Electrostatic Field Enhancement of Al(111) Oxidation

I. Popova, V. Zhukov, and J. T. Yates, Jr.
Department of Chemistry, Surface Science Center, University of Pittsburgh, Pittsburgh, Pennsylvania 15260
(Received 8 July 2002; published 17 December 2002)

We show that the electrostatic charging of an aluminum oxide film by electron-bombardment produces a greatly enhanced rate of Al(111) oxidation by $O_2(g)$ at 90 K, compared to a film which has not been bombarded by electrons. This novel memory effect for prior electron irradiation is caused by the negative electrostatic potential created and stored on the outer oxide film surface as a result of electron bombardment. The high electrostatic field ($\sim 10^7$ V/cm) produced across the depth of the film is postulated to cause an enhancement of ion migration through the film, leading to rapid oxide film growth, as predicted by the Cabrera-Mott theory of low temperature metal oxidation.

DOI: 10.1103/PhysRevLett.89.276101 PACS numbers: 81.65.Mq, 34.80.Ht, 79.20.Hx, 79.60.Dp

We have observed that a high electric field created across an Al_2O_3 film on an Al(111) surface by electron bombardment strongly increases the rate of oxidation at 90 K. The negative electrostatic charge, deposited in the process of electron irradiation of the outer surface of the film, causes rapid oxide film growth, when molecular O_2 is incident on this charged surface. An enhancement of the oxidation rate occurs during electron bombardment [1], but, surprisingly, also *after bombardment is discontinued.* This "memory effect" for prior electron bombardment shows that this phenomenon is not due to electron stimulated excitation of adsorbed O_2 species on the surface, but instead to an electric field effect within the oxide film. This dramatic electric-field-induced oxidation effect could be of importance in the enhancement of the passivation quality of oxide films on structural aluminum surfaces, as well as for enhanced oxide film passivation of aluminum conductors used in microelectronics.

The ultrahigh vacuum chamber used in these experiments has a base pressure of (2–3) $\times 10^{-10}$ Torr and is equipped with x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and a rastering electron gun, as previously described [1]. The electron beam with a diameter of $\sim$0.5 mm and primary beam energy of 100 eV was applied to an area of 1 cm^2 with a current density of 5 $\mu A/cm^2$. The Al(111) crystal in these studies was mounted on W heating wires, and its temperature was measured with a type-K thermocouple. The crystal cleaning procedures were carried out using Ar^+ ion bombardment followed by annealing as described previously [2] and subsequently checked by both XPS and AES measurements. The oxide film thickness was measured by XPS using the relative attenuation of the $Al^0(2p)$ integrated intensity, taking into account the atomic sensitivity factors [3] and the electron attenuation length in Al_2O_3 (16.7 ± 0.6 Å) [4]. Measurements of the O(1s) integrated intensity were correlated with the oxide thickness measurements based on the attenuation of the $Al^0(2p)$ intensity.

The Al_2O_3 films investigated here were initially grown by simultaneous low energy electron irradiation (E_p = 20 eV, $I_p = 5\ \mu A/cm^2$) during oxygen exposure. The oxide growth rate observed for the films grown without electron irradiation in the range of oxygen exposures employed here was much lower, as described in Ref. [1].

Figure 1 shows the oxide film thickness as a function of oxygen exposure after the various electron-assisted oxidation procedures, interrupted for XPS film thickness measurements. At the end of the initial electron-assisted oxidation period (point A), after the 2100 L [1 langmuir (L) = 10^{-6} Torr s] O_2 exposure, the extent of oxidation had reached a near-saturation condition. The oxygen gas was then evacuated, and electron-bombardment was carried out in ultrahigh vacuum at

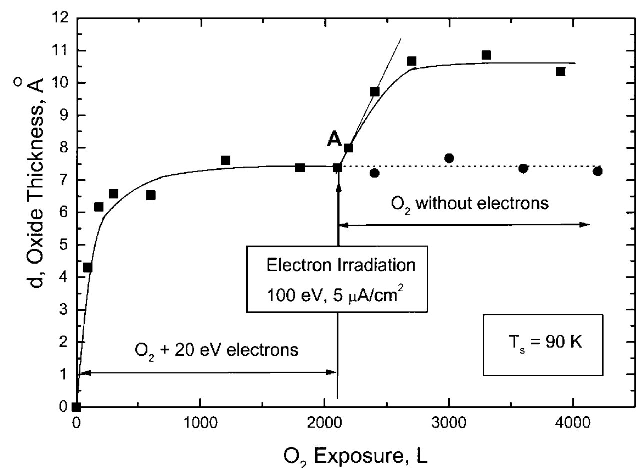

FIG. 1. The uptake curve (oxide film thickness as a function of oxygen exposure). At point A the apparatus was evacuated and the oxide film was subjected to electron bombardment (100 eV, 5 $\mu A/cm^2$, 5 min). Subsequently, oxygen exposures were carried out at 90 K. A dramatic increase of the oxidation rate for O_2 exposures following the electron irradiation is observed (squares). The additional oxidation of the sample beyond point A, carried out without the electron irradiation, does not result in any subsequent oxidation (circles).

