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Dielectric and infrared properties of TiO_2 films containing anatase and rutile

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Abstract

Electrical and optical properties of low-temperature, plasma enhanced chemical vapour deposited films of TiO_2 have been studied; the source gases were $TiCl_4$ and O_2. The amorphous, as-deposited films had a dielectric constant ∼33 consistent with their measured density of 3.2 ± 0.2 g cm^{-3}. Films deposited using a −41 V substrate bias contained the anatase phase and some rutile as evidenced from infrared spectroscopy and x-ray scattering. Annealing of these films at 600 °C resulted in a significant increase in the rutile content of the film.

1. Introduction

Research into binary and ternary oxides continues in an effort to find a high dielectric permittivity material to replace the thin, amorphous SiO_2 films generally used in Si based microelectronics. If microelectronics is to evolve as anticipated in the celebrated 'semiconductor roadmap', a dielectric with permittivity $\varepsilon \geqslant 25$ must be found to enable the technologies of the year 2016 or even earlier. Permittivity is not the only criterion for the dielectric. (a) It should preferably be amorphous to eliminate electrical leakage along grain boundaries (many materials crystallize in the temperature range of 20–1000 °C and this can cause both significant roughness at the dielectric/semiconductor interface which compromises the device quality and gate leakage currents). (b) The optical bandgap should be large. (c) The band offset of the dielectric conduction/valence band and the Si conduction/valence band should be large. (d) The dielectric should be thermodynamically stable with respect to Si at temperatures up to ∼1000 °C. (e) The dielectric should be a good barrier to dopant diffusion if polycrystalline Si gate electrodes are used. (f) The dielectric/Si substrate interface should have interface state densities comparable to those of the Si/SiO_2 interface. Given the large number of criteria, it is perhaps not surprising that no immediate solution to the problem has presented itself.

In the medium term it appears that materials such as $Hf_xSi_yO_pN_q$ may provide an adequate solution to the dielectric dilemma [1]. However, the dielectric which ultimately replaces SiO_2 will most likely be a non-silicate based ternary or quaternary oxide. With this objective in mind we have begun a systematic study of the dielectric properties of potential candidates for inclusion in these compounds beginning with amorphous TiO_2. Although the electronic bandgap of this material is relatively small (∼3.5 eV), the average dielectric constant of the crystalline, rutile phase is very large (∼114) [2]. Therefore, although TiO_2 itself is not adapted to applications in the field of microelectronics, understanding the nature of the electronic and ionic contributions to the dielectric constant of materials such as these may be useful.

Besides the physical issues outlined above, it is important to note that the materials developed must be obtained in a technology-compatible way. This implies that thin films will be deposited using techniques such as chemical vapour deposition (CVD), plasma enhanced CVD (PECVD) or, perhaps, atomic layer CVD (ALCVD). It is not at all clear that the physical properties of the films deposited using such methods will reflect the idealized ones, which we might obtain using specialized 'laboratory' deposition techniques. In the present work, therefore, we have examined the properties of TiO_2 films deposited using a standard technology-compatible PECVD process. It is hoped that the results obtained will give insight into potential problems with deposited films and ultimately render the engineering of an appropriate ternary/quaternary compound easier.

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2. Experimental details

Thin films of TiO_2 were deposited onto Si(1 0 0) wafers using a microwave (2.45 GHz) excited electron cyclotron resonance plasma reactor working in the pressure range 1–10 mTorr. The microwaves were introduce into the reactor via an antenna system described elsewhere [3]. The advantage of this method is that the plasma potential is rather low so that bombardment of the substrate with energetic species in the plasma commonly found in parallel plate type reactors can be avoided. $TiCl_4$ was used as a source of Ti containing molecules and depositions were carried out at substrate temperatures close to room temperature (i.e., <65 °C). Typical deposition conditions were as follows: O_2 partial pressure 8 mTorr, $TiCl_4$ partial pressure 0.15–0.18 mTorr, microwave power 400 W. Two deposition modes were used: (a) a ‘floating’ potential with no substrate bias and (b) a −41 V substrate bias applied using radio frequency (rf) biasing of the substrate. Some of the samples were subjected to post-deposition annealing in N_2 gas, at 600 °C for 30 min.

