Observation of Surface States in the Auger Spectra of Clean and Oxygen-Chemisorbed Si(111) 7×7

M. C. Muñoz, V. Martínez,[a] J. A. Tagle,[b] and J. L. Sacedón
Laboratorio de Lámina Delgada, Instiuto Física de Materiales, Consejo Superior de Investigaciones Científicas, Serrano 144, Madrid, Spain

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The first observation of Si(111) 7×7 intrinsic surface states that uses Auger electron spectroscopy as a valence band spectroscopy is reported. A global inversion method based upon the fast Fourier transform was used to self-deconvolve the Auger spectra. Subsequent oxygen chemisorption is shown to give rise to O_2 electronic levels. Only at the beginning of the oxidation stage are the surface states completely removed.

Self-deconvolution methods have been recently developed in order to use Auger electron spectroscopy (AES) as a valence band spectroscopy.[1,2] With the help of these methods XVV Auger transitions from a number of pure elements and their oxides have been analyzed and their corresponding transition densities (TDOS) compared[3-7] with the bulk density of states (DOS) obtained by other methods. The conclusion from these studies is that once all the unwanted information unrelated to DOS (noise data reduction, secondary electron background subtraction, and deconvolution with the instrumental response function) has been removed,[6] and only when high-resolution self-deconvolution global inversion methods[2] are used, and the TDOS obtained by Auger techniques is in good agreement with that obtained by other techniques. However, in order to predict better the relative intensities of the peaks, the study of basic physical effects (Auger matrix-element energy dependence, initial inner-hole localization, and incomplete screening of the final-state holes) still needs a theoretical effort and an experimental data base.

Electron-spectroscopy studies of the clean Si(111) 7×7 surface and its early stages of oxidation have been many.[8-10] Observation of surface states on the clean surface has been previously reported,[8] but the problem of whether the initial chemisorbed oxygen is in a molecular or a dissociated state is still controversial.[10] Before this work no surface states had been detected directly by AES. Only on a W(100) surface has an indirect observation of surface states been made by comparison of the experimental $N_{67}VV$ Auger spectrum with a self-convoluted theoretical bulk density of states.[11] The main purpose of this Letter is to report the first direct observation, using AES, of Si(111) 7×7 surface states and their further behavior during the chemisorption and initial oxidation stages. We show also that the oxygen-chemisorption stage corresponds to molecular adsorption.

Starting from a Si(111) 7×7 clean surface (C contamination $\theta = 0.005$, where $\theta = 1$ corresponds to 1 monolayer) and a residual pressure of 3×10^{-10} Torr, two kinds of experiments were carried out in order to determine the effect of the electron bombardment, which has been shown to be important on oxygen chemisorption and oxidation of silicon.[8,12] Firstly, the specimen was bombarded with an electron beam of 25-μm diameter and 10 μA at 3 keV while it was exposed to oxygen pressures ranging from 10^{-8} to 10^{-4} Torr. Saturation values of the oxygen (506 eV) and silicon oxide (76 eV) Auger signals were reached for each pressure value. The calibration of Auger intensities in monolayers was made by comparison of the O, Si, and SiO_2 signals during the experiment with use of the general quantitative Auger formalism[13] and will be described elsewhere.[14] The SiO_2 signal began to appear only when the O signal reached an oxygen coverage corresponding to $\theta = 0.8$ ($\theta = 1$ population consists of one O atom for each Si surface atom). The maximum SiO_2 signal observed at the end of the oxidation process corresponded to 16 Å of SiO_2 coverage. Secondly, no electron-beam bombardment was used while the surface was exposed to increasing oxygen pressures. When the pressure dropped again to 3×10^{-10} Torr no measurable SiO_2 signal was detected, regardless of dose (the highest dose was 2 h at 8×10^{-5} Torr). In all these cases the Auger spectrum is the same as the one obtained in the first kind of experiment at the end of the chemisorbed state.

From these experiments we conclude that the chemisorption stage, without traces of SiO_2, appears for coverages lower than 0.8 monolayers of oxygen. After this coverage was reached no oxidation was detected without electron-beam-bombardment stimulation.

