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# Cs adsorption on oxide films $(Al_2O_3, MgO, SiO_2)$

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#### Abstract

Films of alumina, magnesia, and silica were exposed to cesium atoms at room temperature. Cesium adsorption as a function of exposure time was studied with metastable impact electron spectroscopy (MIES) and photoelectron spectroscopy (UPS; He I). On silica, cesium atoms readily chemisorb in the initial stages of exposure. The bonding is apparently due to the interaction with active surface oxygen such as non-bridging oxygen atoms. We suggest that on alumina and magnesia, the chemisorption of cesium, in the form of an ionic state, takes place at surface defects, presumably edge sites such as steps, kinks, corners, etc. In all cases studied, prolonged exposure leads to additional Cs adsorption. Apparently, patches with metallic properties (but no uniform adlayer) develop on the surface; they disappear after the cesium supply is interrupted. © 1997 Elsevier Science B.V.

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#### 1. Introduction

The study of the adsorption of alkali atoms on metals has a long tradition, reaching back to Taylor and Langmuir [1] (see Ref. [2] for a recent review). At low coverages a fairly general picture appears to exist: the alkali atom transfers its valence electron to the substrate. The alkali ions form a dipolar layer which lowers the work function and is responsible for the repulsive dipoledipole interaction between the adatoms. At higher coverages, the delicate balance between the adsor-

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bate-adsorbate and adsorbate-substrate interactions leads to a wealth of overlayer structures.

The adsorption of alkali atoms on semiconductors is less well understood. In general, semiconductors display dangling bonds at the surface which protrude into the vacuum, similar to the surface states of metals. However, even for the extensively studied Si(100)- $(2 \times 1)$  substrate, substantial disagreement exists concerning the overlayer structure and the nature of the alkali bonding to the substrate (for some recent papers on these issues, see Refs. [2–9].

Studies of the interaction of alkali atoms with insulators such as oxide surfaces are limited (see Ref. [10] for a summary). Nevertheless, metal particles and adlayers on oxide surfaces are relevant to crystal growth, catalysis, gas sensor applications, bonding in composites, etc. Many catalysts

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consist of small metal particles on high surfacearea powders of SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>. Often, the interaction of alkali atoms with such surfaces is very weak, and may be confined mainly to interaction with surface defects [10]. However, it was shown that this need not to be the case in general, as was demonstrated for example for alkali adsorption on NiO [11] and TiO<sub>2</sub> [12,13]. Clearly, more work is required to clarify the interaction of electropositive atoms with insulator surfaces.

In this paper we present results from our study of the interaction of cesium atoms with ionic oxides (alumina, magnesia) and the more covalent silica, employing the electron spectroscopic techniques photoelectron spectroscopy (UPS, He I) and metastable impact electron spectroscopy (MIES). The specific merits of MIES for the present study are two-fold: (i) its ability to reveal changes in the valence band surface density of states introduced by the adsorbed species. This is due to the fact that MIES is particularly sensitive to the part of the surface wave functions which protrudes into the vacuum [14,15], and (ii) its high sensitivity (as compared to UPS) for the detection of the charge density of the alkali s-electron. This in turn implies a large sensitivity for the detection of charge transfer from the alkali adsorbates to the surface.

In order to avoid complications due to the charge-up of insulating substrates, our studies were carried out with insulating oxide films, which on the one hand already display the electronic properties of the bulk oxides, but on the other hand are sufficiently thin not to be subject to charge-up phenomena.

