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TiO_2 FILM PROPERTIES AS A FUNCTION OF PROCESSING TEMPERATURE

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PREFACE

Early work on dielectric thin films on silicon showed a discontinuous capacitance-voltage characteristic which might be exploited in several ways to build digital transducers. The device possibilities include complex transducer-integrated circuit hybrids in which the sensitive material regions trigger the discontinuity by various external stimuli.

This report consists of a published paper which describes the technology of depositing thin dielectric films of TiO_2. Previous work by two of the authors (Eugene T. Fitzgibbons and William H. Hartwig) demonstrated the ability to set the C-V discontinuity at zero DC volts, which is an important characteristic in device design. Subsequent work with Karl J. Sladek and his students has led to a better understanding of the deposition parameters. Work on this phase of the research terminated in August 1971.

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TiO_2 Film Properties as a Function of Processing Temperature

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ABSTRACT

Thin film TiO_2 was produced at 150°C by chemical vapor deposition using hydrolysis of tetraisopropyl titanate. Films were amorphous as grown, but annealing in air caused crystallization, with anatase formed beginning at 350°C and rutile at 700°C. Density and index of refraction increased substantially with increasing anneal temperature, while etch susceptibility in HF and H_2SO_4 decreased. Comparison with literature data showed two groups of processes. One group yields films having properties that gradually approach those of rutile with increasing process temperature. The other group gives rutile directly at moderate temperatures. Deposition of amorphous film followed by etching and annealing is suggested as a means for pattern definition.

Thin film TiO_2 has been produced by anodization and thermal oxidation of Ti, evaporation of TiO_2, reactive sputtering of Ti, a variety of chemical vapor deposition (CVD) processes, and even by liquid deposition. The electrical, chemical, and physical properties of TiO_2 films exhibit considerable diversity, which arises from differences in stoichiometry and structure among films formed by different means. The present research began with the discovery of a unique low-temperature process for producing films of readily etchable amorphous TiO_2. Annealing procedures were found to convert these films to the anatase and rutile forms of the material. Film properties could then be determined for a range of well-controlled structures. One purpose of this investigation was to provide a comprehensive set of structure-property data which might serve to explain discrepancies in reported values of density, refractive index, and etch susceptibility. Another purpose was to develop a means for producing thin film TiO_2 for applications requiring pattern definition.

Titanium dioxide exists in two tetragonal structures, anatase and rutile, plus orthorhombic brookite. Rutile is the thermodynamically stable form at all temperatures investigated so far, but anatase and brookite retain their structures until heated to fairly high temperatures, at which they transform irreversibly to rutile. Reported temperatures for significant rates of conversion to rutile are 800°-1100°C for anatase and 700°-1300°C for brookite (1, 2). Theoretical densities of anatase and rutile are calculated to be 3.94 and 4.27 g/cm^3, respectively, using recent values of the unit cell dimensions (1). These agree reasonably well with measured values of 3.90 and 4.23 g/cm^3 (2). Average index of refraction (n) values at 0.55 μm are 2.57 for natural crystals of anatase and 2.74 for synthetic crystals of rutile (1).

While properties of bulk anatase and rutile are well established, little agreement has been reached regarding the properties of thin film TiO_2. One of the most thorough studies is due to Hass (3), who produced films both by thermal oxidation of Ti and by a CVD

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process. Evaporated Ti films were oxidized above 200°C and the resulting oxide was shown to be rutile by electron diffraction. The index of refraction of these films was 98-99% of that of bulk, single-crystal rutile for the whole range from 0.4 to 2.0 μm. In contrast, hydrolysis of $TiCl_4$ produced amorphous films below 280°, and anatase films above 300°C, with n values near 2.3.

Films of TiO_2 have also been produced by anodization (4, 5), reactive sputtering (6), vacuum evaporation (7), and by drying substrates which had been dipped into a titanate solution. Drying at 180°-900°C gave films with n values of 1.95-2.45 (8).

