

# High-resolution electron-energy-loss spectroscopy of vanadium and vanadium oxide thin films on TiO<sub>2</sub>(110)-(1×1)

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Vanadium thin films have been grown on the TiO<sub>2</sub>(110) rutile surface in UHV up to 4 monolayers at room temperature. These thin films have been studied by Auger electron spectroscopy and high-resolution electron-energy-loss spectroscopy (HREELS). Observation of one break in the Auger peak-to-peak ratio plotted as a function of deposition time indicates that the first monolayer formed a two-dimensional overlayer by V atoms. The growth mode of metal V at a monolayer coverage was further confirmed by HREELS results, which showed a rapid decrease of the TiO<sub>2</sub> phonons. Subsequently, the vanadium islands were oxidized to VO<sub>2</sub>, and the obtained HREELS spectra support the growth of a rutile VO<sub>2</sub> structure in the semiconducting phase. The intensity change and energy shift of the surface phonons are explained by consideration of the surface structure and charge transfer between VO<sub>2</sub> overlayers and TiO<sub>2</sub>(110).

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## I. INTRODUCTION

Metal and metal-oxide particles supported on metal oxide have been widely used as catalysts and gas sensors.<sup>1</sup> Among the metal oxides, the TiO<sub>2</sub>(110) surface has become a model for surface studies during the last decade. Recent studies on TiO<sub>2</sub>(110), using different methods under ultrahigh vacuum (UHV) conditions such as low-energy ion scattering (LEIS), x-ray photon spectroscopy (XPS), and Fourier-transform reflection absorption infrared spectroscopy (FT-RAIRS), low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), atomic force microscopy (AFM), and high-resolution electron-energy-loss spectroscopy (HREELS), have begun to provide some interesting information.<sup>1-5</sup> Oxide-oxide systems,<sup>6</sup> in contrast to metal-oxide systems, are less investigated, although they are equally important to the catalyst and sensor applications.

VO<sub>2</sub> is one of the most interesting oxides both because it exhibits a strong metal to semiconductor phase transition (MSPT) as a function of temperature and because it is a lower oxide state to the very important vanadium oxide catalyst V<sub>2</sub>O<sub>5</sub>.<sup>1</sup> In fact, it is thought that VO<sub>2</sub> may be the active species in titania-supported vanadia catalysts. The MSPT temperature for crystalline VO<sub>2</sub> is around  $T_c = 340$  K. Above this temperature, VO<sub>2</sub> is metallic with a rutile structure, while below  $T_c$  it is a semiconductor with an optical band gap of 0.7 eV. Since there are some difficulties in making good quality single crystals, it is worthwhile to use the pseudomorphic VO<sub>2</sub> thin film on TiO<sub>2</sub> as a mimic for the native surface. In addition, the two oxides show a quite different band gap (the TiO<sub>2</sub> band gap is about 3.1 eV), while having the same rutile structure.<sup>1</sup> This system therefore can be used in synthesizing multiple quantum wells with interesting properties obtained through “band designing.”

Recently, the MSPT and the electronic structure of different surfaces of the single-crystal VO<sub>2</sub> were characterized by Goering *et al.*<sup>7</sup> using LEED and photoemission and by Kur-

maev *et al.*<sup>8</sup> using XPS and x-ray emission spectroscopy (XES). In the meantime, thin layers of VO<sub>2</sub> pseudomorphic to the substrate with both short- and long-range orders have been obtained on TiO<sub>2</sub>(110) by Sambri *et al.* and by our group.<sup>6,9,10</sup> The studies of the electron structure and surface morphology indicate that the VO<sub>2</sub> thin films have a rutile structure in a semiconductive phase at room temperature (RT), different from the rutile structure in a metallic phase for the single crystal at temperature  $T > 340$  K. This may add more interest for VO<sub>2</sub> thin films since the surface structure is equally important to the stoichiometry for catalysts and sensors.

The stoichiometry of vanadia seems sensitive to the ambient atmosphere and temperature. Evaporation of vanadium metal onto TiO<sub>2</sub>(110) in an oxygen ambient atmosphere results in the growth of V<sub>2</sub>O<sub>3</sub> overlayers. This was verified by several groups<sup>6,11-14</sup> using Auger electron spectroscopy (AES), XPS, LEED, near-edge x-ray-absorption fine-structure spectroscopy (NEXAFS), HREELS and x-ray photoelectron diffraction (XPD) as the methods of investigation. On the other hand, by depositing V onto TiO<sub>2</sub>(110) in UHV, followed by annealing at 423 K for 2 min in  $2 \times 10^{-6}$  mbar O<sub>2</sub>, epitaxial VO<sub>2</sub> layers were grown on the TiO<sub>2</sub>(110) surface up to thickness of 5 monolayers (MLs).<sup>9</sup> However, the uncertainty of stoichiometry of vanadia films remains, since the peaks in XPS spectra of VO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub> are close to each other.<sup>15,16</sup> In this paper we synthesize the VO<sub>2</sub> thin films following the previously described method.<sup>9</sup> HREELS was used to reveal the change of fundamental surface (Fuchs-Kliwer) phonons, providing some information on the surface structure. HREELS is a useful method to probe the adsorption species and their geometry on surfaces during the gas-solid interaction.<sup>17</sup> Thus HREELS spectra of VO<sub>2</sub> films may provide a basis to investigate their chemical nature towards gases, which is important in catalyst and sensor applications. We report our HREELS spectra on V/TiO<sub>2</sub>(110) in this paper in comparison with the VO<sub>2</sub>/TiO<sub>2</sub> system and other metal/TiO<sub>2</sub>(110) systems.

