Observation of surface optical phonons on TiO_2(100)

L. L. Kesmodel and J. A. Gates
Department of Physics, Indiana University, Bloomington, Indiana 47405

Y. W. Chung
Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60201

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Surface vibrations on a TiO_2(100) surface have been investigated with high-resolution electron-energy-loss spectroscopy at a resolution of 10 meV. The energy-loss spectra are interpreted in terms of single- and multiple-phonon excitation of long-wavelength Fuchs-Kliewer surface optical modes. The observed frequencies are in good agreement with the predictions of dielectric response theory.

I. INTRODUCTION

There has been increasing interest in recent years in the use of high-resolution electron-energy-loss spectroscopy (EELS) to probe the vibrational properties of surfaces.[1] This technique involves the detection of quantum vibrational energy losses (or gains) due to the interaction of an incident, highly monochromatic electron beam of energy 1–20 eV with the surface phonons or with the molecular vibrations of an adsorbed species. Electron spectrometers with the necessary energy resolution of 5–10 meV (40–80 cm^{-1}), first employed in this area by Ibach and co-workers,[1] have recently been constructed by a number of research groups.

In this work we report an EELS study of the (100) surface of (rutile) titanium dioxide. Much of the current interest in this material stems from its use as a catalyst for the photoelectrolysis of water.[2] Recent photoemission studies of TiO_2 and $SrTiO_3$ have therefore focused on the interaction of H_2, O_2, and H_2O with the surfaces of these metal oxides.[3] In this study we find strong excitation of the surface optical phonons of TiO_2 by the incident electron beam. Chemisorption studies on oxide surfaces with EELS technique will thus have to contend with a prominent "background" due to substrate phonon and multiphonon excitations.

II. EXPERIMENTAL TECHNIQUES

The experiments were carried out with an ion-pumped stainless-steel vacuum system having a base pressure of less than 1×10^{-10} Torr. The system is equipped for high-resolution EELS, low-energy electron diffraction (LEED), Auger electron spectroscopy, ion sputtering, and quadrupole mass spectrometry. The sample manipulator provides for a 15-cm vertical translation from the LEED-Auger position to the EELS spectrometer as well as precision x-y sample positioning and rotation. The sample can be heated indirectly by a tungsten filament to 1300 K and liquid nitrogen cooled to 150 K.

The high-resolution EELS spectrometer is based on the electrostatic 127° cylindrical deflection analyzer (CDA) which has been used in several areas of electron spectroscopy. Our instrument was patterned after the spectrometer employed by Froitzheim and Ibach.[4] The reader is referred to the article by Roy and Carette[5] for general design principles of the CDA. The main sectors and lenses of our instrument were precision machined from OFHC copper and coated with colloidal graphite to reduce stray electron scattering. The spectrometer optics is rigidly held in place by machinable ceramic rods and spacers and is shielded with mu-metal and Helmholtz coils to achieve a residual magnetic field of less than 5 mG. The spectrometer is mounted on a stainless-steel base which allows rotation of the analyzer section through 114° in the plane of electron beam incidence.

In the experiments described below the spectrometer was operated at an energy resolution

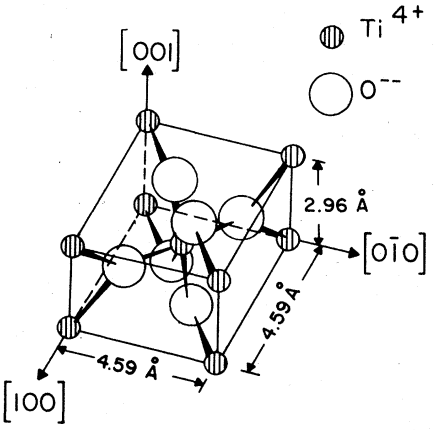

FIG. 1. Rutile structure.

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(FWHM) of 10 meV (~80 cm^{-1}). Optimal count rates were 10^4 Hz in the elastic beam from the TiO_2 (100) surface under study here, although we have obtained much higher count rates (10^5 Hz) on single-crystal metal surfaces. Background count rates were less than 10 Hz.

The single-crystal sample of TiO_2 with (100) orientation was prepared by standard metallographic techniques[6] before introduction to the vacuum system. In order to reduce charging effects from electron beams the sample was reduced by heating in vacuum to 650 K for 12 hours. The sample was routinely cleaned by several minutes of 500-eV argon-ion bombardment at a temperature of 650 K. Surface cleanliness was monitored by Auger electron spectroscopy.

III. RESULTS

The tetragonal unit cell of the rutile form of TiO_2 is depicted in Fig. 1. The (100) surface is known from previous LEED studies[6] to reconstruct to a (1×3) structure when annealed at 850–950 K and cooled to room temperature. For technical reasons the TiO_2 sample was annealed to only 650 K in the present work. Diffuse intensity in the region of the (1×3) diffraction spots was always evident and indicated a reconstructed, but partially disordered surface.