CVD processes include the $TiCl_4$-H_2O reaction near 300°C (3), at 150°C (9), and at 800°C (10). Pyrolysis of tetraisopropyl titanate (TPT) at 300°-700°C gave amorphous and anatase films exhibiting a range in density, refractive index, and etch susceptibility (11). Reaction of $TiCl_4$ with O_2 gave epitaxial rutile on some substrates above 700°C and polycrystalline rutile at lower temperatures (12). In the present work the TPT-H_2O reaction was used, as described next.

Deposition Phenomena

The CVD apparatus is illustrated in Fig. 1. The two liquid feeds are evaporated from heated flasks into metered carrier gas streams. The feed streams then issue from parallel nozzles at the ends of the delivery lines, intermingle with each other and with the room air, and are directed onto the substrate, which is heated from beneath. Film growth is controlled manually by moving the substrate around under the nozzles or by moving the nozzles. By observing the sharp interference colors, the operator can manually control the thickness uniformity of the film to within 100-200Å over a 1.25-in. diameter substrate wafer.

The best temperature range for the TPT evaporator is 75°-85°C. The water evaporator temperature is not critical and films can even be grown without using the CO_2 carrier and water source; in that case, the water vapor in the ambient air is evidently sufficient to maintain the reaction. The growth dynamics appear to be the same with and without the water vapor stream and the structural, optical, and chemical properties are also the same in both cases. The only differences were observed in the reproducibility of electrical properties, and the water vapor source was used to stabilize these.

Under typical conditions, the helium flow rate was 1 l/min, the CO_2 flow rate was ¼ l/min, the TPT and water evaporators were at 75° and 90°C, respectively, and the substrate heater was at 150°C. With these parameters, a 1.25-in. substrate could be covered with a 2000Å film in 10 min.

These conditions were chosen after making a number of observations about the film quality obtained under various deposition conditions. When the TPT evaporator was too hot (90°-100°C) a milky film having diffuse interference colors resulted. Microscopic examination revealed that the film lacked coherence, but rather was made up of tiny stacked spheres. The film had an odor of alcohol or TPT and was soft enough to be smeared with a cloth. Evidently, the TPT condensed after leaving the nozzle and the resulting film was made up of small droplets of TPT which had reacted at their outer surfaces only. Similar results were obtained with the TPT evaporator at 75°C when the He carrier flow exceeded 2 l/min, when the nozzle was closer than 1 in. from the substrate, or when the substrate temperature was below 100°C. Excessive CO_2 carrier flows (> ½ l/min) caused a white powdery deposit, evidently due to premature hydrolysis of TPT, giving a powder product which rained down onto the substrate. The same effect occurred when the nozzle was held more than 3 in. from the substrate. In summary, the conditions chosen above were selected to avoid both incomplete and premature reaction which led to formation of films lacking coherence. Under the chosen conditions, the films were smooth and relatively hole free. No detail could be observed in the scanning electron microscopy at 20,000X, except for an occasional pinhole.

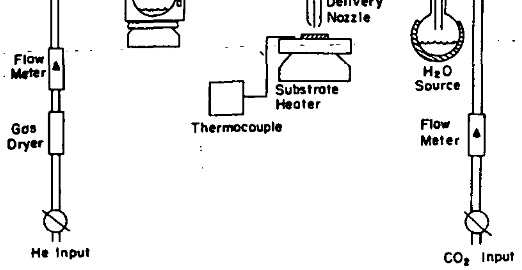

Fig. 1. Chemical vapor deposition system

When film thicknesses of 4000-5000Å were reached during a normal deposition, cracks would appear and propagate over the film, reducing it to a field of small triangular pieces, each separated from the substrate with its points bending upward. This was observed with all the substrates described below at approximately the same film thickness. Several experiments with duplex films were performed. When a film was grown to several thousand angstroms and then later a new film was grown atop the previous one, fracture occurred when the sum of the two thicknesses fell into the 4000-5000Å range. However, when a film was grown and annealed above 350°C (to be described later) and then a new film was grown on the annealed one, fracture occurred when the second film reached 4000-5000Å. This behavior indicates that the film is deposited with an intrinsic tensile stress. Fracture may be associated with a failure of the film-substrate adhesive bond due to increased shear stress as the film thickens.

