



Far-infrared spectra of amorphous titanium dioxide films

G. Scarel^{a,*}, C.R. Aita^a, H. Tanaka^b, K. Hisano^b

^a Department of Materials Engineering, University of Wisconsin–Milwaukee, P.O. Box 784, Milwaukee, WI 53201, USA

^b Department of Applied Physics, The National Defense Academy, Yokosuka 239, Japan

Abstract

The amorphous TiO₂ film structure on an aluminum substrate was studied by far infrared reflection–absorption spectroscopic (IRAS) analysis. The transverse (TO) and longitudinal (LO) optical modes of the amorphous oxide films were studied experimentally and through simulation. These optical modes were compared to those of the corresponding crystal. While TO modes of the films correspond to those of the crystal, the LO modes do not. The best agreement between the experimental and the simulated IRAS spectra is obtained when an appropriate dielectric function $\epsilon_{\text{film}}(\nu)$ is chosen. $\epsilon_{\text{film}}(\nu)$ must be related to the amorphous character of the films e.g. by averaging the anisotropic crystal properties. As a consequence of our findings, the Berreman effect does apply in amorphous films to absorption bands at frequencies of the peaks of the loss function $\text{Im}[-1/\epsilon_{\text{film}}(\nu)]$, which does not correspond to frequencies of the LO modes of the crystal. © 2002 Elsevier Science Ltd. All rights reserved.

PACS: 77.55; 73.80

1. Introduction

Due to its high dielectric constant [1,2], amorphous TiO₂ is a candidate to replace amorphous SiO₂ and SiN as the dielectric layer in ultra-thin film capacitors. For this reason, it is necessary to analyze and precisely characterize the thin TiO₂ films. We observe transverse (TO) and longitudinal (LO) modes to study the effects of the amorphous character of anatase TiO₂ films grown on aluminum substrate. The amorphous character of thin films consists of topological [3] and orienta-

tional disorder. Due to topological disorder, bond length and bond angles are different from those of the crystal. Moreover, due to orientational disorder, the TiO₆ units, typical of anatase, are all randomly oriented. In amorphous films however, even though topological disorder is present, a TO–LO splitting is present which is similar to the one of crystals [4,5]. This information is very important because it allows us to use, for amorphous TiO₂ films, frequencies of corresponding TO and LO modes equal to those in a crystal and reported in Table 1 [6].

The effects of orientational disorder are investigated in this paper using infrared reflection–absorption spectroscopic (IRAS) and the Berreman effect. The latter predicts that the frequency of TO and LO modes of a thin film can be measured

* Corresponding author. Present address: Laboratorio MDM-INFN, Via Olivetti 2, 20041 Agrate Brianza, MI, Italy.

E-mail address: gscarel@mdmlab.mi.infn.it (G. Scarel).

Table 1

Frequencies, damping factors, and high frequency dielectric constants for optical modes in anatase TiO₂ at room temperature [6]

Optical mode	Frequency, ν (cm ⁻¹)	Damping factor, γ (cm ⁻¹)
<i>For optical modes with A_{2u} symmetry in anatase TiO₂</i> ($\epsilon_{\infty} = 5.41$)		
ν_{TO1}	367	68
ν_{LO1}	755	79
<i>For optical modes with E_u symmetry in anatase TiO₂</i> ($\epsilon_{\infty} = 5.82$)		
ν_{TO2}	262	36
ν_{LO2}	366	4.1
ν_{TO3}	435	32
ν_{LO3}	876	33

directly using an oblique polarized infrared beam [7].

2. Experimental procedure

Amorphous TiO₂ films, 0.25 μm thick, were grown at room temperature by reactive sputter deposition technique in a 100% O₂ gas atmosphere [8]. The structure of the films was determined using X-ray diffraction [8] analysis of films grown on fused silica. The presence of an anatase short-range order was established using Raman spectroscopy [9] analysis of films grown on silicon.

Far-IRAS spectra (between 100 and 600 cm⁻¹) of films on aluminum were measured using a Fourier transform infrared spectrometer by Bruker (Model IFS 113v). The instrument is equipped with a 3.5 μm mylar beam-splitter which selects radiation, produced by a glowbar source, in the 50–700 cm⁻¹ frequency range. The instrument is equipped also with a polyethylene polarizer to linearly s- and p-polarize the incoming infrared beam. A TGS pyroelectric detector collects the infrared beam reflected by the sample. For each spectrum, 100 scans were taken with a 4 cm⁻¹ resolution at a fixed angle of incidence $\phi = 45^\circ$. Measurements were made at a pressure of 1×10^{-3} Torr and room temperature. An aluminum-coated glass substrate was used as reference. IRAS spectra were calculated using MATHEMATICA from the Fresnel reflection coefficients [10] for a three-layer system.

