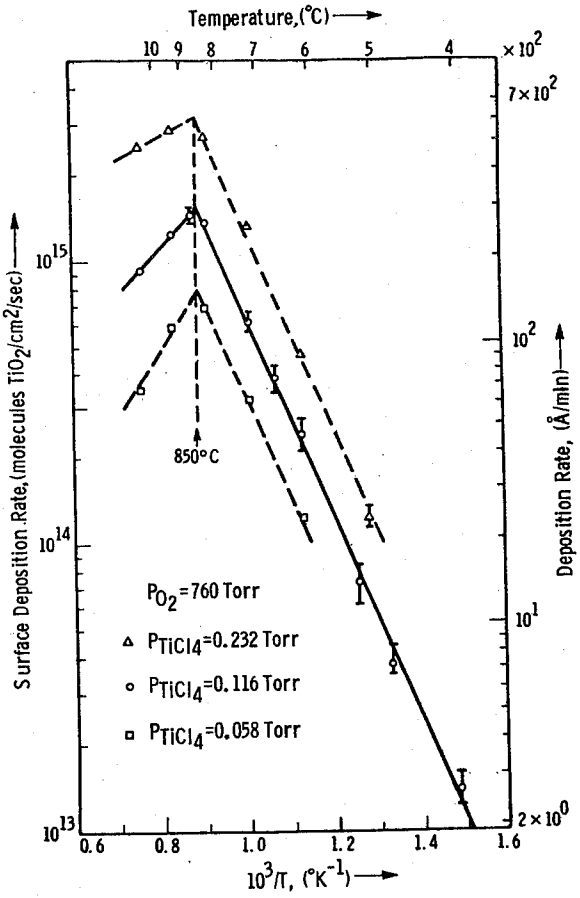
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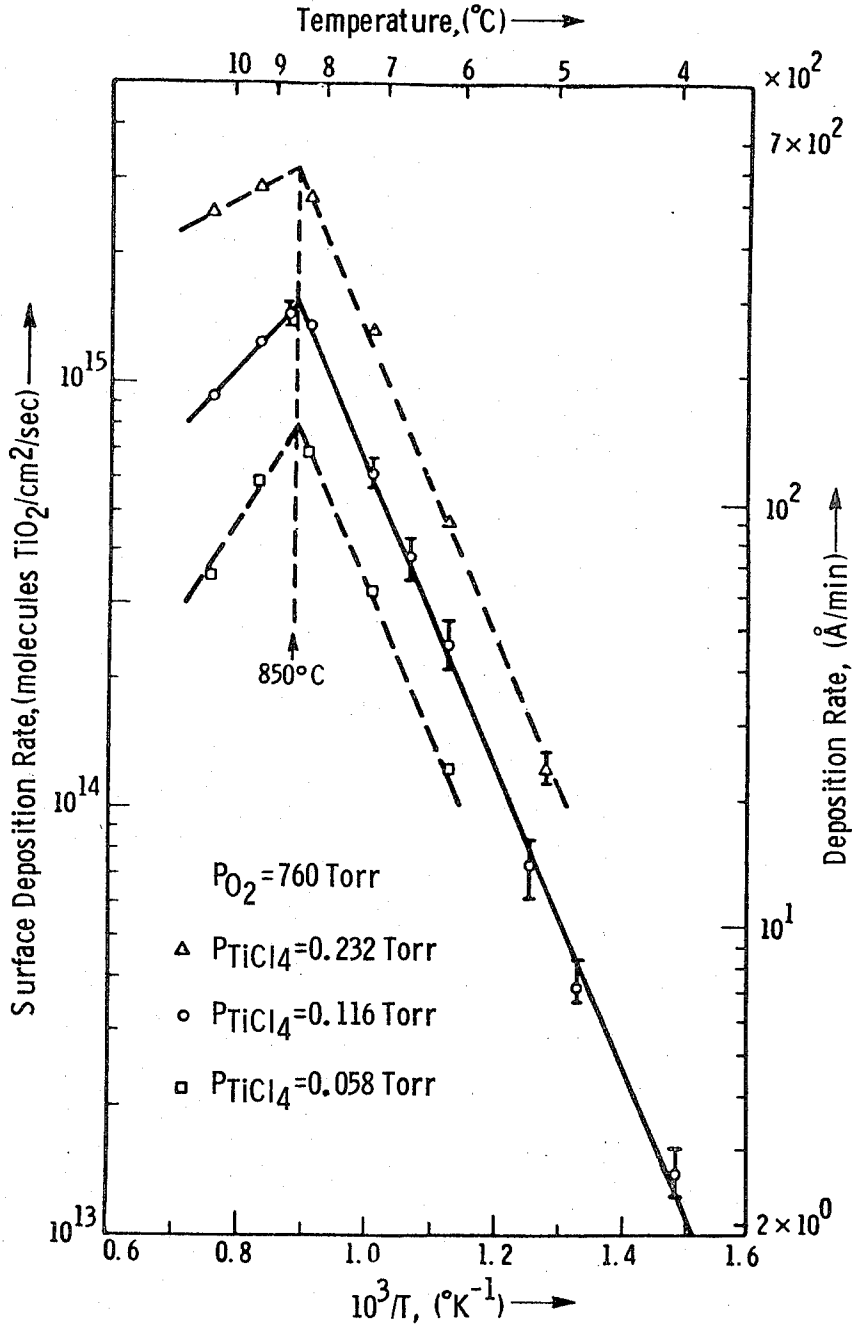
[57] **ABSTRACT**

