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SURFACE STRUCTURAL DEPENDENCE OF CESIUM ADSORPTION ON THE α-Al_2O_3(0001) SURFACE

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Abstract

The structural dependence of Cs adsorption on the α-Al_2O_3(0001) surface has been studied using a combination of surface analytical techniques. The unreconstructed or (1x1) surface shows a high initial Cs adsorption probability of 0.9 based on reflection mass spectrometry (RMS). This value decreases rapidly after a critical Cs coverage of 1.5×10^{14} atoms/cm^2 is reached. Thermally-induced surface reconstruction to form an O deficient surface results in a decrease in the critical coverage, probability and capacity for Cs adsorption. Low energy electron diffraction (LEED) demonstrates that a predominantly $(3\sqrt{3}x3\sqrt{3})R30^\circ$ surface yields an initial adsorption probability of 0.5 while a predominantly $(\sqrt{31}x\sqrt{31})R\pm9^\circ$ yields a value of 0.3. Thermal desorption mass spectrometry (TDMS) shows that surface reconstruction suppresses the high binding energy states of Cs, consistent with the observed changes in adsorption probability. X-ray photoelectron spectroscopy (XPS) provides no direct evidence for formal oxidative/reductive chemistry taking place at the interface. We interpret the facile adsorption and strong binding of Cs on sapphire to result from Cs interacting with coordinatively unsaturated O.

INTRODUCTION

The activity of an alkali metal on a metal oxide surface is of significance to a variety of thermionic systems, including thermionic fuel elements (TFE's) and tacitron devices. Metal oxide ceramics used in the TOPAZ-II TFE's, either as electrode insulators or interelectrode gap spacers, are in constant contact with a reactive environment. This environment is characterized by high partial pressures of Cs (~ 1 torr), high temperatures (900 to 2000 K), and ionizing radiation. Several degradation mechanisms are known to occur in this environment that threaten the longevity of the TFE. These mechanisms include degradation of surface electrical properties and surface erosion. In an attempt to understand the intrinsic limit to operational lifetimes, we have initiated a study to explore the fundamental interaction of Cs at the sapphire surface.

Sapphire is generally thought of as being inert toward the alkali metals (Higgins 1966). However, macroscopic chemical inertness does not preclude the possibility of localized chemical and physical interactions at the sapphire surface. We have previously shown that submonolayer quantities of Cs will adsorb readily on a randomly oriented sapphire surface with an adsorption probability of 0.9 (Zavadil and Ing 1994). We also found that Cs is stabilized on the sapphire surface at temperatures in excess of 1200 K. These findings suggest that localized interactions do occur and that they are present at operational temperatures for sapphire insulators in the TOPAZ-II TFE, typically 920 K. Surface chemistry has been demonstrated for several transition metals on sapphire. Ohuchi and Kohyama (1991) have shown that Ti will react with the $(10\bar{1}2)$ surface at 298 K while Ni and Nb will react on the (0001) surface at 1100 and 1300 K, respectively. Additionally, Moller and Guo (1991) have reported that Cu will bond with oxygen at the (0001) surface at 298 K. The driving force for the Ti and Ni interactions appears to be predominantly intermetallic formation while the activity of Nb and Cu emanates from favorable energetics for bonding with surface oxygen. Surface oxygen bonding is a more likely interaction for Cs on the (0001) surface because intermetallic formation is not favored in the Cs/Al system.

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EXPERIMENTAL

Experiments were conducted in a modified Vacuum Generators ESCALAB 5 spectrometer maintained at a base pressure of 5×10^{-10} torr. X-ray photoelectron spectroscopy (XPS) was performed in a constant resolution mode using a 300 W Mg(K_α) source. Various pass energies were used depending on the resolution required. Low energy electron diffraction (LEED) images were generated with a Princeton Research Instruments reverse view optic system. 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 energies of 60 to 90 eV without charge compensation. Mass spectrometric measurements were made using a quadrupole filter with an electron impact ionization source (UTI 100C). A Cs getter (SAES Getters, Colorado Springs, CO) mounted on a combined electrical/thermocouple feedthrough served as a high purity Cs source. The experimental geometry for reflection mass spectrometric (RMS) measurements has been previously described (Zavadil and Ing 1994).