#### 2. Experimental

The apparatus used has been described previously [16–18]. Of particular relevance to this work are our studies of alkali adsorption on Si(100) [18], the production of alumina layers on tungsten and aluminium [19,20], and the study of the oxygenation of Mg films on silicon [14]. Briefly, a cold-cathode He gas discharge serves both as the source for an intense metastable He beam (for MIES) and as a He I photon source (for UPS). A time-of-flight technique is utilized in order to separate contributions to the electron spectra from the impact of He I photons and He<sup>\*</sup> metastables. The incidence angle of metastables and photons is 45° with respect to the surface. The energy spectra of the ejected electrons are recorded normal to the surface. The time required to collect a complete spectrum is typically 2.5 min for MIES and UPS. The energy scales in the figures are adjusted in such a way that electrons emitted from the Fermi level (i.e. the electrons with the maximum kinetic energy) occur at 21.2 eV in UPS and at 19.8 eV in MIES (because of the 1.4 eV smaller excitation energy of the He metastables (19.8 eV for  $He(2^{3}S)$ ). The energy at which electrons originating from the Fermi level appear in the photoemission or Auger de-excitation spectra (in MIES) is denoted by  $E_{\rm F}$ ; the binding energies quoted in this work refer to this energy. The low energy cut-offs in the spectra correspond to electrons leaving the surface with zero kinetic energy. These cut-offs give directly the change in the surface work function as a function of the Cs coverage, irrespective of the actual interaction process which leads to the production of electrons. The spectra are corrected for the energy-dependent transmission of the electrostatic analyzer.

In addition, there are facilities for AES and LEED. The apparatus is also equipped with a twin-anode (Mg, Al) XPS source. These facilities are of particular value during the preparation stage of the clean silicon substrates and in the determination of the film thickness.

Naturally oxidized Si(100) served as the substrate for the deposition of Cs atoms. Prior to any study, it was heated to 900 K for 24 h. The thickness of the oxide film (determined with XPS) obtained in this way is about 11 Å. Prior to the Cs exposure, the oxide surface was exposed to 500 L oxygen at room temperature in order to obtain an oxygen-terminated surface. This procedure did not introduce additional structures in either the MIES or the UPS spectra. XPS suggests that the surface is SiO<sub>2</sub>.

An Al(111) surface (Mateck Company) served as the substrate for the alumina films. Before starting the oxidation procedure, the Al surface



Fig. 1. MIES spectra during the exposure of a silicon oxide film to cesium. Cs atoms were supplied continuously. The time elapsed between two adjacent spectra is 1 min. The bottom spectrum is for the clean silicon oxide substrate.

was cleaned by repeated cycles of sputtering with  $Ar^+$  and annealing to 873 K.

The following procedure was applied in order to produce the alumina films: the Al(111) surface was exposed to 200 L oxygen at room temperature. This was followed by thermal annealing in several steps up to 850 K. Finally, an additional 500 L oxygen was offered at an elevated temperature of 850 K. This procedure gave UPS (He I) and MIES spectra (see the bottom spectrum of Fig. 5) which are typical for alumina surfaces [19,20].

The magnesia film was obtained as described in Ref. [14]: a Mg film (thickness >10 nm as estimated with XPS) was deposited on Si(100). This film was exposed to oxygen at room temperature under the control of MIES and UPS until a welldeveloped band gap was obtained. The oxygenated Mg film shows features typical of the valence-band emission from MgO(100) [14]. However, apart from this, additional features were seen which were attributed to the presence of oxygen complexes



Fig. 2. UPS (He I) spectra during the exposure of a silicon oxide film to cesium (other details as in Fig. 1).

such as oxygen peroxide ions  $(O_2^{2^-})$  at the surface [14]. MIES and UPS spectra, essentially identical to those from MgO(100) (see Ref. [14] and references therein), were obtained after heating the adlayer to 800 K. The thickness of the MgO layer produced in this way was estimated to be >2 nm from XPS.

Cs atoms were deposited at room temperature onto the oxide surfaces using dispenser sources (SAES Getters Company) which were carefully outgassed. The exposure rate was kept constant during an entire exposure cycle, and small enough so that the work-function change between two adjacent measurements was only of the order of a few tenths of an eV at most. Approximately the same exposure rate was employed for deposition on all substrates. All measurements were carried out at room temperature.

