Phase transformations in TiO$_2$/SiO$_2$ sol–gel films as a function of composition and heat-treatment

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The refractive indices of titania/silica sol–gel films are known to vary over a wide range with composition. However, little work has been done to investigate the possible variations in refractive index that can be produced for one specific sol–gel composition by varying the heat-treatment time and temperature. In this study, three different titania/silica sol–gel compositions containing 40, 60 and 80 mol% titania were studied after thermal processing at temperatures from 175–1050 °C for variable lengths of time. The refractive indices and thicknesses of the sol–gel films spin-coated on to silicon wafers were determined using a combined technique of ellipsometry and reflectance spectroscopy. The microstructural differences in the films were investigated using X-ray diffraction and transmission electron microscopy techniques.

1. Introduction

In previous work, the changes in refractive index of sol–gel films have been studied as a function of the processing conditions used [1–6]. However, the variation in the refractive index as a function of phase changes occurring during a time–temperature–transformation (TTT) study have not been previously reported, to our knowledge. If the correlation between thermal processing, phase transformation and the refractive indices of sol–gels of different composition are known accurately, it becomes possible to use refractive index measurements to determine the phase of a thin film and hence use the technique for quality control.

In a study of this kind, it is important to control other variables that could also affect the refractive index. The film substrate must be inert to avoid changes in refractive index due to diffusion of substrate atoms into the sol–gel film during processing. This has been shown to occur in titania sol–gel films on soda–lime–silica substrates during thermal processing [7]. In this work, silicon was used as the substrate to avoid this problem. The appearance of structural defects such as cracks or pinholes in the films can also affect the refractive index values.

Three titania/silica sol–gels and a pure silica composition were studied in thin film format. A combined ellipsometry and reflectance spectroscopy technique was used to determine the refractive index and absolute thickness of the sol–gel layers. X-ray diffraction (XRD) defined the phase transformation behaviour, and transmission electron microscopy distinguished the microstructure of the crystalline phase or phases present. Both transmission electron microscopy (TEM) planar and cross-section modes were useful in determining the crystallite size, density and dis-tribution. Using both XRD- and TEM-generated domain/crystallite sizes, we were able to obtain a better understanding of the crystalline film microstructure.

2. Experimental procedure

2.1. Synthesis

The TEOS and TIPT sol–gel solutions were each prehydrolysed separately in the following manner. A 1:10:2 molar ratio of tetraethyl silicate (TEOS), ethanol and water was used for the silica prepolymer solution. The water was added dropwise to TEOS and ethanol solution at 60 °C and was refluxed at 60 °C for 30 min in a three-neck round bottom flask fitted with a Teflon stirring paddle, reflux condenser and addition funnel. Tetraisopropyl titanate (TIPT), ethanol, hydrochloric acid (HCl) and water were synthesized in 1:11:0.56:1.0 molar ratio. Titanium alkoxide and ethanol were mixed and stirred together at room temperature and the HCl was added dropwise. The solution was warmed to 40 °C when the water was added dropwise and the solution was stirred for an additional hour. Both the TEOS and TIPT sol–gel solutions were cooled to room temperature and their respective volumes were measured to determine the actual molar concentration of each sol–gel. The TEOS and TIPT solutions were combined to prepare the desired sol–gel molar ratios of 40/60, 60/40 and 80/20 titania/silica and stirred at 40 °C for 30 min. After cooling to room temperature, the titania/silica sol–gels were filtered by syringe using 0.2 μm Gelman CR filters. The initial filtrate was discarded and the remainder kept under refrigeration in a capped Nalgene container until needed. An approximate 5 wt% solids sol–gel was used for the coating ex-

TABLE I Results from heat treatment of 80/20 TiO_2/SiO_2

Temperature (°C)	Time (h)	Thickness (nm)	CYC thickness (nm)	Phase[a]	Refractive index
175	1	114.8, 92.0[c]	183.3, 183.4[c]	Amor	1.930, 1.929[c]
175	10	110.4	181.7	Amor	1.944
175[b]	1	95.4	169.8	Amor	
350	1	100.6	174.1	Amor	2.012
350	10	104.0	173.9	Amor	2.014
350[b]	1	105.9	177.3	Amor	1.983
500	1	91.9[c]	167.7	Amor	2.066
500	5	68.8[c]	167.2	Ana	2.080
500	10	69.3[c]	166.7	Ana	2.085
500	66	68.8[c]	165.8	Ana	2.096
500[b]	1	95.4[c]	169.8	Amor	2.052
700	1	67.6[c]	162.8	Ana	2.126
700	5	68.2[c]	161.8	Ana	2.137
700	10	70.6[c]	161.7	Ana	2.139
700	66	86.2[c]	163.4	Ana	2.120
900	1	85.9[c]	159.8	Ana	2.160
1050	1	[d]	[d]	Ana/Rut	[d]

[a] Titania phase: Amor/amorphous, Ana/anatase, Rut/rutile.
[b] Fast heating rate to designated temperature.
[c] Same coating series.
[d] Crystallite size too large for ellipsometry analysis.

