

Atomic Structure of the (0001) Corundum Surface

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Abstract. The electronic structure and geometry of the Al terminated corundum (0001) surface were studied using a slab model within the *ab-initio* Hartree-Fock technique. The distance between the top Al plane and the next O basal plane is found to be considerably reduced on relaxation (by 0.57 Å, i.e. by 68% of the corresponding interlayer distance in the bulk). An interpretation of experimental photoelectron spectra (UPS HeI) and metastable impact electron spectra (MIES) is given. Calculated projected densities of states exhibit a strong dependence on the relaxation of surface atoms.

Introduction. Alumina surfaces have been studied extensively because of their technological importance [1]. Theoretically, the simplest nonpolar Al terminated (0001) corundum surface was predicted to be the most stable ideal termination of the bulk structure [2,3]. Pioneering *ab initio* Hartree-Fock (HF) calculations using the minimal (STO-3G) basis set of atomic orbitals (AO's) have predicted a large inward displacement (relaxation) of the terminating layer of Al atoms (0.4 Å, or 48% of Al - O interlayer spacing) [4]. Further calculations performed in the local density approximation (LDA) with pseudopotentials and a plane wave basis set predicted an even larger relaxation of about 0.7 Å [5]. The calculations using pair potentials based on the empirical shell-model [3] predict the surface relaxation to be intermediate between the HF [4] and LDA [5] data.

The incentive for this study comes from our recent combined experimental and theoretical study of the MgO (001) surface [6]. It has demonstrated that the UPS (He I) and MIES¹ (He* 1s2s) spectra which have quite different structures in the valence band energy region, can be well approximated by the total density of states (DOS) of a thin crystalline slab and the DOS projected to the surface O ($2p_z$) AO's, respectively (PDOS) [6]. Moreover, the results of these calculations demonstrated that the shape of both DOS and PDOS is very sensitive to the surface relaxation. This leads to the possibility of extracting information on surface atomic structure through the comparison of DOS and PDOS calculated for different surface relaxations with the experimental spectra.

In this paper we explore the above possibility in more detail for the case of the alumina surface. UPS and MIES spectra of the corundum monocrystalline (0001) surface and corundum films on Al (111) and W (110) substrates have recently been published [7-9]. As follows from LEED and ISS data, the films grown on Ta(110) [10] and W(110) [9] are Al terminated (0001) corundum or (111) γ -Al₂O₃ structures. Therefore Al electronic states must contribute to the valence band DOS [4], and the straightforward interpretation of electron spectra given for the simple ionic rocksalt-type insulators like MgO may not be valid for corundum.

We study the relationship between the atomic and electronic structure of the relaxed corundum (0001) surface and the UPS and MIES spectra. A novel method is proposed for the comparison of MIES spectra with theory: in order to simulate in a direct way the projectile-surface interaction (via

¹ For an introduction to MIES see V. Kempter: this volume.

Auger deexcitation connected with electron emission), the DOS projected onto the floating $1s$ orbital of He atom above the surface is calculated and analysed as a function of the He coordinates.

Theoretical method and results. To model the experimental spectra we have used the same method as discussed in ref. [6] for MgO. The electronic structure and the total energy of the corundum slab containing three O and 6 Al atomic layers parallel to (0001) plane terminated by an Al layer were calculated within the Hartree-Fock approximation as implemented in the CRYSTAL computer code [11]. An 85-11G/8-411G basis set augmented with polarization functions was used for Al and O, respectively. [12].

The atomic structure of the surface corresponding to the minimum of the slab total energy with respect to the 7 independent atomic coordinates was found using the least square fit of the energy surface to the quadratic form. The major displacements from the perfect bulk positions are that of Al atoms in the top surface layer. The inward relaxation value of 68% of the Al – O bulk interlayer distance have been found, which is 20% larger than the previous HF result [4]. This difference can be attributed to the more extended basis set and to the larger number of degrees of freedom taken into account in the minimization procedure. Further extension of the basis set with d polarization functions on Al increases this relaxation by 5%. However, our relaxation is still smaller by 17% than that obtained in the LDA calculations [5]. The surface relaxation energy, defined as the difference in total energies of relaxed and unrelaxed slabs, was obtained to be 6.23 eV per unit cell. Three quarters of the relaxation energy gain is due to the inward displacement of the surface Al.

In the MIES experiment the interaction of the He^* probe atom with the surface takes place via the Auger deexcitation process along the entire trajectory in front of the surface. The projectile moves with thermal kinetic energy and the electron emission occurs on the incoming path of the trajectory at comparatively large distances (several atomic units, typically); the transition energy is not strongly influenced by the actual interaction potentials of the initial and final states. We have shown on several occasions [7, 6] that under these conditions the MIES spectra is proportional to the surface density of states relevant for the interaction with He^* .

The spectrum of the emitted electrons may depend on the incident He^* coordinate along the surface. In order to simulate this dependence, we have calculated the DOS projected to the floating He $1s$ orbital as a function of its coordinates. We find that the shape of this DOS does not depend on the distance from the surface (vertical z coordinate) while its magnitude decreases exponentially in the range of z varied between 2 and 4 Å reflecting the average behavior of the overlap integral between the floating AO and surface wave function.

In Fig. 1 we show the He ($1s$) projected DOS averaged along the surface at a distance $z = 2.1$ Å which is close to the typical distance where the Auger deexcitation of He^* projectile takes place. The dotted curve in Fig. 1 was calculated for the slab geometry predicted by the LDA method.

In this paper we do not develop the rigorous theory for the UPS spectra, we merely assume that the structure in the valence band UPS (HeI) spectra is proportional to the valence band DOS of the near-surface region. It was proved to be a good approximation for the case of MgO (100) surface [6] and we believe that this is also the case for Al_2O_3 (0001). The DOS projected to the surface O atom is given in Fig. 1 along with UPS data.