Thin films of titanium dioxide in the rutile form are deposited by chemical vapor deposition technique on a heated surface of a substrate by reacting titanium tetrachloride with oxygen, in the range of temperatures from 700° to 900° C.

17 Claims, 1 Drawing Figure



Temperature dependence of rutile deposition rate at one atmosphere of oxygen partial pressure and different titanium tetrachloride partial pressures.



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CHEMICAL VAPOR DEPOSITION OF DIELECTRIC THIN FILMS OF RUTILE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to dielectric films of rutile titanium dioxide suitable for use as active and passive components in various electrical devices and particularly in solid state devices.

2. Description of the Prior Art

Crystalline titanium dioxide in the rutile crystallographic texture is known to have one of the highest dielectric constants of the TiO_2 textures. Both physical and chemical vapor deposition techniques have been used for the preparation of titanium dioxide films. The physical techniques employed have included the evaporation of titanium followed by oxidation; reactive sputtering of titanium in oxygen; and radio frequency sputtering of titanium dioxide. The pyrolysis of organotitanium esters (e.g., tetraisopropyl titanate), the hydrolysis of titanium tetrachloride, and the anodization of of titanium films are known chemical deposition techniques for titanium dioxide. However, each of these techniques has at least one undesirable feature in producing a layer of device quality titanium dioxide. Some of these desirable features are a lack of flexibility and capacity for device production purposes, contamination particularly from residual hydrogen or water vapor, high porosity of the film grown and lack of control of the stoichiometry of the chemical reaction and the consequent formation of the undesirable crystalline phases of titanium dioxide (anatase and brookite).

An object of this invention is to provide a process for producing titanium dioxide thin films which do not have the undesirable features of prior art titanium dioxide thin films.

An object of this invention is to provide a process for producing a thin film of rutile TiO_2 for electrical devices.

Another object of this invention is to provide a process for producing a thin film of rutile on a suitable substrate by the chemical reaction of titanium tetrachloride with oxygen in a predetermined temperature range.

Other objects of this invention will, in part, be obvious and will, in part, appear hereinafter.