 0031-9007/02/89(27)/276101(4)$20.00 © 2002 The American Physical Society

100 eV, depositing 1.5×10^{-3} C/cm^2 of charge at a current density of 5 μA/cm^2. At this point, irradiation by electrons was discontinued, and the surface was then periodically exposed to $O_2(g)$ at 1×10^{-7} Torr as sequential XPS measurements were made. It was observed that extensive additional oxide film growth occurs on the charged surface after the termination of the electron bombardment. In contrast, if no charging by electron irradiation was carried out, the oxide thickness remained essentially constant upon exposure to O_2 as shown by the horizontal line in Fig. 1 (circles) beyond point A. These data were obtained in a separate experiment and plotted after normalizing the oxygen coverage at point A.

The electron irradiation dose at point A was carried out to different levels, and it was found that after a charge of 1.5×10^{-3} C/cm^2 was applied, independently of the electron-beam current density or electron dose duration, no further enhancement of the oxidation rate was observed, indicating saturation of the stored surface charge density.

The electrostatic charging of the surface by electron bombardment was studied by XPS. Figure 2 shows the creation of the electrostatic potential on the oxide surface as a result of sequential electron-bombardment steps at point A. Surface charging causes the apparent binding energy of both the $Al^{3+}(2p)$ and the $O^{2-}(1s)$ XPS features to shift. In these measurements each electron dose lasted 1 min, and was done consecutively after the previous one. The $Al^{3+}(2p)$ and $O^{2-}(1s)$ XPS peaks shift in parallel to lower apparent binding energy, indicating negative charging of the oxide layer. The maximum peak shift of 1 eV corresponds to an electrostatic field of $\sim 1.4 \times 10^7$ V/cm across the 7 Å thick oxide layer. The electrostatic field created by charging is comparable to the breakdown field for bulk alumina [$(0.3\text{–}1.3) \times 10^7$ V/cm] [5]. This explains why the amount of shift (charging of the layer) cannot be increased even by prolonged electron bombardment of the sample (up to 1.8×10^{-2} C/cm^2 by the 100 eV electron beam). We have also investigated the current dependence of the charging process by the monitoring XPS peak shift with time for a constant current density during electron irradiation. We found that the total amount of charge delivered to the surface determines the created electrostatic potential, independent of current densities in the range of 5–15 μA/cm^2.

The temporal stability of the charged surface was investigated by storage in ultrahigh vacuum at 90 K while periodically monitoring the surface electrostatic potential by XPS. The film gradually discharges with a half-life of about 15 h. In addition, a slow hydroxylation process is observed from the low residual pressure of water vapor present in the ultrahigh vacuum system. The thermal stability of the charged surface was also investigated, and it was found that gradual loss of charge occurred during sequential heating up to 473 K. In addition, a 10%–20% decrease in the $O(1s)$ intensity upon heating was observed. This may be indicative of the loss of a small quantity of weakly adsorbed O_2 from the oxide layer. Trapping of the weakly bound molecular O_2 species on the surface of the oxide film has been previously reported, based on ultraviolet photoelectron spectroscopy measurements [6].

The rate of field-induced oxidation is linearly correlated with the degree of surface charging. This may be seen in Fig. 3, where the rate of oxidation at 90 K is found to be linearly dependent on the change in the surface potential over a range of approximately 0.4 V [as measured by the shift of the $O(1s)$ XPS feature] which is created by electron bombardment. These measurements were made under conditions where the oxidation was

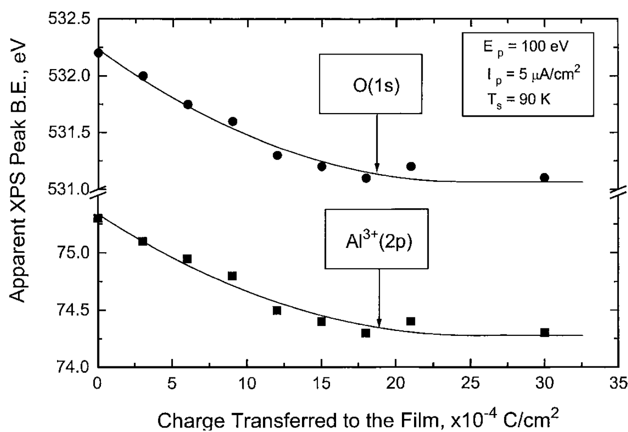

FIG. 2. The charging of the oxide layer by electron irradiation. A parallel shift of both $Al^{3+}(2p)$ and $O^{2-}(1s)$ XPS peaks to lower apparent binding energy (up to 1 eV maximum) was observed upon electron irradiation.