Sapphire crystals of (0001) orientation were obtained with a diameter of 12.5 mm, a thickness of 0.3 mm, an uncertainty in orientation of ± 0.5° and a surface finish of 1 μm (Union Carbide). These crystals were rinsed thoroughly in ethanol prior to insertion into vacuum. The method of mounting the crystals has been previously described and only the salient features will be included in the following discussion (Zavadil and Ing 1994). The rapid substrate heating required for surface cleaning and thermal desorption mass spectrometry (TDMS) studies was achieved by mounting the sample to the leads of a high current feedthrough. The surface temperature was estimated from a W-5%Re/W-26%Re thermocouple bonded to the back of the crystal. We assume a minimal thermal gradient in the crystal due to its limited thickness. TDMS experiments were conducted with temperature ramp rates of 5 K/sec using a temperature programmer (RHK, TM310) to control a DC power supply. A similar configuration was used to regulate the output from the Cs getter for controlled deposition. We have found that temperature control can be used to effectively turn on and off the incident Cs flux. The incident flux is not directly measured in our experiments but has been estimated to be 4.5×10^{12} atoms/cm^2·sec, based on measured Cs surface concentrations and the variation in adsorption probability. For comparison purposes, exposure levels are described in arbitrary units of normalized dose in this paper. Surface temperatures during deposition are typically 320 K due to radiative heating of the crystal by the getter.

RESULTS AND DISCUSSION

Initial Surface Structure and Contamination

Sapphire retains carbonaceous contaminants and must be annealed to temperatures in excess of 1100 K to produce an atomically clean surface (Chang 1971). On an oriented surface, concerns are raised about the changes in surface structure that are produced with high temperature annealing (Chang 1971, French and Somorjai 1970, and Gautier et al. 1991). Chang (1971), among others, has demonstrated that the temperatures necessary for complete carbon

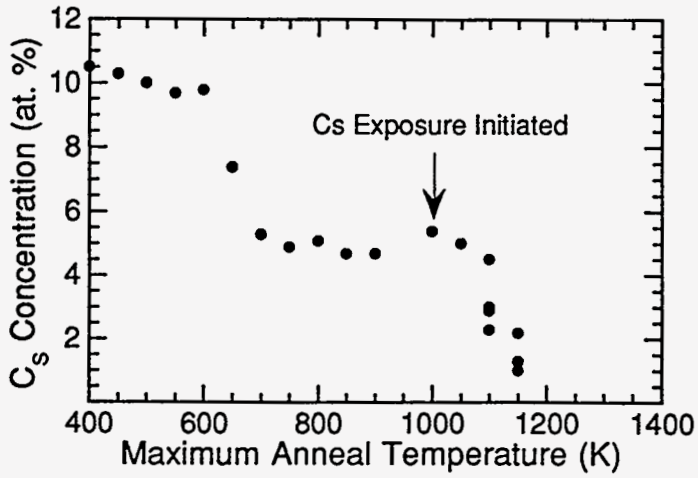

FIGURE 1. Variation in Carbon Surface Concentration with Anneal Temperature.

elimination will also produce surface reconstruction on the (0001) surface. Figure 1 shows the variation in the surface C concentration as a function of maximum anneal temperature. C levels are typically at the 10 at.% level after the crystal has been heated indirectly to 450K due to baking the vacuum chamber. At this stage, a coherent but diffuse (1x1) diffraction pattern is observed, most probably a result of a discontinuous contaminant layer. This level gradually decreases with crystal heating to 600 K, at which point further heating produces a approximate two-fold decrease in the signal. The signal then remains constant until multiple thermal cycles coupled with Cs exposure are employed to produce a decrease below the ~ 1 at % lower limit of detection. The fact that Cs aids in C removal is demonstrated in a more rapid rate of signal decrease when Cs is deposited on the surface compared to thermal cycling in the absence of Cs. This Cs-assisted cleaning temperature is considerably lower than the 1300 to 1500 K reported by other investigators (Chang 1971, French and Somorjai 1970, and Gautier et al. 1991). The sharpest (1x1) diffraction pattern is visible in the 800 to 1100 K region consistent with the initial reduction of surface C. The pattern becomes somewhat diffuse with cycling at 1100 to 1150 K which may indicate the onset for surface reconstruction. The 1100 to 1150 K surface is considered the atomically clean, unreconstructed (1x1) surface in the following studies.