SUMMARY OF THE INVENTION

In accordance with the teachings of this invention there is provided a process for growing a thin film of rutile on a heated surface of a substrate. The thin film of rutile is produced by heating a surface of the substrate to a temperature range of about 400° to 1,100° C. and passing a reactant gas mixture of titanium tetrachloride and oxygen over the heated surface. The titanium tetrachloride and the oxygen chemically react with each other on the heated surface and deposit rutile on the heated surface of the substrate.

DRAWING

For a better understanding of the nature and objects of this invention reference should be had to the graphical representation of the temperature dependence of the deposition rate of rutile at 1 atmosphere of oxygen partial pressure and different titanium tetrachloride partial pressures.

DESCRIPTION OF THE INVENTION

Rutile is produced by the reaction of titanium tetrachloride and oxygen and grown on a substrate surface in accordance with the following chemical equation: $TiCl_4$ (g) + O_2 (g) → TiO_2 (rutile) (solid) + 2 Cl_2 (gas) To provide source material of the highest purity, multiple distillation of the titanium tetrachloride is performed. The multiply distilled titanium tetrachloride is placed in a bubbler apparatus where it is maintained at a predetermined constant temperature. A temperature of 25° C. has been found to be suitable.

A sufficient volume of a carrier gas of oxygen or at least one inert gas selected from the group consisting of argon, neon, krypton, and helium or a gaseous mixture of oxygen and the inert gas is caused to flow through the bubbler containing the titanium tetrachloride to provide the required minimum partial pressure of titanium tetrachloride for the chemical reaction of the process and then passed into a reactor chamber. Before entering the reactor, the carrier gas is joined with oxygen gas in an amount necessary for the chemical reaction of the process and a reactant gas mixture is produced which is caused to flow over and about a substrate disposed on a suitable susceptor and heated within the reactor. The reactor chamber may be made of quartz. Although silicide coated graphite is suitable for making he susceptor, it is desirable that the susceptor be quartz encapsulated graphite to minimize the contamination of the substrate by outgasing of the graphite and rapid consumption or erosion of the susceptor by oxidation.

The substrate may be made of any suitable material which is not adversely affected by oxidation. Materials such, for example, as silicon which will be slightly oxidized in the process, are appropriate as their slightly oxidized surface does not adversely affect the adherence of rutile to the substrate. Such substrates are considered to be substantially non-oxidizable. Other suitable substrate materials are magnesium oxide, quartz, and aluminum oxide. The substrate is heated to a temperature of from about 400° C. to about 1,100° C. The preferred heating range for the substrate is 700° to 900° C. to produce the highest deposition rates of rutile. Rutile is formed below 400° C. and above 1,100° C. but either the rate of growth or the nature of the thin film grown is undesirable.

Should the substrate be silicon and the surface upon which the rutile is to be deposited is to be oxide free, prior to deposition of rutile thereon the silicon substrate is baked at a temperature of from 900° to 1,000° C. in hydrogen gas flowing at a rate of 10 liters per minute for a reactor tube of an internal diameter of 54 mm.

It is desirable that the thin film of rutile grown on a substrate surface should be only one grain in thickness but the thickness of the film should be closely controllable. Therefore, for practical purposes the chemical reaction producing rutile should be carried on at a temperature of no greater than 850° C. At temperatures of 850° C. and lower, the deposit of the grown rutile is single grain in thickness. Above 850° C. the film is multiple grain in thickness which is undesirable since the electrical properties of the grown film are adversely affected thereby. However, rutile deposits which have a physical structure exhibiting a multiple grain thickness are suitable up to a predetermined higher temperature. It has been found that the temperature at which the reaction occurs to produce rutile alone should not exceed 900° C. by a significant amount. As the temperature exceeds 900° C., the proportion of the other crystalline phases of TiO_2 increases accordingly.