Fig. 1 presents the MIES results obtained during the exposure of the silica film to cesium. Electrons emitted from the Fermi level possess 19.8 eV kinetic energy for He<sup>\*</sup> probe atoms. We note several Cs-induced features, labeled Cs(6s),



Fig. 3. MIES spectra during the exposure of a magnesia film to cesium. Cs atoms were supplied continuously. The time elapsed between two adjacent spectra is 2 min. The bottom spectrum is for the clean magnesia film.

Cs(5p), and (1)–(3). It is worth pointing out that feature (1) was seen only if an oxygen-terminated silica surface was prepared in the way described above. The identification of Cs(6s) follows from earlier work on Cs adsorption (see, e.g., Ref. [18]); it is caused by the presence of the Cs 6s electron at the adsorbate atom (see Section 3 for details). The expected position of the doublet caused by the ionization of the Cs  $5p_{1/2;3/2}$  states, labeled Cs(5p), is also indicated. Because of its weakness, feature Cs(5p) cannot be distinguished from substrate emission with certainty. O(2p) and Si–O denote emission from the silica valence band.

Fig. 2 presents the corresponding UPS (He I) results obtained during the exposure of the silica film to cesium. Electrons emitted from the Fermi level possess 21.2 eV kinetic energy. In general, features occur at or near the same binding energies (with respect to the Fermi level) in both the MIES and UPS spectra, and these features are labeled accordingly. The feature labeled "M" is an experi-



Fig. 4. UPS (He 1) spectra during the exposure of a magnesia film to cesium (other details as in Fig. 3).

mental artefact and originates from the incomplete separation of the photoelectron and metastable emission in the UPS spectra. As for Cs adsorption on metals and semiconductors (see Ref. [18] and references therein) Cs(6s) is not seen by UPS.

Figs. 1 and 2 also show the development in time of the spectra after the Cs supply is stopped.

Figs. 3 and 4 display the MIES and UPS results collected during the exposure of the magnesia film to cesium. Apart from the emission due to the ionization of valence band states (labeled O(2p)), intensity involving the Cs 6s electron, labeled accordingly, is seen at  $E_F$  with MIES; the intensity seen beyond  $E_F$  is caused by the small fraction (about 10%) of 2<sup>1</sup>S metastables present in the probe beam. The energetic position where intensity from the ionization of the Cs  $5p_{1/2:3/2}$  states should appear is also indicated. Only at large exposures does a structure develop in the UPS spectra which can be attributed to the ionization of these states.

Fig. 5 presents the MIES results obtained during the exposure of the alumina film to cesium. The



Fig. 5. MIES spectra during the exposure of an alumina film to cesium. Cs atoms were supplied continuously. The time elapsed between two adjacent spectra is 1 min. The bottom spectrum is for the clean alumina film.

emission labeled O(2p) is due to the ionization of states from the alumina valence band (see Section 3). We recognize emission involving the Cs 6s electron in the MIES spectra (Cs(6s)). Cs(5p) cannot be distinguished unambiguously from the substrate emission.

From the general weakness of the Cs 5p emission in Figs. 1–5, and from a comparison with MIES results for the adsorption of Cs on metals, we estimate the coverage at the onset of the feature Cs(6s) to be less than 4% of a monolayer for all cases studied. On the basis of the data presented in Ref. [21] for Cs and water coadsorption on magnesia, we can estimate the Cs coverage in the top spectra of Figs. 3 and 4 to be 0.4 monolayer equivalents (assuming an uniform adlayer).

The development in time of the spectra after terminating the Cs supply was also studied for adsorption on magnesia and alumina. For clarity, these spectra are not reproduced here (see Sections 3.3 and 3.4). Figs. 6a-c (see Section 3) present the exposure dependence of the surface work function, intensity and width of the feature Cs(6s) derived from results such as those shown in Figs. 1–5.