TABLE II Results from heat treatment of 60/40 TiO_2/SiO_2

Temperature (°C)	Time (h)	Thickness (nm)	CYC thickness (nm)	Phase[a]	Refractive index
175	1	129.8	202.7	Amor	1.784
500	1	99.7	189.3	Amor	1.882
500	5	102.0	186.5	Amor	1.904
500	10	101.5	188.7	Amor	1.886
500	66	97.6	184.7	Ana	1.919
600	1	95.6	184.0	Ana	1.925
700	1	94.4	183.3	Ana	1.931
700	5	95.1	181.3	Ana	1.947
700	10	96.2	182.0	Ana	1.941
700	66	108.0	180.2	Ana	1.957
900	1	107.9	176.5	Ana	1.990
1050	1	[b]	[b]	Ana/Rut	[b]

[a] Titania phase: Amor/amorphous, Ana/anatase, Rut/rutile.
[b] Crystallite size too large for ellipsometry analysis.

periments. This was obtained by diluting the as-made sol–gel 1:1 with Punctilious ethanol.

2.2. Sample preparation
All films were spin-coated on to $\langle 100 \rangle$ silicon substrates at 2000 r.p.m. for 30 s using a Headway spin-coater unless otherwise noted. For various low-temperature experiments at or below 350 °C, substrates such as aluminium and carbon-coated mica were also used for TEM work. In this report all coatings investigated were single layers.

2.3. Thin-film thermal processing
Immediately after spin coating, the films were heated at a 5 °C min^{-1} to 150 °C, held for 15 min and then heated at 3 °C min^{-1} to 175 °C and held for 1 h in a model 495 Fisher Ashing Furnace. After cooling with

the furnace door closed, the 4 in. ($\sim$ 10 cm) silicon wafer was split into quarters for additional heat-treatment under controlled conditions of temperature and time. The range of temperatures investigated was 175–1050 °C. The actual processing conditions studied are presented in Tables I–V.

2.4. Analytical characterization
Sections from the same heat-treated sample were used for all the analytical characterization work: refractive index measurement, X-ray diffraction and TEM.

2.5. X-ray diffraction measurement technique and sample preparation
The samples were cut to an area of approximately 10 mm × 10 mm. After cutting, samples were back-mounted, using a soft modelling clay, on to a thin-film

TABLE III Results from heat treatment of 40/60 TiO_2/SiO_2

Temperature (°C)	Time (h)	Thickness (nm)	CYC thickness (nm)	Phase[a]	Refractive index
175	1	143.2	226.4	Amor	1.644
500	1	116.8	188.1	Amor	1.720
500	5	117.0	213.5	Amor	1.716
500	10	114.4	212.3	Amor	1.723
500	66	112.8	210.9	Amor	1.732
700	1	106.4	208.8	Amor	1.745
700	5	107.4	207.7	Amor	1.751
700	10	108.8	218.1	Amor	1.749
700	66	118.3	208.0	Amor	1.750
800	1	205.8[b]	206.6	Ana	1.758
900	1	122.1	204.4	Ana	1.773
1050	1	[b]	[c]	Ana/rut	[b]

[a] Titania phase present: amor/amorphous, ana/anatase, rut/rutile.
[b] Crystallite size too large for ellipsometry analysis.
[c] Inaccurate film thickness value, film thickness within 50.0 nm of cycle thickness.

TABLE IV Results from heat treatment of 100 mol % SiO_2

Temperature (°C)	Time (h)	Thickness (nm)	CYC thickness (nm)	Phase[a]	Refractive index
175	1	182.0	277.8	Amor	1.430
500	1	153.3	280.6	Amor	1.421
500	5	150.2	281.4	Amor	1.419
500	10	148.8	283.3	Amor	1.413
500	66	147.8	280.6	Amor	1.421
700	1	141.8	276.1	Amor	1.436
700	5	145.2	275.9	Amor	1.436
700	10	161.4	274.1	Amor	1.442
700	66	191.2	278.1	Amor	1.429
900	1	158.2	271.9	Amor	1.450
1050	1	212.7	274.5	Amor	1.441

[a] Phase present: amor/amorphous.