Comparison with experiment. The spectra represented by light lines in Fig. 1 were obtained from corundum films grown by coadsorbing Al and O_2 molecules onto a W (110) substrate held at 750K [8]; the film thickness was estimated as 13 Å. Electron energies are given with respect to the vacuum level. The value of 3.8 eV for the surface workfunction of the film was determined from the UPS spectra.

The MIES spectra show very little intensity above the top of the valence band (VB) ($E > 9.3$ eV). We attribute the “soft tail“ of the valence band emission to the ionization of such surface oxygen species which have a lower coordination than in the bulk, located at kinks, steps, etc. The VB emission consists of a pronounced peak ($E = 9.8$ eV) and a shoulder ($E \approx 12.3$ eV) towards higher binding energies. The UPS spectra show the same two VB features ($E = 9.8; 12.3$ eV). The weak intensity above the top of the VB (denoted as B) is not well understood at present: it may be due to emission from the underlying substrate and/or from point defects located underneath the surface. The high energy part of both spectra above 16 eV (denoted as A) is known to be affected by the emission of secondary electrons. Thus this energy region will not be interpreted here.

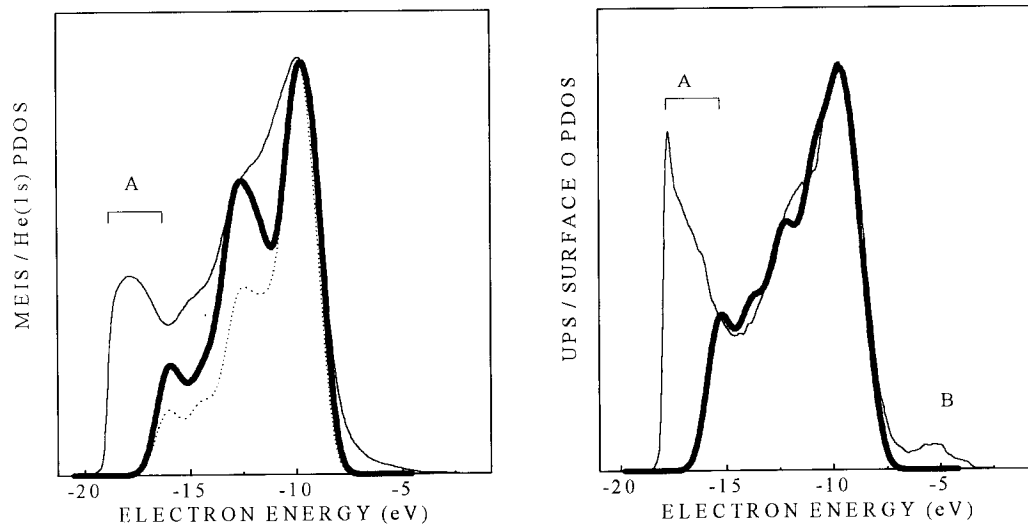


Fig. 1. The experimental MIES (left panel) and UPS (right panel) spectra for corundum films produced by coadsorption of Al and O₂ on W (110) substrate [8] (thin curves). Heavy curves show the result of theoretical simulations of MIES and UPS. Dotted curve is theoretical MIES spectrum for the surface structure predicted by LDA method [5]. HF method have been used to calculate DOS. The energy scale corresponds to the experimental electron binding energy. Theoretical curves are shifted by 1.7 eV in order to match the experimental top of the VB.

The calculated surface DOS is in good agreement with UPS spectra (Fig. 1). This confirms that the photoemission spectrum at HeI incident photon energy is mainly dependent on the initial state electron wavefunction. The final state effects including the dispersion of the conduction band and photoelectron scattering at the surface potential barrier might be important for larger photon energies and angle resolved UPS interpretation, but are probably less important in our case.

The result of the MIES spectra simulation with He 1s orbital as a probe of the surface DOS is close to the experiment. However, the peaks in the experimental spectra appears broader than in the simulated one as it was also the case in MgO. Three possible explanations have been suggested for this discrepancy [6]. As it is seen from Fig. 1, the second peak in the simulated MIES spectrum at the LDA geometry has significantly lower amplitude relatively to the HF geometry, thus giving less satisfactory agreement with experimental spectrum.

From the comparison of the surface DOS and that projected to 1s orbital of the He* projectile with the relevant UPS and MIES spectra, respectively, it is seen that the agreement between theory and

experiment is satisfactory; the positions of the peaks and their relative magnitudes are similar. The comparison of the MIES spectrum with theoretical simulations allows us to discriminate between the HF and LDA optimized slab geometries in favor of that found in this paper using the HF technique.

Conclusion. The results of present calculations demonstrate that in corundum, like in MgO, the shape, relative positions and intensities of the peaks in the surface density of electronic states (DOS) are in satisfactory agreement with the experimental HeI photoelectron spectra (UPS). The metastable impact electron spectrum (MIES), arising from the Auger deexcitation of the He⁺ metastable atom near the surface can be approximated by the DOS projected to a floating 1s atomic orbital (AO) which simulates the probing He atom. This method appears to be more accurate for the simulation of the MIES spectra than just the comparison with DOS projected to the p_z AO of surface atoms used for MgO [6]. We also found that both DOS strongly depend on the surface relaxation. This allows us to study details of the surface atomic structure by means of a comparison of the projected DOS calculated using *ab initio* methods with experimental MIES and UPS spectra. The present Hartree-Fock calculations predict an inward relaxation of the top Al layer as large as 68% of the Al - O interlayer distance. This slab geometry gives the surface projected DOS which is in the best agreement with the experimental MIES and UPS spectra.

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