ABSTRACT

The interaction of cesium at the (0001) and (1102) surfaces of sapphire has been investigated using a variety of surface analytical techniques. Reflection mass spectrometric measurements yield initial Cs adsorption probabilities of 0.9 and 0.85 for the unreconstructed (0001) and (1102) surfaces, respectively. The adsorption probability decreases dramatically for these surfaces at critical Cs coverages of 2.0x10^14 and 3.4x10^14 atoms/cm², respectively. Thermally induced reconstruction of the (0001) surface to form an oxygen deficient surface results in a decrease in the initial probability and capacity for Cs adsorption. Low energy electron diffraction (LEED) demonstrates that an intermediate, mixed domain surface yields an initial adsorption probability of 0.5 while a (VTxVT)xR=90° reconstructed surface yields a value of 0.27. Thermal desorption mass spectrometry (TDMS) shows that surface reconstruction eliminates the high binding energy states of Cs (2.7 eV/atom), consistent with the observed changes in adsorption probability. In contrast, reconstruction of the (1102) surface produces only minor changes in Cs adsorption. X-ray photoelectron spectroscopy (XPS) indicates that no formal reductive/oxidative chemistry takes place at the interface. We interpret the facile adsorption and strong binding of Cs on sapphire to result from Cs interacting with coordinatively unsaturated oxygen.

INTRODUCTION

Sapphire is one of several metal oxide materials used in thermionic energy conversion devices. It is subjected to continuous alkali metal exposure at elevated temperatures, along with ionizing radiation. In such an aggressive environment, concerns are raised about the possibility of interfacial processes that might result in material degradation. Where considerable attention has been given to the interaction of various transition metals at the sapphire surface [1-4], little attention has been given to the alkali metals.

Despite sapphire’s chemical inertness, recent studies indicate that a wide variety of chemistry can occur at the metal/sapphire interface. Ohuchi and Kohyama [1] have shown that Ti will react with the (1012) surface at 298 K while Ni and Nb will react on the (0001) surface at 1100 and 1300 K, respectively. The reactions of Ti and Ni appear to be driven by alloy formation with Al. Nb bonds strongly to surface oxygen and photoelectron emission data indicates formal oxidation of the first metal monolayer. Möller and Guo [2] have reported that Cu will bond with oxygen at the (0001) surface at 298 K to form a Cu(l) surface species based on energy loss measurements and valence band photoemission. Yu and Lad [3] have shown that Mg deposited on the (1012) surface shows little evidence for formal chemical interaction until heated above 573 K, where non-desorbed Mg becomes oxidized.

In this paper, we report on the interaction of Cs at the (0001) and (1102) surfaces of sapphire at temperatures above the sublimation point of Cs. These orientations were chosen because they represent two of the lowest energy surfaces of sapphire [5] and are compositionally distinct; the (0001) surface or C-plane is a cation-terminated surface while the (1102) or R-plane is anion-terminated [6,7]. Both of these surfaces undergo thermally induced reconstruction to yield varying degrees of compositional and structural change within the temperature range of a thermionic system. The impact of these changes are discussed in the context of surface Cs activity.
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EXPERIMENTAL

Experiments were conducted in a modified Vacuum Generators ESCALAB 5 spectrometer maintained at a base pressure of 5x10^{-10} torr. X-ray photoelectron spectroscopy (XPS) was performed in a constant resolution mode using a 600 W Al(Kα) source. Low energy electron diffraction (LEED) was used to monitor changes in surface structure. Depending on the degree of surface cleanliness (in terms of residual carbon or deposited Cs), we found that high quality diffraction images could be generated at primary electron energies of 100 eV without charge compensation. Mass spectrometric measurements were made using a standard quadrupole filter with an electron impact ionization source. The Cs source was a chromate salt getter (SAES Getters, Colorado Springs, CO) that could be rapidly turned on and off using a programmed power supply and temperature feedback.

