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## Abstract

Photoemission spectroscopy was used to investigate the initial oxidation of the Ce/Ta(110) interface at room temperature. The oxidation of Ta(110) is dramatically enhanced by a thin Ce overlayer. A Ta suboxide  $TaO_\chi$  ( $0.5 \leq \chi \leq 1$ ) is formed first in the interface, followed by the rapid formation of  $Ta_2O_5$  upon further oxygen exposure. A weak interface reaction exists in Ce/Ta(110), but is excluded as the main cause of the catalytic oxidation. An earlier suggestion is reconfirmed that the Ce layer converts  $O_2$  to oxygen ions and thus promotes the oxidation of the substrate.

## Keywords

Ames Laboratory, photoemission spectroscopy

## Disciplines

Atomic, Molecular and Optical Physics | Condensed Matter Physics | Physics

## Comments

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## Ce-catalyzed oxidation of Ta(110)

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Photoemission spectroscopy was used to investigate the initial oxidation of the Ce/Ta(110) interface at room temperature. The oxidation of Ta(110) is dramatically enhanced by a thin Ce overlayer. A Ta suboxide  $\text{TaO}_\chi$  ( $0.5 \leq \chi \leq 1$ ) is formed first in the interface, followed by the rapid formation of  $\text{Ta}_2\text{O}_5$  upon further oxygen exposure. A weak interface reaction exists in Ce/Ta(110), but is excluded as the main cause of the catalytic oxidation. An earlier suggestion is reconfirmed that the Ce layer converts  $\text{O}_2$  to oxygen ions and thus promotes the oxidation of the substrate.

### I. INTRODUCTION

Since the discovery of the catalytic effect of Ce on the oxidation of Nb,<sup>1</sup> a series of studies<sup>2-5</sup> on surface oxidation have been carried out in light of the new finding. X-ray photoemission spectroscopy (XPS) measurements of Nb 3*d* levels revealed that at room temperature, significant amounts of bulk  $\text{Nb}_2\text{O}_5$  are formed at low oxygen exposure, promoted by a thin Ce overlayer.<sup>1,2</sup> High oxygen-ion mobility in the Ce overlayer is considered to be the cause of the fast oxygen diffusion. Some other rare-earth metals, such as Pr and Tb, have similar but less impressive capabilities for enhancing the oxidation of Nb.<sup>3</sup> Ce also enhances the oxidation of Si.<sup>4</sup> However, unlike the Ce/Nb interface which was claimed to be non-reactive, Ce itself reacts strongly with Si.<sup>4,6</sup>

Although NbO and various other Nb oxides form in the oxidation of pure Nb, only  $\text{Nb}_2\text{O}_5$  was observed in the growth of a Ce/Nb oxide film. Based on this observation, it was proposed<sup>5</sup> that during the oxidation of pure Nb(110), a Nb suboxide layer (NbO) formed on the surface is a barrier to further oxygen penetration due to higher embedding energy for the oxygen atom. Thus the rapid oxidation of Ce/Nb may be a direct consequence of the lack of a NbO barrier. However, XPS studies of the Nb 3*d* core levels are not very surface sensitive due to the large electron kinetic energy involved ( $10^3$  eV).<sup>1</sup> To study details of the initial stages in the catalytic oxidation, we choose Ta(110) as the substrate, because the Ta 4*f* core levels are very sharp and can be measured by surface-sensitive soft-x-ray photoemission spectroscopy with synchrotron radiation sources. The use of a single crystal as the substrate eliminates possible grain-boundary effects<sup>7</sup> in the oxidation. More important, analyses of the Ta(110) surface core-level shifts allow us to probe the Ce/Ta interface reaction. As compared with the XPS study of Ce/Nb, the better surface sensitivity and resolution in this experiment make it much easier to study the early stages of the catalytic oxidation, which are certainly important for understanding the kinetics of the catalytic action and the general surface oxidation itself.

