

Metallic-to-nonmetallic transition of Na coadsorbed with CO₂ and H₂O on the Cr₂O₃(111)/Cr(110) surface

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Coadsorption of Na with CO₂ and H₂O on a thin Cr₂O₃(111) single crystal epitaxially grown on a single-crystal Cr(110) substrate has been performed to study the effects of the coadsorbates on the electronic properties of the Na species. High-resolution electron-energy-loss spectroscopy spectra as a function of Na overlayer coverage reveal a continuous attenuation of the Fuchs-Kliwer surface-phonon loss modes with near total attenuation by ~ 2 monolayers (ML). Coadsorption with either H₂O or CO₂ returns the substrate Fuchs-Kliwer modes to a relative intensity approximately equal to that observed on the clean Cr₂O₃(111) surface. Angle-resolved photoemission spectroscopy (ARPES) measurements from the Cr₂O₃(111) surface demonstrate almost total attenuation of the Cr₂O₃(111) valence-band emission by a Na coverage of ~ 2 ML with *no return* of Cr₂O₃(111) valence-band emission features upon coadsorption. These observations provide strong evidence that the development of a metallic Na overlayer results in a damping of the coupling interaction between the electron and the Fuchs-Kliwer phonons and that upon reaction with the coadsorbed species, a uniform dielectric overlayer is formed which permits the return of the Fuchs-Kliwer losses. The metallic-to-nonmetallic transition of the overlayer is also supported by the ARPES data which reveal suppression of emission from the Fermi level, the disappearance of the *LVV* Auger transition, and a shifting to higher binding energy of the Na *2p* emission upon compound formation during coadsorption.

Alkali-metal promoters of metal-oxide catalysts are well documented.^{1,2} However, a detailed model of the electronic and geometric properties of these catalytic systems at the microscopic level does not exist. Since the catalytic activity of metal oxides is intimately related to the charge state of the surface atoms,³ a knowledge of the electronic structure at the surface is fundamental to understanding the catalytic activity of these systems. By measuring the various physical properties of the alkali-metal atoms both before and after coadsorption with a molecular species, information about charge-transfer mechanisms at oxide surfaces can be learned. However, the great majority of studies on both alkali-metal-doped oxide⁴ and metal⁵⁻⁷ systems have either ignored or only briefly mentioned the electronic properties of the alkali-metal atoms and how these properties evolve with coadsorption.

Previous studies of the development of metallic overlayers on semiconductor substrates has shown that high-resolution electron-energy-loss spectroscopy (HREELS) can be a very powerful technique for the determination of the electronic properties and growth morphology of these films.⁸⁻¹⁰ In this paper we report a HREELS and angle-resolved photoelectron spectroscopy (ARPES) study of the electronic properties of Na adsorbed on a thin film Cr₂O₃(111) crystal and the resulting effects that the coadsorbates CO₂ and H₂O have on these properties. The primary emphasis of this paper is to study the electronic properties of the adsorbates; therefore, the chemical properties of the coadsorbed species will only be briefly mentioned in this paper with a comprehensive study of the latter effects being published in the future.

The major benefit of studying a thin epitaxially grown oxide film over that of a bulk crystal is that the thin film allows electron tunneling into the substrate which prevents sample charging. The use of a thin oxide film also allows the study of coadsorption on both the clean metal surface and the surface after oxidation without changing the experimental setup. The Cr₂O₃(111) thin films used in this study were prepared by oxidation of single-crystal Cr(110) samples. This oxidation procedure has been described in detail in previous publications.^{11,12} The Cr₂O₃(111) thin films prepared in both systems showed well-ordered hexagonal low-energy electron diffraction patterns with no sign of the Cr(110) substrate beam. Based on the detection of some photoelectrons from the Cr(110) substrate, we estimate the thickness of the Cr₂O₃(111) thin film prepared in the ARPES system to be ~ 10 Å. For the HREELS system, successive oxidations produced a Cr₂O₃(111) film estimated to be ~ 50 Å thick.

The HREELS measurements were made in Bochum, and the ARPES measurements were performed on beamline TGM-3 at the BESSY synchrotron in Berlin. This beamline features a toroidal grating monochromator with a resolution of approximately 150 meV across the energy range of interest for this study. The HREELS and ARPES measurements were both performed in two-stage stainless-steel ultrahigh vacuum chambers. The upper stage of both systems was used primarily for sample preparation and characterization. The lower stage of the HREELS chamber contained a Leybold-Heraeus ELS-22 spectrometer, and the lower stage of the ARPES chamber contained a VSW spectrometer mounted on a

two-axis goniometer.