Film thicknesses and refractive indices (n) were determined *ex situ* using a single wavelength 632.8 nm ellipsometer. In the case of set (a) (zero substrate bias), we obtained a typical deposition rate of 1.1 nm min^{-1}, while for set (b) deposited using a −41 V rf substrate bias, the deposition rate increased to 2.3 nm min^{-1}, indicating that the substrate bias plays a positive role in increasing the density of the reactive species (Ti^+,O^+) near the Si substrate. The typical thickness of all samples used in the present study was 220 nm. The as-deposited oxides appeared to have a smooth surface and the uniformity of the film thickness was typically 5% over a surface area 2 cm by 2 cm.

TiO_2 film densities were determined by glancing angle x-ray reflectivity with a Philips double crystal diffractometer using the Cu Kα(1) radiation (λ = 0.1541 nm) after a four crystal Bartels monochromator and a 0.45 mm receiving slit. The data taken were analysed using the WINGIXA software provided by PANalytical. Film crystallinity was analysed using an x-ray diffractometer (XRD), working with Cu Kα(1) radiation. The dielectric constant of the films was obtained by performing capacitance/voltage $C(V)$ measurements at 100 kHz using a Keithley 590 system on metal-oxide-semiconductor (MOS) capacitors formed by depositing 0.002 cm^2 Al dots on the oxide surface. For recrystallized films, grain boundary related leakage currents were found to be prohibitively high and we were obliged to manufacture metal/oxide/degenerate Si structures in order to be able to measure the capacitance and deduce ε. Film composition was determined by using both secondary ion mass spectroscopy (SIMS) and energy dispersive x-ray analysis. The SIMS profiles reveal a depth-independent, constant concentration of O and ^{47}Ti appropriate to stoichiometric TiO_2. The EDX measurement confirmed the overall film concentration found by SIMS and enabled us to confirm that within experimental error, no Cl from the $TiCl_4$ source was incorporated in the film. Post-oxidation *ex situ* measurements of the infrared absorption spectrum were made using a Fourier transform infrared (FTIR) spectrometer with a resolution of 4 cm^{-1}. The angle between the IR beam and sample was set to 65° in order to stimulate both the transverse optical (TO) and the longitudinal optical (LO) IR active vibrational modes. For these measurements the native oxide on the unpolished Si surfaces was removed with HF.

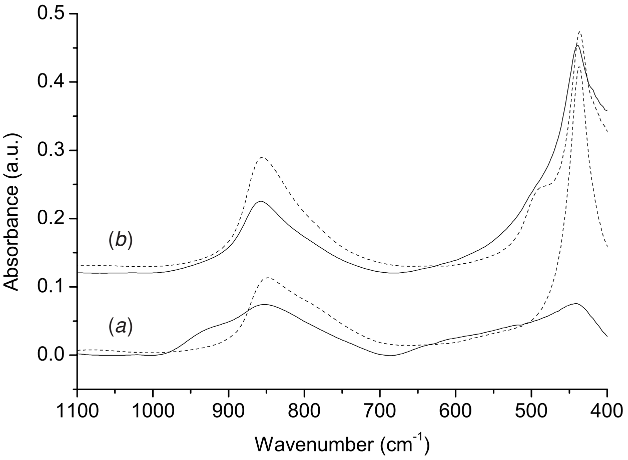

Figure 1. Infrared absorption spectra measured for an incidence angle of 65°. Solid lines: as-deposited TiO_2; dashed lines: the same samples subjected to annealing at 600 °C. (*a*) An oxide deposited with zero bias; (*b*) an oxide deposited with a −41 V RF bias.

3. Results

3.1. Infrared absorption

We present first, in figure 1, the infrared absorption curves. Curves (a) are the IR spectra for the samples deposited with a ‘floating’ bias for 180 min. The solid line is the absorption for the as-deposited TiO_2. The broad peak in the region of 400–600 cm^{-1} is due to the TO vibration of the Ti–O bonds; it is associated with the LO vibrational mode in the region of 700–950 cm^{-1}. In this region, one observes two absorption bands centred at 830 cm^{-1} and 850 cm^{-1} respectively. The EDX measurements confirmed that only low levels of Cl could possibly be included in the films (i.e., less than the experimental accuracy which is ∼3%) so that one might invoke Ti–Cl bonds as the origin of the supplementary infrared absorption. However, Cl related peaks are known to appear at 600 cm^{-1}, so this cannot be the origin. This gives us further confidence that Cl is not present in our deposited films. Detailed investigation of the nature of these extra vibrational modes is required. We conclude that the breadth and position of LO and TO peaks confirm the amorphous nature of the as-deposited film [4] and that the LO peak has two contributions. Following annealing at 600 °C (the dashed line in figure 1(*a*)), two intense, narrow peaks appear at 432 and 853 cm^{-1}. These correspond to the TO and LO modes for the anatase phase [5, 6]. In figure 1(*b*) we show the IR spectra for samples deposited in 90 min using a −41 V substrate bias, we observe that even in the unannealed, as-deposited film, the crystalline, anatase phase vibrational modes are present. Rutile modes, if present, were unobservable.