The rate of deposition of rutile increases, first order equation, with an increase of partial pressure of titanium tetrachloride with 1 atmosphere of oxygen, at all temperatures. The peak deposition rate for all partial pressures of $TiCl_4$ with oxygen at 1 atmosphere, is about 850° C. Above 850° C., the rate of deposition of rutile decreases linearly with temperature increase, but the slope of the deposition rate curves decreases more greatly with decreasing partial pressure of titanium tetrachloride.

In the chemical reaction producing rutile in accordance with the teachings of this invention, the relationship of the minimum partial pressure of oxygen to the partial pressure of titanium tetrachloride in the reactant gas mixture to provide for a deposition rate independent of the oxygen present, is

$$P_{O_2} = 1.8 \times 10^3 (P_{TiCl_4})^3.$$

The partial pressures are in mm. Hg. The reaction is dependent solely on the temperature as shown in the graph.

In the reactant gas mixture the partial pressure of titanium tetrachloride may vary from as low as 0.018 mm. Hg to as high as 0.9 mm. Hg for an oxygen partial pressure of one atmosphere. However, controlled deposition thickness is best achieved when the partial pressure of titanium tetrachloride in

the reactant gas mixture is from about 0.058 mm. Hg to 0.232 mm. Hg for a partial pressure of oxygen of one atmosphere. The deposit thickness of rutile may be controllably achieved at these partial pressures at temperatures of from 700° to 900° C. at a deposition rate of from 50 to 800 A. per minute.

The lateral grain size of the polycrystalline rutile film grown varies with both the film thickness and the temperature of deposition but attains a constant size above 900 A. of film thickness. The final grain sizes are 1,500 A. at 800 C., 3,300 A. at 700° C. and 2,700 A. at 900° C.

Reproducible and uniform rutile thin film growth rates on a heated surface of a silicon substrate are achieved only above a minimum gas flow rate at a given temperature and a given partial pressure of the reactant gases. For example for a 54 mm. I.D. quartz reactor tube at a specific temperature and titanium tetrachloride partial pressure the minimum total gas flow rate is as shown in Table I.

TABLE I

Substrate Surface Temperature	$TiCl_4$ Partial Pressure* (mm. Hg)	Minimum Volume Gas Flow (liters/minutes)
700° C.	0.058	12.5
700° C.	0.116	6.5
700° C.	0.232	3.2
800° C.	0.058	51.0
800° C.	0.116	26.0
800° C.	0.232	13.0

Note: *Partial pressure of oxygen is one atmosphere

As indicated by the tabulated results, an increase in the partial pressure of the titanium tetrachloride resulted in a decrease in the minimum average volume gas flow necessary for reproducible and uniform rutile thin film growth rates.

At any fixed titanium tetrachloride partial pressure and at all temperatures below about 850° C. for the heated surface of the substrate, the growth rate of the thin film of rutile is constant only above a minimum oxygen partial pressure. For a partial pressure of 0.058 mm. Hg for titanium tetrachloride the minimum partial pressure of oxygen required is $3.5 \pm 0.3 \times 10^{-1}$ mm. Hg. At a partial pressure of 0.116 mm. Hg for titanium tetrachloride, the minimum partial pressure of oxygen required is 2.7 ± 0.2 mm. Hg. A minimum partial pressure of oxygen of 20 ± 5 mm. Hg is required for a constant growth rate of a thin film of rutile for a constant partial pressure of titanium tetrachloride of 0.232 mm. Hg. Below these oxygen partial pressure the rutile film deposition rate at any titanium tetrachloride partial pressure decreases as the one half power of the partial pressure of oxygen ($P_{O_2}^{1/2}$).

Stoichiometric rutile can only be deposited below a partial pressure ratio of titanium tetrachloride to oxygen of 1.16×10^{-1} at any temperature between 700° and 850° C.

The graphical representation in the specification shows the temperature dependence of rutile deposition rate at one atmosphere of oxygen partial pressure and different titanium tetrachloride partial pressures.

To be effective as a dielectric film of material, the grown rutile should be at least 100 A. in thickness to assure complete coverage of the surface of the substrate upon which it is deposited.