Na depositions in both systems were made on a sample held at $T \sim 100$ K with well outgassed SAES getter sources which were equipped with collimators and shutters. The base pressure of both chambers was $\sim 1 \times 10^{-10}$ mbar and did not exceed $\sim 8 \times 10^{-10}$ mbar during Na depositions. Overlayer Na coverages were determined from thermal desorption spectroscopy (TDS) measurements where a coverage of 1 monolayer (ML) was defined to be the coverage at which a zero-order kinetics peak with an onset at $T \sim 360$ K first became visible. A second confirmation of Na coverage was made in the ARPES chamber by measuring the work-function change as a function of Na coverage on the Cr(110) surface before oxidation. We observed a minimum in the work function at a coverage based on TDS of ~ 0.5 ML, which is consistent with similar measurements of alkali metals adsorbed on other metal surfaces.¹³ Since no ordered overlayer structures were observed on the $\text{Cr}_2\text{O}_3(111)$ substrate for either the Na or the coadsorbed systems, an estimate of the absolute overlayer density has not been attempted.

HREELS spectra of (a) the clean $\text{Cr}_2\text{O}_3(111)$ surface, (b) the surface with ~ 2.2 ML of Na adsorbed on it, and the surface with (c) 4 L ($1 \text{ L} = 10^{-6}$ Torr s) of D_2O coadsorbed and (d) 20 L of CO_2 coadsorbed with the Na are shown in Fig. 1. The spectrum for the clean $\text{Cr}_2\text{O}_3(111)$ surface exhibits losses corresponding to the two primary Fuchs-Kliewer (FK) surface phonon modes characteristic of this surface at wave numbers of 416 and 708 cm^{-1} . Various losses corresponding to multiple combinations of these losses are also detected at higher energies. These results agree well with previous studies of single-crystal $\text{Cr}_2\text{O}_3(111)$ surfaces.^{11,12} The HREELS spectrum for the Na-dosed surface shows almost total attenuation of all of the surface phonon modes with only the loss feature at 708 cm^{-1} being visible. A measure of the relative intensity of the 708- cm^{-1} loss feature to that of the elastic peak as a function of Na coverage is shown in Fig. 2. It can be seen that this loss feature attenuates with increasing Na coverage with near total attenuation by a coverage of ~ 2.2 ML. As seen in Fig. 1, coadsorption with either CO_2 or H_2O returns the relative intensity of the loss features to values approximately equal to those of the clean $\text{Cr}_2\text{O}_3(111)$ surface. Vibrational losses from the coadsorbed species are also resolved when these spectra are viewed with an expanded scale and will be described in detail in a future publication.

ARPES spectra of (a) the clean $\text{Cr}_2\text{O}_3(111)$ surface, (b) the surface with ~ 2.0 ML of Na adsorbed on it, and the surface with (c) 5 L of H_2O coadsorbed and (d) 10 L of CO_2 coadsorbed with the Na are shown in Fig. 3. For the spectrum from the clean $\text{Cr}_2\text{O}_3(111)$ surface, peaks centered at binding energies (E_b) of 3 and 8 eV are observed which correspond to emission from the Cr 3d and O 2p bands, respectively.^{3,11,12} Some emission from the Fermi level is also observed for this spectra which we attribute to emission from the substrate Cr(110). At a Na coverage of ~ 2.0 ML, the valence-band emission from the Cr_2O_3 is almost fully suppressed with a well-developed Na 2p level peak being observed at $E_b = 31$ eV.