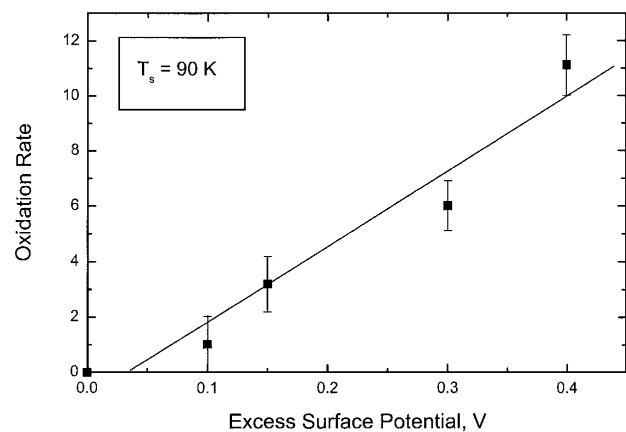

FIG. 3. Linear correlation between the electron-stimulated oxidation rate and negative surface potential. The rate of electron-stimulated Al(111) oxidation was defined as $R = [d\theta/d\mathrm{Exp}]_{\text{with electrons}} - [d\theta/d\mathrm{Exp}]_{\text{w/o electrons}}$. (Exp = O_2 exposure, θ = oxygen coverage) and calculated at the same total oxygen coverage ($\theta \approx 2$ ML) for various beam energies.

carried out simultaneously with electron bombardment at various electron energies in the range of 0–100 eV. From the series of the uptake curves for various electron energies, a correlation of the oxidation rate and electron energy and a correlation of the electron energy and the excess electrostatic potential on the surface were obtained. A cross correlation of these two curves was used to obtain the data shown in Fig. 3.

The enhancement of the oxidation rate after the electron irradiation could also be rationalized by the creation of defect sites upon electron irradiation [7] or by the partial reduction of Al^{3+} to Al^0 in the oxide film [8]. Both of these surface phenomena were previously observed in the process of electron irradiation of oxide surfaces.

In order to distinguish between the field-assisted process and the creation of the defect sites as a possible explanation for the increased oxidation rate, Ar^+ ion irradiation was substituted for electron irradiation at point A in Fig. 1. An ion dose of 1.2×10^{-3} C/cm^2 at 500 eV was applied, causing a slight loss of O(1s) intensity due to sputtering. Subsequent exposure to O_2 at 90 K caused no observable growth of the oxide film, supporting the idea that defect production in the oxide film is not responsible for the enhancement of the oxidation rate.

The partial reduction of the Al_2O_3 surface to metallic Al has been reported for extremely high electron-bombardment fluences at keV energies above 1 C charge deposition [8]. However, in our experiments the electronic charge deposited at point A in Fig. 1 is only $(1.5–2.5) \times 10^{-3}$ C/cm^2. In separate experiments on an Al_2O_3 film we could not observe metallic Al formation by XPS at electron-bombardment energies from 500–800 eV (charge deposited $= 6.0 \times 10^{-3}$ C/cm^2), indicating that at the electron fluences and beam energies used here, no measurable reduction of Al^{3+} takes place. These observations preclude Al_2O_3 reduction by electron bombardment as being involved in the effect reported here.

The charging of the oxide layer observed here is a result of the capacitorlike behavior of the Al_2O_3 insulator film. The grounded Al metal is one of the plates of the capacitor, and the negatively charged outer part of the oxide layer is the other. At 90 K under the O_2 exposure conditions used here, substantial quantities of adsorbed molecular oxygen may be stored on the oxide surface. Electron tunneling from the metal to the surface of the oxide film can lead to conversion of adsorbed O_2 into O_2^- ions, leading to the dissociation and formation of O^{2-} ions. The high electric field induced by the surface charging will enhance the mobility of Al^{3+} and O^{2-} ions through the oxide film, promoting the oxide film growth.

According to the accepted Cabrera-Mott theory of low temperature metal oxidation [9,10], an electrostatic field formed across a growing oxide film promotes ion diffusion—the rate limiting step for mass transport in oxidation. In thermally activated metal oxidation, electron tunneling from the bulk metal to the affinity level of the oxidizing species occurs, and the electric field produced across the oxide film thickness controls the rate of ion transport and concomitant oxide film growth. However, in the case of thermal oxidation, the value of the electrostatic potential on the outer part of the oxide film gradually decreases as $1/d$ (where d is the thickness of the growing oxide film [9–11]), as the electron tunneling through the growing layer diminishes, leading to the parabolic oxide growth rate observed. Creation of the electrostatic potential by means of electron irradiation allows for the artificial stimulation of the ion diffusion, and film growth after the apparent saturation of the thermal growth was achieved.

