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ELECTRON INDUCED SURFACE CHEMISTRY AT THE CS/SAPPHIRE INTERFACE

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Abstract

Electron induced etching of sapphire in the presence of Cs has been studied using a variety of surface analytical techniques. We find that this process occurs on both the (0001) and (1102) orientations of sapphire. Monolayer amounts of Al and sub-oxides of Al are thermally desorbed from the surface at temperatures as low as 1000 K when the surface is irradiated with electrons in the presence of Cs. Etching is highly dependent on Cs coverage with the (0001) and (1102) surfaces requiring 2.0×10^{14} and 3.4×10^{14} atoms/cm² to support etching, respectively. Adsorption profiles demonstrate that these coverages correspond to initial saturation of the surface with Cs. Electron damage of the surface in the absence of Cs also produces desorption of Al and sub-oxides of Al, indicating a possible mechanism for etching. The impact of etching on the surface is to increase the adsorption capacity on the (0001) surface while decreasing both initial adsorption probability and capacity on the (1102) surface.

INTRODUCTION

The chemical and physical stability of metal oxide insulators in a thermionic fuel element (TFE) dictate the overall performance and longevity of a conversion system. In a TOPAZ-II TFE, insulators are used to provide electrical isolation between emitter and collector as well as to maintain the interelectrode gap spacing. Kozlov (1992) has shown that alumina undergoes surface erosion when subjected to the reactive environment of the interelectrode gap. This environment is characterized by high partial pressures of Cs (~ 1 torr), high temperatures (900 to 2000 K), low energy electrons, ultraviolet photons, as well as ionizing and damaging radiation. Material loss may lead to gap spacing changes and possible contamination of emitter and collector surfaces resulting in changes in system performance. Sapphire is used as an insulator in these TFE's and represents a well characterized reference insulator with which to investigate the impact of the interelectrode environment.

In this paper, we report on an observed etching reaction that occurs at the sapphire surface in the presence of Cs and electrons. Two compositionally distinct orientations of sapphire have been studied: the Al³⁺ terminated c-plane or (0001) surface and the O²⁻ terminated r-plane or (1102) surface. We have previously demonstrated that no formal reductive/oxidative chemistry takes place at the Cs/sapphire interface from room temperature up to maximum Cs desorption temperatures in excess of 1100 K (Zavadil and Ing 1995). The fact that Cs can be stabilized on the surface of sapphire creates the possibility that additional forms of energy input may contribute to reactive surface processes. Sapphire is responsive to energy input from both electrons and photons. Electron damage of sapphire that results from excitation of the Al(2p) core-level and stimulated desorption of O⁺ is a well documented phenomenon (Olivier and Poirier 1981). Photon irradiation of sapphire at energies as low as 1.2 eV has been shown to produce Al⁺ and AlO⁺ desorption (Schildbach and Hamza 1992 and 1993). In addition, thermal energy input can change the surface properties of sapphire (Gautier et al. 1994). The presence of Cs is expected to alter the surface electronic properties of sapphire which, in turn, may enhance the chemical activity of the surface.

EXPERIMENTAL

Cs adsorption and desorption experiments were conducted in two separate ultrahigh vacuum systems maintained at base pressures of 2×10^{-10} torr. X-ray photoelectron measurements were conducted on a Vacuum Generators

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ESCALAB 5 system using a 600 W Al(K α) source. Auger electron measurements were made with a Physical Electronics single pass cylindrical mirror analyzer using a 2 keV electron beam with a sample current density of less than 130 $\mu\text{A}/\text{cm}^2$ (assuming a beam diameter of 1 mm). Two separate quadrupole mass analyzers, a Balzers QMG 420 and a UTI 100C, have been used to track adsorption and desorption events. The Balzers quadrupole was fitted with a grounded shield over its electron impact source. Faraday probe measurements have shown that this method is effective at preventing electron emission, producing sample current densities less than 1 nA/cm 2 . Controlled, low energy electron exposure of the sapphire substrate was generated with a separate electron gun (Apex Electronics), modified with a tungsten screen positioned beyond the focusing Einzel lens elements to provide for low energy tuning of the beam. A Physical Electronics Low Energy Electron Diffraction power supply (11-020) was used to control this gun. Low energy electron diffraction (LEED) images were generated with a Princeton Research Instruments reverse view optic system.