## II. EXPERIMENT

The experiments were carried out in a UHV chamber which has been described previously.<sup>18</sup> Briefly, the chamber is equipped with a HREELS instrument (ELS-22, Leybold-Heraeus GmbH), an AES, and a LEED system (Perkin-Elmer Inc.). The HREELS instrument was operated at a base pressure of  $2 \times 10^{-10}$  mbar. Spectra were acquired by using a primary beam energy of 2–5 eV and an incident angle of  $80^\circ$  with respect to the surface normal. A typical elastic peak count rate after specular reflection from clean stoichiometric  $\text{TiO}_2(110)$  was about 12 000 cps with a full width at half maximum (FWHM) in the range of 9–13 meV. The AES's were recorded using a cylindrical mirror analyzer (CMA) and a lock-in amplifier and were recorded in the  $dN/dE$  mode. The intensities of AES's were measured using the peak-to-peak ratio for each individual peak.

The  $\text{TiO}_2$  sample (Pi-Kem Ltd.) was cut (to 0.25 mm) and polished to within  $0.5^\circ$  of the (110) plane, as determined by Laue diffraction. It was cleaned by  $\text{Ar}^+$  sputtering at energies lower than 1 keV, followed by annealing at 863 K in  $2 \times 10^{-6}$  mbar of  $\text{O}_2$  (99.9998% purity, Hede Nielsen A/S) for 30 min and cooling down to room temperature in the same oxygen atmosphere in an attempt to restore the surface stoichiometry. This procedure was repeated until a very sharp  $1 \times 1$  LEED pattern was seen. The cleanness of the sample was further checked by AES.

Pure vanadium (99.8% purity, Goodfellow Ltd.) was deposited onto  $\text{TiO}_2(110)$  at room temperature (RT) using an electron beam evaporator (Caburn MDC Ltd., model EB90). The deposition rate was estimated to be  $\sim 0.04$  ML/min as determined by AES calibration. An ordered vanadium oxide  $\text{VO}_2$  film was obtained through steps of 0.2-ML metal V depositions onto the sample surface followed by annealing at  $\sim 423$  K for 2 min in  $2 \times 10^{-6}$  mbar  $\text{O}_2$ , as described in our previous study.<sup>10</sup> At each step, the  $(1 \times 1)$  LEED pattern disappears during V deposition and it is recovered after annealing in  $\text{O}_2$ . This recipe was proposed by Sambri *et al.*<sup>9</sup> from PES and XPD measurements. However, the overall LEED pattern became blurred with the growth of  $\text{VO}_2$ .  $\text{VO}_2$  ultrathin films were grown up to a thickness of 19.2 ML's. All the data acquisitions, both for AES and HREELS, were performed at room temperature unless specified otherwise.

## III. RESULTS AND DISCUSSION

### A. Vanadium films

Figure 1 shows the data for AES growth curves obtained for deposition of vanadium upon  $\text{TiO}_2(110)$  at RT. The AES intensities (peak-to-peak ratio) of the Ti (LMM, 390 eV), Ti (LMM, 421 eV), V (LMM, 440 eV), V (LMM, 475 eV), and O (KLL, 510 eV) are plotted as a function of nominal V coverage, while the deposition rate of vanadium is maintained at the same level. There is an overlap between the O (KLL 510 eV) and V (LMM, 511 eV) peaks. The intensities of the O (KLL 510 eV) peaks are therefore corrected by subtracting the intensities of the V (LMM, 511 eV) peaks, which was deduced by considering the sensitivities of different V LMM peaks (e.g., 440, 475, and 511 eV) in the stan-

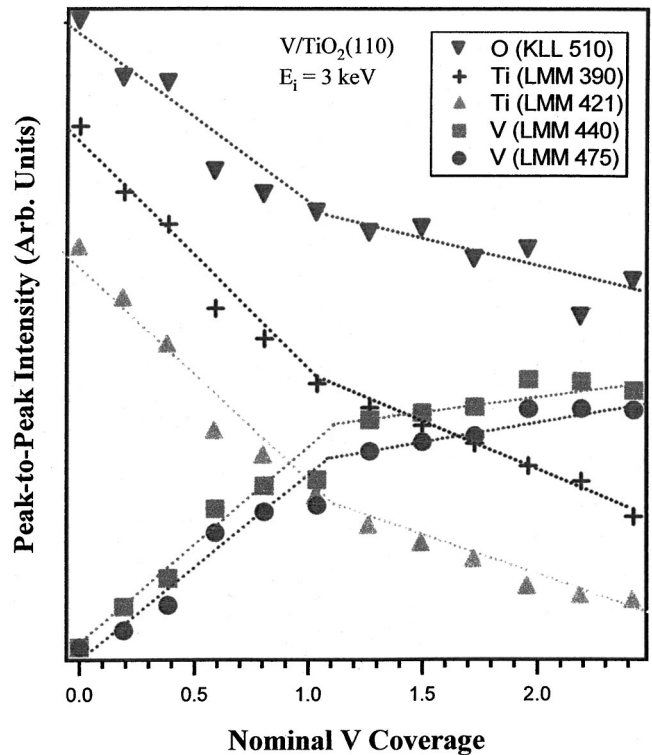


FIG. 1. Peak-to-peak intensities of Auger spectra for Ti (LMM, 390 eV), Ti (LMM, 421 eV), V (LMM, 440 eV), V (LMM, 475 eV) and O (KLL, 510 eV) plotted as a function of nominal V coverage. The intensities of O (KLL, 510 eV) peaks are corrected by subtracting the intensities of V (LMM, 511 eV) peaks, which was deduced by considering sensitivities of different V LMM peaks (e.g., 440, 475, and 511 eV) in the standard Auger spectra.<sup>19</sup> The deposition rate is maintained constant at  $\sim 0.04$  ML/min at RT.

dard Auger spectra.<sup>19</sup> No visible shift is observed for all the peaks. As seen in this figure, straight lines can be fitted to the data for an initial growth, and clear breakpoints are observed for all Ti, V, and O intensities at the same coverage point. We define this point as 1 monolayer (ML). The number of atoms of 1-ML V is roughly equal to that of surface Ti atoms, which is  $5.06 \times 10^{14}$  atoms/cm<sup>2</sup>. In this kind of plot, one expects a straight line during growth of the first layer and a break at completion of this layer<sup>20</sup> if we assume a constant sticking coefficient of vanadium on  $\text{TiO}_2(110)$ . The absence of a break for the further deposition (not shown in Fig. 1) suggests a Stranski-Krastanov-type growth mode for vanadium on  $\text{TiO}_2(110)$ . However, the relatively large scatters in it prevents a more precise explanation.