#### 3. Discussion

## 3.1. The oxide substrates

Our UPS (He I) and MIES spectra from the silica films in general agree well with those of Ref. [22]: both the UPS (He I) and MIES spectra display the two structures Si-O and O(2p) (see bottom spectra of Figs. 1 and 2) at  $E_{\rm B} = 7.8$  and 11.3 eV for UPS, and  $E_B = 7.8$  and 10.7 eV for MIES, characteristic of the non-bonding O(2p)and the  $\sigma$ -type Si–O–Si bond of the silicon oxide surface, respectively [22]. We would like to discuss one particular aspect which has obviously not yet addressed: while O(2p)been occurs at  $E_{\rm B} = 7.8$  eV both in UPS and MIES, this is not the case for Si–O (seen at  $E_{\rm B} = 10.7$  and 11.3 eV in MIES and UPS, respectively). On the basis of the results of Ref. [23], we propose the following explanation for the different energetic position of the Si-O structure in MIES and UPS. Although the termination of the silicon oxide surface by oxygen does not introduce an additional state above the valence band, the oxygenation procedure pulls out the band labeled O<sub>2</sub> in Ref. [23] from the bulk  $O_{\sigma}$  bands.  $O_2$  is located only about 2 eV below the  $O_{\pi}$  bands. While UPS detects mainly emission from the ionization of  $O_{\pi}$  and  $O_{\sigma}$ , MIES instead sees, besides the emission from  $O_{\pi}$ , a superposition of  $O_{\sigma}$  and  $O_2$ , i.e. MIES is sensitive to the changes in the surface electronic structure introduced by the oxygen termination.

We have shown in Ref. [15] that the UPS and MIES spectra from the alumina films produced in the way described in Section 2 agree well with those calculated for a corundum (0001) surface. There is considerable evidence that the surface is Al-terminated; nevertheless, the emission seen with both methods is mainly due to the O 2p orbitals of the uppermost oxygen layer. MIES is particularly sensitive to the 2p orbitals protruding into the vacuum. The UPS and MIES spectra from the magnesia films agree well with those reported previously and with those from MgO(100) surfaces [14]. On the basis of ab initio calculations for MgO(100), we have explained why the valence band emission seen with UPS (He I) and MIES is different [14]: MIES is sensitive mainly to the O  $2p_z$  orbital protruding into the vacuum, while UPS also detects the O  $2p_{x;y}$  orbitals oriented within the surface plane. This fact accounts for the additional peak seen at  $E_B = 9$  eV.

## 3.2. Cesium adsorption on silica

Several Cs-induced features appear in the MIES spectra during the first phase of the exposure to Cs atoms: the intensity at the Fermi level (labeled Cs(6s)) and two features at  $E_B = 3.5 \text{ eV}$  (1) and at around  $E_B = 6 \text{ eV}$  (2). We cannot exclude that there is another feature at 10 eV (3). This is suggested by the change in the shape of the structure O(2p) with exposure. Only (2) is also seen clearly with UPS. In particular, no signal corresponding to Cs(6s) appears in UPS.

We consider (1) and (2) as the signature for the bonding of the cesium atoms via the active oxygen which terminates the surface. Although this emission cannot be assigned without electronic structure calculations, we can state the following: the peak energies with respect to the Fermi level are reminiscent of similar structures seen when adsorbing alkali atoms on faceted MgO [24] and on TiO<sub>2</sub> surfaces [12,13]. In these cases it was proposed that a Na<sub>2</sub>O dimer structure is formed which involves protruding oxygen surface atoms. The structure is also reminiscent of the three-peaked structure which is expected when peroxo- or peroxy-type molecular oxygen complexes are ionized, e.g. when one electron is removed from either one of the three weakest-bound orbitals of oxygen  $(\pi_{g}, \pi_{u} \text{ and } \sigma_{g})$  [25–28]. The occurrence of a peroxy-type species has been claimed during the growth of MgO films by the exposure of Mg films to oxygen molecules [14]. Oxygen-induced peaks in the same energy region are also obtained from the oxygenation of Cs adlayers on metals (W(110)) [25]) and semiconductors (Si(100) [29–31] and InP [32]; see also Ref. [33]). In these cases the most convincing explanation proposed for its origin is the adsorption of an atomic oxygen species in the vicinity of Cs atoms.