In this experiment, we evaporated 4.5 Å of Ce on Ta(110). Changes in the Ta 4*f* core levels are evident

upon Ce adsorption. Curve fitting is used to reveal changes of the surface components. The Ce/Ta interface reaction is discussed in terms of the Ta surface core-level shifts. After exposing the Ce/Ta(110) surface to  $1 \times 10^{-8}$  Torr  $\text{O}_2$  at room temperature, it is seen that the Ce overlayer significantly promotes the oxidation of Ta(110). The growth pattern of the Ta oxides is totally different from that without the Ce catalyst. Two Ta oxide states,  $\text{TaO}_\chi$  ( $0.5 \leq \chi \leq 1$ ) and  $\text{Ta}_2\text{O}_5$ , dominate the initial oxidation. A thin  $\text{TaO}_\chi$  layer is formed first, but is further oxidized to  $\text{Ta}_2\text{O}_5$  quickly upon more oxidation. The Ce overlayer was studied by measurements of the valence spectra and the Ce 4*d* absorption spectra. Observation of the Ce oxide states reconfirms earlier suggestions<sup>1-3</sup> that changes between the two Ce valence states ( $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ ) promote the oxygen-ion diffusion from surface to substrate.

### II. EXPERIMENTAL

The photoemission experiments were performed at the Iowa State University–Montana State University ERG-Seya beamline<sup>8</sup> at the Synchrotron Radiation Center (Stoughton, WI), University of Wisconsin–Madison. The combined ERG-Seya monochromators provide photon energies from 5 to 1200 eV. The Ta(110) crystal,  $2 \times 2 \times 1$  mm<sup>3</sup>, was prepared by the Ames Laboratory. The Ta crystal was cleaned by annealing *in situ* at an extremely high temperature ( $\sim 2600^\circ\text{C}$ ) to expel oxygen from the bulk Ta. High-voltage electron-beam bombardment was employed to heat the sample efficiently. The temperature was monitored by an optical pyrometer. After 4 h of annealing, the Ta(110) was clean, as checked by the valence spectrum (Fig. 1, curve A) and the Ta 4*f* core-level spectrum (Fig. 2, curve A). The line shape of the Ta 4*f* levels is very sensitive to the surface condition. Oxygen contamination will cause the surface components to shift to higher binding energies. The (110) low-energy electron-diffraction (LEED) pattern was checked in another chamber after similar cleaning procedures. Before each experiment, the sample was flashed to high temperature to remove any residual contamination from the surface. The base pressure was about  $1 \times 10^{-10}$  Torr. The pressure only rose to  $3 \times 10^{-10}$  Torr during the high-

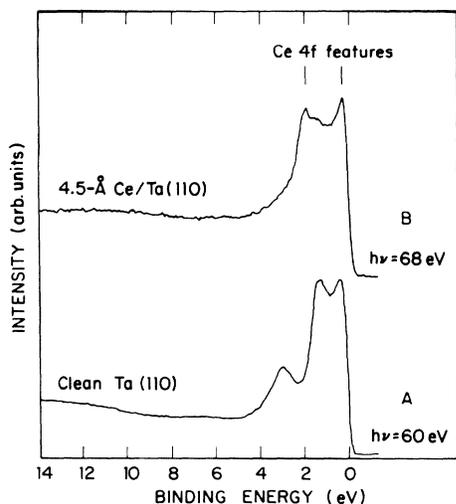


FIG. 1. Valence-band spectra of clean Ta(110) and Ce/Ta(110). In *B* two Ce 4*f*-related features are identified at 2.0 and 0.2 eV.

temperature flashing. A piece of high-purity Ce metal was also provided by the Ames Laboratory. The Ce metal was melted and degassed thoroughly. After 8 h of degassing, 4.5 Å of Ce was evaporated onto the Ta(110) surface. Figure 1, curve *B* shows the valence-band spectrum taken after the evaporation with  $h\nu = 68$  eV. Two Ce 4*f*-related features<sup>9,10</sup> can be seen at 2 eV and near the Fermi level (0.2 eV). There is no sign of oxygen contamination around 6-eV binding energy.

### III. RESULTS AND DISCUSSION

#### A. Ta surface core-level shifts: The Ce/Ta interface reaction

Figure 3 shows the detailed Ta 4*f*<sub>7/2</sub> levels before and after Ce adsorption. The surface core-level shifts for various Ta surfaces are well known.<sup>11</sup> For Ta(110), only the first surface layer contributes significant core-level shifts.<sup>11</sup> Therefore the Ta 4*f*<sub>7/2</sub> spectra can be fitted by one surface level (*S*) in addition to the bulk level (*B*). Each component has the Doniach-Šunjić (DS) line shape<sup>12</sup> convolved with a Gaussian broadening function. To reduce the number of independent parameters, we may assume the hole lifetime ( $1/\gamma$ ) and the singularity index ( $\alpha$ ) in the surface component are the same as in the bulk component.<sup>13</sup> However, as noted in Ref. 13, the Gaussian widths ( $\Gamma^G$ ) may be different. The Gaussian broadening represents contributions from the instrumental resolution function, phonon excitation, and other possible sources of inhomogeneous broadening. It was found that the surface components in Ta(111) have broader Gaussian features than the bulk components.<sup>13</sup> The differences in the Gaussian widths were tentatively attributed to unresolved surface crystal-field splitting.<sup>13</sup>