$\text{TiO}_2(110)$ , the most thermodynamically stable surface of rutile  $\text{TiO}_2$ , has three surface phonons at  $\sim 47(S_1)$ ,  $55(S_2)$ , and  $95 \text{ meV}(S_3)$ ,<sup>21–23</sup> respectively. Figure 2 shows a HREELS spectrum of clean  $\text{TiO}_2(110)-(1 \times 1)$  along with a result calculated from the dielectric theory.<sup>24</sup> The spectrum shows two fundamental surface phonons at  $55 \text{ meV}(S_2)$  and  $94.6 \text{ meV}(S_3)$ , respectively. The other surface phonon mode ( $S_1$ ) is not resolved from  $S_2$  but is indicated by the asymmetric nature of the 55-meV loss. The calculation was performed using the same method as for  $\alpha\text{-Al}_2\text{O}_3(0001)$  by Liehr *et al.*<sup>25</sup> In Fig. 2, the discrepancies in loss energy, be-

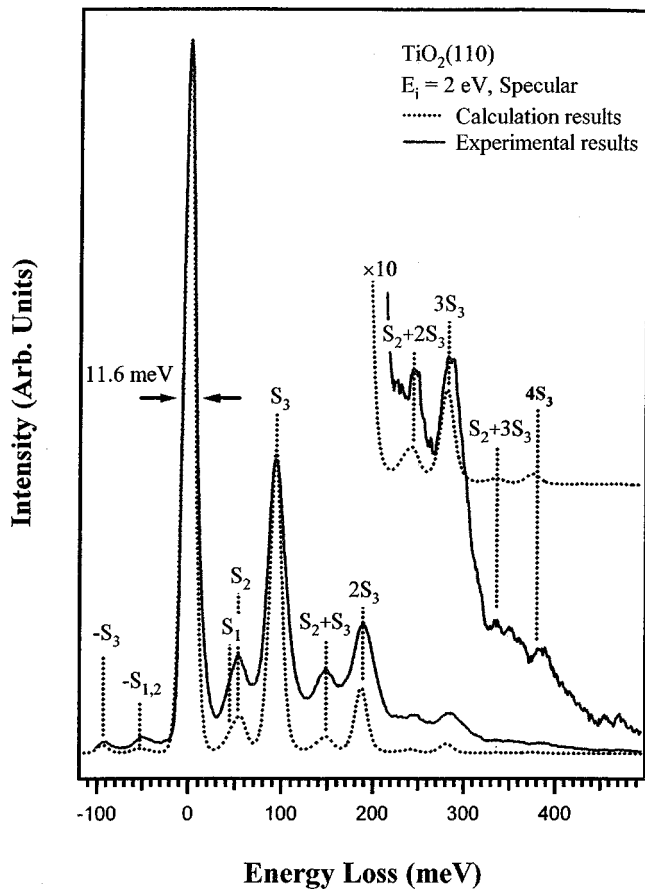


FIG. 2. HREELS spectra from a clean  $\text{TiO}_2(110)$  surface. Comparison of the experimental result with a calculation result based upon the dielectric theory. The appropriate normalization results from the conservation of the total number of particles. See the text for details.

tween the experiments and calculations, for the fundamental surface phonons and their multiple combinations, are small. The results also agree very well with previous HREELS studies on  $\text{TiO}_2(110)$ .<sup>21-23</sup>

A set of HREELS spectra recorded as a function of vanadium coverage is shown in Fig. 3. In this figure, the fundamental optical-phonon modes experience a decrease in intensity in line with an increase in the vanadium coverage. These changes are shown in Fig. 4. The attenuation of the surface phonons is a consequence of the screening of the coupling of the electric field of the incident electron with the oscillating dipoles of the  $\text{TiO}_2$  surface phonons by the vanadium overlayers. Previous HREELS studies on metal/oxide systems have revealed a similar type of screening interaction by metal overlayers, for example,  $\text{Pt/ZnO}(0001)\text{-Zn}$ ,<sup>26</sup>  $\text{Pt/ZnO}(000\bar{1})\text{-O}$ ,<sup>26</sup>  $\text{Na/Cr}_2\text{O}_3(111)/\text{Cr}(110)$ ,<sup>27</sup>  $\text{K/TiO}_2(100)$ ,<sup>28</sup>  $\text{Pd/TiO}_2(110)$ ,<sup>29</sup> and  $\text{Cu/ZnO}(000\bar{1})\text{-O}$ .<sup>30</sup> Recent calculations predicted<sup>26,29</sup> that the slope of the curve of intensity vs metal coverage decreases with coverage for the fundamental surface phonons and that this could be employed to monitor the growth mode of the metal overlayers on the oxide substrate. The more rapid the decrease in intensity of surface phonons, the more area of the surface is cov-

