The Study of Oxidation of Magnesium(0001).

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THE STUDY OF OXIDATION OF Mg (0001)

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Physics and Astronomy

by

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This work is dedicated to my parents for their life long guidance, support, and love.
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ABSTRACT

The oxidation of Mg(0001) was studied using ESDIAD (Electron Stimulated Desorption Ion Angular Distributions), LEED (Low Energy Electron Diffraction) and STM (Scanning Tunneling Microscopy). Disassociated oxygen and two species of oxygen were observed morphologically by STM and were identified as incorporated oxygen (mixed layer) and ionic oxide MgO(111). We observed that the step terraces and the dissociated oxygen are highly mobile and interact easily with the STM tip at room temperature. The true oxide was first observed on a double step pinning site as a protrusion elongated along the step edge. These sites pin the top terrace to the one underneath forming a double step at the pinning site. A form of oxygen (incorporated) characterized by bumps of 1.2 Å in height was observed on the plane of terraces. The bumps and protrusions grow in area and height as a function of oxygen exposure. At 12 L oxygen exposure, bumps coalesce to completely cover the surface. By 13 L, LEED show a diffuse 1x1 pattern indicating this growth was in registry with the Mg substrate. At larger oxygen exposures, most of the bumps observed are precursors for the formation of protrusions which leads to the thickening of the oxide. ESDIAD indicates that the initial oxygen is subsurface and that the step edges are not involved in the ion desorption. Formation of the oxide surface was complete by 200 L exposure.
CHAPTER 1: INTRODUCTION

Oxidation of Mg(0001) has been studied extensively by several groups with the aim that such a simple system will provide a better understanding of the oxidation process that can be extended to more complicated systems.\(^1\) Mg oxidation has also been investigated from a standpoint of corrosion since magnesium alloys have poor corrosion resistance that restricts their use in some applications, for example in the aerospace industry, in spite of their high strength/weight ratios.\(^2\) MgO is also useful as a thin film insulator in semiconductor devices since it has one of the largest band gaps,\(^2\) as a ceramic that is easily bonded to metals,\(^3\) and as a catalyst support.\(^4\)-\(^6\) In this latter application, the reactive metal is deposited on the surface of MgO as a thin film which increases the effective surface area of the catalyst. MgO is also used as a buffer material for high \(T_c\) superconducting thin films, to prevent inter-diffusion between the substrate materials which can react with the high \(T_c\) overlayer.\(^7\) The MgO buffer also helps to enhance the \(c\)-axis growth of such films and hence is potentially important in future microelectronics applications.\(^7\)

Previous work on the oxidation of Mg classifies the oxygen present in the surface layer into two chemical states. The first has been referred to as interstitial oxygen, incorporated oxygen, chemisorbed oxygen, defective oxide, MgO\(_2\). The second is the true ionic oxide (i.e. the bulk oxide). In order to avoid confusion and maintain a consistent terminology, the present work refers to the first type of oxide as incorporated oxygen and the second type, as ionic oxide or MgO.

One of the first studies on oxidation of the Mg(0001) single crystal was performed by Namba et al.\(^8\),\(^9\), using Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED) and Electron Energy Loss Spectroscopy.
(EELS). Their oxidation experiment was carried out on a sample that did not have a mirror like surface finish due to 24 hr continuous ion sputtering and one time annealing at 200 °C. Such long ion sputtering tends to roughen the Mg surface and evaporation from the surface caused by annealing at that temp roughens the surface further.\textsuperscript{10} As the sample preparation and surface condition is critical to the oxidation process, their results are suspect and will not be given further consideration.

A later study of oxidation of Mg(0001) was performed by Hayden \textit{et al.}\textsuperscript{10} and Kötz \textit{et al.}\textsuperscript{11} using LEED, EELS, work function and ellipsometric measurements on a well prepared surface. They found that the initial stage of oxidation occurs in the range 0 - 6 L (One Langmuir, L=1x10\textsuperscript{-6} torr-sec) oxygen exposure characterized by a Mg(0001) 1x1 diffuse LEED pattern and a sharp decrease in the work function. The model they used to interpret their ellipsometry data was limited to one in which the areas of Mg and MgO had to remain distinct, i.e., individual islands of Mg and MgO. The results of their measurements indicated that if the surface could be so modeled, the thickness of the mixed Mg, MgO layer was 4 Å.