The derivative forms of Auger spectra corresponding to Si(111) 7×7 clean surface and different oxygen coverages are shown in Fig. 1. The spectrum with $\theta = 0.8$ corresponds to 1 Å of O_2 chemisorbed at the surface. At the initial oxidation stage the Auger spectrum is characterized by a fractional coverage of $\theta = 0.2$ of SiO_2 (1 Å of SiO_2 equivalent to $\theta = 0.37$) and $\theta = 0.8$ of O_2, giving a total amount of 1.6 Å. Because of the progressive overlapping of SiO_2 and Si spectra when the oxidation increases, self-deconvolution of more advanced oxidation stages was not feasible at this time. The spectra were self-deconvoluted using a recent global method based upon the discrete Fourier transform.[2] Inelastic and instrumental-response effects were removed in three steps: (i) Background subtraction was performed employing Sickafus's procedure[15]; (ii) integration of dN/dE was performed with use of a trapezoidal algorithm which does not involve data smoothing; and (iii) deconvolution was performed with the elastic peak and its associated losses taken at the same incident electron energy as the Auger spectrum. The signal-to-noise ratio of data was very high ($\simeq 10^3$) and no numerical smoothing was necessary.

Figure 2 shows the TDOS obtained by self-deconvolution of the $L_{23}VV$ spectrum of the clean Si(111) 7×7 surface (Fig. 1, $\theta = 0.0$). A richer structure appears in this TDOS, compared to previously published data,[6] as a result of a finer sampling of data of higher resolution together with some improvements in data handling.[14] We compare our result with the theoretical DOS corresponding to a 25% vacancy model of this surface.[16] The peak positions obtained [−0.30 (*A*), 1.0 (*B*), 2.0, 2.7 (*s*), 3.7 (*s*), 5.5, 6.5, and 8.7 eV, where *s* stands for shoulder] are in good agreement with those of the theoretical model[16] [−0.45, 1.2, 2.0, 3.0, 3.8, 5.5 (*s*), 6.5 and 9.5 eV]. The maximum (*A*) above $E_v = 0$ is well resolved in our result and it is attributed to a surface state due to the dangling bond pointing perpendicular to the surface. The peak (*B*) corresponds to a dangling bond pointing towards the vacancy site of the second layer. The low intensities of the other peaks have been attributed to a strong matrix-element effect involving the relative increase of the *p*-state contribution to the $L_{23}VV$ Auger spectrum of the Si(111) surface.[17]

The behavior of these surface states with the oxygen chemisorption is shown in Fig. 3. When the oxygen adsorbed is ≃0.8 ml [Fig. 3(b)] the first surface state (−0.3 eV) disappears (oxygen-chemisorption stage) and if we reach an oxide coverage of 0.2 ml of SiO_2 (initial oxidation stage) the two surface states (−0.3 and 1.0 eV) are suppressed [Fig. 3(a)].