Films could be grown on any smooth object that could be heated. In the present work, different substrates were used for different experiments. Fused quartz was used for optical transmission measurements. Fused quartz covered with evaporated Pt and also polished Si were used as substrates in determining refractive index and thickness relationships by ellipsometry and interferometry. Soft glass microscope slides, as well as some of the other materials, were used in x-ray analysis. Before deposition, the fused quartz and the soft glass substrates were cleaned thoroughly in low residue detergent, were rinsed in deionized water, and were heated in air at 1000° and 350°C, respectively, to drive off surface contaminants. The Pt/quartz substrates were annealed in air at 1000°C to stabilize them, and no further cleaning was performed. The Si wafers had been commercially prepared using mechanical and electrochemical polishing and were used as supplied.

Annealing and Crystallization

Films produced by the CVD method described above underwent dramatic changes in physical and chemical properties during annealing. The changes in crystal structure are described here.

Crystalline phases were identified using an x-ray diffractometer with copper $K_{\alpha 1}$ radiation. Four types of samples were used. Powder samples were obtained by allowing the standard deposition process to continue for several hours until a thick white powdery deposit had built up; this was then scraped off and divided into samples for testing. The other three types of samples consisted of 3000-4000Å films grown on fused quartz, soft glass, and polished Si.

The powder in the as-grown condition showed no sign of crystallinity and was evidently amorphous. No

Table I. Crystalline phase and anneal temperature for TiO_2 on several substrates

Anneal temperature,[a] °C	Substrate[b]			
	Powder sample	Soft glass	Polished Si	Fused quartz
150 (as grown)	Amorphous	Amorphous	Amorphous	Amorphous
350	Amorphous + anatase	Amorphous + anatase	Amorphous + anatase	Amorphous + anatase
700	Rutile + anatase	Rutile + anatase	Rutile + anatase	Anatase
1000	Rutile	—	Rutile	Anatase

[a] All anneals carried out in air.

[b] Crystalline phases identified in all films showed no orientation.

crystallization occurred during aging at room temperature in air for one week. Annealing the powder for 10 min at 350°C resulted in the appearance of the two strongest diffraction peaks of the anatase form of TiO_2. A sample annealed at 700°C for 2 hr showed the five strongest anatase peaks and the three strongest rutile peaks. A 20-hr anneal at 1000°C completely converted the powder to rutile; many rutile peaks were observed, and no anatase peaks were detectable.

Table I summarizes the data for all four types of samples. In every case the as-grown material is amorphous, and material annealed at 350°C shows some anatase. However, the weakness of the anatase patterns suggested that only partial crystallization occurred at 350°C. This temperature can be regarded roughly, as an amorphous-anatase transition temperature. Additional anneals at 300°-400°C indicate that the transition is not sharp, but rather occurs over a range of about 50°C in which the extent of crystallization gradually progresses. The temperature, 700°C, appears similarly to be characteristic of the anatase-rutile transition. This transition appears to be less sharp and progresses over a range of about 300°C. An important exception is the films on fused quartz which persist in the anatase form, even after annealing at 1000°C. Somehow, the quartz-TiO_2 interface stabilizes the anatase structure, perhaps by preventing nucleation of rutile.

The present data are in accord with some of the literature data described earlier. The anatase-rutile transition occurs in bulk samples at 800°-1100°C (1, 2). In films produced by CVD or liquid dipping, a change from amorphous to anatase structures was found at 280°-300°C (3), and at 250°-350° (8). An anatase-rutile transition was observed at 800°C (3), and several investigators produced rutile directly at 800°C or above (10, 13). In contrast, rutile films were produced as low as 400°C from Ti oxidation (3) and from the $TiCl_4$-O_2 reaction (12).