It has been postulated that the migration of oxygen ions through the oxide film dominates in the growth kinetics for thermal oxidation [12]. It is not possible in the work described here, involving electron-bombardment-induced surface charging, to determine whether the negatively charged outer layer consists of trapped electrons or an excess of negative oxygen anions. The observed surface charging of -1.0 V on a 7 Å thick Al_2O_3 film could be caused by an accumulation of about 4×10^{13} O^{2-}/cm^2 or about 0.02 of a monolayer of O^{2-} ions [13].

In these experiments, the artificial production of enhanced negative charge on the surface of a stable oxide film has been shown to induce additional metal oxidation when oxygen is subsequently added to the charged surface. An enhancement of oxidation rate in the electron-beam induced oxidation of Al(111) by bombardment of adsorbed water layers has been reported. The possible presence of a memory effect for electron-bombardment-induced oxidation using water as the oxidant was not investigated [14].

In summary, we have shown that an aluminum oxide film on an Al(111) surface may be charged by electron impact. The effect of the electric field induced across the oxide film thickness on the additional oxidation was seen

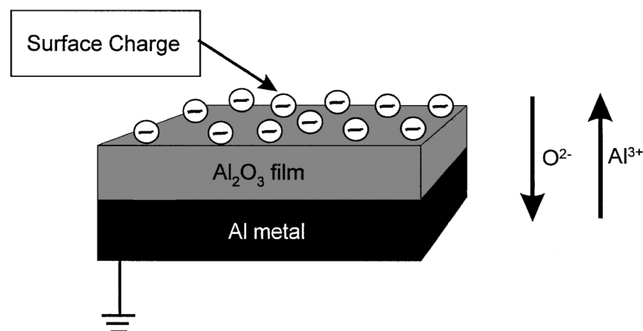

FIG. 4. Schematic model for electrostatic field enhancement of Al(111) oxidation, indicating the creation of the electrostatic charge on the oxide surface, enhancing the ion diffusion process, the rate limiting step of the Al oxidation process.

long after the electron irradiation was discontinued, a memory effect which has not been observed previously. The presence of this field is found to dramatically enhance the kinetics of Al(111) oxidation, when O_2 molecules interact with the charged surface after electron bombardment. It is postulated that the rate of ion migration through the growing oxide film is strongly enhanced by the electric field in accordance with the general ideas within the Cabrera-Mott theory of metal oxidation. A schematic diagram of the effect described here is shown in Fig. 4.

We thank Air Force Office of Scientific Research for the full support of this work.

[1] V. Zhukov, I. Popova, and J. T. Yates, Jr., Phys. Rev. B **65**, 195409 (2002).
[2] V. Zhukov, I. Popova, V. Fomenko, and J. T. Yates, Jr., Surf. Sci. **441**, 240 (1999).
[3] C. D. Wagner, W. M. Riggs, and L. E. Davis, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer Corp., Physical Electronics Division, Eden Prairie, MN, 1979).
[4] D. R. Penn, J. Electron Spectrosc. Relat. Phenom. **9**, 29 (1976).
[5] N. Klein and M. Albert, J. Appl. Phys. **53**, 5840 (1982).
[6] P. Hoffman, K. Horn, A. M. Bradshaw, and K. Jacobi, Surf. Sci. **82**, L610 (1979).
[7] J. A. Slezak, B. D. Zion, and S. J. Sibener, Surf. Sci. **442**, L983 (1999).
[8] A. Hoffman and P. J. K. Paterson, Surf. Sci. **352–354**, 993 (1996).
[9] N. Cabrera and N. F. Mott, Rep. Prog. Phys. **12**, 163 (1949).
[10] A. T. Fromhold, Jr., *Fundamental Theory of Metal Oxidation* (North-Holland Publishing Company, Amsterdam, 1976).
[11] F. P. Fehlner and N. F. Mott, Oxid. Met. **2**, 59 (1970).
[12] C. Ocal, S. Ferrer, and N. Garcia, Surf. Sci. **163**, 335 (1985).
[13] The excess surface charge [$\sigma(\mathrm{C\,m^{-2}})$] due to electron bombardment is calculated from the relationship $\sigma = \varepsilon\varepsilon_0 \Delta V/d$, where $\varepsilon = 10$ is assumed for the dielectric constant of the Al_2O_3 film. The surface density of O^{2-} ions on the neutral Al_2O_3 surface, based on the crystallographic bulk density of Al_2O_3 is 1.7×10^{15} cm^2.
[14] H. D. Ebinger and J. T. Yates, Jr., Phys. Rev. B **57**, 1976 (1998).