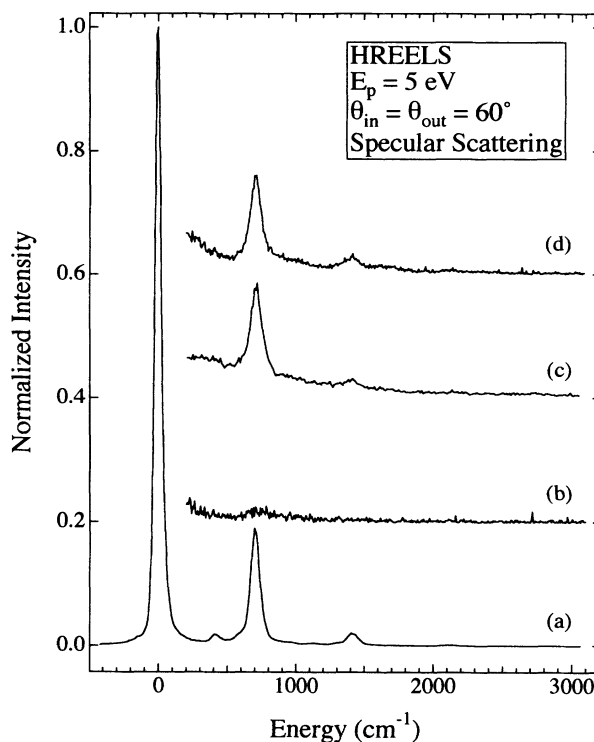


FIG. 1. HREELS spectra of (a) the clean $\text{Cr}_2\text{O}_3(111)$ surface, (b) the surface with ~ 2.2 ML of Na adsorbed on it, and the surface with (c) 4 L of D_2O coadsorbed and (d) 20 L of CO_2 coadsorbed with ~ 2.2 ML of Na. Peaks at wave numbers of 416 and 708 cm^{-1} correspond to the excitation of the two primary Fuchs-Kliewer surface phonon modes characteristic of the $\text{Cr}_2\text{O}_3(111)$ surface. The FWHM of the elastic peak of the clean spectrum was $\Delta E_{el} = 7$ meV.

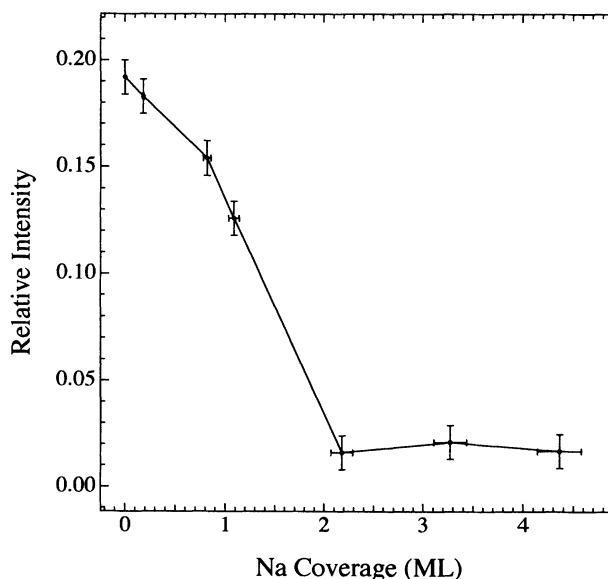


FIG. 2. Intensity of the HREELS peak corresponding to the excitation of the 708- cm^{-1} surface mode relative to that of the elastic peak as a function of Na overlayer coverage (line drawn to guide the eye).

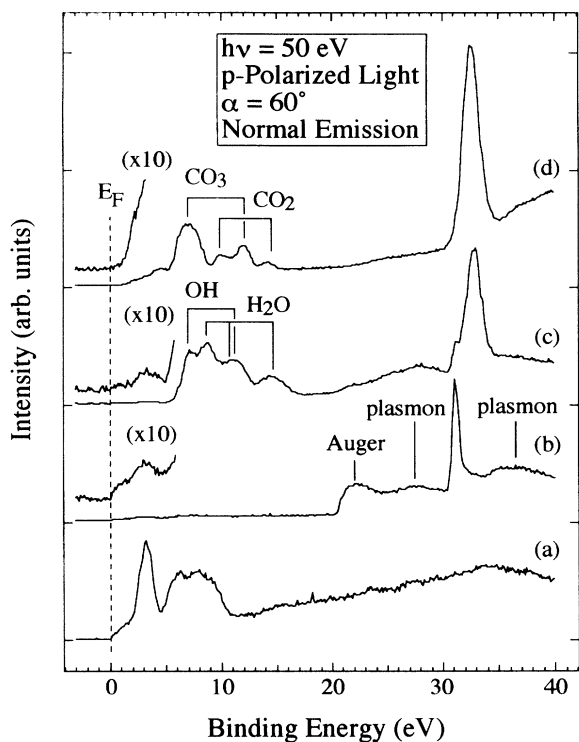


FIG. 3. ARPES spectra of (a) the clean $\text{Cr}_2\text{O}_3(111)$ surface, (b) the surface with ~ 2.0 ML of Na adsorbed on it, and the surface with (c) 5 L of H_2O coadsorbed and (d) 10 L of CO_2 coadsorbed with ~ 2.0 ML of Na where α is the angle between the surface normal and the wave vector of the incident light.