In the next stage of oxidation from 6 - 10 L, their LEED data showed no extra features but only a broadening of the integral spots and an increase in the background intensity. They interpreted this result as an incorporated 1x1 layer of oxygen. The sharp decrease in the work function observed in the initial stage continued. Their EELS data showed the onset of MgO plasmon losses in this region while their ellipsometry results showed that part of the mixed layer formed in the initial stage transformed into three dimensional MgO either as a continuous layer or as islands. Their ellipsometry data further showed that the effective thickness of the mixed layer decreased from 4 to 1.5 Å.
At ~ 12 L in LEED, they observed growth of a new pattern superimposed on the diffuse Mg(0001) spots. They interpreted the new spots as due to a square lattice structure of Mg(100) growing epitaxially in three equivalent domains on the hexagonal Mg(0001) surface. The work function became a minimum at 12 L and then increased, which they associated with the epitaxial growth of MgO. Above 12 L oxygen exposure, they found EELS measurements that support the growth of bulk MgO.

In the exposure range 16 to 5000 L, their ellipsometry data was modeled as a full MgO layer together with a mixed Mg/MgO layer of thickness 1.4 Å. It was not possible from their data to distinguish whether the two layers were on top of each other or whether they existed as adjacent islands of Mg and MgO. They observed the mixed layer throughout this range with almost no change in its properties except for an increase in MgO.

The oxidation of Mg(0001) was also investigated by Flodstrom and Martinsson using AES, LEED, and EELS. Their data indicated the following two step model for the initial oxidation process. The first step was the exposure range 0-2 L and the second was between 2-10 L range.

In the 0-2 L exposure range their AES data (O(KLL) peak) showed a linear uptake and their LEED data showed a Mg(0001) 1x1 pattern that decreased in intensity. Their LEED data indicated that the adsorption sites for oxygen were disordered. The EELS data showed only the Mg metal vacuum loss peak. They concluded that, in the 0-2 L exposure range, incorporated oxygen is formed.

In the 2-10 L oxygen exposure range, the original LEED pattern disappeared and a "new" diffuse 1x1 pattern reappeared at about 8 L. In AES at 10 L, they observed an upward break in the slope of the linear oxygen uptake consistent with the growth of islands. In addition, the EELS data showed the
coexistence of a Mg metal vacuum loss peak and a Mg/MgO interface loss peak in this region confirming the formation of islands. They also estimated the thickness of the MgO islands in this exposure range to be three layers of MgO based on an electron scattering length of 5 Å for the 44.5 eV electrons in the Mg(L_{2,3}VV) peak. Hence, their data indicated that MgO(111) islands are formed in this range and grow to completely cover the surface by 10 L. This picture is also consistent with their AES data where two interfacial peaks at 39 and 27 eV appear at 2 L and reach a maxima at 8 and 11 L respectively. The interfacial peaks reaching a maximum indicates that the thin oxide layer is completely covering the surface before the bulk like oxide formation starts. With further oxygen exposure up to 25 L, their EELS data showed the start and increase of loss peaks at 16.5 and 22.0 eV close to the bulk-like MgO features at 17 and 24 eV. This indicated that the thickness of the oxide increased to form a bulk-like MgO by 25 L oxygen exposure.

X-ray Photoelectron Spectroscopy (XPS) studies support the concept of two kinds of oxide being found on the surface. Ghijsen et al. observed at the initial stage of oxygen exposure only one peak in the O 1s binding energy region at 530 eV. At 0.2 L exposure, a second structure appeared at a higher binding energy of 533 eV. They found that the intensity of both peaks evolved in a similar manner during oxidation. After a slow increase up to 2-3 L, the total intensity of the O 1s peaks increased sharply and finally leveled off at 100-200 L. The intensity ratios of the O 1s peaks, I_{HBE}/I_{LBE}, increased at the beginning of the adsorption but became nearly constant above an exposure of about 20 L. In order to identify the two peaks, they heated an oxygen exposed sample and observed the evolution of the two peaks. They found that the intensity of the high binding energy (HBE) at 533 eV decreased while the low binding energy peak
(LBE) at 530 eV increased proportionately. By assuming that this treatment would convert the incorporated oxygen to MgO, they identified the HBE peak as incorporated oxygen and the LBE peak, as MgO. Moreover, the total area under both curves remained unchanged indicating that the HBE oxygen species (incorporated oxygen) changed into the LBE oxygen species (MgO) with no loss of oxygen from the surface. Apparently the incorporated oxygen penetrates the oxide barrier at higher temperature to carry out further oxidation of the substrate.