Sapphire crystals of (0001) and (1102) orientation were obtained as either discs (12.5 mm dia.) or squares (10 mm x 10 mm) with a thickness of 0.3 mm, an uncertainty in orientation of ± 0.5° and an epitaxial-quality surface finish (Union Carbide). The crystals were cleaned prior to introduction into vacuum to eliminate excessive levels of surface carbon contamination. They were first immersed in trichlorotrifluoroethane, followed by an extensive ethanol rinse, drying under a flowing stream of nitrogen, and annealing under ambient atmosphere for one hour. (0001) crystals were annealed at 1200K while (1102) crystals were annealed at 600K. With this approach, we found that surface carbon levels could be reduced to 1 at.% prior to any thermal cleaning in vacuum. The cleaned crystals were mounted onto a tungsten grid (0.005 inch dia., 50 lines/inch) using an alumina-based ceramic adhesive. Sample temperature was controlled by resistively heating the W grid and measuring the sample temperature with a W-5%Re/W-26%Re thermocouple bonded to the back of the crystal. We assume that the temperature at the back of the crystal closely approximates the surface temperature given the high thermal conductivity of sapphire and the minimal sample thickness.

RESULTS AND DISCUSSION

Cs will adsorb onto a sapphire surface at temperatures above its sublimation point. Evidence for adsorption can be found by monitoring Cs(3d) and Al(2p) photoelectron emission as a function of Cs exposure at substrate temperatures of 320 K. A set of spectra for the unreconstructed or (1x1) surface of (1102) orientation are shown in Figure 1. These spectra are indexed according to Cs coverage where \( \theta_c \) and \( \theta_{sat} \) represent the initial (or critical) and saturation adsorption capacities of

![Figure 1: Variation in Cs(3d) and Al(2p) Photoelectron Emission with Cs Coverage: \( \theta_c \) is the critical Cs coverage or initial adsorption capacity.](image-url)
the surface, as discussed below. The maximum intensities of the Cs(3d) spectra have been normalized to emphasize the similarities in lineshape over this coverage range. Peak positions have been referenced to the conduction band minimum by measuring the valence band maximum and assuming a band gap of 8.5 eV [8]. The appearance of the Cs(3d_{5,2,3/2}) transitions at 731.2 and 745.1 eV are readily observed with increased exposure. In addition, the Cs(4d_{5,2,3/2}) transitions positioned on the high binding energy tail of the Al(2p) at 82.1 and 84.3 eV become increasingly more visible with increased exposure. These spectra demonstrate that a finite quantity of Cs is stabilized on the sapphire surface at 320 K.

The XPS spectra show no evidence for reductive/oxidative chemistry. The Al(2p) transition shows little response to the presence of Cs. There is a lack of a reduced-state Al feature, expected to lie 2-3 eV lower in binding energy [1], throughout the exposure range. In addition, the half-width of the Al(2p) transition remains at a nearly constant value of 1.7 eV, indicating that the lack of resolution in these spectra does not mask the appearance of a second state of Al. The Cs(3d) transitions undergo little change with increased exposure indicative of a single state of Cs on the surface. The presence of an oxidized form of Cs would result in two sets of 3d transitions (oxidized and metallic) at saturation coverages separated by 0.4 eV, based on measurements made by Hrbek for substoichiometric cesium oxide [9]. The only spectroscopic indication that Cs perturbs the surface is a gradual -0.8 eV shift in all of the core levels monitored (including the O(1s) and Al(2s)) with a minimum value reached beyond \( \theta_{c} \). This shift is not shown in the data of Figure 1 due to the charge correction method applied. We assume this shift results from a surface potential change given the uniformity of the shift and a minimum degree of lineshape broadening. We have also found no evidence for reaction at elevated temperatures including deposition at substrate temperatures up to 800 K and Cs-saturated surfaces heated to 1100 K. These findings are consistent with the predicted stability of \( \text{Al}_2\text{O}_3 (\Delta G_r^{f,298} = -260 \text{ kcal/mole } \text{O}_2) \) versus Cs\(_2\text{O} (\Delta G_r^{f,298} = -130 \text{ kcal/mole } \text{O}_2) \) over the temperature range explored [10].