Cs Adsorption on the Unreconstructed Surface

The top trace in Figure 2 shows the variation in the adsorption probability as a function of Cs exposure for the (1x1) surface. The adsorption probability increases with initial exposure, limits at a maximum value and then rapidly decays. The maximum value measured is 0.9 which is equivalent to the adsorption probability measured on randomly oriented sapphire (Zavadil and Ing 1994). This value is also significantly larger than 0.7 reported for Cs on NiO(100) (Kennou et al. 1991). This great an adsorption probability indicates a strong interaction between the adsorbate and substrate. The fact that a maximum value is maintained for some period of increased exposure indicates that the surface has a significant density of high energy adsorption sites. The rapid decrease in adsorption probability signals a critical coverage at which these sites become fully saturated and adsorption must proceed through an alternate mechanism. Adsorption clearly continues after this critical coverage is reached, based on our measurements of a limiting probability of ~ 0.1. The initial increase in adsorption probability with exposure may signal an activated adsorption process. One such mechanism postulated to explain this behavior is the nucleation of Cs clusters with continued adsorption at an increasing number of perimeter sites.

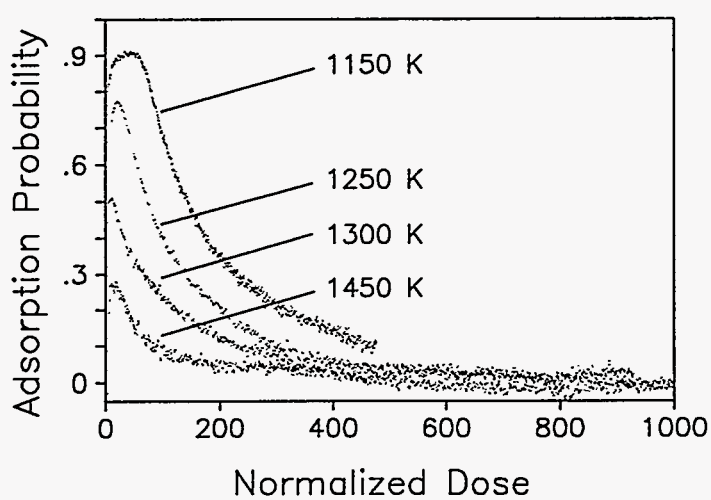

FIGURE 2. Variation in Adsorption Probability with Maximum Anneal Temperature.

An estimate of the critical coverage of Cs on the unreconstructed (0001) surface can be made by examining XPS data. A surface coverage for Cs has been calculated based on the relative Cs($3d_{5/2}$), Al(2s) and O(1s) peak areas. This quantitative correlation between electron emission and atomic concentration can be made based on the known areal densities of O and Al for the (0001) orientation, assuming simple exponential attenuation of electron transmission in the solid state and calculating inelastic mean free paths based on empirically derived scattering models (Seah and Dench 1979). We estimate a critical coverage value for Cs of 1.5×10^{14} atoms/cm^2. This value is approximately one third the value observed for hexagonal packing of Cs on several metal surfaces (Stolz et al. 1993). The magnitude of this value precludes the possibility that adsorption is occurring only at defect sites on the surface. A continuous

adsorbate layer, one possibility being Cs sitting at Al^{3+} vacancy sites on the compressed hexagonal close packed O sublattice, can be ruled out because of the lack of a coherent diffraction pattern at this critical coverage. The adsorption probability data suggest that there is a tendency toward cluster formation. The variation in $Cs(3d_{5/2})$, Al(2s) and O(1s) signals with increasing exposure also provide evidence of Cs clustering. Cluster formation for Cs on other metal oxides has been previously observed (Kennou et al. 1991).

Core level spectroscopic data show no evidence for formal oxidative/reductive chemistry at the Cs/sapphire interface. The $Cs(3d_{5/2})$ emission yields a single transition from submonolayer to saturation exposures of Cs. It could be argued that the -0.4 eV oxidative shift expected for Cs bonding to low coordinate O (Hrbek et al. 1993) would not be resolved, given a full width at half maximum of 2.5 eV for this transition, as measured on our system. O(1s), Al(2p) and Al(2s) emission also yield single transitions. Angle resolved XPS has been employed for both the O(1s) and Al(2s) to enhance emission from the surface layer relative to the near-surface region with no indication of multiple states of O or Al. In this experiment, the Al(2s) level was chosen due to Cs(4d) interference with the Al(2p). To ensure that significant chemistry does not occur at elevated temperatures, XPS was conducted on the surface after high temperature deposition of Cs at 800 K. No evidence for changes in the Cs, O and Al core levels were observed. The only spectroscopic indication that Cs deposition perturbs the surface is a gradual -0.8 eV shift in the core levels with a local minimum occurring within the transition region of exposure where the adsorption probability decreases. This shift most likely results from a change in surface potential with the addition of a charge injecting species to the surface.