Thickness and Index of Refraction

Changes in interference colors occurred as a result of annealing, and these indicated a change in thickness, *d*, and/or index of refraction, *n*. If a standard color chart for SiO_2 was used, the changes indicated that annealing a 150°C film at 1000°C caused an increase in *d*. However, measurements using an ellipsometer indicated a substantial decrease in *d*, accompanied by an increase in *n*, and indicating that a single color chart, based on fixed *n*, would be misleading. To obtain additional independent values of *d* and *n*, a multiple beam interferometric technique was used. Both the ellipsometer and the interferometer used the 5460A green line of Hg.

Coated and uncoated portions of a step were used to find both *d* and *nd* with the interference method (14). The ellipsometer yields separate values of *d* and *n* (15). A cross check was provided by a color chart, which gives *nd* (14).

Results obtained before and after annealing at 1000°C are shown in Table II. The several methods give good agreement, and it is clear that annealing causes a substantial decrease in *d* and increase in *n*.

Table II. Change in thickness and index of refraction due to annealing at 1000°C

Sample condition	Thickness, A (method)[a]	Index of refraction (method)[a]
As grown, 150°	3820(I), 3870(E)	1.98(I), 2.10(E)
Annealed, 1000°	2510(I)	2.49(I)
As grown, 150°	2400(E)	2.00(E), 1.95(C)
Annealed, 1000°	1580(E)	2.40(E), 2.47(C)
As grown, 150°	1900(E)	2.10(E), 2.06(C)
Annealed, 1000°	1220(E)	2.60(E), 2.50(C)

[a] I = interferometer; E = ellipsometer, C = color chart plus ellipsometer-determined thickness.

To complete these measurements, a final series of data was obtained as a function of anneal temperature. A film was deposited on Pt/quartz and data were obtained by ellipsometry, using averages of two to four measurements. Figure 2 is a plot of resulting values of thickness and index of refraction.

The thickness shrinkage of 35% is quite remarkable in magnitude. Since the film is constrained to a fixed area, any density changes are evidently exhibited only in one dimension. One might suspect that such a violent dimensional change would set up stresses which might rupture the film. However, examination of a 1000°C annealed film in the scanning electron microscope at 20,000X showed no cracks, tears, or eruptions.

It was suspected that the shrinkage might be accompanied by a mass loss, as would be expected if the as-grown material were a hydroxide or hydrate. A hydroxide, $Ti(OH)_4$, would lose 31% of its initial weight if complete dehydration occurred. Several experiments were carried out in an effort to detect a weight change on annealing. In the most sensitive experiment, a sample was weighed on a vacuum microbalance and annealed *in situ*. No weight change could be detected within the experimental uncertainty of ± 7% of the initial film weight. Although the sensitivity of this experiment was rather low, the result does rule out mass reduction as a primary cause of the volume shrinkage.

It is possible that the films are microporous and that shrinkage occurs by sintering. Swaroop (16) and Pliskin and Lehman (17) attributed densification of SiO_2 films to sintering. Sladek and Herron (18) investigated TiO_2 film growth by the TPT-H_2O reaction at 25°C, and suggested that voids are incorporated when isopropyl groups are removed from the growing film during surface reaction.

The difference between a microporous material and a "homogeneous" one of abnormally low density is only in the size of the void spaces. Our observations using the scanning electron microscope detected no pores. Qualitatively, the optical transparency and sharp interference colors of our films indicate negligible scattering by void spaces. However, both of these

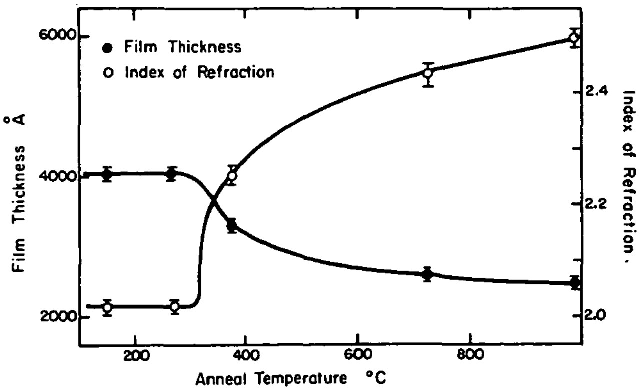

Fig. 2. Thickness and index of refraction as a function of anneal temperature. TiO_2 on Pt/quartz.