The feature (2) may be attributed to the ionization of a structural element of the type  $Si-O^--Cs^+$ , e.g. to the ionization from the 2p orbital of non-bridging oxygen (NBO) atoms in the vicinity of the Cs species. We propose that feature (1) is caused by the ionization of a molecular oxygen (peroxy- or peroxo-type) species eventually bridging two silicon atoms. We note that the intensity of (1) decreases at the expense of (2) upon further Cs exposure. This could signal that Cs exposure leads to the dissociation of the molecular oxygen species.

Fig. 6a displays the exposure dependence (intensity and width) of the feature Cs(6s) and of the work function (its change with respect to the clean film). In the early stage of exposure, the charge transfer from Cs to the surface manifests itself only in a considerable decrease of the work function during Cs exposure (by about 3.5 eV), but, on the other hand, it manifests itself in the absence of emission at the Fermi level (denoted by  $E_{\rm F}$ ). Such emission should, however, be present if the Cs 6s electron remained localized at the Cs core. Intensity at the Fermi level becomes clearly noticeable when the work function starts to saturate. The peak labeled Cs(6s) with about 1 eV FWHM (rather independent of exposure time) develops. A feature which is similar in shape and energetic position is commonly found when alkali atoms are adsorbed on metals [16, 17, 25, 34] and semiconductors [18,29]. In these cases it appears that when the work function minimum (typically found around 0.5 monolayer alkali coverage) is passed, the metallization of the alkali adlayer begins. Feature Cs(6s) is predominantly caused by the autodetachment of the He<sup> $-*(2^2S)$ </sup> Feshbach resonance formed by the resonant transfer of a surface electron to the metastable probe atom [34,35]. In the present situation, Cs(6s) is wider than in the case of Cs adsorption on metals (where it is typically 0.6 eV). Therefore, we cannot be sure that it originates mainly from autodetachment of He<sup>-\*</sup>; in particular, at small exposures, Auger de-excitation involving single neutral alkali atoms or small alkali clusters could dominate. We will



Fig. 6. The exposure dependence of the surface work function (its change with respect to that of the clean film) and the intensity and FWHM of the Cs(6s) peak for Cs adsorption on (a)  $SiO_2$ , (b) MgO and (c)  $Al_2O_3$ .

address this question in a future publication. For the present situation, it suffices that both processes can only take place when the 6s electron is localized at the Cs core. Therefore, we suggest that the appearance of Cs(6s), i.e. the presence of intensity at the Fermi level  $E_F$ , is evidence of areas with metallic properties on the surface. Substrate emission remains strong when metallic regions are present, suggesting that no uniform Cs adlayer is formed.

The metallization is dynamic in the sense that the Cs(6s) feature disappears quickly (decreases to about half of its intensity within 1 min) and practically completely when the Cs supply is interrupted. However, some cesium remains bonded to the surface, as signaled in particular by the fact that the work function stays low.

We must distinguish between two modes for Cs adsorption: (i) chemisorption as  $Cs^+$  ions at exposures where Cs(6s) is not yet apparent and after the desorption of the metallic areas following the interruption of the Cs supply. At this stage, the cesium bonds to the active surface oxygen, such as NBO atoms. (ii) Weak physisorption, whereby the additional cesium is subject to little charge transfer with the surface: the 6s electron is actively involved in the electronic processes between the He probe atom and the surface, and must therefore be localized at the Cs core (see also adsorption mode (ii) in Section 3.3).