We also observe the appearance of another peak at 493 cm^{-1} following annealing at 600 °C for 30 min in an N_2 atmosphere (the dashed line). This peak corresponds to the Ti–O vibration in the rutile [7] phase, which indicates that the sample must be a mixture of anatase and rutile. Because of

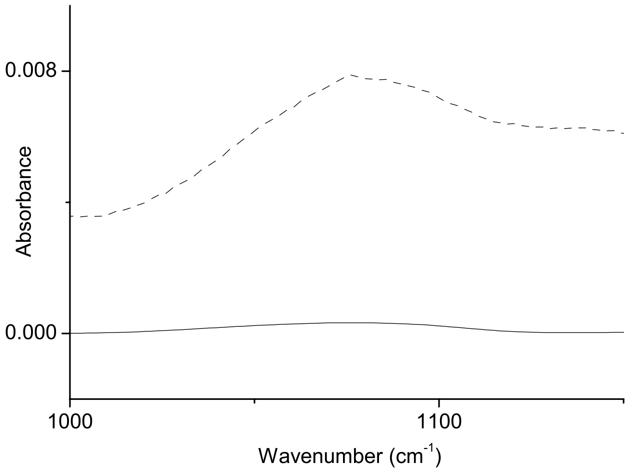

Figure 2. The infrared absorption spectrum of the Si–O–Si stretching vibrational mode in 5 nm of thermally grown SiO_2 (the dashed curve). Solid line: a spectrum for TiO_2 deposited with a −41 V bias then annealed at 600 °C, expanded in the same spectral region.

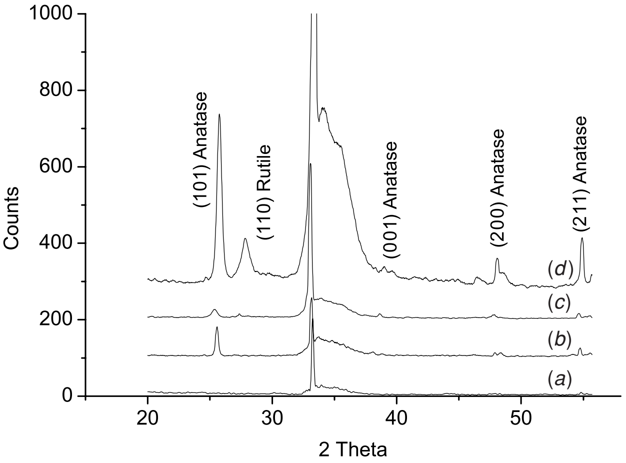

Figure 3. The x-ray diffraction pattern for (*a*) as-deposited at room temperature without a −41 V bias (*b*) zero bias deposited, 600 °C annealed samples (*c*) a −41 V bias as-deposited films (*d*) films as in (*c*) but annealed at 600 °C.

the lower frequency limit of our FTIR instrument, we were unable to measure with precision the full width of half maximum for the TO peaks. From the IR measurement we were further unable to ascertain the degree of crystallinity of the films.

It has been demonstrated [8] that annealing of TiO_2 on Si above 800 °C results in an interaction with the formation of Ti silicate or SiO_2. Because of concerns about the potential reactivity of the TiO_2 film with the Si substrate during annealing particular attention was paid to the IR absorption peak around 1070 cm^{-1} where the strongest mode associated with Si–O vibrations occurs in thin films. In figure 2 we show the IR absorption for a 5 nm thick SiO_2 film grown on Si (the dashed line) and the expanded data (the solid line) from figure 1(*b*) associated with the 600 °C annealed film deposited with a −41 V bias. It is clear from this comparison that any SiO_2 interfacial layer present in the annealed TiO_2/Si structure is less than 1 nm thick.