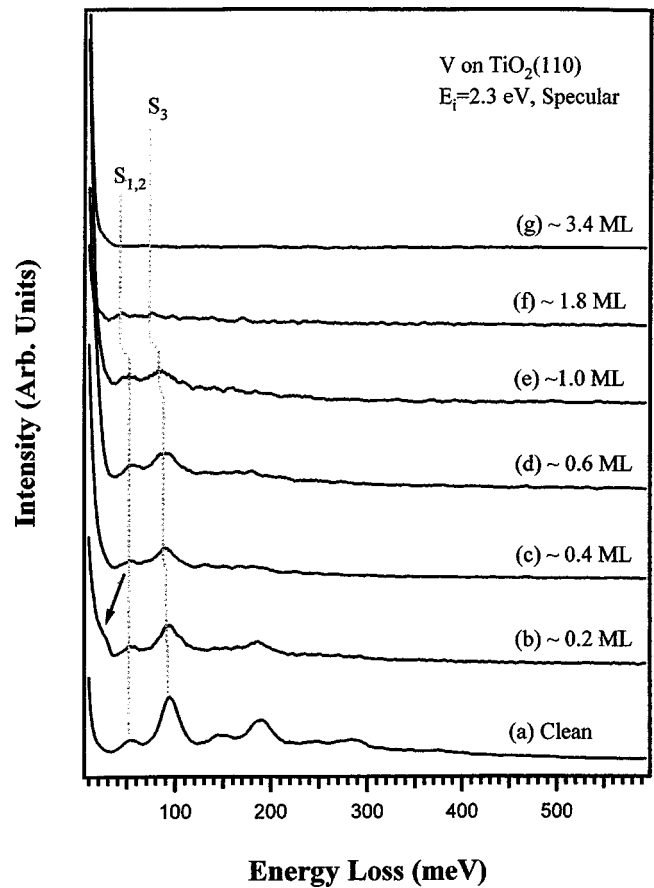


FIG. 3. HREELS spectra of  $\text{V/TiO}_2(110)\text{-}1\times 1$  as a function of vanadium coverage at RT. The electrons strike the surface at a specular geometry ( $\theta_i = \theta_s = 80^\circ$ ). The spectra are normalized to the elastic peak.

ered by the metal overlayer. In our study, a complete attenuation of the phonon modes at  $\sim 1$  ML suggests a two-dimensional growth of vanadium on  $\text{TiO}_2(110)$ . The attenuation behavior is similar to two-dimensional growth systems such as  $\text{Pt/ZnO}(0001)\text{-Zn}$  (Ref. 26) or  $\text{Ag}$  on  $\text{GaAs}$  at 170 K,<sup>31</sup> but in contrast to the three-dimensional island growth systems such as  $\text{Pd/TiO}_2(110)$  (Ref. 29) or  $\text{Cu/ZnO}(000\bar{1})\text{-O}$ .<sup>30</sup>

The loss energy shift of the phonons and their multiple losses with vanadium coverages are also observed in our experiment (Fig. 5). In earlier works these changes were understood simply in terms of a modification of the dielectric function at the surface.<sup>26,32-34</sup> Charge transfer between the metal overlayer and the  $\text{TiO}_2$  substrate causes the modification of the dielectric function; therefore it causes intensity change and energy shift of the surface phonons. There will be a downward shift in energy for the three surface phonons if the charge transfers from the V overlayer to the  $\text{TiO}_2$  substrate.<sup>26,33,34</sup> The largest change will be for the high-energy  $S_3$  mode. Our observation agrees well with these conclusions. As discussed there should be two contributions for the phonon peaks, one for the V-covered and one for V-free  $\text{TiO}_2$  surface regions. However, they are difficult to resolve from each other due to the broad nature of the phonon peaks. Only shift can be observed in the HREELS spectra.

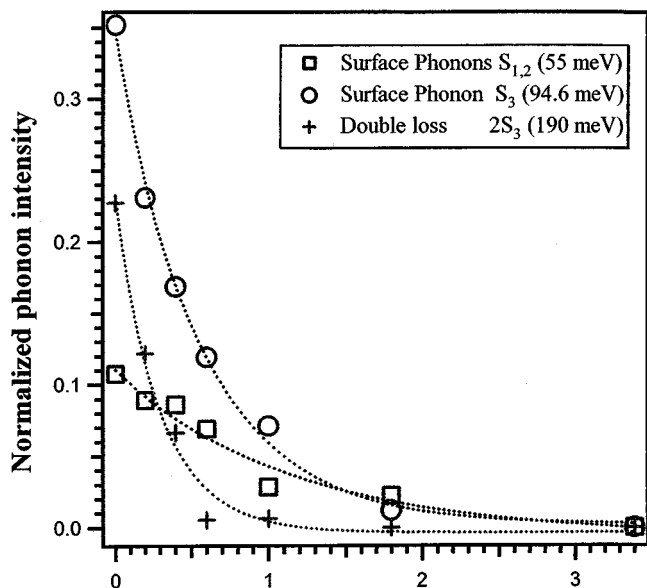


FIG. 4. The intensity of surface phonons as a function of vanadium coverage. The circles, squares, and crosses are experimental data. The lines are guides to the eye only. The figures in the parentheses are loss energy from the clean  $\text{TiO}_2(110)-1 \times 1$  surface.

There is a drastic change in intensities for the elastic peak when the vanadium was deposited onto the surface. In Fig. 6, the change was plotted as a function of vanadium coverage with identical spectrometer parameters. In the framework of dielectric theory, the electron is treated as a classical particle; the discussion of the interaction between the incident electron and the surface can be carried out without considering a