We will not discuss in detail the time development of the peaks (1), (2), and (3) after the Cs supply has been interrupted because oxygen from the residual gas of the vacuum chamber may become incorporated to some extent into the top layer. We cannot exclude that the change of the surface stoichiometry, manifesting itself in a change in the intensity of (1) relative to (2), is caused in this way. In addition, we cannot exclude at this stage that the Cs atoms may extract cations from the underlying oxide substrate [10]. A Cs/O surface layer could then be formed (with the oxide substrate being reduced). At first glance this suggestion may appear unexpected because the heat of formation of the oxide is larger for Si (475 kJ per mole O) than for Cs (350 kJ per mole O). However, a surface phase may be formed which does not follow the predictions of bulk thermodynamics.

#### 3.3. Cesium adsorption on magnesia films

Our results support and supplement the photoemission data (hv = 80 to 125 eV) for Cs and Na adsorption on MgO(100) [36]. It was found that trace amounts of Cs and Na could be chemisorbed at defect sites at room temperature. Larger amounts of Na (but not of Cs) could be physisorbed to the surface, but easily desorbed at room temperature. It was concluded that the physisorbed Na at large exposures corresponds to metallic clusters nucleated around the defect sites which are occupied by the chemisorbed Na atoms. The metallic nature was confirmed by plasmon losses seen in the photoemission spectra. On the other hand, the weak attenuation of the substrate emission suggested that no uniform adlayer was formed. For Cs, no metallic clusters were found.

The new result which we obtain from our UPS spectra is the decrease in the work function upon cesiation (see Fig. 6b); it signals that cesium indeed sticks to the surface. Very weak intensity from Cs 5p ionization becomes visible at large exposures. The substrate emission is not attenuated in the studied exposure range.

More information can be extracted from the MIES results (see Fig. 6b). Initially, the workfunction decrease is also seen, providing evidence for cesium adsorption. Cs-induced intensity at  $E_{\rm F}$ appears at a relatively early stage of exposure. The feature develops into the peak labeled Cs(6s) (1 eV FWHM, rather independent of exposure). As for Cs on silica, and in agreement with Ref. [36], we attribute the Cs(6s) feature to the presence of metallic areas (in the sense that emission appears at the Fermi level) on the surface. Practically no emission is seen, which can be attributed to the ionization of Cs 5p. As for silica, Cs(6s) disappears when the Cs supply is stopped (decreases to less than half of its intensity within 1 min). Even after it has disappeared, the work function of the surface stays low, indicating that some cesium still remains on the surface. Furthermore, the substrate emission is reduced by 20% at most by the adsorbed Cs, indicating that no closed homogeneous adlayer is formed.

Again we find two adsorption modes: (i) chemisorption of Cs as ions. This is suggested by the persistence of a low work function after Cs(6s) has disappeared. Covalent bonding should lead to intensity at  $E_{\rm F}$  in the MIES spectra because the Cs 6s electron would be involved in either the Auger de-excitation or the autodetachment process. From the absence (weakness) of the Cs 5p doublet structure in the MIES (UPS) spectra, and as estimated from the small intensity change of the valence band emission following exposure, we conclude (see Section 3) that the Cs coverage at this stage is well below 0.1 monolayers. Therefore, as in Ref. [36], we conclude that the adsorption takes place at defects only. Because MIES does not detect any occupied point defects on the clean magnesia surface (such as F-centers as a consequence of oxygen vacancies), the adsorption of Cs presumably occurs at edge sites such as corners, kinks etc., where the anions have a lower coordination than at the perfect surface. The presence of such defects is suggested by the presence of the soft tails on the high-energy side of the valence band emission. Apparently, these surface defects fulfil the function of the active oxygen in the case of SiO<sub>2</sub>. (ii) At larger exposures, there is physisorption of additional cesium. The weak adsorbatesubstrate bonding is signaled by the fact that the additional Cs atoms are desorbed at room temperature as soon as the Cs supply stops. The occurrence of Cs(6s) is a consequence of the localization of the 6s electron at the adsorbate atom. Therefore, at this stage the 6s electron is no longer transferred to the surface. The fast appearance of  $C_{s}(6s)$  upon exposure suggests that the number of possible adsorption sites is much larger than those available for chemisorption. Similar to what was suggested in Ref. [36], condensation of Cs atoms in the form of two-dimensional islands may take place around the Cs species chemisorbed to defect sites.