TABLE V Results from heat treatment of bare silicon wafer

Temperature (°C)	Time (h)	Thickness (nm)	CYC thickness (nm)	Phase[a]	Refractive index
500	1	2.33	269.1	Amor	1.460[b]
500	5	3.34	269.1	Amor	1.460[b]
500	10	3.33	269.1	Amor	1.460[b]
500	66	9.23	269.1	Amor	1.460[b]
700	1	10.6	270.3	Amor	1.456[b]
700	5	20.3	269.1	Amor	1.460[b]
700	10	32.1	270.5	Amor	1.460[b]
700	66	63.2	268.9	Amor	1.460
900	1	56.7	269.3	Amor	1.459
1050	1	136.4	270.2	Amor	1.456

[a] Phase present: amor/amorphous.
[b] Film thickness less than 50.0 nm, set refractive index value used for analysis.

sample holder. All data were collected using a Rigaku RU-300 rotating anode generator, equipped with a horizontal Bragg–Brentano goniometer, copper anode, diffracted beam flat graphite monochromator, and scintillation detector. The filament settings were 50 kV, 280 mA and the monochromator was tuned for CuK_α radiation. Analysis for all X-ray diffraction data was performed using the Rigaku DMAXB-II version 2.2 software. The average crystallite size measurements were made using the Scherrer technique [8]. The instrument peak width was determined using NIST SRM640A silicon powder. For the anatase TiO_2 phase the $\langle 1\,0\,1 \rangle$ reflection [9] was utilized for peak width measurements, and for rutile the $\langle 1\,1\,0 \rangle$ reflection [10] was used.

2.6. Transmission electron microscopy techniques and sample preparation

Two types of samples were used for TEM examination: planar sections parallel to the sol–gel layer

and cross-sections perpendicular to the plane of the film.

Some planar sections were prepared by coating the sol–gel films directly on to substrates other than the usual silicon wafers. These alternate substrates included a carbon film evaporated on to mica, and aluminium foil. Samples heat-treated at temperatures above 500 °C could not be coated on to the alternate substrates, as oxidation of the substrates occurred during heat-treatment, but had to be prepared from layers coated on to silicon wafers. Planar sections from these samples were prepared by cutting 3 mm diameter discs from the wafer using an ultrasonic drill. These discs were then ground down from the silicon side to a total thickness of less than 50 µm and finally thinned to perforation, again from the silicon side only, in an ion-mill.

For preparation of the cross-sectional samples, a portion of the silicon wafer was sliced into 3 mm × 1 mm rectangles. These rectangular pieces were stuck together in groups of six to form a block. The block was ground down to a total thickness of less than 50 µm and then ion-milled to perforation.

2.7. Measurement of refractive index

A Rudolph Auto EL II ellipsometer in a null-seeking configuration equipped with a He–Ne laser light source was used to determine the refractive index of sol–gel coated silicon wafers. Reduction of the Δ, Ψ data was carried out with the McCracken software package [11]. A minimum of ten readings was averaged for each sample condition analysed. The exact cycle thickness of the 5 wt % sol–gel films was determined using reflectance spectroscopy. The reflectance spectra were taken on a Varian 2300 spectrophotometer equipped with an integrating sphere (single-beam reflection optics). The model employed to calculate spectra was the Rouard [12] multilayer description using the formalism described by Vasicek

[13, 14]. These two techniques are explained in greater detail in Part I of this series [1]. An appropriate film thickness for reliable ellipsometry analysis of each sol–gel composition was determined from concentration and spin-speed series experiments [15].

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction showed all the titania/silica compositions to be amorphous when heat treated to 500 °C for 1 h. Diffraction peaks from crystalline material are defined as those reflections which have an intensity three times the square root of the background intensity. Samples of the 80/20 and 60/40 titania/silica sol–gels heated to 700 °C for 1 h were found to contain the anatase TiO_2 phase, Fig. 1.

The 40/60 titania/silica samples given a similar heat treatment were still found to be amorphous. The 80/20, 60/40, 40/60 titania/silica samples heated to 1050 °C for 1 h were all found to contain the crystalline phases of anatase and rutile TiO_2 as shown in Fig. 2. In all thin film samples, including the 100 mol % silica, no crystalline silica was detected.

It should be noted here that the average crystallite size measure by XRD is not necessarily the grain size found in a sample. Quite often a grain is made up of several crystallites resulting from large edge dislocations, twins, subgrain boundaries, etc. Therefore, crystallite size values can be equal to or, more often, less than grain size values obtained by TEM.