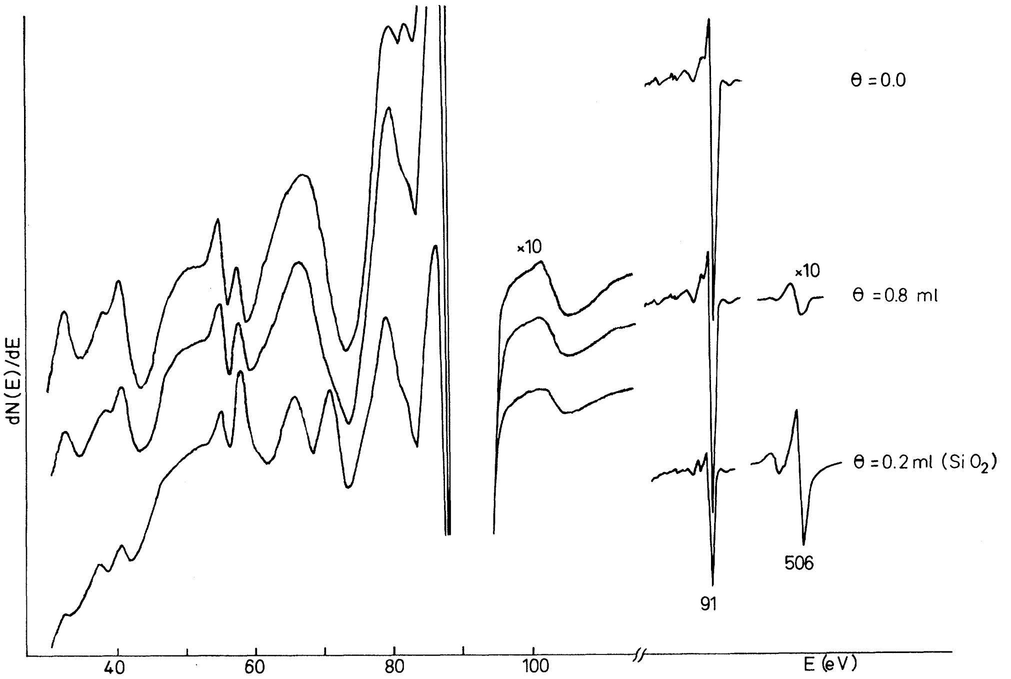

FIG. 1. $L_{23}VV$ Auger spectra for clean, oxygen-chemisorbed, and initial oxidation stages of Si(111) 7×7 surface. Left part shows detail of Si spectra. Right part shows the complete Si and O spectra.

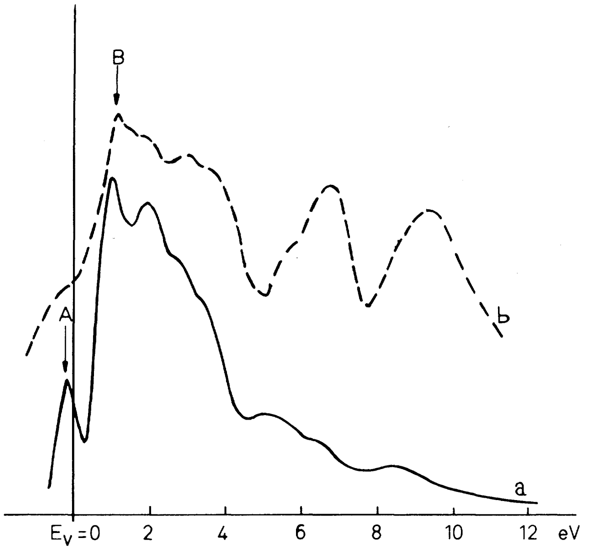

FIG. 2. (a) Self-deconvoluted Si $L_{23}VV$ transition density from Si(111) 7× 7 clean surface, and (b) 25%-vacancy model density-of-states calculations (Ref. 16).

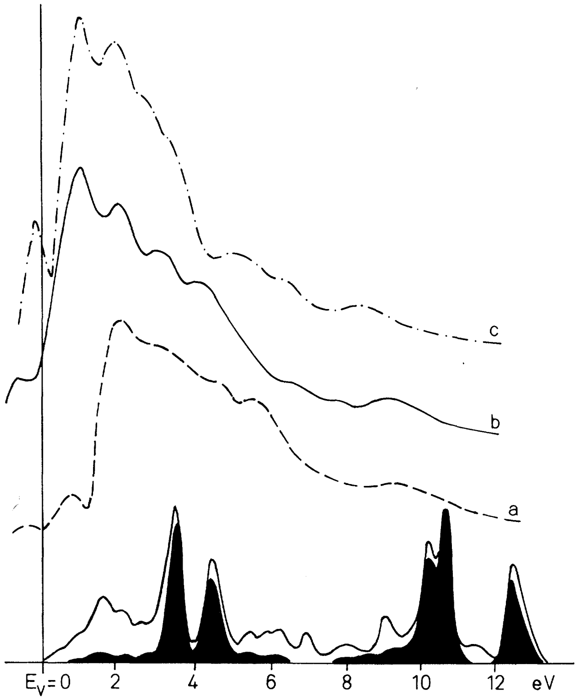

FIG. 3. Auger transition densities from (a) the initial oxidation stage, (b) the oxygen-chemisorbed stage, and (c) the Si(111) 7× 7 clean surface. Bottom panel: theoretical DOS of a monolayer of O_2 on Si(111) surface (Ref. 10); shaded areas show the partial oxygen DOS.