Electron diffraction studies indicate that all the thin films of rutile grown on the various substrates have a fiber texture and a preferred orientation which is determined by the temperature of the substrate upon which is deposited. Table II tabulates the results of experiments in which thin films of rutile were grown in accordance with the teachings of this invention on silicon substrates whose surface temperature was varied.

TABLE II

Substrate surface temperature (° C.)	Major preferred orientation: (hkl)TiO_2 ‖ (111)Si [1]	Major preferred orientation: c-axis of TiO_2 w.r.t. surface, deg.[2]	Minor orientation, (hkl)TiO_2 ‖ (111)Si
400	(110)	0	None detected.
457	(101)	57	Do.
515	(101)	57	Do.
600	(101)	57	(100).
700	(101)	57	None detected.
800	(301)	78.5	(100).
900	(100)	0	None detected.

[1] h, k and l are standard reference axes in crystallography and the figures given are for those parallel to the silicon surface upon which it was deposited.

[2] Orientation of c-axis of rutile grown with respect to the surface of substrate upon which it was grown.

The most desirable material is produced at 800° C. since the c-axis of the grown rutile is 78.5° with respect to the silicon surface upon which it was grown. The relative dielectric constant is the highest approaching density for pure rutile. The refractive index is also the largest being 2.83+. Other desirable films are those grown at 457° C., 515° C., 600° C., and 700° C. The two remaining growth temperatures, namely 400° and 900° C., produce a suitable rutile thin film but they have the lowest refractive index and the lowest relative dielectric constant when compared to air.

In all instances in the temperature range of from about 400° to about 1,100° C., the adherence of the thin film of rutile on a heated surface of the substrate was very good and uniform polycrystalline rutile thin film resulted. In the preferred temperature range of 700° to 900° C., the most desirable rutile thin film properties were obtained. These were such, for example:

Dielectric constant ~ 50–100
Dielectric loss ~ 0.1 at 50 kc.; 0.05 at 500 kc.
Thickness - 100 A. to greater than 1 micron
Grain size - 0.15 to 0.33 micron
Porosity - substantially zero percent
Refractive Index - 2.6 to 2.9

Although specific reference has been made to thin films of rutile grown on silicon, the same properties are evident when rutile is grown on silicon dioxide films and other substrate surfaces in accordance with the teachings of this invention. Metal-insulator-semiconductor devices of Al-SiO_2-TiO_2(rutile)-SiO_2-Si, Al-TiO_2(rutile)-SiO_2-Si, Al-SiO_2-TiO_2(rutile)-Si, and Al-TiO_2-Si structures have been successfully prepared and show acceptance and full incorporation of rutile as a component layer in the structures. The silicon wafers employed were of both n and P-type material and both types employed had resistives as low as 0.01 ohm-cm. and as high as 20 to 40 ohm-cm.

Titanium dioxide produced in accordance with the teachings of this invention is the rutile form and has no hydrogen entrapped within the film as is the case in prior art processes using hydrogen as a reducing gas. Consequently the thin films of rutile grown in accordance with the teachings of this invention are much superior to prior art thin films as far as electron charge stability is concerned. The detrimental effect of protons in prior art rutile thin films is therefore avoided.

We claim as our invention:

1. A process for growing the rutile form of titanium dioxide on a heated surface of a substrate comprising the steps of;

a. heating a surface of a substantially nonoxidizable substrate to an elevated temperature of from 400° to 1,100° C.; and

b. passing a gaseous mixture of oxygen and titanium tetrachloride over the heated surface whereby the titanium tetrachloride reacts with the oxygen at the heated surface to produce titanium dioxide which is then deposited on the heated surface in the rutile form, the minimum partial pressure of oxygen in the reactant gas mixture having a relationship to the partial pressure of titanium tetrachloride contained therein expressed by the formula

$$P_{O_2} = 1.8 \times 10^3 (P_{TiCl_4})^3$$

wherein the partial pressures are in mm. Hg, and the partial pressure of titanium tetrachloride being from 0.028 to 0.90 mm. Hg.