3. Results and discussion

Experimental and calculated far IRAS spectra measured using a s- and a p-polarized beam at $\phi = 45^\circ$ for the 0.25 μm anatase TiO₂ film on aluminum are shown in Figs. 1 and 2.

The frequencies of the relevant absorption bands measured using a s-polarized beam are reported both in Fig. 1 and in Table 2. The frequencies of the absorption bands measured using a p-polarized beam are reported both in Fig. 2 and in Table 2.

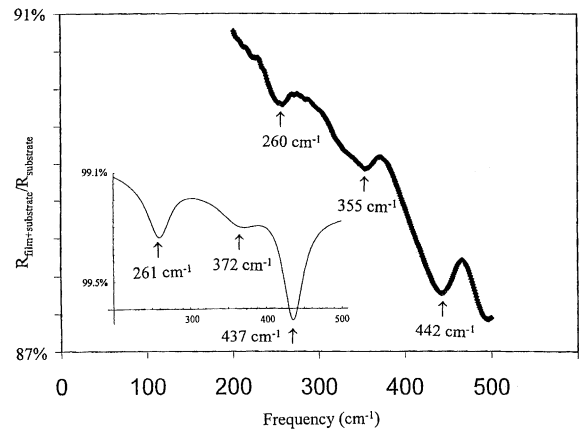


Fig. 1. Experimental and calculated (inset) far IRAS spectra measured with s-polarized beam.

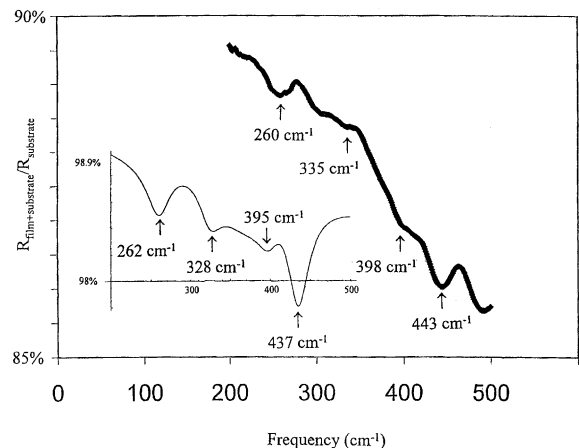


Fig. 2. Experimental and calculated (inset) far IRAS spectra measured with p-polarized beam.

Table 2

Comparison of experimental and calculated frequencies of absorption bands in IRAS spectra ($\phi = 45^\circ$) of the 0.25 μm thick TiO_2 film on aluminum with those of peaks of loss functions and those of optical modes for anatase TiO_2 in Table 1

Beam polariz.	Exp. freq. (cm^{-1})	Calc. freq. (cm^{-1})	$\text{Im}[\varepsilon(\nu)]$ (cm^{-1})	$\text{Im}[-1/\varepsilon(\nu)]$ (cm^{-1})	ν_{TO} (cm^{-1})	ν_{LO} (cm^{-1})
s	260	261	262	–	262- $\nu_{\text{TO}2}$	–
	355	372	366	–	367- $\nu_{\text{TO}1}$	–
	442	437	436	–	435- $\nu_{\text{TO}3}$	–
p	260	262	262	–	262- $\nu_{\text{TO}2}$	–
	335 ^a	328	–	326	–	–
	398	395	–	396	–	–
	443	437	436	–	435- $\nu_{\text{TO}3}$	–
	853	839	–	838	–	–

^a Weak.

For the calculation of the reflection coefficient and, consequently, of the IRAS spectra, an expression for $\varepsilon_{\text{film}}(\nu)$ is used that is an average of its value in the anisotropic crystal [11]. This expression, shown in Eq. (1), has been successfully applied in amorphous [11] and polycrystalline films [12]:

$$\varepsilon_{\text{film}}(\nu) = [\varepsilon_{\parallel}(\nu) + 2\varepsilon_{\perp}(\nu)]/3. \quad (1)$$

In Eq. (1), $\varepsilon_{\parallel}(\nu)$ and $\varepsilon_{\perp}(\nu)$ are the dielectric functions of anatase TiO_2 in the A_{2u} and the E_u symmetries respectively. These functions are expressed according to the factorized form [13]. Absorption is expected at the frequencies of the peaks of loss functions $\text{Im}[\varepsilon_{\text{film}}(\nu)]$ and $\text{Im}[-1/\varepsilon_{\text{film}}(\nu)]$. These functions are calculated and plotted versus frequency in Fig. 3. The frequencies where peaks occur in the loss functions are reported both in Fig. 3 and in Table 2.