Table III. Chemical susceptibility to several etches

Anneal temperature, °C	Etch rate and behavior 0.5% HF	 48% HF	 100% H_2SO_4	 85% H_3PO_4
150	50-75 A/sec	Very rapid	Slow at 25°C 25-40 A/sec at 50°C	Leaves residue
350	On Pt: very slow On Si: undercutting	Slow and uneven	About 15 A/sec at 50°-100°C	
700	No etching	On Pt: slow On Si: undercutting	Very slow	
1000	No etching	On Pt: slow On Si: undercutting	About 1000 A/hr at 120°C	Very slow at 120°C

observations would be insensitive to voids of size below about 200A. We attribute the abnormally low density of the present amorphous films to voids of size somewhere in the range between atomic dimensions and about 200A.

Susceptibility to Chemical Etch

Etch susceptibility is a prerequisite for electronic applications of TiO_2. Some past work indicates that amorphous TiO_2 is readily etched while high-temperature and hence crystalline forms are quite impervious to chemical attack. Barksdale (19) observed in 1949 that, while bulk TiO_2 is known to be slightly soluble in H_2SO_4, HF, and a few strong alkalies, material annealed near 1000°C is almost completely inert chemically.

Etchability of TiO_2 as a function of anneal temperature was determined for films grown on Si and on Pt substrates. Results are summarized in Table III. Again there is a wide, controllable gradation in properties, with the low-temperature form showing high chemical susceptibility while the 1000°C material is nearly inert. Films on Si behaved the same as those on Pt except for the 48% HF case. This etch lifted the TiO_2 off the surface of Si, evidently by dissolving a thin interfacial layer of SiO_2 and undercutting the TiO_2.

These results are in accord with data of Yokozawa *et al.* (11), who reported that their amorphous TiO_2 films etched in dilute HF at 4-60 Å/sec, while anatase films etched only slowly in concentrated HF. Feuersanger (9) reported that his films were easily etched in 10% HF; this suggests that they were amorphous, as would be expected for a 150°C process. His high index of refraction (discussed later) is then the only property that does not agree with the present results. Harbison and Taylor (10) reported an etch rate of 700 Å/min in 48% HF for material grown at 800°C. This is much higher than would be expected from our results.

Optical Absorption

An optical transmission spectrum of a 350°C annealed film is shown in Fig. 3. This was obtained by measuring the difference between the transmission of the film on fused quartz and the transmission of the fused quartz alone. We attribute the maxima and minima above 0.35 μm to interference due to multiple internal reflection, and the strong absorption peak at 0.32 μm (3.9 eV) to an electronic transition. Transmission in an amorphous TiO_2 film was also measured and similar results were obtained, except that the strong absorption peak was much broader, although still centered at 0.32 μm. In agreement with these results, Maserjian (20) found an absorption peak at 0.32 μm with a rutile film. In contrast, however, single-crystal rutile exhibits an absorption edge (21) at 0.41 μm (3.0 eV). The cause of the discrepancy between bulk single-crystal and thin film TiO_2 is not known. However, in both this work and that of Maserjian (20) the 0.32 μm peak has been established.

Discussion

Present data on density and index of refraction are compared with literature values in Fig. 4. Since absolute values of density were not obtained in this work, it was necessary to choose a value for one condition, and 2.5 g/cm³ for the amorphous films was used, based on the results of Yokozawa *et al.* (11).