The EELS spectrum of TiO_2 (100) near room temperature is shown in Fig. 2. The spectrum was obtained on the specular reflection at a beam energy of 14 V and incidence angle of 50 degrees from the surface normal. Two principal loss features are observed at 436 and 766 cm^{-1}. Note that the 766-cm^{-1} loss is very strong and in some spectra was ~30% of the elastic beam intensity. There are also weaker and broader loss features observed in the 1000–3000 cm^{-1} range as well as energy-*gain* peaks at 436 and 766 cm^{-1}. A magnified spectrum of the higher-energy-loss region is shown in Fig. 3. If one considers the loss peaks at 436 cm^{-1} and 766 cm^{-1} to be associated with phonon frequencies ν_1 and ν_2, respectively, then all other observed spectral features can be attributed to multiple and combination phonon losses as listed in Table I. Moreover, the ratio of the intensities of the one-phonon energy-gain peaks to the one-phonon loss peaks agrees with the Boltzmann factor $\exp(-h\nu_i/k_B T)$ within experimental error.

The angular dependence of the ν_1 and ν_2 loss intensities away from specular reflection was also investigated and is shown in Fig. 4 for the ν_2 phonon. We note that both the elastic beam and phonon loss decay rapidly from the specular direction with angular half-width of ~2.5 degrees.

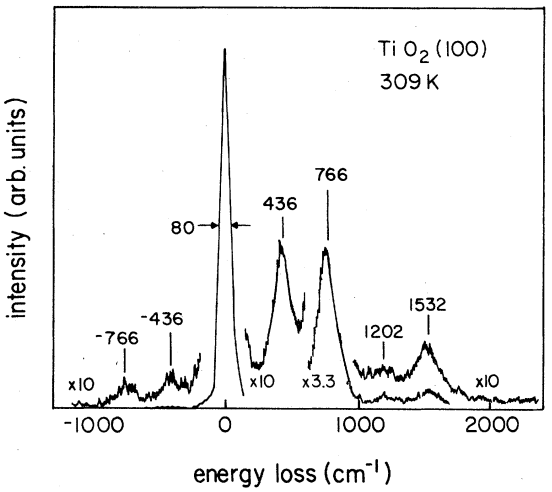

FIG. 2. Energy-loss spectrum of 14-eV electrons in specular reflection. Angle of incidence is 50 degrees.

Such a sharp angular behavior for the phonon loss is usually attributed to a long-range electron-dipole interaction rather than short-range "impact" scattering.[1] This angular dependence is similar to that observed in earlier studies on ZnO surfaces.[7]

The bulk optical phonon modes of TiO_2 are known from infrared[8] and neutron scattering[9] studies. The highest-frequency LO phonon mode at long wavelength occurs at 842 cm^{-1} in the neutron data and 806 cm^{-1} in the infrared measurements. In the present EELS study the 766-cm^{-1} phonon has been measured on a large number of spectra and the experimental error is ±8 cm^{-1}. Hence, we are led to identify this mode as a *surface* optical phonon mode rather than a bulk mode. This is a long-wavelength surface mode since the loss is confined to small momentum trans-

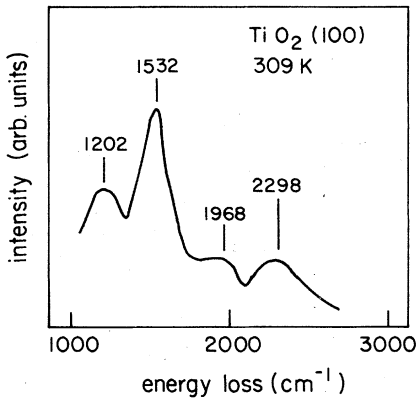

FIG. 3. Energy-loss spectrum as in Fig. 2 showing higher-energy region. Vertical lines indicate the predicted positions of multiphonon excitations of ν_1, ν_2 as in Table I.

TABLE I. Surface optical phonons on (rutile) TiO_2(100).

Frequency (cm^{-1})	Mode assignment
436[a] ± 8	ν_1
766[a] ± 8	ν_2
1202[b]	$\nu_1 + \nu_2$
1532[b]	$2\nu_2$
1968[b]	$\nu_1 + 2\nu_2$
2298[b]	$3\nu_2$

[a] Measured value of single-phonon excitation.
[b] Predicted multiple-phonon excitation. See Fig. 3 for comparison to experiment.

fer ($\Delta k_{\parallel} \approx 0$) parallel to the surface. The situation is not as clear for the second LO phonon branch since the neutron determination is 429 cm^{-1} and the infrared measurements give 458 cm^{-1}. The EELS mode ν_1 at 436 (± 8) cm^{-1} lies within experimental error of the neutron scattering value, but well outside of the infrared measurement. Theoretical calculations discussed below, however, suggest that the ν_1 mode is also a surface optical phonon.