The crystallite size data for this study can be found in Table VI. The data show that for the 700 °C samples, the crystallite size is small, < 7 nm, and consistent with grain-size measurements made by TEM. The samples heated to 1050 °C showed an increase in crystallite size relative to the 700 °C samples, and again sizes were consistent with observations made by TEM. An interesting observation from these data is that as the mol % titania is decreased in a
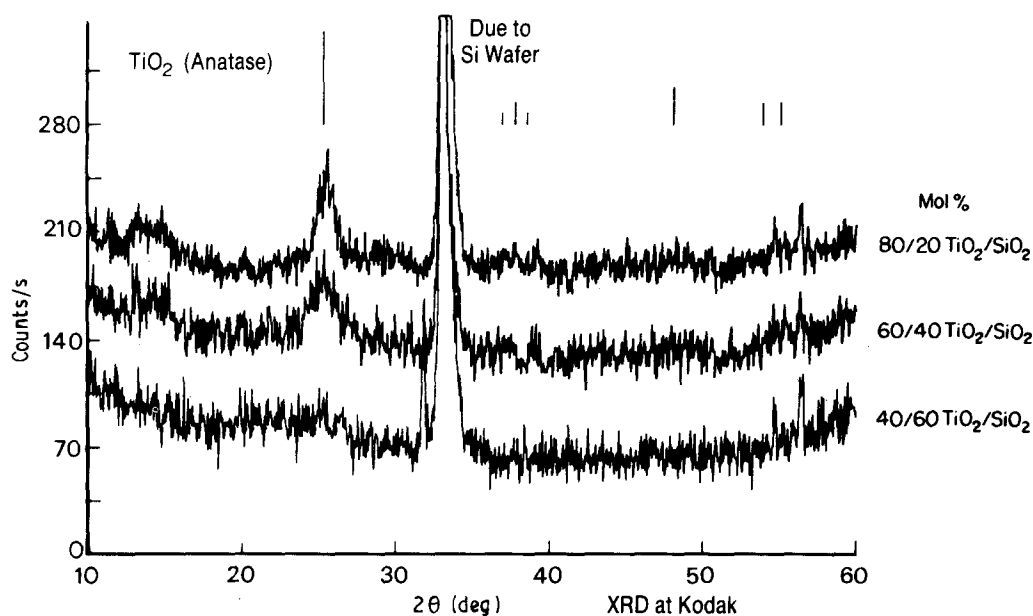

Figure 1 X-ray diffraction spectra of titania/silica sol–gel films heat-treated to 700 °C.
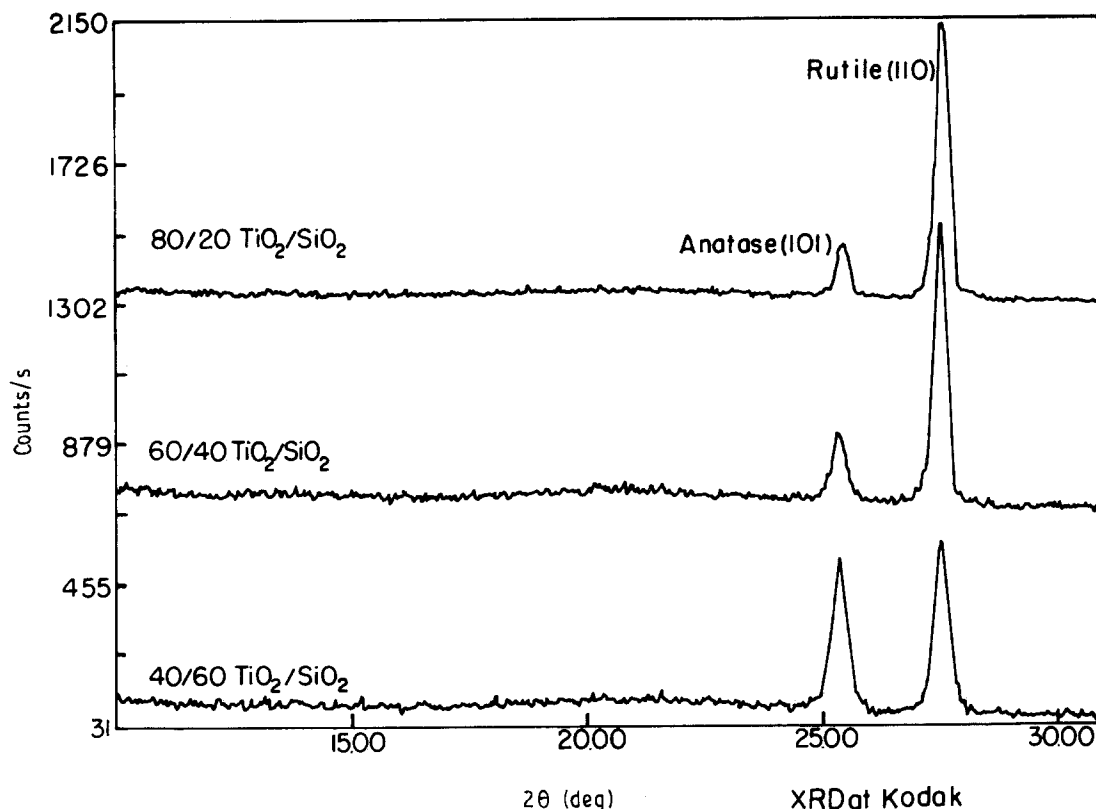
Figure 2 X-ray diffraction spectra of titania/silica sol–gel films heat-treated to 1050 °C.

