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LASER RAMAN MEASUREMENTS OF DIELECTRIC
COATINGS AS A FUNCTION OF TEMPERATURE

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Laser Raman measurements of dielectric coatings as a function of temperature

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ABSTRACT

Single crystal Raman spectra of the anatase phase of titania have been acquired as a simultaneous function of temperature and pressure in a heated diamond anvil cell. Measured data are used to construct frequency contours in P,T space for particular allowed vibrational modes. The magnitude of stress in thin films deposited on various substrates and its temperature evolution have been evaluated from correlations between the P,T frequency maps and measured temperature-dependent mode frequencies exhibited by the films. A simple anharmonic oscillator model has been used to relate the temperature-dependence of the square of the mode frequency to the first order anharmonic contribution to the potential energy from which the thermal expansion coefficient (α) of polycrystalline films may be estimated. The stress dependence of α for bulk titania has been determined from this data and is compared with the predicted response of several stressed titania films.

1. INTRODUCTION

Anharmonicity in the lattice potential energy is manifested in condensed phase materials by temperature- or pressure-induced variations in mode vibrational frequencies resulting from lattice expansion or contraction. Therefore, measurements of the molecular vibrational spectrum under varied conditions of pressure and temperature can be used as a probe of the anharmonicity which then is used to estimate intrinsic thermophysical properties of the material. For example, the pressure dependence of a localized mode vibrational frequency (ω_0) is directly proportional to the product of the isothermal compressibility (κ), ω_0 , and the mode Grüneisen parameter, γ , which indicates the magnitude of the anharmonicity.¹

Measured vibrational frequencies and their temperature variation in bulk materials often are different from those observed when the material is deposited as a thin film. Residual stress in the film resulting from thermal properties mismatch between the film and the supporting substrate contributes to this disparity. Alterations in the film microstructure also will influence intrinsic vibrational frequencies and their variations under an applied stress. For example, sol-gel deposited titania films (anatase phase) exhibit larger frequency shifts with applied pressure than seen in PVD films of the same phase or from a single anatase crystal. A 15% increase in the isothermal compressibility of the sol-gel film is inferred from such measurements and can be understood in terms of the spheroidal microstructure exhibited by these films.^{2,3}

Variation in sample temperature leads to perturbation of the vibrational spectrum. In extreme cases, the available thermal energy is sufficient to promote transformation of the material to a new crystalline phase which exhibits marked changes in the number of allowed modes and mode intensities. Recent work has demonstrated that time-dependent Raman measurements can be used to follow the isothermal transformation kinetics as an amorphous titania film crystallizes into the anatase crystalline phase.⁴ Under milder conditions where transformation phenomena do not occur, shifts in mode frequencies and changes in linewidth are expected and have been observed. The subject of work reported here concerns the temperature dependence of mode frequencies in titania films deposited on several different substrates. Films, deposited in either tensile or compressive stress states, have been analyzed and, for a particular mode, exhibit differences in mode frequency and its temperature variation which are dependent on the residual stress in the film. Measured data are used to estimate the thermal expansivity of the film based upon an anharmonic oscillator model. From measurements on single crystal anatase as a simultaneous function of both temperature and pressure, the stress dependence of the thermal expansion coefficient, α , is calculated and compared with estimated values for several anatase films deposited on glass, silica, and silicon substrates. Deviations between the behavior exhibited by the bulk material and deposited films can be attributed to the influence of film microstructure.

2. EXPERIMENTAL

Titania films were deposited onto silicon, glass, and silica substrates using sol-gel and reactive sputter deposition techniques (PVD, and IAD) discussed previously.^{5,6,7} Substrate thicknesses were 0.4 mm, 0.1 mm, and 2.0 mm respectively. In all films studied here the presence of a homogeneous anatase phase material was confirmed from measured Raman spectra. Film properties are described in Table 1. A single crystal of anatase was obtained from the Grao Mogol locality in Minas Gerais, Brazil and used as a standard.

Table 1. Characteristics of TiO₂ (anatase phase) films

Identification	Substrate	Index	Thickness
A (IAD)	Si(100)	2.522	286 nm
B (PVD)	Glass	2.382	853 nm
C (sol-gel)	Silica	2.230	176 nm
D (PVD)	Silica	2.410	560 nm
E (PVD)	Silica	2.403	Multilayer coating 3-cav Fabry Perot $\lambda/4$ at 500 nm

A flake from the anatase single crystal was loaded into a diamond anvil cell of the Merrill-Bassett design⁸ which could be heated under pressure by means of a resistance furnace encompassing the cell. Argon was used as the pressure transmitting fluid and was added to the cell along with a small crystal of Sm:YAG which was used to determine the internal cell pressure by means of pressure-induced frequency shifts of the laser-induced fluorescence doublet near 617 nm.^{9,10} To confirm hydrostatic conditions within the cell, the fluorescence bandwidth, doublet splitting and relative intensity of the doublet components were monitored for all measurements.