3.2. X-ray measurements

3.2.1. X-ray diffraction. In figure 3 we show the x-ray diffraction (XRD) patterns for the same samples as presented in figure 1. The most intense peaks in all three data sets shown, in the region of $2\theta \sim 32$–$37°$, come from the single crystal Si substrate. Similar observations have been reported by others [9]. As-deposited, zero bias films show a featureless spectrum typical of an amorphous network and is shown in figure 3(*a*). The narrow peak at 33.2 is the (0 0 2) diffraction of the Si (1 0 0) substrate. The 600 °C annealed oxide deposited under 'floating' bias conditions (figure 3(*b*)) consists of an intense line at 25.4° and less intense lines at 38.9°, 48.1° and 55.5°, which correspond to the (1 0 1), (0 0 4), (2 0 0) and (2 1 1) plane reflections of the crystalline phase anatase respectively. The anatase (1 0 1) peak is expected at $2\theta = 25.28°$. The experimental angles are very slightly displaced compared to the single crystal values, and this may be due to a variety of reasons: imperfect alignment between the samples and the substrate holder in the *xy* plane, roughness of the film, misalignment of the omega/2 theta goniometer, etc. Stress effects in the oxide film have been neglected even though the contact between the Si(1 0 0) single crystal and the TiO_2 could, potentially, introduce this variable. The anatase (1 0 3) reflection expected for an angle of 36.9° is confused with the Si substrate reflection mentioned previously. Figure 3(*c*) shows the data obtained for samples deposited in the presence of a −41 V substrate bias but not subjected to subsequent annealing. We again see peaks associated with anatase but there is also a weak peak at $2\theta \sim 27°$ which can be identified as due to the rutile (1 1 0) reflection [10]. In figure 3(*d*) we show the data for samples shown in figure 3(*b*) but subsequent to annealing at 600 °C. The peak at 27.1° attributed to the rutile (1 1 0) plane is seen to intensify consistently with the transformation of some of the sample into the rutile phase. As far as we are able to tell, the appearance of the rutile peak does not occur at the expense of the anatase peak therefore suggesting that an anatase to rutile phase transformation does not occur for the temperature used.

A final check was made to investigate the possibility of preferred orientation in the deposited films. To this end, sample rotation experiments were carried out and the intensity of the anatase and rutile peaks observed in the standard manner [11] used to ascertain if a preferred orientation is present. There was no evidence for this effect.

3.2.2. Glancing incidence x-rays. The glancing incidence data were analysed using the WINGIXA software from PANalytical. The film density was ascertained for three samples. For the amorphous films deposited in the absence of a substrate bias and without further annealing, the density was 3.2 ± 0.1 g cm^{-3}. Annealed films deposited with no bias had a density of 3.62 ± 0.2 g cm^{-3} whilst films deposited with the a −41 V bias then annealed at 600 °C had densities ∼3.85 ± 0.2 g cm^{-3}. These values were obtained allowing for surface roughness and beam divergence. From the fitting procedure we ascertained the surface roughness in the different films to be 1.2 nm (130 nm thick, as-deposited), 6.5 nm (204 nm, zero bias, annealed) and 7.4 nm (225 nm, deposited with a bias then annealed). Increase of the roughness resulted from the densification and/or the recrystallization process in the TiO_2 films. This is not surprising since it is known that the formation of polycrystalline films results in a higher surface roughness because of the random orientation of adjacent grains.

3.3. Electrical measurements

Measurements were possible for the three types of samples studied. We reiterate that for the annealed films it was necessary to use metal/oxide/degenerate Si structures in order to determine ε. The dielectric constants were as follows: 33 (amorphous films deposited with no bias and no anneal), 74–78 (amorphous films deposited with zero bias then annealed at 600 °C) and 105–117 (films deposited with a -41 V bias then annealed at 600 °C). The latter values are very high, exceeding the known single crystal values [2]. For the unbiased/annealed sample which ostensibly contained amorphous and anatase TiO_2 the value exceeds that of pure anatase [12]. ε is of the same order as pure rutile for the biased/annealed sample which actually contains a mixture of anatase and rutile as evidenced from our x-ray studies.

3.4. The refractive index

The refractive index was measured by ellipsometry using a single wavelength (632.8 nm) system. The as-deposited film indices were 2.25 ± 0.005 (deposited with no substrate bias) and 2.30 (deposited with a substrate bias of -41 V) increasing to 2.30 and 2.48, respectively, following annealing at 600 °C. These values are consistent with those usually observed for amorphous films but a little low for the recrystallized films. One must remember that rutile is birefringent and also that our polycrystalline samples are predominately composed of anatase, or a mixture of anatase and rutile. The refractive index measured with the ellipsometer results an average value that takes into account all these aspects.