TABLE VI Crystallite sizes measured by XRD

Sample ratio titania/silica	Corrected FWHM (deg)	Phase[a]	Average crystallite size (nm)
700 °C			
80/20	1.166	Ana	7.0
60/40	1.799	Ana	4.5
40/60		Not observed	
1050 °C			
80/20	0.182	Ana	45.0
	0.145	Rut	56.5
60/40	0.209	Ana	39.0
	0.167	Rut	49.0
40/60	0.298	Ana	27.5
	0.269	Rut	30.5

[a] Phase present: ana/anatase, rut/rutile.

sample film, there is a decrease in the average crystallite size for a sample, indicating that the presence of silica inhibits crystallite (grain) growth. In the 1050 °C samples, the rutile phase crystallite size is observed to be larger than the corresponding anatase crystallite size.

3.2. Transmission electron microscopy

All the 80/20 titania/silica samples heat treated below 500 °C were amorphous, in agreement with the X-ray diffraction data.

Micrographs from the series of samples heat-treated for 1 h at 700 °C are shown in Fig. 3a–c. Cross-sections were prepared from these samples so that the

distribution of grains and grain sizes could be observed across the whole layer from the area adjacent to the substrate up to the free surface. XRD showed that the 40/60 sample was still amorphous and TEM examination confirmed this. The 60/40 and 80/20 samples both contained very small, equiaxed, crystalline grains. The maximum grain size in the 80/20 sample appeared to be about 10 nm, while the maximum for the 60/40 sample was of the order of 7 nm. There appeared to be no preferential nucleation and growth of the grains at the silicon/sol–gel interface. The distribution of the grains can be seen more clearly in Fig. 4a and b which show the same region of the 60/40 layer taken under two different imaging conditions: bright-field and dark-field. The dark-field image is formed from electrons which have been diffracted by the crystalline grains only and this makes them easier to distinguish from the matrix.

All the samples heat treated at 1050 °C contained crystalline, equiaxed grains. In each case, an amorphous layer had formed on the silicon substrate and the grains formed a second layer on top of this. There was a variation in grain sizes between the different sample compositions. In the 80/20 sample, the grains formed a monolayer with a maximum grain size of approximately 0.2 µm, Fig. 5c, while the 40/60 sample contained a layer several grains thick with grain sizes in the range of 7–70 nm, Fig. 5a. The 60/40 sample also had a monolayer of grains with a size range from 14 nm–0.2 µm, Fig. 5b.