Cs adsorbs readily onto the sapphire surface despite the lack of formal reductive/oxidative chemistry. Figure 2 shows the variation in adsorption probability with exposure for both of the unreconstructed (0001) and (1102) planes at 320 K, designated by the (1x1) label. These curves were generated from reflection mass spectrometric traces for Cs adsorption onto clean and Cs-saturated surfaces [11]. Both surfaces show high initial adsorption probabilities with the (0001) plane yielding a value of 0.9 and the (1102) plane a value of 0.85. These values are significantly greater than the value of 0.7 reported for Cs adsorption on NiO(100) [12]. This high value is maintained for some length of exposure, after which the probability decays rapidly to a minimum value. LEED images generated across this exposure range show only an increasing background intensity indicative of the lack of long range ordering for the Cs layer. The point at which the

![Figure 2: Adsorption Probability as a Function of Exposure for Cs Adsorption on the (0001) and the (1102) Surface at 320 K.](image-url)
probability begins to decay represents a critical coverage of Cs ($\theta_c$) and it varies for these two orientations. Based on the relative Cs(3d), O(1s) and Al(2s) core level intensities, we estimate the critical coverages to be $(2.0\pm0.6)x10^{14}$ and $(3.4\pm0.8)x10^{14}$ Cs atoms/cm$^2$ for the (0001) and (1102) planes, respectively. These values represent sub-monolayer coverages when considering an areal density of $4.8x10^{14}$ atoms/cm$^2$ for a hexagonal close packed monolayer of Cs adsorbed on a metal surface [13]. This difference in initial capacity may be a result of the chemical nature of these two surfaces. The (0001) surface is considered to be Al cation terminated [6] while the (1102) surface is considered to be O anion terminated [7]. The compressed hexagonal packed O sublattice of the (0001) has one third of its three-fold hollow sites occupied by an Al cation, potentially restricting access to Cs. The O sublattice of the (1102) surface assumes a pseudo-square surface net and is considerably more available for adatom interaction without surface Al cations. The fact that no long-range order is observed may result from a mismatch between the Cs atomic diameter (potentially as great as 4.9 Å) and the lattice parameters for these surfaces [6].

Thermally induced reconstruction of the (0001) surface changes both the initial capacity and adsorption probability for Cs at 320 K. These changes are clearly seen in the remaining adsorption probability plots of Figure 2. Annealing the crystal to successively higher temperatures results in a decrease in the initial adsorption probability from 0.9, to 0.76, 0.5 and 0.27 for anneals to 1100 K, 1250 K, 1300 K and 1450 K, respectively. LEED shows that the surface is undergoing reconstruction over this temperature range. A mixed domain surface appears to form after annealing to 1250 and 1300 K that is characterized by regions that yield a diffuse (1x1) diffraction pattern with growing intensity in the fractional order zones and regions that yield a clear (3$/sqrt{3}$x$3$/sqrt{3})R30° pattern. The formation of mixed domains or facets on sapphire has been a frequently observed phenomenon [6,14]. Annealing the crystal to 1450 K produces a predominantly (3$/sqrt{3}$x$3$/sqrt{3})R30° surface. This structure can also be formed at equivalent temperatures without the surface being previously exposed to Cs, indicating that Cs does not significantly alter the activation energy for thermal reconstruction. Integration of the area under the probability curves for the (0001) surface show that the critical coverage is decreased by as much as an order of magnitude after increased temperature annealing. This result is confirmed by XPS measurements. The (3$/sqrt{3}$x$3$/sqrt{3})R30° surface has been interpreted to consist of hexagonal domains of Al(111), possibly two atomic layers thick, based on recent x-ray reflectivity measurements [15]. This structure represents a condition of total loss of surface oxygen. The fact that we observe decreased affinity for Cs suggests that the strong interaction of Cs at the (1x1) surface results from selective interaction with surface oxygen. The observed enhancement in initial adsorption of Cs after the appearance of the (3$/sqrt{3}$x$3$/sqrt{3})R30° pattern may result from adsorption on remaining unreconstructed domains or selective adsorption at the Al(111) domain boundaries. These domain boundaries are expected to contain defect structure that might yield stable sites for Cs adsorption.