#### 3.4. Cesium adsorption on alumina films

The MIES results for Cs adsorption on alumina show a number of features similar to those for cesium on magnesia (see Fig. 6c). (i) Right from the beginning of the exposure, the work function decreases significantly. We take this as evidence that considerable charge transfer to the substrate takes place. However, other than for magnesia, no emission can be detected at  $E_{\rm F}$  in this early stage of the exposure. (ii) When the work function has decreased by about 1.5 eV, intensity appears at the Fermi level. At this stage, the intensity appearing at and below  $E_{\rm F}$  is most probably due to Auger de-excitation involving the Cs 6s electron. The small width of the feature (only about 1 eV, even at larger exposures) indicates that there is no band formation (i.e. no homogeneous metallic adlayer exists on the surface). (iii) The feature Cs(6s) at  $E_{\rm F}$  develops into a well-defined peak located directly below the Fermi level. Its width is below 0.5 eV FWHM when it first becomes recognizable. and amounts to 1.1 eV FWHM when the work function goes into saturation. In analogy to silica and magnesia, we consider the occurrence of Cs(6s) as evidence that the surface possesses regions with metallic properties at this stage. (iv) The substrate emission is only partly attenuated by the Cs adsorbate. This also speaks against the formation of a homogeneous closed Cs adlayer. The absence of any noticeable emission (as compared to Cs adsorption on metallic substrates) from the ionization of Cs 5p also speaks against the formation of a uniform adlayer. (v) As for silica and magnesia, the metallization is dynamic in the sense that it disappears rapidly (decrease of Cs(6s) to less than half its intensity within 1 min) when the Cs supply is stopped. Nevertheless, the surface work function stays low, indicating that some Cs remains chemisorbed on the surface. (vi) From the analogy with magnesia, we conclude that the initial chemisorption as ions takes place at surface defects only. MIES does not detect any occupied point defects (such as F-centers) at the clean alumina surface (which would manifest themselves by discrete features within the band gap). Therefore, chemisorption presumably takes place at edge sites such as corners, kinks, etc.

To summarize, as for magnesia, two adsorption stages appear to exist. (i) Initially, Cs chemisorbs, forming an ionic bond at defect sites, presumably with low-coordinated oxygen ions. (ii) Additional Cs is physisorbed, whereby, as suggested in Ref. [24] for MgO, metallic clusters may nucleate around the chemisorbed atoms located at the defect sites. These clusters are unstable at room temperature and disappear as soon as the Cs supply is interrupted.

## 4. Summary

The metastable impact electron (MIES) and photoelectron (UPS (He I)) spectra from films of alumina, magnesia and silica are presented. Furthermore, the spectra obtained when adsorbing cesium atoms on these films are also given. On silica, initial chemisorption appears to take place at surface sites with active oxygen, such as nonbridging oxygen atoms: spectral features appear which are typical for the formation of Cs-O complexes. For magnesia we can support earlier results which claim that the initial chemisorption of Cs as ions occurs at surface defects (edge sites featuring low-coordinated oxygen atoms). For alumina, we suggest that the adsorption takes place in the same way. For all the films studied, prolonged exposure to Cs at a sufficiently large evaporation rate appears to lead to dynamic metallization of the surface. No homogeneous closed metallic adlayer is formed. The metallic areas on the surface are thermally unstable and disappear rapidly after the Cs supply is interrupted.

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