A constant kinetic-energy feature ($E_{\text{KE}} \sim 24$ eV) is resolved at $E_b \sim 22$ eV. This feature is attributed to an $L_{2,3}VV$ Auger transition, which results from an initial ionization from the $2p$ level with the resulting hole being filled by a $3s$ valence electron with a corresponding emission of a second $3s$ electron. The two broad peaks centered at $E_b \sim 27.5$ and ~ 36.5 eV have been interpreted as resulting from Na plasmon losses from the Auger and $2p$ peaks, respectively.^{5,14,15} An asymmetry in the Na $2p$ peak is observed which has been observed for p -band emission from alkali overlayers on many metal and semiconducting surfaces.^{5,16} The origin of this asymmetry is attributed to the creation of electron-hole pairs near the Fermi level as the photoelectron is ejected from the surface (i.e., a Doniach-Sunjić line shape).^{17,18}

As can be seen in Fig. 3, coadsorption of either CO_2 or H_2O both result in significant broadening of the $2p$ emission from a full width at half maximum (FWHM) of ~ 0.75 to ~ 1.5 eV. The binding energies are also increased by ~ 2 eV for the H_2O and ~ 1.5 eV for the CO_2 . The $L_{2,3}VV$ Auger transition and the plasmon-loss features are totally or almost totally attenuated. Although the cross section for emission from the Na $3s$ level is very low at a photon energy of 50 eV, some Fermi-level emission is observed for the Na spectra before coadsorption that is not observed after coadsorption. It is also noted that there is no signature of a return of valence-band emission

from the Cr_2O_3 substrate, which indicates that the coadsorbed species must form a somewhat uniform overlayer. In other words, significant clustering of the Na upon coadsorption can be ruled out. From comparison of the valence-band emission from the Na/ CO_2 coadsorbed spectrum with that from a previous coadsorption study on Pd(111),¹⁹ we attribute the valence-band features of the coadsorbed system to emission primarily from Na_2CO_3 with traces of emission from physisorbed CO_2 as indicated in Fig. 3. Comparison of the valence-band emission for the Na/ H_2O coadsorption spectrum with that of NaOH (Ref. 20) and thick films of ice²¹ gives evidence that a mixture of these two species is present at the surface. A shoulder on the low binding-energy side of the Na $2p$ level emission for the Na/ H_2O spectrum lies at approximately the same energy as that for the $2p$ emission from 2-ML Na without coadsorption, probably indicating that there is some unreacted Na remaining in the surface region as well.

The observation of emission from the Fermi level coupled with the existence of an $L_{2,3}VV$ Auger transition, plasmon losses, and a Doniach-Sunjić line shape for the $2p$ emission give considerable evidence that the Na overlayer at ~ 2.0 ML is in a metallic state on the Cr_2O_3 substrate. The almost complete attenuation of the valence-band emission from the Cr_2O_3 substrate at this coverage implies relatively uniform layer by layer growth of the Na. The analysis of the valence-band emission after coadsorption which gave evidence for compound formation indicates that the Na reacts strongly with the coadsorbates. The nonmetallic nature of the coadsorbed overlayer is confirmed by the lack of emission from the Fermi level and the observation that Auger and plasmon-loss features are no longer present. We attribute the shift to higher binding energy of the Na $2p$ emission upon coadsorption to the metallic-to-nonmetallic transition of the overlayer species. The ionic nature of the Na after compound formation will result in an initial-state shift of the core level to higher binding energy. In addition, the transformation of the $3s$ electrons to a nonitinerant state after compound formation will result in a reduction in screening and a resultant increase in the measured binding energy as well. Therefore, both initial- and final-state effects must be considered when interpreting the shift of the $2p$ peak to higher binding energy. The $2p$ peak was also observed to broaden and increase in intensity after coadsorption. The most probable origin of this broadening is that a distribution of local binding sites is being occupied after compound formation. The increase in the integrated intensity of the $2p$ peak after coadsorption may be due to the shift of the spectral weight from the plasmon losses and Doniach-Sunjić losses into the main $2p$ peak.

The ARPES data provide strong evidence that the Na overlayer at ~ 2.0 ML undergoes a metallic-to-nonmetallic transition upon coadsorption with either H_2O or CO_2 . This gives strong support to our interpretation that the degree of attenuation of the FK modes is directly related to the electronic state of the overlayer species. In essence, the presence of free-charge carriers at the surface acts to damp out the coupling interaction

of the incident HREELS electrons with the FK surface phonons and that upon localization of these charge carriers the FK losses are allowed to return. This behavior is entirely consistent with the original theoretical predictions of the behavior of the FK surface modes of an ionic substrate terminated by a conducting layer.²² Although there are not enough data points in Fig. 2 to determine the exact functional dependence of relative attenuation of the 708-cm⁻¹ mode, it can be seen that only ~2.2 ML of Na are sufficient to almost fully attenuate the FK loss modes. This behavior is in good agreement with the observed FK attenuation on the Ag/GaAs(100) surface by Dubois *et al.*⁸ In this study the GaAs FK loss mode was observed to be nearly fully attenuated by a Ag overlayer coverage of 2.5 Å. They were also able to partially return the FK losses by annealing the surface which they attribute to islanding of the Ag at higher temperatures. To the best of our knowledge, our results are the only published ones where one has been able to attenuate a FK loss mode by the addition of an adsorbate and then have it return *without* reexposing the substrate to the vacuum. We would also like to note that significant shifts in the loss energies of the FK modes after adsorbate deposition were not observed with our system or in the study by Dubois *et al.*⁸