Cs Adsorption on the Reconstructed Surface

The variation in the adsorption probability traces for the surface annealed to temperatures greater than 1150 K are also shown in Figure 2. This series of traces demonstrates that higher annealing temperature produces a decrease in the maximum value of the adsorption probability. This value decreases from 0.9 at 1150 K to 0.5 at 1300 K and 0.3 at 1450 K. The critical coverage is also decreasing with maximum anneal temperature based on the observed shift in the transition of the adsorption probability to lower exposure. These two observations indicate that the adsorptive site density is decreasing with increased anneal temperature. One impact of this change is that the initial capacity for Cs adsorption also decreases. This result is demonstrated in Figure 3 where the $Cs(3d_{5/2})$ intensity is plotted as a function of maximum anneal temperature for a normalized dose of 2000. The data demonstrates a monotonic decrease in the surface concentration with temperature. If the surface is disordered using Ar^+ bombardment (3 keV, 1 $\mu m/cm^2$) after annealing to 1450 K, the adsorption probability trace tracks that shown for 1200 K in Figure 2. Disordering the surface also restores some of adsorption capacity as evidenced by an increased Cs signal (see Fig. 3).

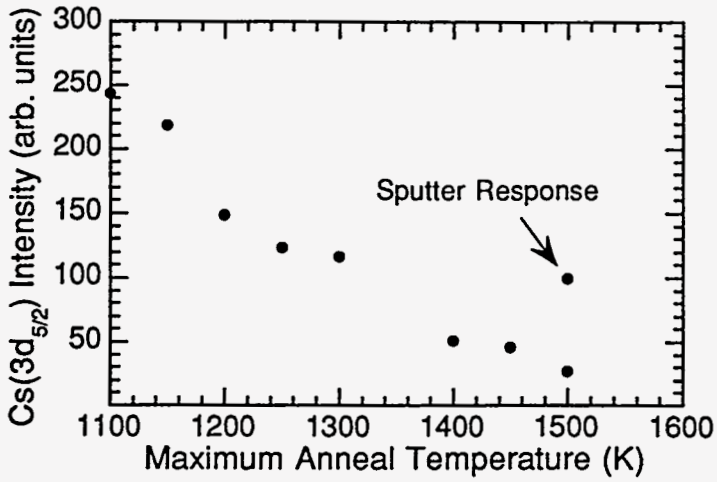

FIGURE 3. Variation in Cs Signal with Maximum Anneal Temperature.

Desorption of Cs from the sapphire surface should be highly sensitive to the degree of surface reconstruction. Figure 4 shows the thermal desorption profiles for near-saturation doses of Cs (2000) as a function of maximum

anneal temperature. The unreconstructed surface shows a predominant low-temperature desorption feature at 600 K with a shoulder at 520 K. The majority of Cs actually desorbs at temperatures greater than 800 K described by a broad feature with a maximum at 1000 K. Coverage dependent TDMS data shows that these high temperature states fill first with increasing coverage. These high temperature states are consistent with high energy binding of Cs at the sapphire surface and explain the existence of the initial high adsorption probability. Surface reconstruction results in a loss of these high temperature states while the low temperature state characterized by desorption at 600 to 620 K is maintained. The signal detected at temperatures in excess of 1300 K appears to result from Cs desorbing from alternate surfaces in the chamber due to radiative heating, as evidenced by a lack of a $Cs(3d_{5/2})$ signal at 1300 K.

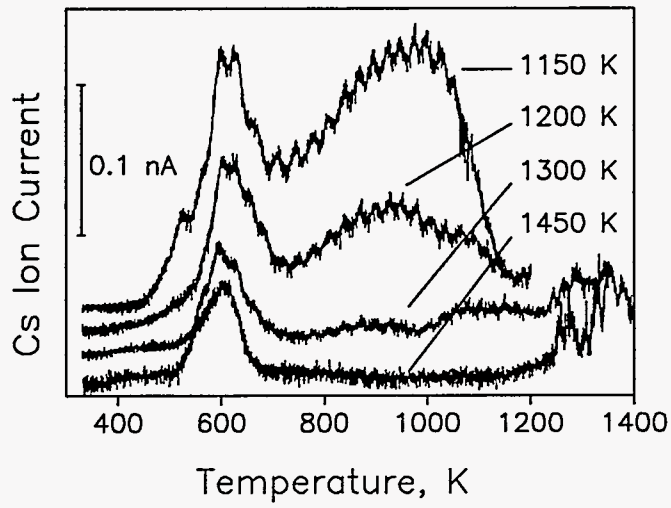

FIGURE 4. TDMS Spectra for Saturation Doses of Cs on Deposited on Annealed α-Al_2O_3(0001).