The best least-squares fit for Ta 4*f*<sub>7/2</sub> of clean Ta(110) is obtained by adjusting the parameters to the values tabulated in Table I. The background is approximated by a straight line. For comparison, some parameters given by

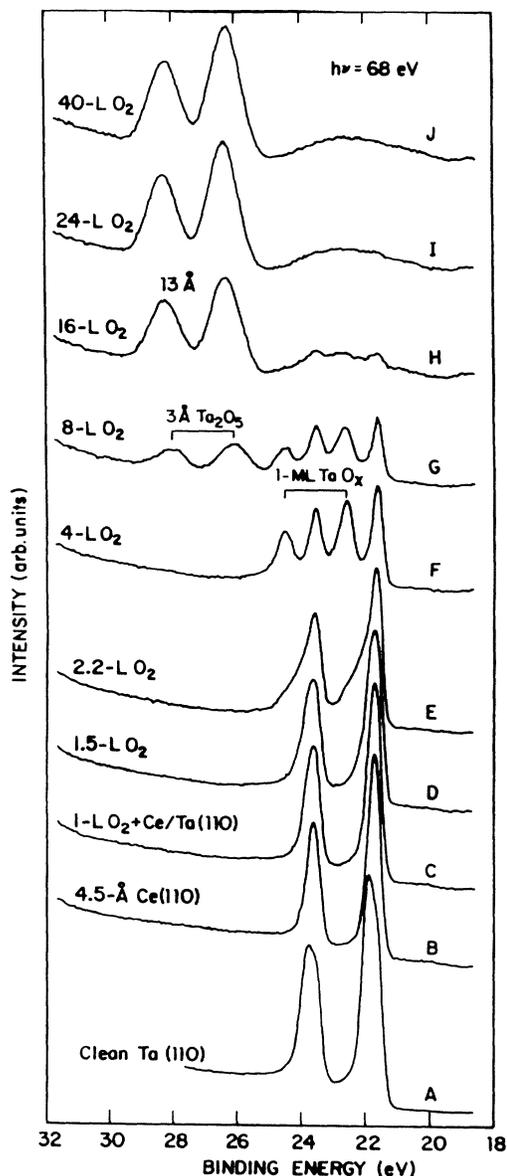


FIG. 2. Ta 4*f* spectra. *A* and *B* are for clean Ta(110) and Ce/Ta(110), respectively. *C*-*J* were taken after Ce/Ta(110) was exposed to various amounts of O<sub>2</sub> at 1 × 10<sup>-8</sup> Torr.

other work are also listed. Values of the Lorentzian width  $\Gamma$  ( $=2\gamma$ ), the singularity index  $\alpha$ , and the surface 4*f* level shift  $\Delta_{\text{surf}}$  are generally in agreement with other work. The instrumental resolution in the experiment is 265 meV. The phonon broadening in Ta can be as much as 167 meV, as estimated by Flynn.<sup>14</sup> Thus the combined Gaussian width should be about 313 meV, very close to the bulk Gaussian width ( $\Gamma_{\text{bulk}}^G$ ) obtained in our fit. The Gaussian width in the surface component  $\Gamma_{\text{surf}}^G$  is larger than  $\Gamma_{\text{bulk}}^G$ . As in Ta(111), unresolved surface crystal-field splitting may be considered as the source of the extra broadening.