A more recent XPS study by Thiry et al.\textsuperscript{13} showed similar results. However, since the surface of their Mg crystal was not very smooth and the LEED patterns they obtained were diffuse, their results are suspect and will not be considered further. XPS studies of oxidation of polycrystalline Mg\textsuperscript{14}, Mg adsorbed on Ru(001),\textsuperscript{15} and ultra thin MgO films on Mo(100)\textsuperscript{16} all show two peaks in the O 1s spectra with the HBE peak identified as the incorporated oxygen and the LBE peak as the ionic oxide.

A High Resolution EELS (HREELS) study of oxidation of Mg(0001) by Thiry et al.\textsuperscript{13,17} confirmed the two kinds of oxygen. We assume their results are reliable since their crystal showed sharp LEED patterns and AES showed no contaminants. They found that the incorporated oxygen given by a peak at 460 cm\textsuperscript{-1} saturated by \(\sim 46\) L after showing a maximum at \(\sim 20\) L and that the ionic oxide given by a peak at 620 cm\textsuperscript{-1} saturated only after 200 L. By comparing spectra obtained at 10 L of a non-annealed Mg(0001) sample with one taken a half hour later without further exposure to oxygen, they found that residual roughness favored the formation of the incorporated oxygen which then converted into the ionic oxide. Hence they concluded that the incorporated oxygen can diffuse through the ionic oxide barrier to carry the oxidation further inside the metal.
To summarize, Hayden et al.\textsuperscript{10} and Flodstrom et al.\textsuperscript{12} found different LEED patterns with oxygen exposure. Namely, Flodstrom et al.\textsuperscript{12} observed MgO(111) 1x1 growth while Hayden et al.\textsuperscript{10} observed additional spots due to MgO(100) 1x1 growth. They claim different exposure ranges for the formation of the thin layer of ionic oxide. Hayden et al.\textsuperscript{10} gives 5 - 12 L, and Flodstrom et al.\textsuperscript{12} gives 2 - 10 L. They also do not agree at what exposure the bulk-like ionic oxide first appears. Hayden et al.\textsuperscript{10} gave 12 L and Flodstrom et al.\textsuperscript{12} gave 25 L. Flodstrom et al.\textsuperscript{12} also state that the islands formed at 2 - 10 L consist of three layers of MgO while Hayden et al.\textsuperscript{10} state that there is a mixed layer until 6 L which, in the exposure range 6 -10 L transforms into a three dimensional oxide where mixed layer thickness reduces to 1.5 Å. We are lead to the assumption that differences in the two experiments are due to slight differences in sample preparation. However, the models proposed by Hayden et al.\textsuperscript{10} and Flodstrom et al.\textsuperscript{12} basically agree that incorporated oxygen is the first to form followed by an island-like ionic oxide growth. The results of T. Ghijsen et al.\textsuperscript{2} and P. A. Thiry et al.\textsuperscript{13,17} confirm the existence of incorporated oxygen which saturates above an exposure of ~46 L after a maximum at ~ 20L and the monotonic increase of ionic oxide until saturation above 200L.

The purpose of this research is to address the differences in the above results utilizing the additional probe of Electron Stimulated Desorption Ion Angular Distributions (ESDIAD) and to probe the morphology of the surface during these different stages of oxide growth using Scanning Tunneling Microscope (STM). ESDIAD probes the local geometry and the dynamics of O⁺ desorption. In this technique, ions are emitted only from the top-most layers and direction of the ion emission revealed by their angular distribution is determined.
by their initial bonding geometry.\textsuperscript{18} For example, if step edges are the main sites in the oxidation process, then the ESDIAD pattern will show off-normal ion emission. If the oxygen is initially subsurface, then the oxygen ion yield in the ESDIAD should be low or nonexistent. In addition, LEED will be used to confirm the surface order and to compare with previous results. STM probes the surface morphology of the oxidation process on an atomic scale. It will be shown that Mg presents an interesting challenge to the STM probe as the Debye temperature of Mg is low enough that the atoms at the surface are extremely mobile at room temperature under the influence of the STM tip. Furthermore, this paper will identify the morphology of the previously observed incorporated oxygen and the ionic oxide, \textsuperscript{2, 13, 17} in that the two forms of oxide can be associated with distinct features observed on the surface by STM.
CHAPTER 2: EXPERIMENTAL TECHNIQUES