2. The process of claim 1 wherein
the reactant gas mixture includes a carrier gas selected from the group consisting argon, neon, krypton, and helium.

3. The process of claim 1 wherein
the partial pressure of oxygen in the reactant gas mixture is one atmosphere, and
the partial pressure of titanium tetrachloride ranges from 0.028 mm. Hg to 0.9 mm. Hg.

4. The process of claim 1 wherein
the partial pressure of titanium tetrachloride is from 0.058 mm. Hg to 0.232 mm. Hg.

5. The process of claim 1 wherein
the surface of the substrate is heated to a temperature of from about 700° to about 900° C.

6. The process of claim 1 wherein
the surface of the substrate is heated to a temperature of from 700° to 850° C., and
the ratio of the partial pressure of titanium tetrachloride to the partial pressure of oxygen in the reactant gas mixture is less than 1.16×10^{-1}, the partial pressure of titanium tetrachloride being from 0.028 to 0.90 mm. Hg.

7. The process of claim 6 wherein
the thin film of titanium dioxide grown on the heated surface of the substrate is one grain in thickness.

8. The process of claim 1 wherein
the surface of the substrate is heated to an elevated temperature no greater than 850° C., and
the thin film of titanium dioxide grown on the heated surface of the substrate is one grain in thickness.

9. The process of claim 1 wherein
the surface of the substrate is heated to a temperature of approximately 800° C.,
the thin film of titanium dioxide is grown to a thickness of at least 100 A., and
the major preferred orientation of titanium dioxide crystallites parallel to the surface of the substrate is (301) and the major preferred orientation of the c-axes of the titanium dioxide crystal with respect to the substrate is 78.5°.

10. The process of claim 9 wherein the substrate is made of silicon.

11. The process of claim 1 wherein
the substrate is made of a material selected from the group consisting of silicon, magnesium oxide, quartz, and aluminum oxide.

12. The process of claim 1 wherein
the temperature of the substrate surface is 700° C.;
the partial pressure of oxygen in the reactant gas mixture is one atmosphere;
the partial pressure of titanium tetrachloride in the reactant gas mixture is at least 0.058 and does not
the minimum average reactant gas mixture volume flow is the equivalent of 12.5 liters per minute for a 54 mm. I.D. quartz reactor tube.

13. The process of claim 1 wherein
the partial pressure of titanium tetrachloride is 0.116 mm. Hg; and
the minimum average reactant gas mixture volume flow is the equivalent of 6.5 liters per minute for a 54 mm. I.D. quartz reactor tube.

14. The process of claim 1 wherein
the partial pressure of titanium tetrachloride is 0.232 mm. Hg; and
the minimum average reactant gas mixture flow is the equivalent of 3.2 liters per minute for a 54 mm. I.D. quartz reactor.

15. The process of claim 1 wherein
the temperature of the substrate surface is 800° C.;
the partial pressure of titanium tetrachloride in the reactant gas mixture is at least 0.058 and does not exceed 0.90 mm. Hg, the partial pressure of oxygen in the reactant gas mixture being one atmosphere; and
the minimum average reactant gas mixture volume flow is the equivalent of 51.0 liters per minute for a 54 mm. I.D. quartz reactor.

16. The process of claim 1 wherein
the partial pressure of titanium tetrachloride is 0.116 mm. Hg; and
the minimum average reactant gas mixture flow is the equivalent of 26.0 liters per minute for a 54 mm. I.D. quartz reactor.

17. The process of claim 1 wherein
the partial pressure of titanium tetrachloride is 0.232 mm. Hg; and
the minimum average reactant gas mixture flow is the equivalent of 13.0 liters per minute for a 54 mm. I.D. quartz reactor.

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