After 4.5 Å of Ce was evaporated on the Ta(110) surface, the Ta 4*f*<sub>7/2</sub> surface component shifts toward the

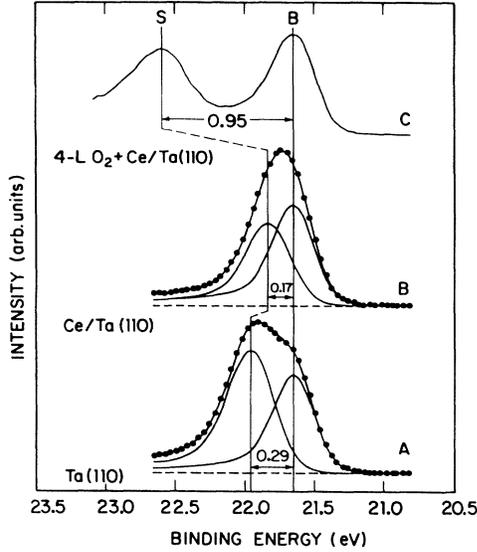


FIG. 3. Ta  $4f_{7/2}$  spectra in which the surface and bulk components are separated by either curve fitting *A*, *B*, or oxidation *C*.

bulk core level by 0.12 eV, making the overall line shape much sharper (Fig. 3, curve *B*). The same values of  $\Gamma(2\gamma)$ ,  $\alpha$ , and  $\Gamma_{\text{bulk}}^G$  have been used in the fitting. The Gaussian width for the surface component is found to be closer to the bulk value, indicating that the surface crystal-field splitting is weaker for the Ta/Ce interface than the Ta/vacuum interface.

The smaller surface core-level shift in Ce/Ta(110) can be the result of two effects: (1) electron donation from Ce to the Ta valence band and (2) the rebroadening of the Ta surface valence band due to bonding between Ce and Ta. The influence of a donor adsorbate (Cs) on Ta(100) and W(100) was reported before.<sup>15</sup> In our case, Ce may also be considered an electron donor since Ce has a lower electronegativity (1.03) than Ta (1.33).<sup>16</sup> A small amount of electron charge may be transferred from Ce to Ta. Therefore the Ta surface core level should shift to lower binding energy due to increased electron screening. To understand the second effect, we need to consider the origin of the surface core-level shifts for transition metals like Ta.<sup>17</sup> The reduced coordination number of atoms on metal surfaces usually results in a narrowing of the valence band. The major effect of the band narrowing is to raise (or lower) the Fermi level of the surface band, de-

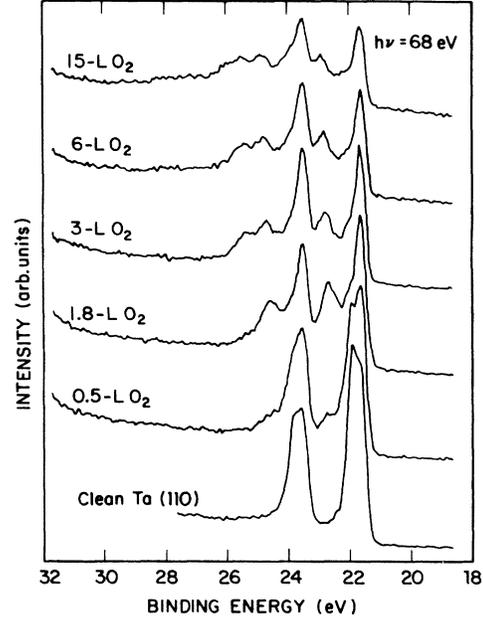


FIG. 4. Ta  $4f$  spectra after Ta(110) was exposed to  $1 \times 10^{-8}$  Torr  $O_2$  for various periods.

pending on whether the  $d$  band is less (or more) than half-filled. To restore equilibrium and bring the Fermi level back to the bulk level, a small amount of charge must transfer out of (or into) the surface bands. The small charge change in the surface thus lowers (or raises) the energies of all electrons in the surface. For Ta, the  $d$  band is less than half-filled, so the surface core levels shift to higher binding energies. The Ce overlayer makes the Ta surface more bulklike. Ce—Ta bonding rebroadens the narrowed Ta surface valence band. The resulting Ta surface line-shape parameters are closer to the bulk. Since the Ta surface layer still exhibits a shift of +0.17 eV, the Ce—Ta bond is weaker than the Ta—Ta bond. Thus a reaction between Ta and the physisorbed Ce exists but it tends to be small. We further believe that at room temperature there is no interdiffusion between Ce and Ta, as illustrated later in the oxidation of Ce/Ta.

### B. Oxidation of Ce/Ta(110): The catalytic effect

For purposes of comparison, the oxidation of Ta(110) itself was investigated. Figure 4 shows a sequence of Ta  $4f$  spectra after clean Ta(110) was exposed to oxygen

TABLE I. Summary of Ta  $4f_{7/2}$  line-shape parameters.