2.1 Electron Stimulated Desorption (ESD) Ion Angular Distribution (ESDIAD)

2.1.1 ESD

Electron stimulated desorption is the process in which an incident mono-energetic electron beam excites the surface atoms or molecules of a sample, resulting in ionization and ejection of the ions from the surface. Since the ionization and ejection are fast (10⁻¹⁶ to 10⁻¹⁴ seconds) compared to the typical vibrational time (10⁻¹² seconds), the ion is ejected along the direction of its surface bond. The resulting angular distribution of the ejected ions represents the bonding geometry.¹⁸,¹⁹

The process of ion desorption consists of three very general steps.¹⁸ First, an initial excitation occurs on the time scale of 10⁻¹⁶ seconds with the electron interacting with a surface atom.¹⁸ Second, the resulting excited state relaxes either by displacement of the atom or by electronic energy transfer processes which re-distribute the energy in the time scale of 10⁻¹⁵ sec.¹⁸ Finally the desorbing species ejects and leaves the surface in the time scale of 10⁻¹⁴ sec.¹⁸

Two models have been put forward over the years, to explain the basic features observed in this process. The first model was proposed by Menzel, Gower and Redhead and is known as the MGR model.²⁰,²¹ The basis for this model is the Frank-Condon principle, which states that, the nuclear separation and relative velocity are essentially unchanged during an electronic transition in a molecule, that is, the electronic transition takes place quickly compared with the time required for appreciable nuclear motion.²² If a repulsive neutral or ionic state is produced by a Frank-Condon type excitation, the surface atom or ion will desorb as a response to the repulsive force. This model appears to describe
desorption of neutral atoms and low electron energy desorption. The MGR model, however, can explain neither the desorption of O\(^+\) from an ionic oxide such as TiO\(_2\) or MgO, in which oxygen is originally configured as O\(^2-\), and therefore must lose three electrons, nor the large threshold energies observed in such systems. This was the motivation for the second model proposed by Knotek and Feibelman and illustrated in Fig. 1 for MgO. This model explains the large change in charge required for O\(^+\) desorption from so called maximum valent compounds where the metal ion is in its maximum valence configuration. Ionic oxides are prime examples of maximum valent compounds.

The starting point for this model is the creation of the core hole in the Mg atom. This core hole is then filled by an electron from the oxygen valence band. This inter-atomic Auger decay causes either one or two additional electrons in the valence band to escape. If two electrons escape, the original O\(^2-\) loses one electron from the valence band to fill the core hole in the Mg 2p and two other electrons escape from the valence band resulting in O\(^2-\) going to O\(^+\). Because the Auger process takes place much faster than ion movement, O\(^+\) suddenly finds itself in a repulsive Coulomb potential which ejects it from the surface. Since the ESD process is launched by the creation of a core hole, ESD cross-sections as a function of excitation energy follow the cross-sections for the creation of the core hole. Moreover, the desorption is independent of the method of initial core hole creation. Therefore, the ion desorption should take place no matter how the surface is stimulated, e.g., with electrons, photons or ions. This model explains the large charge transfer found in the desorbing oxygen ion (O\(^2-\) to O\(^+\)) and the large threshold energies. The atom to which the desorbing ion is bonded can be easily identified by measuring the threshold for the desorption. This can be very
Fig. 1: Schematic illustration of the inter-atomic Auger decay, the model proposed by Knotek and Feibelman for ESD applied for the case of the maxi-valency system MgO.
convenient if there are more than one atomic species on the surface. This is a very atom specific model in that it explains the observed features of the desorption by considering a specific bonded pair of atoms on the surface. Since the Knotek-Feibelman model explained ESD of O\(^+\) from the maximum valency system TiO\(_2\) quite well,\(^{25}\) it could be expected to describe MgO as well.