IV. DISCUSSION

Surface optical (SO) phonon modes at long wavelength were first treated theoretically by Fuchs and Kliewer[10] and were detected experimentally on ZnO.[7] Their basic properties are entirely

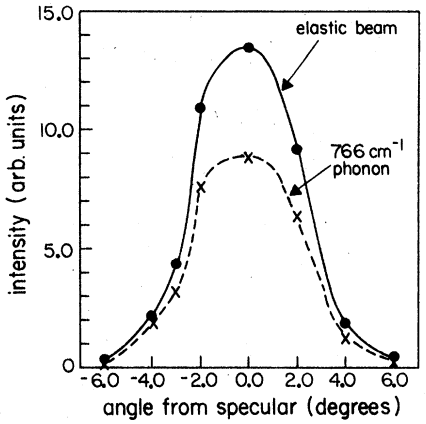

FIG. 4. Intensity versus angle from specular beam direction for 14-eV electrons on TiO_2(100), $T = 309$ K. The phonon loss intensity is multiplied by 2.

classical in nature and may be derived from Maxwell's equations with appropriate surface boundary conditions.[11] In the case of a semi-finite crystal the SO modes obey the eigenvalue equation

$$\mathrm{Re}\,\epsilon_n(\omega) = -1, \tag{1}$$

where $\epsilon_n(\omega)$ is the component of the dielectric function normal to the surface. One important aspect of these modes at long wavelength is that their penetration depth is hundreds of angstroms, and they are therefore insensitive to specific

TABLE II. Summary of bulk and surface optical phonon frequencies (cm^{-1}) for (rutile) TiO_2.

				Surface modes		
Infrared active bulk modes	(a)	(b)	Theory (c)	(d)	(e)	Experiment (100) surface (f)
Γ_1^-(TO)	173	167				
Γ_5^+(TO)	189	183	SO(xy)	374	373	Not observed
Γ_5^+(LO)	375	373	SO(xz)	375	374	
Γ_5^+(TO)	388	388				
Γ_5^+(LO)	429	458	SO(xy)	426	455	(ν_1) 436 ± 8
			SO(xz)	429	458	
Γ_5^+(TO)	494	500				
Γ_1^-(LO)	812	811	SO(xy)	797	757	(ν_2) 766 ± 8
Γ_5^+(LO)	842	806	SO(xz)	781	761	

[a] Neutron scattering data from Ref. 9.
[b] Infrared data from Ref. 8.
[c] Plane of polarization of electric field in surface mode, x = [100], y = [010], z = [001].
[d] Calculation from Ref. 12 using parameters from neutron data.
[e] Calculation from Ref. 12 using parameters from infrared data.
[f] EELS data of present work.

surface features on the monolayer scale.

Mahan has recently carried out a surface phonon calculation for TiO_2 (100).[12] The basic approach involves representing the dielectric function by a set of classical oscillators

$$\epsilon_n(\omega) = \epsilon_n(\infty) + \sum_{j=1}^{3} \frac{a_j}{1 - \omega^2/\omega_j^2}, \quad (2)$$

where the parameters a_j are determined from the conditions that $\epsilon = \infty$ for the TO bulk modes and $\epsilon = 0$ for the LO bulk modes. The surface mode frequencies predicted by this procedure are given in Table II along with a summary of the surface and bulk data. The calculations were made using both the infrared[8] and neutron data[9] sets of bulk parameters. The predicted frequencies from the two calculations tend to closely bracket each of the EELS experimental results (ν_1, ν_2). The calculation correctly predicts the ν_1 surface mode to lie close to the Γ_5^+ bulk LO phonon and the ν_2 surface mode to lie considerably below the corresponding Γ_5^+ mode. The calculation further estimates the intensities of the 374 cm^{-1} and 426 cm^{-1} SO modes to be 1% and 3%, respectively, of the SO mode at 797 cm^{-1}. This explains why the 374-cm^{-1} mode is not apparent in the EELS spectra but greatly underestimates the observed ν_1 intensity which is approximately 25% of ν_2. However, given the inherent simplicity and lack of free parameters in the calculation the overall agreement is encouraging.

V. CONCLUSIONS

We have presented experimental evidence for strong excitation of surface optical phonons on TiO_2 (100) by slow electron scattering. The observed frequencies are in rather good agreement with a calculation of Fuchs-Kliewer-type SO phonons by Mahan. This holds in spite of the known local surface reconstruction of TiO_2 (100) because of the insensitivity of these long-wavelength modes to specific surface properties. Bulk phonon excitations were not observed in the experiments apparently because of the short penetration depth of the electrons at these low impact energies.[13] The qualitative features of these results are similar to those reported previously on ZnO[7].

Finally, we note that the surface phonons on TiO_2 and other compound semiconductors will have important implications for chemisorption studies by high-resolution EELS on these materials. The presence of numerous, relatively strong multiple phonon bands extending to ~3000 cm^{-1} will hinder the detection of many adsorbate vibrations on these surfaces. The $2\nu_2$ peak on TiO_2 (100) at 1532 cm^{-1}, for example, has an intensity of ~5% of the elastic peak in many spectra we have recorded. This peak would be expected to obscure the 1600 cm^{-1} bending mode for chemisorbed H_2O on TiO_2 surfaces. Improved energy resolution will alleviate this problem.

ACKNOWLEDGMENTS

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[13]The Γ_1^- bulk modes would not be excited in any case since these modes have no dipole moment normal to the (100) surface.