The sapphire crystals of both (0001) and (1 $\bar{1}$ 02) orientations were supplied by Union Carbide. These crystals were supplied as 10x10 mm substrates with a thickness of 0.3 mm, an uncertainty in orientation of $\pm 0.5^\circ$ and a surface finish of 1 μm . Substrates were cleaned using trichlorotrifluoroethane immersion, ethanol rinsing, drying under a flowing nitrogen stream, and annealing in air for one hour. Optimum annealing temperatures have been found to be 1200 K and 900 K for (0001) and (1102) crystals, respectively, based on minimization of initial carbon contamination to approximately 1 at.%. These crystals could be heated by temperature programming to 1400 K using resistive heating as previously described (Zavadil and Ing 1994). Thermal desorption data was collected using a heating rate of 5 K/sec. Controlled deposition of Cs was conducted with a chromate salt getter (SAES Getters) that could be rapidly turned on and off using temperature programming. Typical incident fluxes were on the order of 5×10^{12} atoms/cm 2 ·sec (Zavadil and Ing 1995).

RESULTS AND DISCUSSION

Evidence for surface chemistry can be found by monitoring thermal desorption from sapphire after extended Cs and electron exposure. Figure 1 shows the relationship between measured ion current and sample temperature for a series of masses desorbing from both (0001) and (1102) surfaces with initial Cs coverages (θ_{Cs}) of 2×10^{14} and 5×10^{14} atoms/cm 2 , respectively. The significance of these values is that they represent coverages at which the most active adsorption sites are saturated with Cs; the point at which the adsorption probability decreases to a near-zero value (Zavadil and Ing 1995). The (1102) data was generated for a single deposit while the (0001) data was generated from a sequence of deposits of equivalent coverage. The data shows that species of 27 and 43 amu desorb from the surface at