MgO is a very good example of a maximum valency ionic system. Therefore, ESD of O\(^+\) should be easily observed for electron beam energies greater than 52 eV which is the energy of the 2p core state of Mg shown schematically in Fig. 1.\(^{24}\) Surprisingly the O\(^+\) ion yield from MgO is very low and was observed only recently by T. Gotoh et al.\(^{26,27}\) who investigated ESD O\(^+\) desorption from MgO(001). They found that the O\(^+\) desorption has a threshold energy of 80 eV and that ESD process occurring in MgO was described by the Knotek-Feibelman mechanism. They also identify the initial core hole created to be Mg 2p. An O\(^+\) created in this system feels an explosive coulomb force pushing it away from the surface as explained above. In order for it to be observed, however, it must escape the surface without re-neutralization or recapture by the lattice. Walkup and Avouris\(^ {28}\) have shown that the lattice dynamics can be a crucial factor in the ESD process. They found that even when all the conditions are correct for ESD (i.e. the localization of the electron excitation and the initial state is repulsive), the lattice can rearrange in the time scale of the desorption process to recapture the ion. They found that this ability of the lattice to rearrange has a major effect on the desorption yields, on the ion kinetic energy distributions and on determining the nature of the desorption sites. For instance, when discussing particular sites such as atop, inplane, edge, etc. the rearrangement of the lattice should also be considered as the lattice can not be thought of as being fixed during the ion desorption process. This effect should be particularly
apparent in the case of the MgO where the metal ions are very light, so the lattice dynamics play a much larger role in the desorption process than in a lattice of heavier ions such as Ti or W. As the O⁺ ion starts to desorb, the neighboring Mg ions in the lattice will respond changing their original positions favorable for desorption. This may be the reason for such a low O⁺ desorption yield from MgO. Hence what happens as the ion moves away from the surface and how the lattice itself responds to the repulsive force is just as important as the formation of the ion itself.

2.1.2 ESDIAD

ESDIAD patterns and ion yields have been obtained from a variety of sample surfaces and adsorbates. These patterns contain well defined cones of ion emission both normal and non-normal to the surface.¹⁹ Since the Coulomb repulsion is strong and the desorption takes place in a time scale that is short compared to a vibrational period, the ion typically desorbs along the direction of its bond. The ESDIAD patterns then represent the original bonding configuration of the atom on the surface. As noted above, no ESD was observed from MgO until recently.²⁶,²⁷ Subsequently ESDIAD, patterns were also obtained by Gotoh and Takagi²⁹ for MgO(001). They show only normal emission indicating that step edges are not involved in the desorption.

2.2 Low Energy Electron Diffraction (LEED)

Low Energy Electron Diffraction (LEED) is one of the primary tools that determine surface structure and long range order.⁴ LEED patterns are observed when an electron beam of low energy is elastically scattered, i.e., diffracted, from the surface of a single crystal sample. The diffracted beams are observed as spots on a viewing screen, and are characterized by the points of reciprocal lattice of the sample, i.e. the location of the spots gives direct evidence of the crystallographic
structure. The observed diffraction pattern is simply the projection of the surface reciprocal net at a "magnification" determined by the incident electron energy. Hence LEED can readily determine the periodicity or the translational symmetry of the sample. The diffusiveness of the spots gives the degree of local order and the amount of contaminants on the surface. This is a surface sensitive tool since the electron mean free path in the sample for electron energies less than 100 eV is a few angstroms restricting useful information to the near surface region. The typical incident beam size of the electron gun is about ~ 1 mm resulting in a pattern that is an average over this area, rendering LEED as best utilized for crystallographic studies of surfaces with nearly ideal structures and very good long range structural order. If point defects or steps form commensurate ordered structures on the surface, then the LEED patterns will remain sharp giving no indication of this type of disorder. Therefore it is useful to study the local structure directly with STM, especially in the case at hand when LEED pattern becomes diffuse and disappear.

2.3 Scanning Tunneling Microscopy (STM)

Scanning Tunneling Microscopy (STM) is the most powerful surface structure analysis tool developed to date. It provides direct real space images of surface topography on an atomic scale. It is non-destructive, does not require periodicity of the surface or even ultra-high vacuum conditions. In this experiment a specifically prepared tip is scanned about 5 Å above a surface. A fixed biased voltage is applied between the tip and the sample causing the electrons to tunnel through the vacuum gap. A feedback mechanism regulates the vertical motion of the tip with a piezoelectric drive element to keep the tunneling current constant. This vertical motion of the tip traces contours of constant tunneling current which reflect the surface topography.
STM revolves around the principle of vacuum tunneling between the tip (typically W or Pt/Ir wire) and the atoms of the sample. It can be shown by solving the Schrödinger's equation for a rectangular barrier (in the simplest case) that the tunneling current, \( I \), decays exponentially with the barrier width, \( d \), as,

\[
I \propto e^{-2\kappa d}
\]

(1)

where \( \kappa^2 = 2m(V_B - E)/\hbar^2 \)