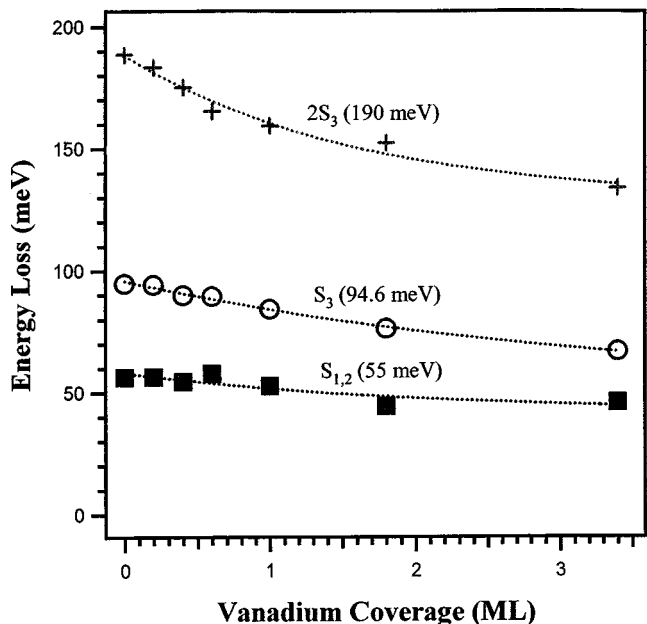


FIG. 5. The loss energy of surface phonons as a function of vanadium coverage. The circles, squares, and crosses are experimental data. The lines are guides to the eye only. The figures in the parentheses are loss energies from the clean  $\text{TiO}_2(110)-1 \times 1$  surface.

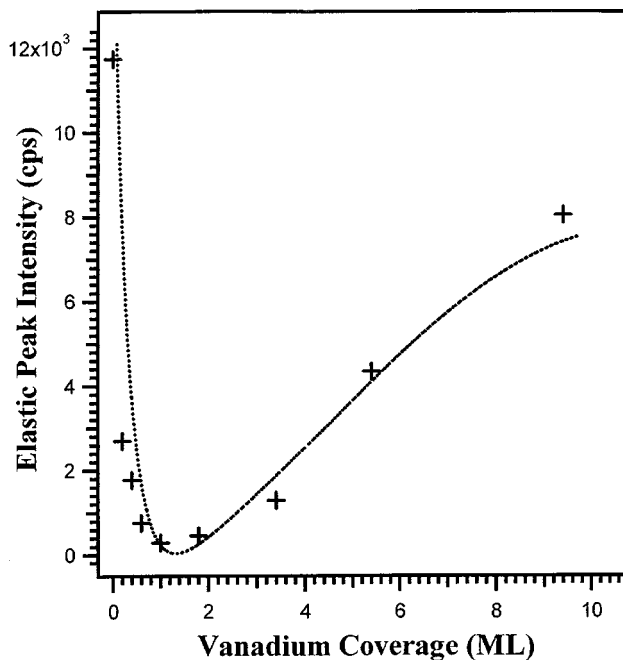


FIG. 6. The intensity of the elastic peak as a function of vanadium coverage. The line is a guide to the eye only. The crosses are experimental data.

fully microscopic treatment. According to this approach, the elastic peak of the spectra arises from the noninteracting electrons scattering from the surface. The inhomogeneous scattering from a rough surface will inevitably decrease the specularly of this scattering. The decrease in intensity of the elastic peak is therefore good evidence for surface roughening when metal is deposited on  $\text{TiO}_2(110)$ . Such a phenomenon has been observed in previous studies of thin metal films on oxide surfaces such as  $\text{Pt/ZnO}(000\bar{1})\text{-O}$ ,<sup>26</sup>  $\text{Pt/ZnO}(0001)\text{-Zn}$ ,<sup>26</sup>  $\text{Na/Cr}_2\text{O}_3(111)/\text{Cr}(110)$ ,<sup>27</sup>  $\text{K/TiO}_2(100)$ ,<sup>28</sup>  $\text{Pd/TiO}_2(110)$ ,<sup>29</sup>  $\text{Cu/ZnO}(000\bar{1})\text{-O}$ ,<sup>30</sup> and  $\text{Pd/SiO}_2$ .<sup>35</sup>

The first overlayer is disordered, as evidenced by the LEED pattern, which gradually disappeared after depositing 1 ML of V.<sup>36</sup> The elastic peak is presumably originating from the exposed well-ordered substrate at a submonolayer stage.<sup>31</sup> So the two-dimensional (2D) growth mode will cause more reduction in intensities of the elastic peak than the 3D growth mode. For example, silver forms a uniform overlayer on  $\text{GaAs}(100)$  at 170 K and reduces the elastic peak intensity by  $\sim 100$  times, while it forms 3D islands at 300 K and reduces the elastic peak intensity by  $\sim 10$  times.<sup>31</sup> The same conclusion can also be made by comparing  $\text{Pt/ZnO}(000\bar{1})\text{-O}$  and  $\text{Pt/ZnO}(0001)\text{-Zn}$  systems.<sup>26</sup> In our experiments the elastic peak is reduced by a factor of approximately 100 by the vanadium overlayer, indicating a well-covered surface of vanadium metal. This is in contrast with a previous study on the same  $\text{TiO}_2(110)$  substrate in which the elastic peak was reduced by a factor of approximately 30 by the 3D palladium island growth (combined with a 2D island growth at coverage below 0.2 ML).<sup>29</sup>

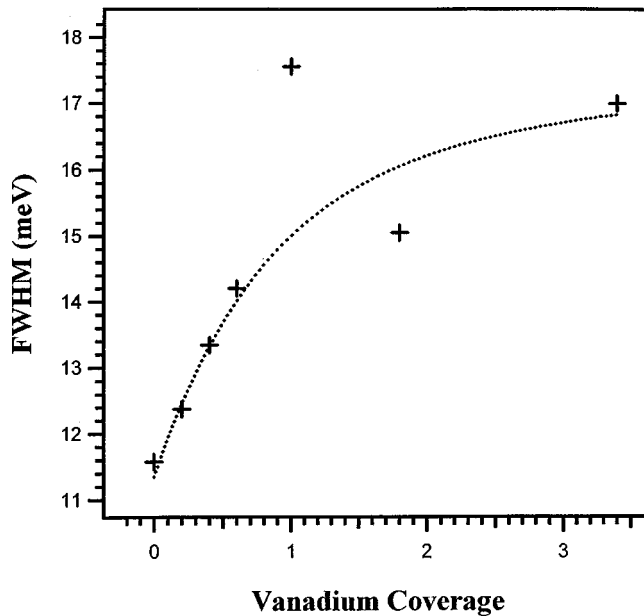


FIG. 7. The width of the elastic peak as a function of vanadium coverage. The crosses are experimental data. The line is a guide to the eye with no free-carrier effect on the surface. See text for details.