In contrast, the (1102) surface shows only minor changes as the surface reconstructs from its (1x1) to (2x1) state at 1300 K. A small increase in adsorption probability from 0.85 to 0.87 occurs with reconstruction. We find that the critical coverage of Cs actually increases by approximately 10% with (2x1) formation. These changes indicate an increase in the surface activity for Cs. However, XPS measurements show an overall decrease in saturation surface coverage suggesting that the structure of the Cs deposit may differ significantly for the (1x1) and (2x1) surfaces. Further annealing of this surface to 1450 K produces no further changes in subsequent adsorption profiles. The reconstruction of the (1102) surface has been interpreted to result from the formation and ordering of oxygen vacancies [7]. The generation of vacancies represents a less severe change in the surface composition than the de-oxygenation thought to produce the (3$/sqrt{3}$x$3$/sqrt{3})R30° structure. The fact that the (1102) surface retains its activity for Cs even after reconstruction is consistent with a selective Cs-surface oxygen interaction.

Thermal desorption of Cs from the sapphire surface shows that Cs desorbs from a wide range of states. Figure 3 show the thermal desorption traces for the Cs-saturated (0001) surface after undergoing the thermal annealing treatment previously discussed. The (1x1) surface shows three predominate features with a broad desorption maximum at 1000 K and a sharp maximum and shoulder at 620 and 520 K, respectively. A coverage-dependent experiment shows that the 1000 K feature saturates first followed by filling of the lower temperature states. This trend is expected based on the fact that Cs should saturate the highest binding energy adsorption sites first. The
high temperature feature at 1000 K equates to a Cs binding energy of 2.7 eV/atom, assuming first order desorption kinetics, a pre-exponential, frequency factor of $10^{13}$ sec$^{-1}$ and a measured temperature ramp rate of 5 K/sec [16]. De-oxygenation of the surface results in elimination of this high energy state while the lower energy states are maintained. The spurious signal that appears around 1300 K in the reconstructed traces results from Cs desorption from alternate surfaces in the chamber. The fact that Cs does not reside on the reconstructed surface at these temperatures was verified with XPS. This loss in Cs stability with surface reconstruction is consistent with the decreased activity found in the adsorption probability measurements. In contrast, thermal desorption spectra generated from the (1102)-(2x1) surface (not shown) demonstrate that a state as high as 1250 K or 3.4 eV/atom exists. This result suggests that sub-monolayer quantities of Cs may be bound more strongly to the (0001)-(1x1) surface than indicated in the desorption profiles, but surface reconstruction aids in its removal.

![Figure 3: Cs Thermal Desorption Spectra for the (0001) Surface.](image)

CONCLUSIONS

The interaction of Cs on the (0001) and (1102) planes of α-Al$_2$O$_3$ has been investigated. We have found that Cs adsorbs readily on these surfaces yielding initial adsorption probabilities of 0.9 and 0.85, respectively. Initial adsorption capacity is limited to sub-monolayer coverages of 2.0x10$^{14}$ and 3.4x10$^{14}$ atoms/cm$^2$, respectively. Thermal desorption measurements show that high binding energy states in excess of 2.7 eV/atom exist for both surfaces. Thermally-induced surface reconstruction results in attenuation of both the adsorption capacity and probability of Cs adsorption on the (0001) surface. This orientation of sapphire is more severely affected by reconstruction resulting in surface de-oxygenation. Cs activity is minimally impacted by reconstruction on the (1102) surface. These results suggest that the driving force for Cs adsorption is a selective interaction with the coordinatively unsaturated oxygen at the surface. Formal reductive/oxidative chemistry has been ruled out as a possible explanation for the observed strong Cs binding.

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