Raman spectra collected from ambient temperature and pressure to 40 kbar and 700 K. were excited at normal incidence to the diamond anvil faces in a backscattering geometry using a Raman microprobe (SPEX Model 1482). A long focal length objective (10X, 0.3 NA) was used to view inside the cell and to image the CW probe excitation (488.0 nm, 250 mW) onto the sample. Scattered light collected by the objective was directed to a 0.5 m triple spectrometer (SPEX Model 1877) and dispersed onto the active elements of an intensified gated array detector (TN Model 6133). Multiple spectra acquired at 1 sec exposure times were averaged to improve the signal to noise ratio. Spectra were calibrated using the known Raman frequencies of anatase under ambient conditions. The spectral region around 617 nm (Sm:YAG fluorescence) was calibrated using known emission lines from a neon source.

Raman spectra of anatase films mounted in a resistively heated furnace were acquired in a 60 degree forward scattering geometry from ambient temperature to 700 K. Scattered light was analyzed using a 0.85 m double monochromator (SPEX model 1403) equipped with a photomultiplier detector. Raman line frequencies and linewidths were determined from best Lorentzian line fits to all measured spectra.

3. RESULTS

The Raman spectrum of the anatase phase of TiO_2 is characterized by 5 predominant lines at 141, 194, 395, 512, and 635 cm^{-1} as shown for the single crystal in Fig. 1a. Titanium atoms in this structure are coordinated by six oxygen atoms, each of which is three-fold coordinate with titanium as shown in Fig. 1b. The high frequency E_g mode at 635 cm^{-1} is described principally in terms of symmetric oxygen atom displacements about the titanium atom in the x,y plane.

Fig. 1. (a) Raman spectrum of single crystal anatase. (b) The atomic structure for the anatase phase of TiO_2 .

Frequency variations as a simultaneous function of applied pressure and temperature have been measured for this localized mode in the single crystal standard and are summarized below in Fig. 2a and 2b.

Fig. 2. The frequency dependence of the 635 cm⁻¹ E_g mode in single crystal TiO₂ (anatase) as a function of applied temperature and pressure. (a) Three-dimensional representation of the frequency shift (ω_{T,P} - ω₀), where ω₀ is the measured frequency at 293 K and 1 bar. (b) Contours of constant frequency in P-T space.

Frequency variations of the 635 cm⁻¹ E_g mode correlate with the magnitude of external stress applied to the bulk material. In general, compressive stress usually induces positive frequency shifts resulting from lattice contraction while thermal stress induces negative frequency shifts owing to lattice expansion. However, for anisotropic crystal space groups, thermally induced lattice expansion may generate a contraction of the unit cell in one or two dimensions and slight expansion in the other dimension(s) leading to mode frequency increases for modes with co-directional displacements. The two low frequency modes in anatase exhibit this type of behavior to temperatures approaching 800 K. At higher temperatures, little change in the mode frequency is observed.

Raman spectra of thin anatase films exhibit mode vibrational frequencies that depend upon the nature of the substrate and the type of processing used for their deposition. Mode frequency variations also are found to vary from those measured in single crystal standards as the film is heated. Fig. 3 compares the temperature dependence of the 635 cm⁻¹ E_g mode frequency measured for the film samples listed in Table 1 with the response of the single crystal under applied pressures of 1 bar and 7.1 kbar.

Fig. 3. Temperature dependent Raman frequencies (E_g mode) for anatase films deposited on various substrates compared with the observed temperature-dependent frequency response of a compressed anatase crystal under the indicated hydrostatic pressures. (solid lines) Film A (*); Film B (x); Film C (-); Film D (o); Film E (+).

The E_g resonance frequencies at 300 K deviate from the frequency of the unstressed crystal standard at the same temperature. Frequency shifts reflect the magnitude of inherent stress in the film which can be quantified from comparison with measured pressure dependent frequencies for the single crystal. Figure 3 suggests that films B and C are in compressive stress, and that films A, D, and E are in tensile stress. While differences in thermal expansivities between film and substrate often can be used to predict whether the film stress will be tensile or compressive, the influence of the film microstructure should not be overlooked. For example, the sol-gel film deposited on silica is highly compressive, yet single and multilayer titania coatings on silica are seen to be in tensile stress. The temperature dependence of the mode frequency also varies from film to film. This behavior suggests that the mode anharmonicity can be influenced by the method used to deposit the film. Crystal lattice expansion and contraction under an applied stress will influence mode vibrational frequencies. Therefore, vibrational measurements of materials as a function of applied stress can be used to estimate the degree of lattice expansion or contraction that occurs when the material is subjected to perturbations in temperature or pressure.