We also report the first correlation between the TDOS obtained by AES of the Si(111) 7×7 surface in the course of oxygen chemisorption and subsequent oxidation and the theoretical calculations of the corresponding system. In the chemisorption stage [Fig. 3(b)] two new subbands appear at 4 and 10 eV. The subband at 4 eV splits into two peaks at 3.5 and 4.2 eV. We compare this result with a recent calculation for one monolayer of molecular oxygen chemisorbed on a Si(111) 7×7 surface,[10] which assumes that the O_2 molecule axis is parallel to the surface and the bond of O_2 molecule with the Si surface is the one corresponding to the SiO_2 molecule. In this model the subbands at 4 and 10 eV correspond to O_2 molecule orbitals which split and shift slightly when the O_2 molecules reach a monolayer (Fig. 3, bottom panel). Only when charge transfer between O and Si electronic levels is considered does the peak at 12.5 eV appear. This peak has no counterpart in our result. The above results suggest that the present spectrum can be explained in terms of interatomic transitions[18] whic show the contribution of the molecular adsorbate electronic levels to the substrate Auger line shape. The above mentioned theoretical DOS makes a clear difference between the adsorbate electronic levels and those corresponding to the total system, allowing us to assign clearly the interatomic character of these peaks. The former comparison enables us to conclude that in the chemisorption stage the oxygen is adsorbed in molecular form on Si(111) with its molecular axis parallel to the surface.

Once the initial oxidation stage is reached a new peak at 5.6 eV ($E_v=0$) appears. This peak has the position of an interatomic transition from a P_x or P_y oxygen orbital in the SiO_2 molecule to a hole in the $2p$ level of the silicon ion. This interatomic transition has also been observed previously in the SiO_2 DOS,[7] and we associated it with the main peaks at 6 eV $(E_F=0)$[19] and 11.8 eV $(E_{vac}=0)$[20] observed in ultraviolet photoelectron spectroscopy. Our result shows clearly that this peak is only present in the oxidation stage. A previous report[20] associated this peak to a chemisorption stage, but this might be due to the presence of a certain amount of SiO_2.

In conclusion, AES has been shown to have the capability of detecting surface states on Si(111) 7×7 clean surfaces and also of detecting a molecular-oxygen chemisorption state. It should be remarked that a fair agreement with theoretical DOS was also reached. The fact that these calculations are very sensitive to surface bonding allows us to conclude that, as was previously suggested,[21,22] the use of AES as a sensitive probe of the electron environment of surface atoms, especially as a surface bonding probe, is experimentally well established.

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[a] Permanent address: Centro de Investigación UAM-IBM, Canto Blanco, Madrid, Spain.

[b] Permanent address: Laboratorio de Física de Superficies, UAM, Canto Blanco, Mardrid, Spain.

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Screening and Configuration-Interaction Effects in the 5*p* X-Ray-Photoelectron Spectrum of Th Metal

T. K. Sham and G. Wendin[a]
Brookhaven National Laboratory, Upton, New York 11973

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This paper reports unusual structures in the x-ray photoelectron spectrum of the 5*p* level of thorium metal and proposes that the low-lying empty 5*f* levels are responsible for such a complicated 5*p* spectrum through two mechanisms: (i) fluctuation of the core hole between $5\underline{p}$ and $5\underline{d}^2 5f$ configurations (underline denotes a hole level) and (ii) shake-up from filled valence levels to empty low-lying 5*f* levels.

Relaxation and decay of the core holes left behind in photoemission processes have recently attracted large experimental and theoretical interest.[1-15] It has been observed in many cases that the core-level spectra strongly deviate from what can be expected on the basis of a one-electron picture. These situations are usually connected with the core hole pulling down empty levels to the vicinity of the occupied valence levels. The low-lying orbitals are important particularly in two ways. They sometimes allow a core hole to fluctuate between nearly degenerate configurations which may lead to very strong level shifts, satellite structure, and damping.[14,15] They may also lead to localization of screening charge to atomiclike orbitals, resulting in shake-up and even shakedown satellite structures.[14-16]

In this Letter, we report the 5*p* spectrum of thorium metal[17] and attempt to interpret the Th 5*p* spectra based on these mechanisms. X-ray photoemission spectra of Th metal were obtained with a VG ADES 400 spectrometer. The metal films were prepared by *in situ* evaporation of Th metal onto either Au or Al foils at liquid-nitrogen temperature. The backing materials were etched with clean Ar^+ and then annealed in high vacuum. The operating pressure inside the spectrometer was less than 1×10^{-10} Torr during the