Electron diffraction patterns were obtained from all the samples. However, for a cross-section, the volume sampled in each pattern was so small that the titania phase or phases present could not be identified conclusively. In the case of the samples heat treated at
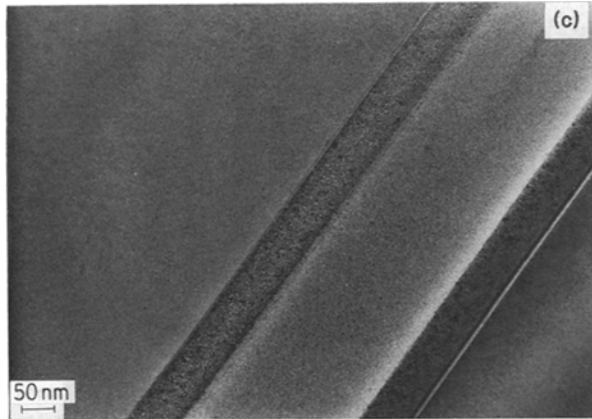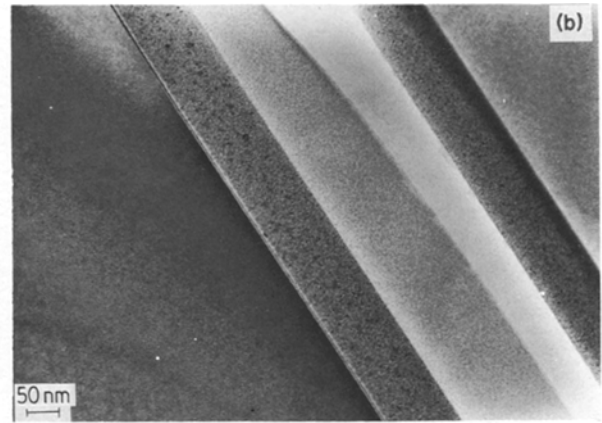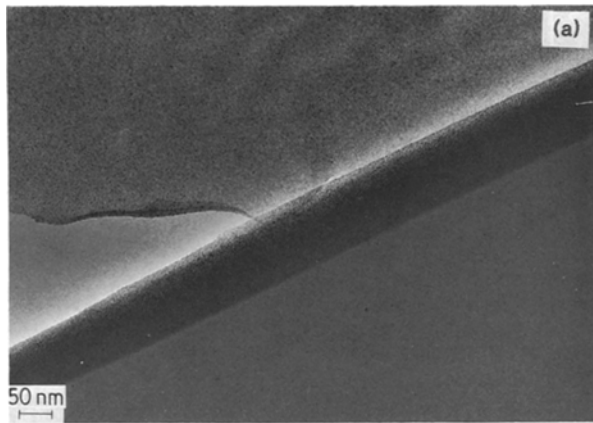
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Figure 3 TEM cross-sections of 700 °C heat-treated titania/silica films: (a) 40/60, (b) 60/40 and (c) 80/20.

1050 °C, XRD data had shown that they all contained both titania phases, anatase and rutile. TEM examination of the crystalline layers showed a range of grain sizes but no obvious bimodal distribution corresponding to the two phases. Dark-field TEM was not possible as the diffraction rings were very faint when viewed on the TEM screen and could not easily be identified as belonging to either the anatase or rutile phases.

Variations in the heat treatment of titania/silica sol–gels can produce crystalline grain sizes from < 10 nm–0.2 μm in the titania phase. As expected for a phase change produced by a nucleation and growth mechanism, the grains in the samples heat treated at

700 °C were far smaller than those at 1050 °C, growth of the crystalline nuclei being far more rapid at 1050 °C.

Although formation of the crystalline titania grains is far more likely to be nucleated heterogeneously than homogeneously in the system, there was no evidence of preferential nucleation at the sol–gel/substrate interface. Crystallization occurred uniformly throughout the layer to give an even distribution of grains in the 80/20 and 60/40 samples heat treated at 700 °C. Although the grain distributions appeared homogeneous, nucleation could still have occurred heterogeneously. Possible nucleation sites could be the porosity remaining in the structure after the low-temperature pre-bake of 175 °C.

The grain structure of the layers heat treated at 1050 °C was non-uniform: all layers contained a wide range of grain sizes. The grains appeared relatively defect-free, as would be expected for crystals formed at high temperature as the result of a phase change.

There was good agreement between the crystallite size as measured by XRD and grain size as measured by TEM, see Table VI. This is also an indication that the grains were relatively defect-free so the grain and domain sizes were approximately equal.
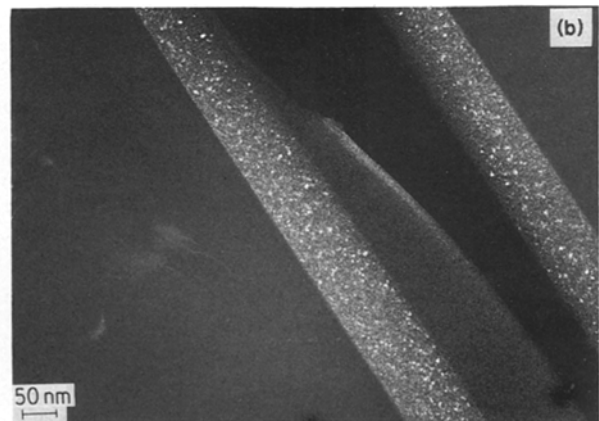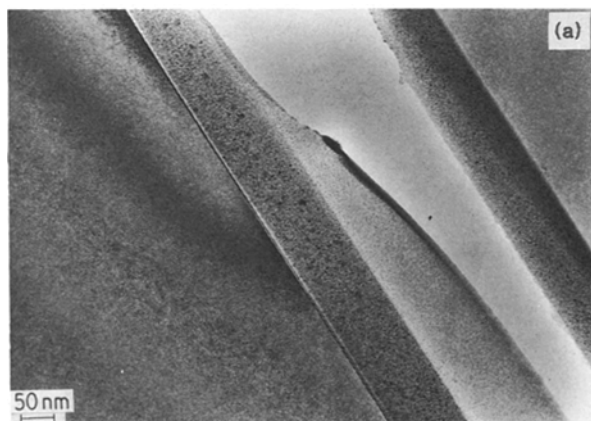