4. DISCUSSION

To extract thermophysical properties from vibrational spectra requires a model which relates lattice volume changes to variations in phonon frequency and force constant as a function of an applied stress. The *quasiharmonic approximation*, discussed in a review by Bruesch,¹¹ treats the

response of diatomic molecules, linear chains, and isotropic lattices to an applied thermal stress. Application of this formalism to anisotropic systems is complicated by the directionality of the vibrational mode displacements which contribute to the lattice expansion. Nevertheless, the model can be used to estimate the thermal expansion behavior of thin films where random polycrystallite orientation usually pervades. This discussion will be restricted to the high frequency localized E_g mode of anatase which involves displacement of oxygen atoms from titanium atom centers in the x,y plane. The thermal expansion of the film, then results from temperature-induced expansion of the equilibrium Ti-O bond length which describes the mode.

A Taylor's series expansion of the potential energy associated with this normal mode, $V(Q)$, can be written in terms of the mode displacement (Q), where f_o is the unperturbed force constant for the mode under consideration, and g_o , and h_o represent the anharmonic contributions to the potential. In general, g_o is a negative number.

$$V(Q) = 1/2 f_o Q^2 + 1/6 g_o Q^3 + 1/24 h_o Q^4 + \dots, \quad (1)$$

The equation of motion to first order in the anharmonicity appears in the expression below.

$$\mu \partial^2 Q / \partial t^2 + f_o Q + g_o Q^2 = 0. \quad (2)$$

Here, μ is the reduced mass of the oscillator, and t is time. The time average of the interatomic separation, written in terms of the mean square vibrational amplitude, is obtained to first order in the anharmonicity from the solution to equation (2).¹¹ The average available thermal energy, $k_B T$, where k_B is Boltzmann's constant, then is equated to the vibrational energy leading to the following two relationships:

$$a(T) = a_o - 1/2 (g_o / f_o^2) k_B T, \quad (3)$$

$$\omega^2(T) = \omega_o^2 \{1 - (g_o^2 / 2 f_o^3) k_B T\}, \quad (4)$$

where $a(T)$ is the temperature-dependent lattice constant co-directional with the normal mode, a_o is the equilibrium lattice constant, and $\omega(T)$ is the temperature-dependent vibrational frequency. An average value for the linear thermal expansion coefficient, α , can be written from equation (3).

$$\alpha = 1/a_o [\partial a(T) / \partial T] = -1/2 (g_o k_B / a_o f_o^2). \quad (5)$$

Equation (4) can be rewritten, and is used to evaluate the first order contribution to the anharmonicity. Also, the harmonic force constant is defined in the usual manner. For the E_g mode in anatase, the reduced mass (μ) is taken to be the mass of the oxygen atom, and a_o then becomes the equilibrium Ti-O bond length in the x-y plane and c is the speed of light.

$$f_o = 4 \pi^2 c^2 \omega_o^2 \mu. \quad (6)$$

$$\Delta \omega^2 = [\omega(T)^2 - \omega_o^2] = -(\omega_o^2 g_o^2 / 2 f_o^3) k_B T. \quad (7)$$

Fig. 4 shows the variation in the quantity $\Delta \omega^2$ with sample temperature for the bulk material at several pressures and for the anatase films. Changes in slope are evident and attest to the dependence of both the harmonic and anharmonic force constants on stress.

Fig. 4. Linear variation of $\Delta\omega^2 (= \omega^2(T) - \omega_0^2)$ with temperature. The solid curves represent measurements on bulk anatase crystals contained within the diamond anvil cell and subjected to changes in hydrostatic pressure.

Film A (*); Film B (x); Film C (-); Film D (o); Film E (+).

The data represented in Fig. 4, summarized in Table 2, can be used to estimate the thermal expansion coefficient of bulk anatase crystal and to study the influence of stress on the magnitude of α . Equation (5) can be rewritten in terms of the slope (S) of the $\Delta\omega^2$ vs T curve in Figure 4.

$$\alpha = [k_B/2\mu]^{1/2} (1/2\pi c) (1/a_0) \{S^{1/2}/\omega_0^2\}. \quad (8)$$