High temperature annealing produces changes in surface crystallography that have been related to surface oxygen loss (Chang 1971, French and Somorjai 1970, Guatier et al. 1991). The highest order reconstruction of the (0001) surface yields a $(\sqrt{31}x\sqrt{31})R\pm9°$ diffraction pattern. The surface structure that gives rise to this pattern is thought to be an oxygen deficient cubic surface mesh sitting on top of the original compressed hexagonal close packed lattice of the bulk. LEED patterns observed in our experiments indicate that at 1400 K the surface contains facets of the $(\sqrt{31}x\sqrt{31})$ structure as well as a lower order $(3\sqrt{3}x3\sqrt{3})R30°$ structure. We observe that the $(3\sqrt{3}x3\sqrt{3})R30°$ structure predominates at temperatures below 1400 K while the $(\sqrt{31}x\sqrt{31})R\pm9°$ structure predominates at temperatures above 1400 K. This tendency toward facetting for the (0001) surface has been previously observed (Chang 1971). No consistent arguments have been proposed in the literature for whether the $(3\sqrt{3}x3\sqrt{3})R30°$ structure represents an intermediate stage of oxygen loss. It is clear from our data that the affinity for Cs adsorption decreases as the surface reconstructs and eventually loses oxygen. This result strongly implicates the role of O in the stabilization of Cs at the surface. However, a structural component must also exist for Cs stabilization based on the observed reactivation of the reconstructed surface after Ar^+ bombardment. Sputtering is believed to disorder the surface without significantly changing the surface stoichiometry (Gautier et al. 1991). We believe that coordinatively unsaturated O generated through disordering, as well as excess O in the (1x1) structure, are responsible for the observed stability of Cs.

The implication of the decreased adsorption probability with surface reconstruction on the (0001) surface appears to be that thermal treatments deactivate the surface. From the view of surface property degradation, this result should benefit the material if a degradation mechanism scales with Cs surface concentration. However, not all low energy sapphire surfaces are expected to demonstrate similar behavior. Previously, we found that randomly oriented sapphire could be heated to 1500 K and still show an initial adsorption probability of 0.9. Clearly, this structurally complex surface is not deactivated through thermal treatment. Any non-planar structure will possess several low energy surfaces at which Cs may interact to different extents. Additionally, a surface damage mechanism (potentially neutron bombardment) may reactivate a surface similar to the observed effects of ion bombardment. Although these results with the (0001) surface are promising, they do not preclude the possibility of Cs-assisted degradation of insulators within the TFE environment.

CONCLUSIONS

The role of surface structure in determining the adsorption/desorption characteristics of Cs on α-Al_2O_3(0001) has been investigated. We have found that thermally induced surface reconstruction significantly impacts the adsorption probability and capacity for Cs. The (1x1) surface yields an initial adsorption probability of 0.9 for Cs deposition at 320 K. This value is maintained until a critical coverage, estimated to be 1.5×10^{14} atoms/cm^2, is reached and the adsorption probability exponentially decreases to a value of 0.1. Thermally induced reconstruction produces an increasingly facetted surface with domains that yield $(3\sqrt{3} \times 3\sqrt{3})R30°$ and $(\sqrt{31} \times \sqrt{31})R\pm 9°$ diffraction patterns, the former being predominant at lower temperatures. The initial adsorption probability and capacity decrease as the surface reconstructs to produce an O deficient surface layer while the high temperature desorption states of Cs are eliminated. Ion bombardment partially restores the surface's probability and capacity for Cs adsorption. These results support the argument that the facile adsorption of Cs on sapphire is due to an interaction between Cs and coordinatively unsaturated surface O. However, core level spectroscopy shows no direct evidence of formal oxidative/reductive chemistry at the interface.

Acknowledgments

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