Whereas the two-dimensional island is thought to be rough (no LEED pattern observed<sup>36</sup>), the recovery of the elastic peak intensity with increased vanadium coverage can be understood as increased scattering from larger metal islands (>5 nm in diameter) which are formed by coalescing small islands and which have a smooth top surface. In many cases, the large metal islands have (111)-like structures which can be observed by LEED.<sup>4</sup> The elastic peak intensity starts to recover at a higher coverage (~2.0 ML's) for V/TiO<sub>2</sub>(110) in comparison with Pd/TiO<sub>2</sub>(110), where the elastic peak starts to increase at ~0.5 ML.<sup>29</sup> This perhaps suggests a different surface structure (island sizes and locations, etc.) for the two systems.

If the interaction between the metal overlayer and the substrate is weak, a free-electron carrier would be created at monolayer coverage. The free carrier would give rise to a plasmonlike mode ranging from zero to higher energies. The elastic peak would then be broadened asymmetrically toward the positive side. For vanadium on TiO<sub>2</sub>(110), however, the trend to broaden the elastic peak is rather small. At ~1.0 ML there is a factor of about 0.5 of increase in width for the elastic peak, as shown in Fig. 7. The reason lies probably in the strong interaction between V and the TiO<sub>2</sub>(110) substrate, unlike the weak interaction system Ag/GaAs(100) at 170 K.<sup>31</sup> The monolayer V atoms probably have chemical bonds with surface O and therefore cannot carry free electrons. The support for this assessment comes from the energy shift of surface phonons during the deposition of vanadium, which suggests a charge transfer from V to TiO<sub>2</sub>(110). A similar shift was not observed for weak interaction systems such as Ag/GaAs at 170 K.<sup>31</sup>

At a coverage of 0.2-ML V [Fig. 3(b)] there is a distinct shoulder (marked by the arrow in Fig. 3) near the elastic

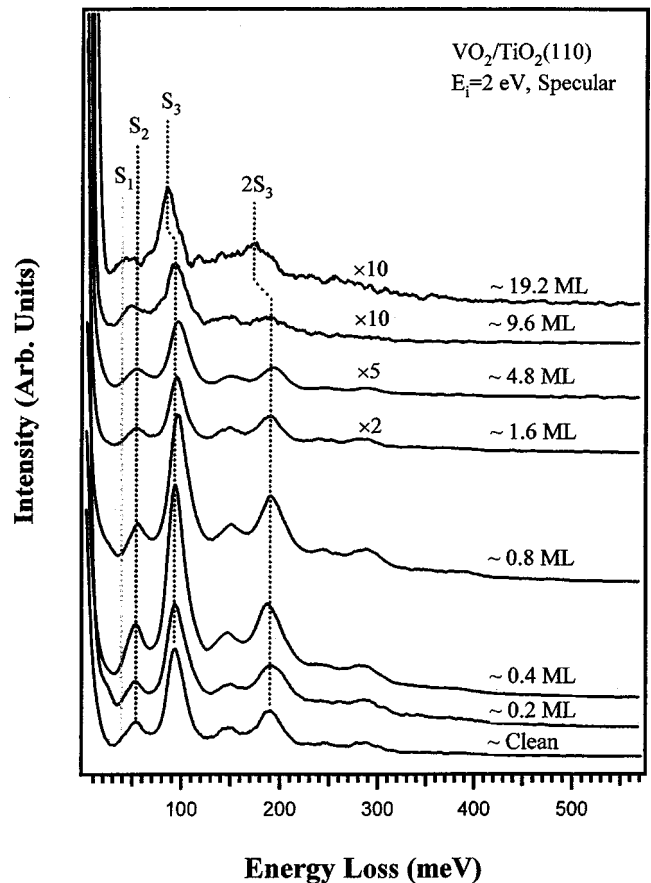


FIG. 8. HREELS spectra of VO<sub>2</sub>/TiO<sub>2</sub>(110)-1×1 as a function of VO<sub>2</sub> coverage at RT. The electrons strike the surface at a specular geometry ( $\theta_i = \theta_s = 80^\circ$ ). The spectra are normalized to the elastic peak.

peak. The assignment for this feature is not clear, although a similar phenomenon has been observed for the Cu/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) system.<sup>18</sup>

## B. VO<sub>2</sub> films

A set of HREELS spectra recorded as a function of VO<sub>2</sub> coverage is shown in Fig. 8. The shapes of the spectra as a function of VO<sub>2</sub> coverages up to 4 ML's are rather similar to those from a spectrum of clean TiO<sub>2</sub>(110). There is no additional peak for even a thick (~9.6 ML) VO<sub>2</sub> overlayer, indicating that the VO<sub>2</sub> films have a structure similar to the substrate.

To our knowledge there is no HREELS spectrum reported for the VO<sub>2</sub> single crystal. Previously obtained HREELS spectra from V<sub>2</sub>O<sub>5</sub>(001) showed nine fundamental surface phonon losses with the most pronounced loss at 73 meV.<sup>37</sup> In another study on V<sub>6</sub>O<sub>13</sub>(001), seven fundamental phonon losses were observed, with the largest intensity at an energy loss of 70 meV.<sup>38</sup> A recent HREELS study, reported by Guo *et al.* on V<sub>2</sub>O<sub>3</sub> films on Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>(110),<sup>13,39</sup> exhibited two energy losses, at ~48 and ~79 meV.