For the unstressed anatase crystal, the reduced mass (μ) can be replaced by the mass of an oxygen atom; a_0 is then taken as the equilibrium Ti-O equatorial bond length (1.937 Å).¹² The computed value for α of $5.0 \times 10^{-6} \text{ deg}^{-1}$ is in good agreement with the reported value of the bulk crystal of $6 \times 10^{-6} \text{ deg}^{-1}$, suggesting that analysis of the temperature dependence of this mode alone is sufficient to provide a good estimate to α .¹³

Values appearing in the last column of Table 2 are directly proportional to the thermal expansion coefficient according to equation (8), and can be used to estimate the stress dependence of that quantity. However, α also is inversely proportional to the Ti-O equilibrium bond length with decreases in magnitude with increasing pressure. A change of 1% over this pressure range is estimated and will act to increase α accordingly. Therefore, in the absence of bond compressibility data, a lower limit to the stress dependence of the thermal expansion coefficient can be determined from vibrational measurements of the bulk crystal.

Table 2. Summary of parameters extracted from Figure 4. (SC refers to an anatase single crystal under the indicated hydrostatic pressure.)

Sample	ω_0^2 (cm ⁻²)	S (cm ⁻² /deg)	$[-S^{1/2}]/\omega_0^2$ (cm/deg ^{1/2})
SC 0 kb	4.108 E5	-20.69	1.107 E-5
SC 7 kb	4.142 E5	-23.80	1.178 E-5
SC 25 kb	4.218 E5	-27.61	1.246 E-5
SC 39 kb	4.250 E5	-28.69	1.260 E-5
Film A	4.029 E5	-18.34	1.063 E-5
Film B	4.126 E5	-21.39	1.121 E-5
Film C	4.152 E5	-25.36	1.213 E-5
Film D	4.027 E5	-13.49	0.912 E-5
Film E	4.054 E5	-17.39	1.029 E-5

Fig. 5 depicts the pressure dependence of the parameter $[S^{1/2}]/\omega_0^2$, which is directly proportional to α , and shows that increasing pressure (stress) tends to increase the thermal expansion coefficient. The $[S^{1/2}]/\omega_0^2$ value for the sol-gel film corresponds to an applied stress equivalent to 16 kbar. Since the measured vibrational frequency for the E_g mode in this film suggests that the film is under only 7-8 kbar of stress, the film microstructure also must influence the value of α . This is not surprising since previous work already has established that the microstructure of sol-gel films leads to an increase in the compressibility.²

Fig. 5. Pressure dependence of normalized values of $[S^{1/2}]/\omega_0^2$.

5. CONCLUSIONS

Laser Raman investigations of the pressure and temperature dependence of normal vibrational mode frequencies probe the anharmonicity in the lattice potential energy from which various thermophysical properties of the material can be estimated. The thermal response of vibrational frequencies intrinsic to thin films often contrasts with that observed from the corresponding bulk material. Such differences are thought to arise from stress in the film introduced during the film deposition process (internal stress) and resulting from thermal mismatch between the film and substrate. The film microstructure influences the magnitude of the internal stress and can be altered from changes in deposition parameters. Both factors lead to perturbation in the optical and mechanical properties exhibited by a particular film and also can influence film compressibility and expansivity.

Raman spectroscopy has been used to determine the extent of residual stress in thin titania films deposited on several different substrates using various techniques, and to estimate the influence of stress on the thermal expansion coefficient (α). Titania films, formed on silica and silicon substrates using reactive sputter or ion assisted deposition procedures, are found to be under tensile stress as would be expected for systems where $\alpha(\text{substrate}) < \alpha(\text{film})$. For sputtered titania films on a glass substrate, the film is in a compressive state since $\alpha(\text{glass}) > \alpha(\text{titania})$. However, sol-gel deposited titania films on silica substrates are found to be compressive. This apparent anomaly indicates the importance of film microstructure in controlling internal stress. While PVD films are characterized by a columnar grain structure, the sol-gel films consist of a spheroidal microstructure. Previous work has suggested that this morphology is responsible for the higher compressibility of these films over that intrinsic to PVD films.²

A relative increase in the thermal expansion coefficient of single crystal anatase was determined from the temperature dependence of the high frequency E_g mode. The lower limit to the increase in α at an applied hydrostatic pressure of 40 kbar was determined to be on the order of 15 percent. The sputter deposited film on glass exhibits a compressive stress of 4 kbar. This corresponds to an increase in α of about 4 percent from interpolation of Fig. 5. A somewhat smaller value is computed for this film (using the anharmonic oscillator formalism) from the frequency dependence of the square of the resonance frequency. Anomalous behavior again is noted for the sol-gel film. Here, the predicted increase in α based on the film stress alone is approximately one-half of the value computed from the model. Results support the contention that film microstructure influences the internal stress of a film and therefore plays an important role in determining the thermal expansion properties of a thin film.

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