	Present		Others
	Ta(110)	Ce/Ta(110)	
$\Delta_{\text{surf}}$ (eV)	0.29	0.17	0.28 [Ta(110), Ref. 11]
$\Gamma(2\gamma)$ (eV)	0.05	0.05	0.04 [Ta(111), Ref. 13]
$\alpha$	0.12	0.12	0.15 [Ta(111), Ref. 13]
$\Gamma_{\text{bulk}}^G$ (eV)	0.31	0.31	
$\Gamma_{\text{surf}}^G$ (eV)	0.35	0.33	

at  $1 \times 10^{-8}$  Torr. (We want to point out that in this work oxidations were performed cumulatively and the  $O_2$  exposure values shown are the total amounts. Spectra in Figs. 2, 4, 5, and 6 are normalized by the photoyield current from a monitoring mesh which is approximately proportional to the photon flux.) We note that a small amount of  $O_2$  exposure (0.5 L) can induce noticeable chemical shifts. After a total of 15 L  $O_2$  exposure, some Ta suboxides with chemical shifts of less than 3 eV are formed in the surface. [1 langmuir (L)  $\equiv 10^{-6}$  Torr sec.]

Figure 2 shows the Ta 4f spectra for the oxidation of Ce/Ta(110) at the same  $O_2$  pressure. From spectra C and D one can see virtually no Ta oxidation during the initial exposures ( $\leq 1.5$  L), since the Ce layer on top was oxidized first. In fact, assuming that the Ce atoms stay on top of Ta uniformly and are all oxidized to  $Ce_2O_3$ , one may estimate that the Ta under 4.5 Å Ce would not be reached by oxygen until 2.7 L  $O_2$  exposure. In our experiment, the Ta oxidation "threshold" is near 2.2 L  $O_2$  exposure (spectrum E), which is a good indication that Ce covered the Ta surface quite uniformly and no significant Ce/Ta mixture or interdiffusion occurs. After a total of 4 L  $O_2$  exposure, a pair of well-defined shifted peaks appears at binding energies 0.95 eV higher than the bulk levels, indicating the formation of a Ta suboxide, which we call  $TaO_x$ . More oxygen exposures (from G to J) result in the fast growth of  $Ta_2O_5$ , which is represented by a large chemical shift ( $\sim +5$  eV) in the core levels. The very broad feature near 22 eV in G–J is the  $O 2s$  level. After 16 L  $O_2$  exposure, 13 Å of  $Ta_2O_5$  have grown.<sup>18</sup> In I after 24 L  $O_2$  exposure the thickness of  $Ta_2O_5$  is already beyond the probing depth. Comparing with the oxidation of pure Ta(110) (Fig. 4), we conclude that the oxidation of Ta is dramatically enhanced by the Ce on top.

The formation of the Ta suboxide  $TaO_x$  surprised us since no Nb suboxide was observed in the Ce/Nb oxidation. It is also very interesting to note that the well-defined  $TaO_x$  is the only suboxide in the oxidation. If we compare the  $4f_{7/2}$  components after 4 L  $O_2$  exposure with the fitted Ta  $4f_{7/2}$  level in Ce/Ta(110) (Fig. 3, curves C and B), it is obvious that almost the entire first Ta layer becomes  $TaO_x$ , as the whole surface component shifts from the bulk level by +0.95 eV.

Meanwhile, the identification of  $TaO_x$  proves to be less straightforward. Oxidation of Ta under different conditions (usually at elevated temperatures) has been investi-