Results of two of the CVD studies (11, 13) and the liquid deposition (8) show good agreement with present data in both properties plotted. Results of Hass (3) on films formed by $TiCl_4$ hydrolysis and by oxidation of "TiO" (formed by exaporating Ti with O_2 present) show an increase in n with temperature similar to that observed here, although with somewhat higher values of n.

In contrast, Hass (3) obtained nearly the bulk rutile value of n with oxidized Ti, and Ghoshtagore and Noreika (12) found an even higher value with films formed from $TiCl_4 + O_2$ in the whole temperature range studied. (We have applied a small correction to their reported value of n_D to obtain a value applicable at 0.55 μm.) The fact that their n exceeds the random-orientation average for bulk rutile could have been due to preferred orientation of their films.

In summary, one group of processes produces films which show a characteristic variation in physical and

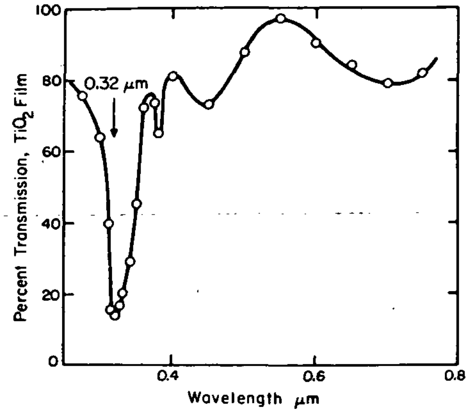

Fig. 3. Optical transmission spectrum. 2600Å film of TiO_2 annealed at 350°C.

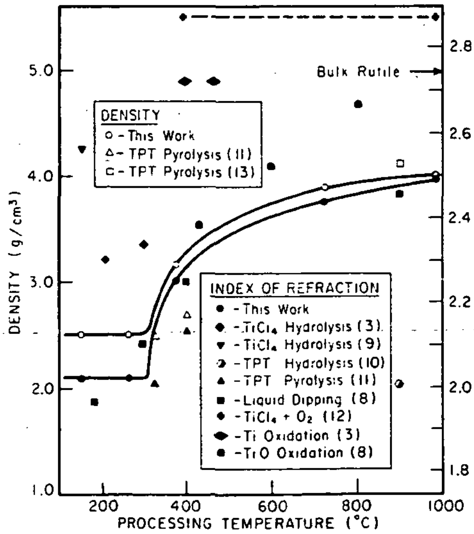

Fig. 4. Density and refractive index vs. processing temperature: a comparison with other work.

chemical properties with maximum processing temperature, whether this temperature is reached during deposition or during postdeposition anneal. These variations arise from densification and crystallization and ultimately yield material with properties approaching those of the equilibrium (rutile) bulk state. However, it is also possible to bypass these intermediate stages and obtain rutile directly at moderate temperatures.

We have found that, of the several forms produced, rutile or anatase-rutile mixtures have superior dielectric properties. The relative dielectric constant/dissipation factor at 1 kHz was about 100/0.04 for material annealed at 700°-1000°C. The sign of the surface charge of TiO_2 on Si was negative, and positive, negative and zero, values could be obtained by growing duplex TiO_2/SiO_2 films. (Details of these electrical studies will be reported later.) These properties suggest a number of applications for rutile in integrated circuit technology.

Although it is possible to produce rutile films directly, they are almost impossible to etch (Table III). In contrast, the deposition-annealing process used here could lend itself readily to the various etch steps needed for integrated circuit production. Standard photomasking techniques could be used to define a desired pattern in the as-grown film, and a later anneal would convert the material to its stable form.

The fact that the TiO_2 itself changes chemical susceptibility suggests that patterns might be defined without photoresists, if a means were found for selective conversion in desired areas. This idea has led to some further work (to be reported later) in which an electron or photon beam is used to define positive patterns in amorphous TiO_2.

In conclusion, it is possible to produce rutile films either directly or via a series of stages progressing in density, refractive index, and etch susceptibility. The present method of low-temperature deposition followed by annealing is promising for applications requiring pattern definition.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1972 JOURNAL.

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