Table 2 shows that there are absorption bands measured using a p-polarized beam at frequencies

higher than 800 cm^{-1} , which are not shown in the spectra of Figs. 1 and 2. Table 2 shows that all the absorption bands detected using a s-polarized beam, both in the experimental and in the calculated spectra, appear at frequencies of the peaks of $\text{Im}[\varepsilon_{\text{film}}(\nu)]$ and of TO modes (Table 1). Two absorption bands detected using a p-polarized beam, both in the experimental and in the calculated spectra, do also appear at frequencies of peaks of $\text{Im}[\varepsilon_{\text{film}}(\nu)]$ and of TO modes. The other absorption bands, also detected using a p-polarized beam, do appear at frequencies of peaks of $\text{Im}[-1/\varepsilon_{\text{film}}(\nu)]$ and these absorption bands obey the Berreman effect, because they are absent in spectra measured using a s-polarized beam [7]. None of the detected absorption bands, however, appears at frequencies of LO modes. This fact is interesting, given that originally the Berreman effect is expected to affect absorption bands appearing at frequencies of LO modes.

4. Conclusions

We conclude that, from the microscopic point of view, the TO and the LO modes keep their identity in the anatase TiO_6 unit. Macroscopically however, the random orientation of the anatase TiO_6 units has a dominant effect in IRAS spectra. As a clear consequence, we see from Table 2 that in IRAS spectra of amorphous films, only the frequencies of the TO modes can be measured directly but the frequencies of LO modes can not be

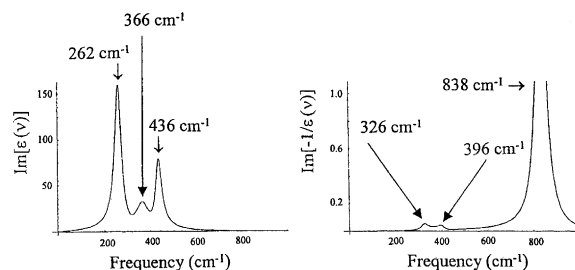


Fig. 3. The loss functions as a function of frequency for anatase TiO_2 .

measured at all. This is very different than the case of crystalline films for whom both the frequencies of TO and LO modes can be directly measured [14].

Acknowledgements

The authors would like to acknowledge C.J. Hirschmugl (Physics, UWM), R.S. Sorbello (Physics, UWM) and A.S. Sklyarov (Advanced Analysis Facility, UWM) for assistance and fruitful discussions.

References

- [1] R.J. Gonzalez, R. Zallen, in: M.F. Thorpe, M.I. Mitkova (Eds.), *Amorphous Insulators and Semiconductors*, Kluwer Academic, Norwell, MA, USA, 1997, p. 395.
- [2] W.L. Gladfelter, C.J. Taylor, D.C. Gilmer, D.G. Colombo, G.D. Wilk, S.A. Campbell, J. Roberts, *Mater. Res. Soc. Symp. Proc.* 567 (1999) 349.
- [3] F. Wooten, K. Winer, D. Weaire, *Phys. Rev. Lett.* 54 (1985) 1392.
- [4] F.L. Galeener, G. Lucovsky, *Phys. Rev. Lett.* 37 (1976) 1474.
- [5] S.W. de Leeuw, M.F. Thorpe, *Phys. Rev. Lett.* 55 (1985) 2879.
- [6] R.J. Gonzalez, R. Zallen, H. Berger, *Phys. Rev. B* 55 (1997) 7014.
- [7] D.W. Berreman, *Phys. Rev.* 130 (1963) 2193.
- [8] J.D. DeLoach, G. Scarel, C.R. Aita, *J. Appl. Phys.* 85 (1999) 2377.
- [9] V.V. Yakovlev, G. Scarel, C.R. Aita, S. Mochizuki, *Appl. Phys. Lett.* 76 (2000) 1107.
- [10] W.N. Hansen, *J. Opt. Soc. Am.* 58 (1968) 380.
- [11] P. Grosse, B. Harbecke, B. Heinz, R. Meyer, M. Offenberg, *Appl. Phys. A* 39 (1986) 257.
- [12] A. Aoki, H. Tanaka, K. Hisano, in: *Proc. 12th Jpn. Symp. Thermophys. Prop. A*, vol. 103, 1991, p. 9.
- [13] T. Kurosawa, *J. Phys. Soc. Jap.* 16 (1961) 1298.
- [14] M.D. Sciacca, A.J. Mayur, E. Oh, A.K. Ramdas, S. Rodriguez, J.K. Furdyna, M.R. Melloch, C.B. Beetz, W.S. Yoo, *Phys. Rev. B* 51 (1995) 7744.