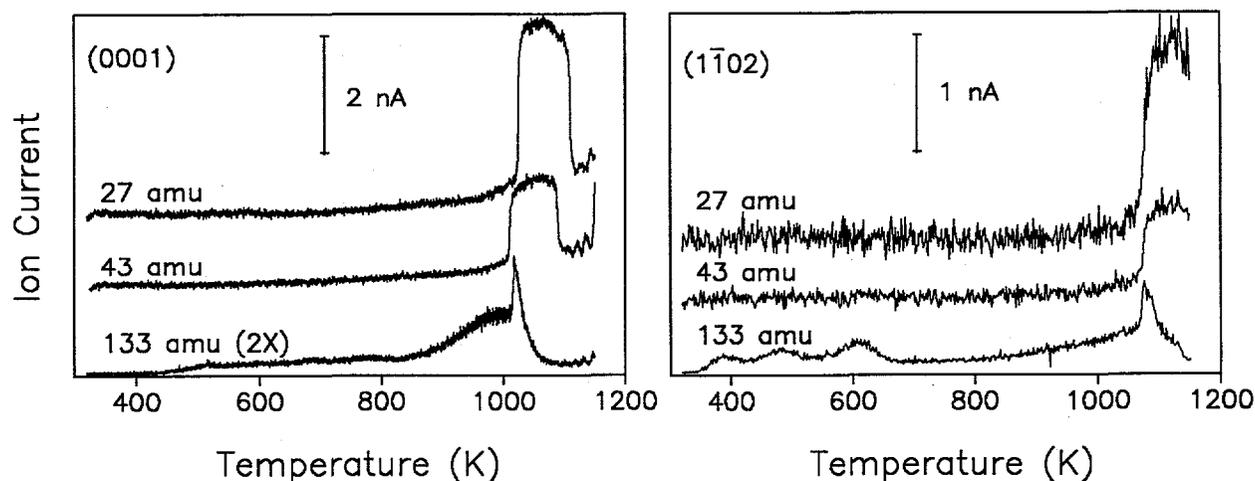


FIGURE 1. Desorption Profiles for Cs Covered (0001) and (1102) Surfaces: (0001), $\theta_{\text{Cs}} = 2 \times 10^{14}$ atoms/cm 2 and (1102), $\theta_{\text{Cs}} = 5 \times 10^{14}$ atoms/cm 2 .

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temperatures greater than 1000 K and their appearance coincides with the desorption of Cs (133 amu). We attribute these signals to the production of Al and AlO. The difference in measured ion current between these two sets of spectra is a result of variation in the spectrometer gain. Control desorption experiments run in the absence of Cs do not yield these signals. This result demonstrates that spectral interference due to limited mass resolution, yielding a contribution at 27 amu due to CO and at 43 amu due to CO₂, can be excluded as a possible explanation for the origin of these signals. The desorption of Al and AlO indicates that the surface is being etched at elevated temperatures in the presence of Cs. The fact that this process is observed on both orientations demonstrates that the composition of the surface, whether O²⁻ or Al³⁺ terminated, plays a limited role in the etch.

The shape of the Cs desorption traces of Figure 1 appears to be characteristic of this etching process. The low temperature region (< 800 K) of the Cs trace shows an onset for desorption and various desorption maxima whose positions and intensities are dependent on Cs coverage. The high temperature region (> 800 K) of the Cs trace shows a gradual increase in signal beyond 800 K, followed by a rapid rise in desorption at a temperature between 1000 K and 1100 K and an exponential decay to background signal levels. This rapid onset of increased Cs desorption at high temperatures occurs simultaneously with the onset of Al and AlO desorption. This relationship is more apparent in the (1102) data. The 100 K shift in the onset for desorption, evident when comparing the (0001) and (1102) data, is a result of variation in Cs coverage. Coverage dependent studies on these two surfaces yield a gradual shift in this onset with increased Cs coverage. The small mismatch in the onsets for the (0001) traces is a result of this same coverage dependent variation. Cs coverage below 2×10^{14} atoms/cm² for the (0001) surface results in the absence of this high temperature onset along with only partial removal (~ 50%) of the Cs deposit below temperatures of 1150 K. Etching is observed if this surface is subsequently dosed with just enough Cs to saturate the surface. Similar results are observed for a coverage of 2×10^{14} atoms/cm² on the (1102) surface. This result indicates that a critical coverage of Cs is required to produce etching.

Cs does not appear to be thermally etching the sapphire substrate. The best known case of thermal etching of sapphire is in its activity with Si. Chang (1971) has shown that Si will etch sapphire at elevated temperatures (> 1300 K) resulting in the desorption of SiO and Al. In this situation, Si is responsible for reducing the Al center, forming a volatile monoxide, and desorbing along with Al. The fact that an analogous process is not taking place between Cs and sapphire is demonstrated by the absence of a CsO⁺ fragment in the desorption spectra. This result is consistent with free energy of formation calculations that show Al₂O₃ is more stable at 1100 K than any of the oxides of Cs. The traces of Figure 1 also show that the majority of Cs has desorbed from the surface while near-maximum rates of Al and AlO desorption continue to higher temperatures. These results suggest that Cs is playing a mediating role in the etching of the surface. We can obtain an estimate of the amount of product formed by integrating the ion current under these features, estimating the quadrupole sensitivity based on the known Cs surface concentration, and correcting for ion energy dependence with the quadrupole transmission function. We find that the Al and AlO signals correspond to 1×10^{14} and 6×10^{13} atoms/cm², respectively. These values are consistent with partial monolayer removal, assuming that ionization probabilities for Cs, Al and AlO are approximately equivalent. The greater value for Al may be related to possible fragmentation of AlO which has not been taken into account in these calculations. Preservation of stoichiometry requires that oxygen be lost from the surface as O (either atomic or diatomic) or higher order oxides of aluminum given the absence of an oxide of cesium. Neither of these species have been detected in significant quantities indicating that oxygen must be lost by an alternate mechanism, possibly an electron damage process.