4. Discussion

The x-ray diffraction data and the infrared absorption measurements are consistent with the samples being amorphous when deposited in the absence of a substrate bias. The samples obtained using a substrate bias clearly evidence the presence of some crystalline anatase and some rutile. The infrared absorption spectrum reveals only the anatase and amorphous signatures. Upon annealing, films deposited in the absence of polarization evidence the appearance of anatase whilst the films deposited with a substrate bias reveal an increasing amount of rutile. As mentioned previously, the appearance of the rutile does not seem to be to the detriment of the anatase. Deposited films are, of course, not in thermodynamic equilibrium so that any temperature induced changes cannot be simply compared with the behaviour seen in bulk samples. The primary effect of high temperature annealing is for anatase to transform into rutile but the appearance of rutile does not coincide with anatase disappearance for us. Generally [13] the transformation occurs at temperatures in excess of 800 °C (note that such anneals could not be performed in our case because of the risk of film/substrate interaction [8]).

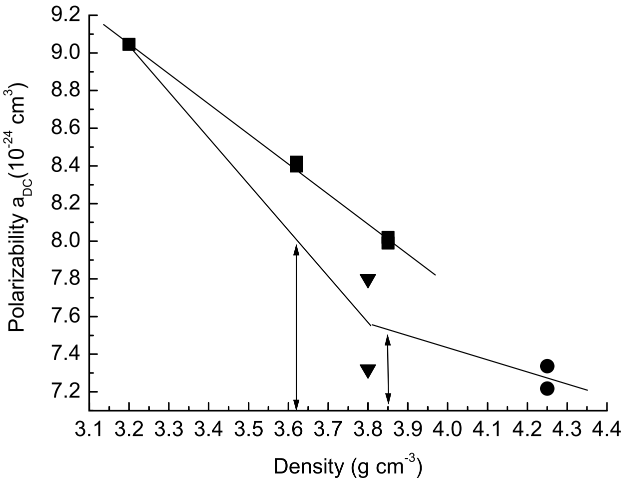

Figure 4. Low-frequency molecular polarizability for anatase (▼) and rutile (●) deduced from their anisotropic dielectric constants. The experimental values of the dielectric constant of the thin films studied here (■).

The film densities determined from the glancing incidence x-ray scattering measurements enable us to conclude that the amorphous, as-deposited film has a density significantly lower than either of the crystalline phases (3.8 g cm^{-3} for anatase and 4.2 g cm^{-3} for rutile [14]). The 600 °C annealed film deposited with zero bias appears to contain primarily anatase (figures 1 and 3), so it is not surprising that the measured density, 3.62 g cm^{-3}, is close to the pure anatase value. The sample containing both anatase and rutile phases obtained by annealing the film deposited in the presence of a substrate bias unsurprisingly has a density which appears to be between the pure anatase and pure rutile values.

In the simple approach described by the Clausius–Mossotti equation, the dielectric constant is written as [15]

$$\varepsilon = \frac{(1 + (8\pi/3)\,\alpha_{\mathrm{dc}}/V_{\mathrm{m}})}{(1 - (4\pi/3)\,\alpha_{\mathrm{dc}}/V_{\mathrm{m}})} \tag{1}$$

where α_{dc} is the low-frequency molecular polarizability and V_{m} is the molecular volume. In consequence, it is related to the densityρ, of the material since $\rho = M/V_{\mathrm{m}}$ with M equal to the molecular mass. Although we have no *a priori* reason to assume that α_{dc} is density independent, we can use the measured values of the dielectric constant and density to ascertain the sample dependence of $\alpha_{\mathrm{dc.}}$ The values obtained for α_{dc} are shown in figure 4 where we include also the values for crystalline anatase and rutile determined from their anisotropic dielectric constants [16, 17]. Comparison of the film derived data and the crystalline values suggests that the effective polarizabilities for the annealed samples containing anatase and rutile are too large and should be more than the values indicated by the arrows in figure 4. One can, in consequence, assume that we have overestimated the values of the dielectric constants in the deposited films (in particular the annealed ones). Using the hypothetical polarizabilities as indicated by the arrows in figure 4, we can estimate the 'real' value of the dielectric constant we should have measured. For the anatase containing sample deposited under zero bias and then annealed we deduce $\varepsilon \sim 34$ (as opposed to 74–78). Note that other authors have reported $\varepsilon \sim 78$ in deposited films