gated for many years.<sup>20–27</sup> A few types of Ta suboxide,  $TaO_x$  ( $Ta_6O$ ),  $TaO_y$  ( $Ta_2O$ ),  $TaO_z$  ( $Ta_2O$ ), TaO, and  $TaO_2$ , were detected by x-ray-diffraction and weight-gain measurements.<sup>20</sup> Unfortunately, almost all of them were not in pure form, thus the assigned formulae are stoichiometrically approximate. In the photoemission spectroscopy area, interpretations of chemical shifts in Ta suboxides are correspondingly controversial<sup>21–24</sup> (see Table II), since the suboxides cannot be prepared well enough. Sanz and Hofmann<sup>21</sup> oxidized Ta at room temperature and analyzed the core-level spectra (obtained by XPS) in an analogy with the oxidation of Nb. Three chemical shifts were identified in their deconvolution of the oxide spectra. TaO and  $TaO_2$  were assigned to the chemical shifts of 2.0 and 3.9 eV, respectively. However, with better resolution and higher surface sensitivity, our Ta oxidation spectra (Fig. 4) clearly reveal the existence of two chemical shifts of less than 2.5 eV. We also note that these shifted peaks may move to higher binding energies upon further oxidation. Chemical shifts ranging from 0.5 to 2.4 eV were reported in the initial oxidation of Ta(111) at room temperature.<sup>25</sup> A similar experiment was done on Ta(100), and a shift of  $\sim 1.5$  eV was thought to be related to TaO.<sup>22</sup> LEED studies<sup>26,27</sup> on the oxidation of Ta surfaces did show some ordered structures, but only after annealing. It is generally accepted that at room temperature Ta surfaces oxidize in an almost amorphous fashion. So the deconvolution of Ta oxide spectra shown in Ref. 21 can only be considered as a rough evaluation of the Ta oxidation states. Photoemission studies on Ta oxidation at higher temperatures were carried out by Legma *et al.*<sup>23</sup> and Himpfel *et al.*<sup>24</sup> At elevated temperatures, oxygen diffusion and oxidation are much faster. The oxide products are quite different under varied conditions. Reference 23 identified the oxidation products after comparing them with Nb oxides. Reference 24 is a parallel oxidation study of W and Ta. One of the key conclusions in Ref. 24 is that there is a significant discontinuity of binding energy (2–3 eV) between metallic and dielectric (insulating) screening. Consequently, chemical shifts of less than 2 eV were assigned to Ta oxide states relatively higher than in other studies, and the 2.05-eV shift was referred to as a formal metallic  $Ta^{5+}$  state, which is unknown so far.

The oxidation of Ce/Ta(110) is unlike that of Ta reported at any temperature region. Therefore as we com-

TABLE II. Chemical shifts of Ta 4f levels (in eV relative to the bulk) for Ta surface oxides. The notion (metallic) is used only for the convenience to accommodate the results of Ref. 24. Some values shown are the averages of all data given in the literature. The  $TaO_x$  with a 0.95-eV shift is close to  $Ta^{1+}$  and  $Ta^{2+}$ . See text for details.

Ta Oxides	(Metallic)					Insulating
	1+	2+	3+	4+	5+	5+
Ref. 21		2.0		3.9		5.0
Ref. 22		1.5				
Ref. 23	0.5	1.3	> 1.8			5.2
Ref. 24	0.48		1.22		2.05	5.2
Ce/Ta(110)+ $O_2$		0.95				5.1

pare  $\text{TaO}_x$  to the results shown in Table II, it is not justified to favor or disfavor any of these studies based on oxidation conditions. Considering all earlier work and data in Table II, we feel it is appropriate to assign  $\text{Ta}^{2+}$  ( $\text{TaO}$ ) as the upper limit and  $\text{Ta}^{1+}$  ( $\text{Ta}_2\text{O}$ ) as the lower limit for the oxidation state of  $\text{TaO}_x$  ( $0.5 \leq \chi \leq 1$ ). Since the  $\text{TaO}_x$  is actually very thin (1 ML), this kind of estimate seems reasonable.

In Fig. 2, curves *G* and *H*, the  $\text{TaO}_x$  and Ta signals become smaller, and  $\text{Ta}_2\text{O}_5$  shows up during oxidation. It was mentioned earlier that all spectra in Fig. 2 are normalized and the thicknesses of  $\text{Ta}_2\text{O}_5$  were estimated in Ref. 18. Some possibilities regarding the growth of  $\text{Ta}_2\text{O}_5$  and  $\text{TaO}_x$  can be evaluated by studying Fig. 2, curves *F*–*H*. Since there is not much Ce/Ta mixture, the oxidation can be assumed to be relatively homogeneous. Thus it is natural to believe the interface layer  $\text{TaO}_x$  should be first oxidized to  $\text{Ta}_2\text{O}_5$  in Fig. 2, curve *G*. On the other hand, because the relative intensity of  $\text{TaO}_x$  compared with that of Ta does not change much, it has to be recognized that some new  $\text{TaO}_x$  is formed at the same time. (The electron mean free path in  $\text{Ta}_2\text{O}_5$  is much larger than that in Ta or  $\text{TaO}_x$ , the transformation of  $\text{TaO}_x$  to  $\text{Ta}_2\text{O}_5$  in Fig. 2, curve *G* should not reduce the Ta signals.) From Fig. 2, curves *G* and *H*, it may be estimated that the average amount of  $\text{TaO}_x$  never exceeds the initial 1 ML at any time.