The stoichiometry of vanadium oxides films on ordered metal-oxide surfaces has been shown to be strongly dependent on oxygen pressure and temperature.<sup>40-42</sup> Thus VO<sub>2</sub> has

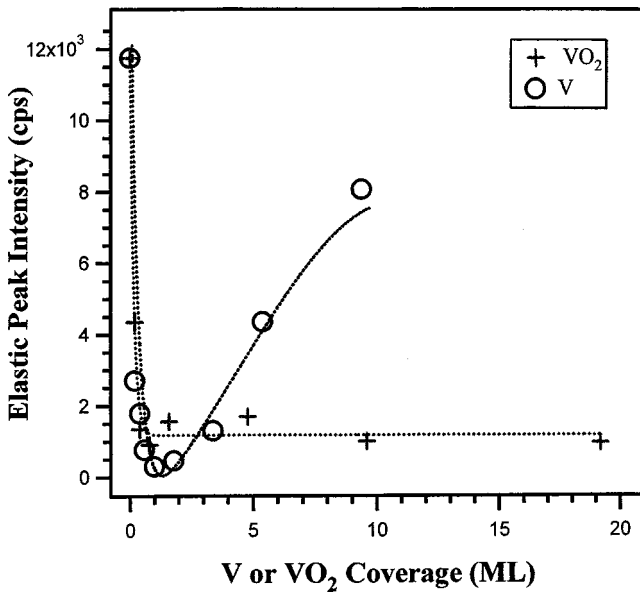


FIG. 9. A comparison of intensities of the elastic peak from V and VO<sub>2</sub> films on TiO<sub>2</sub>(110)-1×1. The lines are guides to the eye only.

been grown on SiO<sub>2</sub>/Si,<sup>40</sup> and on the (0001) and (10 $\bar{1}$ 0) surfaces of sapphire.<sup>41</sup> V<sub>2</sub>O<sub>3</sub> films, on the other hand, have been grown on TiO<sub>2</sub>(110) and Al<sub>2</sub>O<sub>3</sub>/Mo(110) by depositing vanadium in a lower oxygen background.<sup>6,11–14,39</sup> The growth of VO<sub>2</sub> on TiO<sub>2</sub>(110) by depositing vanadium metal in vacuum followed by annealing in 2×10<sup>-6</sup>-mbar oxygen atmosphere was supported by LEED, XPD, and PES<sup>9,10</sup> with a binding energy (BE) of 516.5 eV for V 2p<sub>3/2</sub>, in agreement with the spectra from the single-crystal VO<sub>2</sub>.<sup>15</sup> By contrast, the BE for V 2p<sub>3/2</sub> of V<sub>2</sub>O<sub>3</sub> at RT is 515.7 eV.<sup>15</sup> It appears that the structure and stoichiometry are affected drastically by the background gases. As vanadium metal is active towards oxygen, V atoms could react with background oxygen before they reach the TiO<sub>2</sub>(110) substrate. The obvious influence of background gases on the metal nucleation and growth was also observed previously.<sup>43</sup>

In both this study and previous studies,<sup>9,10</sup> the 1×1LEED pattern of VO<sub>2</sub> remains the same as the pattern for the substrate TiO<sub>2</sub>(110), without even lateral mismatch, up to several monolayers, although the overall brightness of the LEED pattern gradually decreases. To our knowledge, neither STM nor AFM image have been published for the VO<sub>2</sub> epitaxy on rutile TiO<sub>2</sub>(110), perhaps because the rutile-structured VO<sub>2</sub> film so closely matches the substrate that it would be difficult to distinguish between them.

XPD and SRPES studies also suggested that the VO<sub>2</sub> thin film has a rutile structure in a semiconducting phase.<sup>9,10</sup> The elastic peak intensity changes with the VO<sub>2</sub> coverages are plotted in Fig. 9 in comparison with that of V overlayers. Unlike V on TiO<sub>2</sub>(110), there is an initial decrease (~15 times) of the intensity of the elastic peak, and no recovery after that, indicating a similar roughness during the VO<sub>2</sub> growth.

For the intensity change and energy shift of surface phonons, it is convenient to divide the data into three parts as

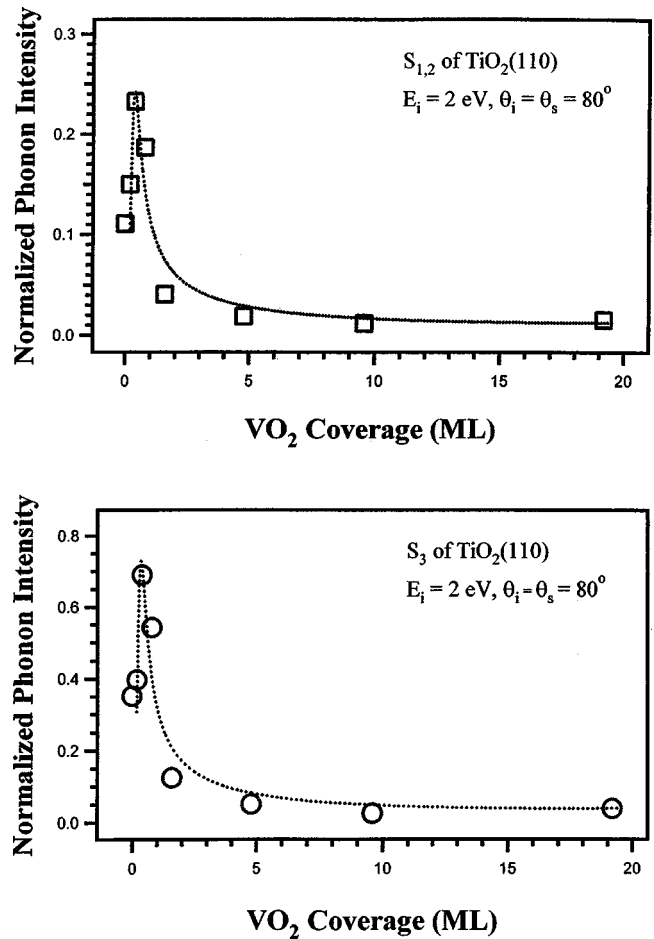


FIG. 10. The intensity of surface phonons as a function of VO<sub>2</sub> coverage. The squares and circles are experimental data. The lines are guides to the eye only.