Figure 4 TEM cross-section of 700 °C heat-treated 60/40 titania/silica film: (a) bright-field and (b) dark-field.
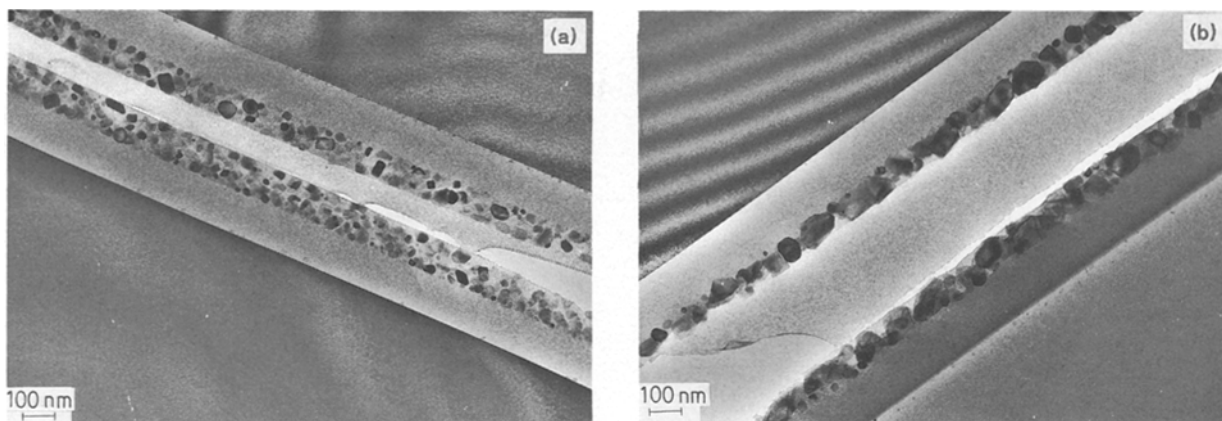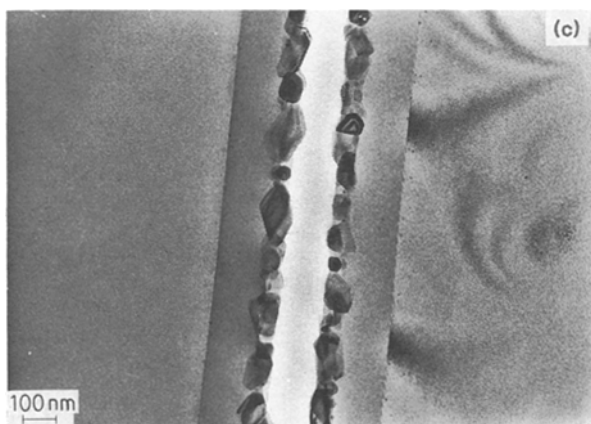
Figure 5 TEM cross-section of 1050 °C heat-treated titania/silica films: (a) 40/60, (b) 60/40 and (c) 80/20.

3.3. Refractive index measurements

Samples of all the titania/silica sol–gel compositions and a 100% silica sol–gel were heat treated for 1 h at temperatures of 175, 350 and 500 °C, using both slow and fast heating rates, and for 10 h at a slow ramp only. The refractive index results for these films are tabulated in Tables I–IV.

Similar samples plus a bare silicon wafer were heat treated to a maximum of 1050 °C and held from 1–66 h. The refractive index and crystalline phase of
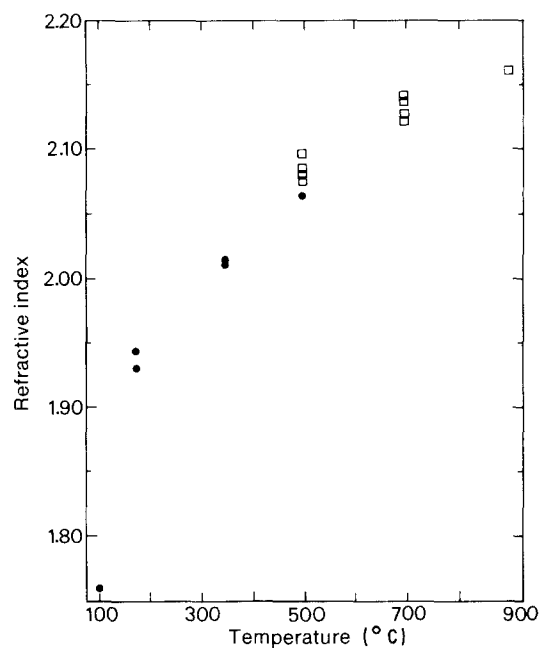