To study the role of the Ce layer in the oxidation, we measured the valence spectra (Fig. 5) and constant final-state (CFS) spectra in the region of Ce  $4d$  absorption edges (Fig. 6). The valence spectrum of clean Ce/Ta(110) mainly exhibits Ce features due to the uniform Ce coverage and the small electron escape depth in the range of kinetic energies involved (see Fig. 1 for a better view). As mentioned earlier, there are two Ce  $4f$ -related

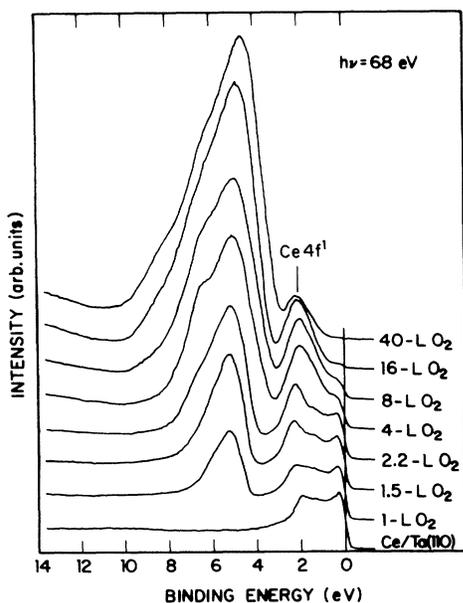


FIG. 5. Valence-band spectra of Ce/Ta(110) as a function of  $\text{O}_2$  exposure.

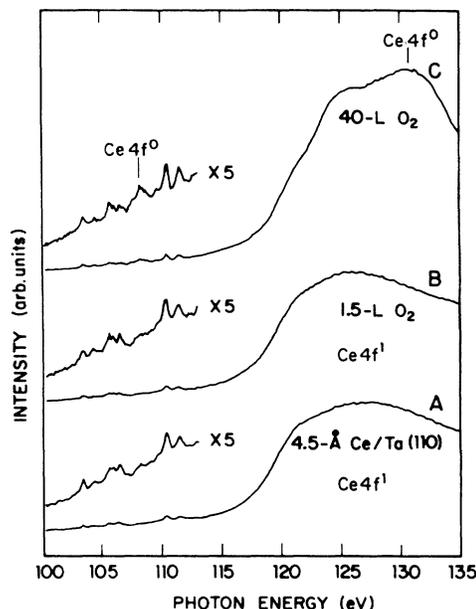


FIG. 6. CFS spectra in the region of Ce  $4d$  absorption edges.

features<sup>9,10</sup> located at 2.0 and 0.2 eV, respectively. The first one is regarded as the (shifted) localized  $4f^1$  core level. The second feature near  $E_f$  (not well resolved) is due to the hybridization between  $4f$  and the valence band. Upon oxidation, broad  $\text{O}2p$ -related structures emerge around 5–6 eV, while the density of states near  $E_f$  decreases. The Ce  $4f$  level at 2.0 eV shifts to about 2.4 eV after oxidation, consistent with other work.<sup>28</sup> The intensity ratio between this Ce  $4f$  level and the peak near  $E_f$  increases after 1.5–4 L  $\text{O}_2$  exposure. This may be the result of the decreased hybridization, since the valence band near  $E_f$  disappears under oxidation. After 40 L  $\text{O}_2$ , the density of states close to the Fermi level ceases to exist, corresponding to the formation of an insulator at the surface. At the same time, the intensity of the Ce  $4f$  level drops, indicating the transformation of some  $\text{Ce}_2\text{O}_3$  ( $\text{Ce}^{3+}$ ,  $4f^1$ ) to  $\text{CeO}_2$  ( $\text{Ce}^{4+}$ ,  $4f^0$ ).