Electron exposure of the surface appears to play a role in this etching process. There are several sources of electrons in our experimental configuration which contribute to the occurrence of etching. The sapphire surfaces are exposed to electrons generated from the quadrupoles' ionization sources, unless specific shielding precautions are taken. Irradiation of the surface with 70 eV electrons occurs during both adsorption and desorption of Cs when monitoring events with the optimized UTI quadrupole. We find that the appearance of the etching feature depends only on electrons being present during desorption. Attempts to desorb Cs with the ionization source turned off resulted in retention of a significant fraction (30 to 50%) of the original deposit, based on XPS measurements. Etching results in the complete removal of Cs from the surface. In addition, movement of the sample out of line-of-sight of the ionization source does not yield an etching profile and shows residual Cs on the surface after annealing. A second source of electrons results from x-ray irradiation of the surface during XPS. While Al K α photons are not

expected to generate damage at the sapphire surface, the secondary electrons produced in the near surface region could alter the surface. Al $K\alpha$ irradiation generates a broad energy range of secondary electrons from 1487 eV to some minimum (trapping) energy. We have only observed etching to occur on substrates that have been subjected to x-ray irradiation. The primary electron source used for generating Auger emission is less of a concern in this study because irradiation is localized to less than 1% of the surface area monitored during desorption and, as discussed below, surface damage is easily controlled and detected.

Electron induced damage can account for the observed desorption of Al. This sensitivity to electron irradiation raises concerns of electron induced damage of the surface which is known to occur with sapphire (Olivier and Poirier 1981). Electron irradiation of sapphire produces selective oxygen loss from the surface. Oxygen loss is attributed to stimulated desorption resulting from excitation of the Al(2p) and an interatomic Auger decay from the O (2p) (Feibelman and Knotek 1975). The Al(LVV) Auger transition is quite sensitive to the appearance of reduced state Al produced by the desorption of O. Figure 2 shows a series of derivative mode Al(LVV) spectra generated from a (1102) surface prior to electron exposure, after 4 minute increments of 1.6 keV, 400 $\mu\text{A}/\text{cm}^2$ electron exposure, and after subsequent annealing to 1350 K. This electron energy was chosen to simulate the energy of the x-ray source in previous XPS measurements. It should be noted that an energy equivalent to the Al(2p) core level (~ 80 eV) is all that is needed to produce O desorption and any further energy increase only alters the desorption efficiency. The atomically clean (1102) surface shows an unresolved doublet with a minima at 35 eV and 51 eV. This spectrum is characteristic of a stoichiometric sapphire surface. Electron exposure produces a third feature with a minimum at 63 eV. Continued exposure produces continued growth in the amplitude of this feature. Annealing the surface to 1350 K results in a loss of the 63 eV transition and apparent restoration of surface stoichiometry. Figure 3 shows the resulting desorption traces for Al and AlO during the post-electron exposure anneal. These spectra show the both Al and AlO start to desorb from the surface at a temperature of 950 K in an approximate 1.3:1 ratio. This ratio is slightly less than the 1.6:1 ratio observed for the Cs mediated etching process. Neither O or AlO_2 are detected during the desorption process in agreement with the Al-rich nature of the surface. Subsequent desorption spectra with no additional electron exposure do not yield Al or AlO signals indicative of complete removal of the damaged surface layer upon annealing. These results are consistent with Chang's (1971) observation that electron exposure of the oxygenated (0001) surface at elevated temperature could produce the original (1x1) stoichiometric surface.