Figure 6 Phase transformation temperature and refractive index of 80/20 titania/silica sol–gel film. (□) Anatase, (●) Amorphous.
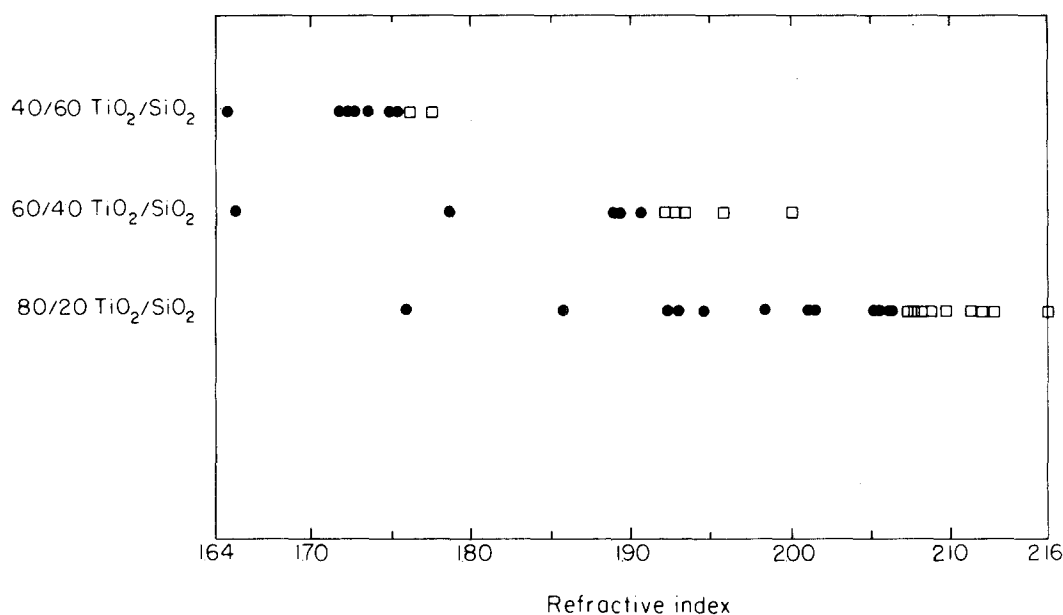

Figure 7 Refractive index values for titania/silica sol–gel films as a function of phase transformation. (□) Anatase, (●) Amorphous.

each film are given in the same tables. Crystallinity is defined by XRD. The phase transformation data in terms of refractive index and heat treatment temperature for the 80/20 titania/silica composition are plotted in Fig. 6. The refractive index and phase of the 100% silica film were invariant under the processing conditions studied. Data from the three refractive index/heat treatment sets show the titania phase transformation temperature to be related directly to the silica dopant concentration. As the concentration of silica is increased, the transformation temperature increases. Fig. 7 is a composite plot of the phase transformation in terms of refractive index for all three compositions.

Using the knowledge that refractive index is an additive quantity [15], one can predict the refractive index for crystallization for any titania/silica sol-gel composition. In this estimate the refractive index of the crystalline anatase phase and the amorphous silica component are assumed to be 2.3 and 1.42, respectively, as determined in this study. Substituting the molar composition of titania and silica, one can estimate the transformation refractive index. The calculated values agree well with the experimental data.

4. Conclusions

The data presented have shown that the phase transformation for titania/silica films is dependent on the heat treatment parameters and the particular composition of sol-gel processed. Of special interest is the ability of the silica dopant concentration to control the titania transformation. The greater the concentration of silica, the higher the temperature and/or longer the time the film must be heated to cause the titanium phase transformation from amorphous to either anatase or rutile. Under similar heat treatment regimes, films with higher silica concentration will require greater energy input for crystalline phase transformation and will have reduced crystallite domain size. The refractive index and phase of 100% silica sol-gel films were found to be invariant under similar heat treatment regimes. Using information gained from both TEM and XRD studies of the same film, the refractive index can be used as a method to determine the phase of titania/silica sol-gel films. A method for estimating the refractive index at which a specific titania/silica sol-gel will exhibit XRD-defined crystallization correlated in the three compositions studied.

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