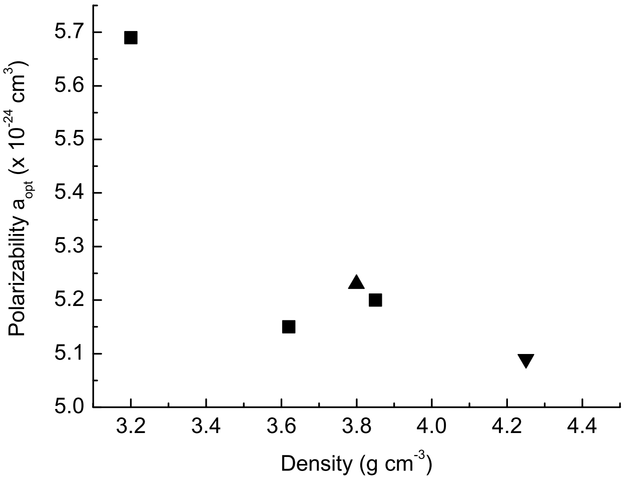

Figure 5. High-frequency molecular polarizability determined for anatase (▲), rutile (▼) and the thin films studied in this work (■).

containing anatase [8] and 33.2 (as opposed to 105–117) for the sample deposited under a bias and then annealed. At the present time, we have no explanation for the appearance of such an anomalously high dielectric constant in the thin films.

The refractive indices, n, are related to the high-frequency polarizability, α_{opt}, through the Lorentz–Lorenz equation:

$$\frac{(n^2-1)}{(n^2+2)} = \frac{4\pi}{3}(\alpha_{\mathrm{opt}}/V_{\mathrm{m}}). \qquad (2)$$

From our measurements we can deduce the polarizability and compare it with the values measured in crystalline anatase and rutile. These data are shown in figure 5. In this case, we observe that the polarizability in our films and in the crystalline phases does not appear to be significantly different as it was in the case of the low-frequency polarizability, α_{dc} (figure 4). This suggests that our optical measurements are reliable. In general, this would be expected since the optical polarizability derives from the electronic structure of the component ions (O^- and Ti^+) which may remain relatively constant from phase to phase. The low-frequency polarizability, however, is directly related to the electronic part and a vibrational energy part, the latter clearly depends upon the structure and bonding of the Ti and the O [15], i.e., the structure of the TiO network.

In figure 3, our x-ray data indicate that films deposited in the presence of an RF bias already contain anatase and some rutile crystals. Following a short anneal at 600 °C the amount of rutile increases substantially (figure 3) although not, apparently, to the detriment of the anatase present. This conclusion is confirmed by the infrared absorption data shown in figure 1. Conversion of anatase to rutile does not appear to be occurring at the anneal temperature of 600 °C. This leads us to suggest that rutile 'precursors' may be generated during the ion-assisted deposition process that can grow/convert during subsequent annealing without transiting via the anatase phase. Ion-assisted phenomena of the crystallization kind are not totally unknown and have been observed in the formation of α-cristobalite and α-quartz from amorphous SiO_2, using a low energy (400 eV) neutral or ion beam to bombard amorphous silica [18]. Interestingly, our data contrast with that obtained on thin films of TiO_2 deposited using ion assistance of an O ion beam of energy 400 eV [6]. In this case no evidence was found for rutile formation in the as-deposited films, only the anatase phase. Comparison with our data suggests that the energy of the ions assisting deposition may play a crucial role in determining if rutile/rutile 'precursors' will be formed during the deposition process. This is a particularly interesting problem which requires further investigation.

5. Conclusions

We have studied PECVD TiO_2 films deposited from $TiCl_4$ and O_2 within the context of understanding their physical properties as far as they might be useful for microelectronics applications. We observe that amorphous films have rather low dielectric constants (∼33) consistent with their measured densities. We can thus conclude that dilution of TiO_2 in other amorphous hosts such as SiO_2 will not result in high dielectric constant ternaries. Films deposited with or without an RF bias do, however, appear to have surprisingly large dielectric constants. These films do contain crystalline anatase and rutile as evidenced from x-ray and infrared absorption measurements. However, the dielectric constants are too large to be simply interpreted as due to the presence of the aforesaid crystalline phases. Note that these data are consistent with observations of other authors in the case of anatase containing films. We have no explanation for this effect. We do find evidence for ion beam assisted generation of polycrystalline rutile in films deposited in the presence of an RF bias and the amount grows if the films are subsequently annealed at high temperature. Both rutile and anatase phases coexist in these samples. The presence of crystalline phases in the deposited thin films is clearly undesirable given the magnitude of the resulting surface roughness we have observed.

Further effort is required to understand the physical origin of the anomalously large dielectric constants and the deposition conditions which result in the appearance of the rutile phase simultaneously with the anatase phase.

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