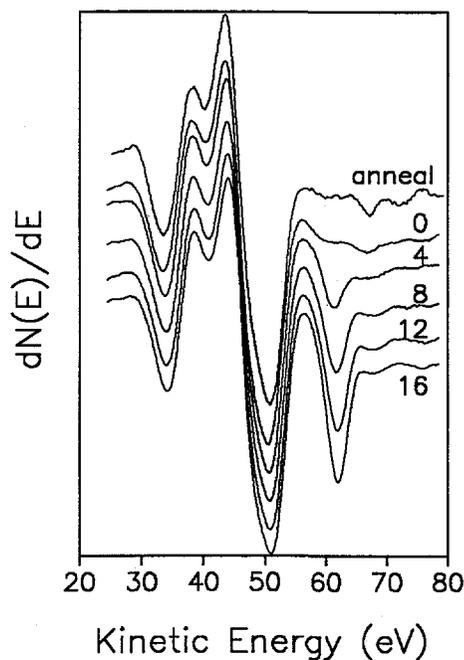


FIGURE 2. Variation in Al(LVV) Derivative Lineshape as a Function of Electron Irradiation: 4 Minute Intervals at 1.6 keV and 400 $\mu\text{A}/\text{cm}^2$.

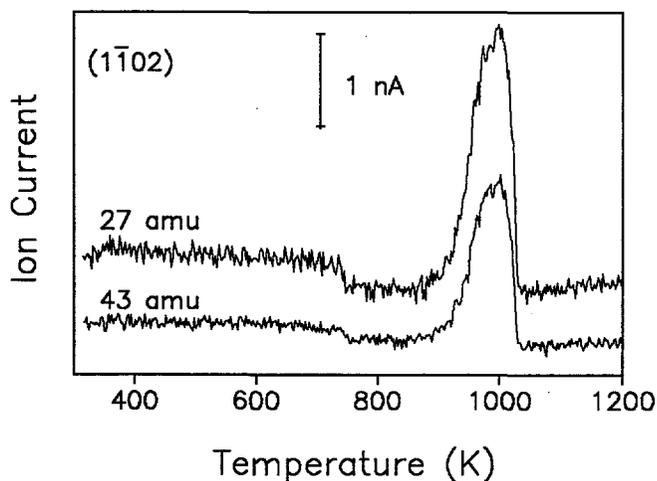


FIGURE 3. Desorption Profiles for Electron Irradiated (1102) Sapphire: 30 Minutes at 1.6 keV and 400 $\mu\text{A}/\text{cm}^2$.

The above discussion demonstrates that electron irradiation alone produces similar desorption results to those observed with Cs exposure. A possible conclusion is that the etching observed in the presence of Cs is strictly a result of damage generated by electron irradiation. However, there are several additional observations that argue that both Cs and electrons participate in the etching process. We have found that the levels of electron exposure necessary to produce comparable Al and AlO signals with an electron beam will remove Cs that has been previously deposited on the surface. This result contrasts with combined XPS and adsorption measurements that show that detectable levels of Cs are not lost as a result of x-ray exposure. Cs desorption from a surface that has been previously electron damaged does not yield the characteristic etch feature which indicates that Cs must be present during irradiation. The results above demonstrate that electron damage is annealed out of the surface which suggests that Cs deposited on a freshly annealed surface and desorbed with no additional electron irradiation should not yield etching. However, we find that etching can occur on such a surface.