The formation of  $\text{Ce}^{4+}$  is also demonstrated by the CFS spectra taken in the region of the Ce  $4d^{10}4f^n \rightarrow 4d^94f^{n+1}$  absorption edges (Fig. 6). The absorption spectra consist of two parts: a fine-structure part from 100 to 113 eV (enlarged), and a strong wide band in the region of 120–135 eV. The absorption structures are very sensitive to the occupancy of the  $4f$  level.<sup>10,29</sup> The spectra of pure Ce and  $\text{Ce}_2\text{O}_3$  are similar (Fig. 6, curves *A* and *B*) since the Ce is trivalent ( $4f^1$ ) in both materials. However, as Ce becomes nominally tetravalent ( $4f^0$ ) in  $\text{CeO}_2$ , the spectrum looks very different, resembling that of  $\text{La}^{3+}$ , but shifted in energy.<sup>29</sup> In Fig. 6, curve *C*, after 40 L  $\text{O}_2$  exposure, a mixture of  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  spectra is found. A new peak at 108 eV in the fine structure and another new broad feature around 130 eV are characteristic of the tetravalent Ce. From the relative intensities of the  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  features in the fine structure, we learn that a significant

portion of  $\text{Ce}_2\text{O}_3$  still remains on the surface. Actually, in the valence spectra, the intensity of the Ce 4*f* level after 40 L  $\text{O}_2$  drops about 40%, so there is 60% of  $\text{Ce}_2\text{O}_3$  on the surface. The unusually slow oxidation saturation of the very thin Ce layer (4.5 Å) is directly related to its role in the oxidation of the Ta substrate. In fact, it was proposed that the catalytic oxidation is connected to the valence changes between 3+ and 4+ in the oxidized Ce.<sup>1-3</sup> The  $\text{Ce}_2\text{O}_3$  layer on the surface reacts with adsorbed oxygen atoms to form  $\text{CeO}_2$ . However,  $\text{CeO}_2$  is an oxygen-ion conductor with a high oxygen-ion mobility.<sup>1</sup> The  $\text{CeO}_2$  may easily lose oxygen ions to the substrate and change back to  $\text{Ce}_2\text{O}_3$ . Therefore, the Ce oxide layer converts adsorbed  $\text{O}_2$  to oxygen ions which may diffuse into the substrate below. As long as the oxygen-ion diffusion into Ta is not slow compared with the oxygen dose ( $1 \times 10^{-8}$  Torr), the Ce overlayer should appear to be in the lower-oxidation state as  $\text{Ce}_2\text{O}_3$ . In this experiment, the Ce layer remains as  $\text{Ce}_2\text{O}_3$  until the oxidation of Ta begins to slow down after  $\sim 40$  L  $\text{O}_2$  exposure. Therefore we believe the earlier suggestion on the role of Ce is correct.

The weak Ce/Ta interface reaction mentioned earlier might initially help the oxygen-ion transfer from Ce to Ta. But after  $\text{Ta}_2\text{O}_5$  forms beneath Ce, the interface reaction is totally lost, therefore further fast oxidation could not be explained by this mechanism.

#### IV. SUMMARY

From the experimental results discussed, the conclusions are summarized as follows.

Oxidation of Ta(110) is dramatically enhanced by a Ce overlayer at room temperature. One monolayer of Ta is oxidized to  $\text{TaO}_\chi$  ( $0.5 \leq \chi \leq 1$ ) first, in contrast with ear-

lier observations on the Ce/Nb oxidation. The catalytic oxidation of Ta does not slow down after the formation of  $\text{TaO}_\chi$ . Bulk  $\text{Ta}_2\text{O}_5$  forms after only 8 L  $\text{O}_2$  exposure.

From the analyses of the Ta surface 4*f* core levels, we conclude the Ce overlayer only weakly reacts with the Ta substrate by a weak bonding to Ta and/or a small amount of electron donation to Ta. No Ce/Ta interdiffusion or mixture was found. The weak Ce/Ta reaction is not considered to be the main cause of the catalytic reaction.

We have confirmed that the Ce oxidation state changes between  $\text{CeO}_2$  and  $\text{Ce}_2\text{O}_3$ , providing oxygen ions (instead of  $\text{O}_2$  molecules), thus promoting the oxidation of the metal substrate.

After this paper was submitted, a paper by Braaten *et al.*<sup>30</sup> appeared. Polycrystalline Ta was used in their experiments. The same conclusions were reached on the existence of the catalytic effect of Ce on Ta oxidation and the corresponding mechanism. Our work differs in the findings of the weak Ce/Ta(110) interface reaction and the clear formation of  $\text{TaO}_\chi$  in the oxidation of Ce/Ta(110). These detailed insights might be attributed to the use of single crystal Ta as the substrate.

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