a function of VO<sub>2</sub> coverages: low coverages (<2 ML's) with the substrate structure strongly involved, medium coverages (~10 ML's) with the rutile VO<sub>2</sub> dominating, and high coverages (~20 ML's) with the defective structure dominating. At low VO<sub>2</sub> coverages (<2.0 ML's), the HREELS spectra are still dominated by TiO<sub>2</sub>(110) surface phonons. As we discussed earlier, the intensities of substrate surface phonons can be quenched either by the formation of a metallic free carrier or by the charge transfer from the overlayer to the substrate (for S<sub>3</sub>). In this study the surface phonons increase in intensity at VO<sub>2</sub> coverages below 1 ML, as shown in Fig. 10. In line with the enhancement of surface phonons, an upward shift in energy for the surface phonons is observed. At a VO<sub>2</sub> coverage of 0.8 ML, S<sub>3</sub> was observed at 97 meV, 2.4 meV higher than for clean TiO<sub>2</sub>(110). At lower coverages the shift is very small and is not distinguished in the spectra. The shift in energy of the surface phonons is shown in Fig. 11. The intensity enhancement and upwards shift of surface phonons are probably due to a modification of the dielectric function.<sup>33,34</sup> A similar enhancement was observed in previous studies.<sup>26,29</sup> That VO<sub>2</sub> modes are superimposed upon the TiO<sub>2</sub> modes seems unlikely since this should cause downwards shifts.

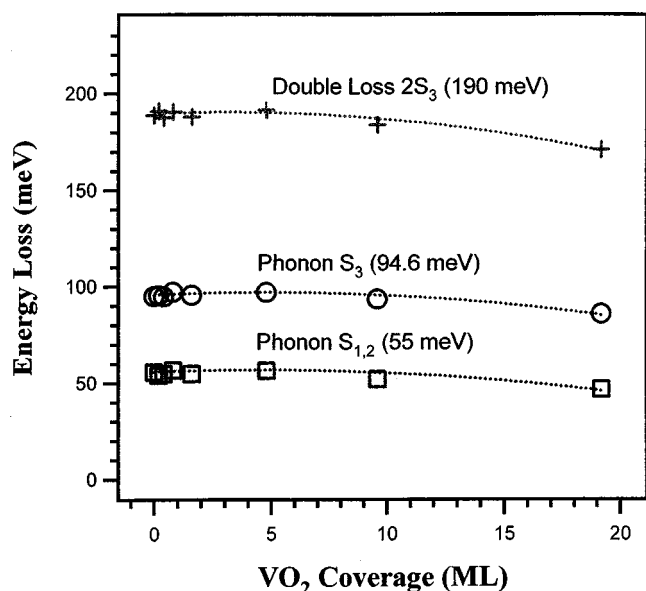


FIG. 11. The loss energy of surface phonons as a function of VO<sub>2</sub> coverage. The squares, circles, and crosses are experimental data. The lines are guides to the eye only.

For an overlayer of  $\sim 10$  ML's, the effect caused by the substrate will be small. As far as the classical theory is concerned, the surface phonons are considered as harmonic vibrations. The energy shift of surface phonons (from rutile TiO<sub>2</sub> to rutile-structured VO<sub>2</sub>) will be induced either by the difference between the Ti-O and V-O bond length or by the mass difference between Ti and V atoms. The bond length difference between Ti-O and V-O can be neglected since no lattice distortion was observed in LEED. All three surface phonon modes shift to lower energies (Fig. 11), in agreement with the smaller mass of the vanadium atoms.

With more VO<sub>2</sub> deposited onto the surface, the LEED pattern gradually becomes blurred, indicating that the epitax-

ial overlayer can no longer match the substrate lattice. The lattice distortion from VO<sub>2</sub>(110) is also evidenced from HREELS. The shift of surface phonons to lower energies ( $S_{1,2}$  to  $\sim 47$  meV and  $S_3$  to  $\sim 86$  meV) for a thick VO<sub>2</sub> thin film ( $\sim 19.2$  ML's) can be understood as due to formation of another phase of VO<sub>2</sub> or perhaps presence of V<sub>2</sub>O<sub>3</sub>, which was found to form upon TiO<sub>2</sub>(110) under different experimental conditions and which has surface phonon modes at  $\sim 48$  and  $\sim 79$  meV,<sup>13,39</sup> respectively. If we have both VO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub> on the surface, we are perhaps observing a mixture of HREELS spectra from these. The surface phonons of VO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub>, both with a broad nature, are difficult to resolve from each other. There is a 7–9-fold attenuation in intensity of the surface phonons (Fig. 10), which indicates that the structure of the vanadium oxide film may have changed.

#### IV. CONCLUSION

The first monolayer of vanadium thin films on TiO<sub>2</sub>(110) shows a two-dimensional layer growth, as evidenced by both AES and HREELS. The submonolayer vanadium thin films interact strongly with the substrate TiO<sub>2</sub>(110).

Epitaxial VO<sub>2</sub> overlayers have been grown on TiO<sub>2</sub>(110). The VO<sub>2</sub> overlayers with coverages up to 10 ML's have a structure similar to TiO<sub>2</sub>, as evidenced by the constancy of the loss energy of surface phonons. A small amount of charge transfer from substrate to overlayer is evidenced by an enhancement of the surface phonons at submonolayer coverages. At high coverages ( $\sim 20$  ML's) the overlayer can no longer match the substrate lattice.

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