From HREELS measurements of the FK surface-mode losses of the Cr₂O₃(111) film as a function of Na coverage, we show that the development of a metallic Na overlayer causes the FK loss modes to attenuate. We also show that coadsorption of the metallic Na species with

CO₂ or H₂O results in the creation of a uniform dielectric overlayer and a resulting return of the FK loss features. ARPES measurements reveal suppression of emission from the Fermi level, the disappearance of the *LVV* Auger transition, and an increase in the binding energy of the Na 2*p* electron emission upon coadsorption which we attribute to the 3*s* valence electrons of Na becoming non-itinerant. Therefore, we have shown that the electronic state of an overlayer adsorbed on a polar substrate has a direct bearing on the coupling interaction of the HREELS electrons with the Fuchs-Kliewer modes of the substrate. Since the electronic state of adsorbed alkali-metal atoms is not only of great interest for understanding catalytic processes but also for a general understanding of the development of the metallic state of matter, the ability to measure overlayer metallization by observing the degree of attenuation of Fuchs-Kliewer modes with HREELS can provide new insight into the metallization process on oxide substrates.

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¹C. Lin, T. Ito, J. Wang, and J. H. Lunsford, *J. Am. Chem. Soc.* **109**, 4808 (1987).

²X. Zhang, R. K. Ungar, and R. M. Lambert, *J. Chem. Soc. Chem. Commun.* **8**, 473 (1989).

³C. Xu, B. Dillmann, H. Kuhlenbeck, and H.-J. Freund, *Phys. Rev. Lett.* **67**, 3551 (1991).

⁴S. Kennou, M. Kamaratos, and C. A. Papageorgopoulos, *Surf. Sci.* **256**, 312 (1991).

⁵D. Heskett, I. Strathy, E. W. Plummer, and R. A. de Paola, *Phys. Rev. B* **32**, 6222 (1985).

⁶R. A. de Paola, F. M. Hoffmann, D. Heskett, and E. W. Plummer, *J. Chem. Phys.* **87**, 1361 (1987).

⁷S. Mizuno, H. Tochihara, T. Kadowaki, H. Minagawa, and I. Toyoshima, *Surf. Sci.* **264**, 103 (1992).

⁸L. H. Dubois, G. P. Schwartz, R. E. Camley, and D. L. Mills, *Phys. Rev. B* **29**, 3208 (1984).

⁹J. E. Demuth and B. N. J. Persson, *Phys. Rev. Lett.* **54**, 584 (1985).

¹⁰N. J. DiNardo, T. M. Wong, and E. W. Plummer, *Phys. Rev. Lett.* **65**, 2177 (1990).

¹¹C. Xu, M. Hassel, H. Kuhlenbeck, and H.-J. Freund, *Surf. Sci.* **258**, 23 (1991).

¹²H. Kuhlenbeck *et al.*, *Ber. Bunsenges. Phys. Chem.* **96**, 15 (1992).

¹³*Physics and Chemistry of Alkali Metal Adsorption*, edited by H. P. Bonzel, A. M. Bradshaw, and G. Ertl, *Materials Science Monographs*, Vol. 57 (Elsevier, New York, 1989).

¹⁴C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1986).

¹⁵L.-G. Petersson and S.-E. Karlsson, *Phys. Scr.* **16**, 425 (1977).

¹⁶B. Itchkawitz, Ph.D. dissertation, University of Pennsylvania, 1991.

¹⁷S. Doniach and M. Sunjic, *J. Phys. C* **3**, 285 (1970).

¹⁸D. C. Langreth, *Phys. Rev. B* **1**, 471 (1970).

¹⁹J. Wambach, G. Odörfer, H.-J. Freund, H. Kuhlenbeck, and M. Neumann, *Surf. Sci.* **209**, 159 (1989).

²⁰J. A. Connor, M. Considine, and I. H. Hillier, *J. Electron. Spectrosc. Relat. Phenom.* **12**, 143 (1977).

²¹P. A. Thiel and T. E. Madey, *Surf. Sci. Rep.* **7**, 211 (1987).

²²R. Fuchs and K. L. Kliewer, *Phys. Rev.* **140**, A2076 (1965).