Surface etching impacts the adsorption of Cs on both the (0001) and (1102) surfaces. Figure 4 shows the variation in Cs adsorption probability with exposure as a function of the number of etch cycles for both orientations. These curves are calculated by monitoring the adsorption process by measuring the reflected Cs signal (Zavadil and Ing 1993). The (0001) data show that the surface maintains a high initial adsorption probability of 0.9 with etching and that this facile adsorption is extended to higher exposure. The (1102) data show that etching produces a small decrease in the initial adsorption probability from 0.9 to 0.88. The initial adsorption capacity can be calculated by integrating these curves. The (0001) surface shows a 50% increase in initial capacity with increased etch cycle whereas the (1102) surface shows a 5% decrease. This increase in Cs capacity for the (0001) surface is in contrast to previously reported measurements that show that surface de-oxygenation decreases the capacity for Cs adsorption on the c-plane (Zavadil and Ing 1994). XPS measurements show no significant increase in Cs surface concentration which indicates that the morphology of the deposit changes with etching. The combined decrease in adsorption probability and capacity observed for the (1102) surface suggest either a decrease in residence time on the surface and/or a decrease in nucleation centers for the Cs adsorbate with etching. These types of change would result in an increased probability of desorption at room temperature.

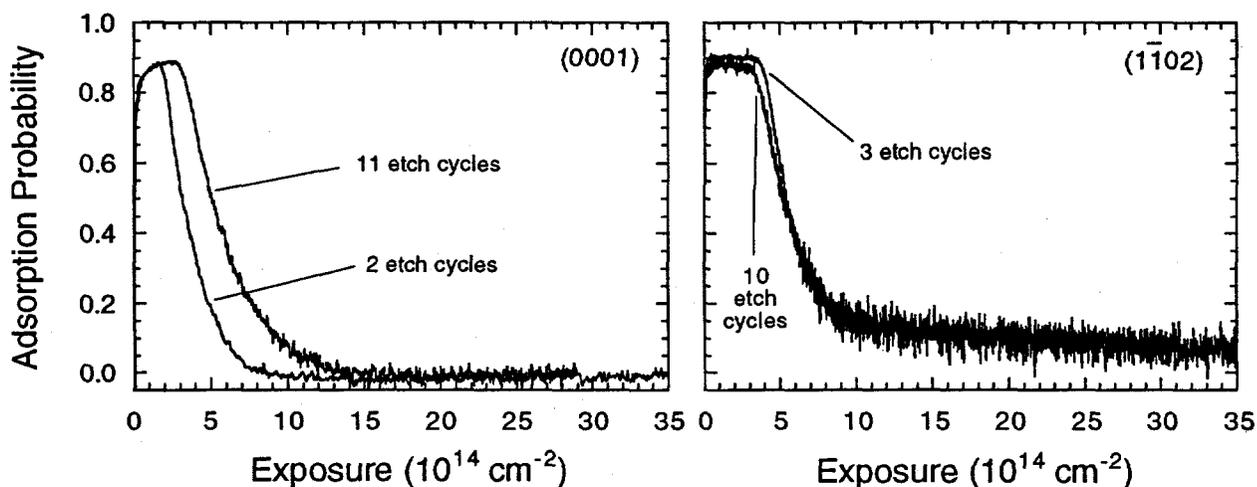


FIGURE 4. Cs Adsorption Probability Curves for Etched (0001) and (1102) Sapphire as a Function of Etch Cycles.

CONCLUSIONS

We have demonstrated that a material loss process can occur on sapphire in the presence of a Cs deposit and electron irradiation. The desorbing species detected are Al and sub-oxides of Al. Results show that the level of desorbing product is consistent with monolayer removal. Etching is dependent on initial Cs coverage, with coverages

greater than an initial saturation value required to produce etching. Etching is also independent of the chemical composition of the surface, occurring on both the (0001) and (1102) orientations of sapphire. The role of electrons is unclear based on our studies to date, but may be related to a damage mechanism that results in the stimulated desorption of oxygen. This oxygen loss is consistent with apparent oxygen deficiency observed in the desorbed product. Etching produces changes in the adsorption characteristics of both orientations of sapphire studied. Whether this damage mechanism is a likely contributor to insulator degradation in a thermionic system depends upon the energy and fluence profiles for electron emission from the fuel. It is unlikely that electrons generated at the emitter surface could induce etching because of the low energies in the interelectrode gap region. This study demonstrates that added energy input to the surface of an insulator can stimulate processes that would not normally occur.

Acknowledgments

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