(2)

and \( m \) is the mass of the electron, \( V_B \) is the barrier height and \( E \) is the energy of the electron.\(^{33}\) In the simplest case \( V_B \) is the vacuum level and for states at Fermi level, \( V_B - E \) is just the work function. Since most work functions are about \(-4\) eV, eq (2) gives \( 2\kappa \approx 2 \text{ Å}^{-1} \). From eq(1) it is possible to see that the tunneling current drops by nearly an order of magnitude for every 1 Å of vacuum between the tip and sample. Therefore, the separation must be very small to obtain tunneling and very precise control of the tip is required to keep the tunneling current stable. This includes the limiting of the vibrations of the tip, to much less than 1 Å.\(^{33}\)

The position of the tip is accurately controlled by three piezoelectric drivers scanning the surface of the sample in two dimensions (X,Y) and controlling the height above the sample in the third dimension (Z). STM can be operated in two modes. The first mode is the "constant current" mode, in which a feedback circuit constantly adjusts the tip height to keep the current constant as described above. In this mode, the surface topography is reproduced by the path of the tip that is inferred directly from the voltage supplied to the piezoelectric drivers. The second mode is the "constant height" mode in which the tip height is held constant above the surface and the surface topography produces fluctuations in current which can in turn be used to generate an image of the surface. It is
worthwhile to note that this later mode is practical only when the sample surface is extremely flat.

To obtain good atomically resolved images, the tip and the sample preparation always plays a very crucial role. The best STM images result from tunneling at a single atom on the tip.\textsuperscript{33} Hence the preparation of the tip is very important. The sample surface should also be extremely flat. If there are large hills, say 5 mm, the tip will have to move by this amount. The piezoelectric mechanism will not always allow such large excursions of the tip and therefore the tip may crash into the surface damaging both.

The strength of the STM lies in its capability to image individual atoms. STM yields direct information about point defects, kinks and other surface morphology without requiring large samples.\textsuperscript{30} STM also provides reliable information about symmetry, atomic spacing and vertical distortion in the surface layer,\textsuperscript{30} making it an ideal tool to investigate surfaces. STM is an invaluable tool for this study because it provides information on the geometry of the surface during Mg oxidation, and on the physical differences between the two forms of oxide.
CHAPTER 3: EXPERIMENT

3.1 Sample Preparation

The first step in the experiment was to obtain a single crystal sample of Mg whose surface was parallel to the (0001) crystal plane. The sample was cut from a Mg (0001) single crystal boule ~1 cm in diameter and the orientation of the cut was established using Laué X-ray diffraction in the following manner. The boule was mounted on a South Bay Technology goniometer head and placed on the track in a Diffractis 601 X-ray diffraction generator manufactured by Enraf Nonius, Inc. A Polaroid XR-7 camera system was mounted in the diffractometer in a configuration to obtain photographs of the back scattered Laué diffraction patterns. With the sample 3 cm from the camera, exposure times varied from 10-20 minutes. By comparing the diffracted spots on the photograph (3000 ISO Polaroid 57 film) with the reference marks on the film holder, it was possible to re-adjust the goniometer to center the diffraction pattern on the reference axes of the camera. For higher accuracy, the sample/goniometer was moved 5 cm away from the camera requiring a exposure of about 30-40 minutes. An accuracy of $1/4^\circ$ orientation in the alignment was obtained. The oriented crystal mounted on the goniometer was installed in a Servomet spark cutter in a position to slice the boule perpendicular to the axis of the goniometer. Several samples of ~1 mm thickness were made.

The spark cutter was used instead of a wire saw since there was no physical contact between the spark cutting tool and the sample. This minimized the thermal and mechanical damage to the surface of the crystal. This machine operates by producing a rapid series of spark discharges between the tool and the sample which are immersed in a dielectric oil. The spark erodes the work at a rate...
dependent on the energy and the frequency of the discharges; high energies are used for fast rough work and low energies for producing finer finishes. The spark is produced by rectifying the A.C. supply voltage and applying the resulting D.C. to a relaxation circuit. A capacitor is charged until it reaches the breakdown voltage of the dielectric oil, and then discharged through a spark across the work gap. The capacitor is then recharged and the cycle is repeated. The breakdown voltage is proportional to the work gap, which must be controlled within close limits for efficient operation. This voltage is therefore used to control a servo system which maintains the work gap at its optimum value. The extent of depth of surface damage depends on the nature of the work material and on the spark energy and may typically be about 100 μm. Kerosene was used as the dielectric and was circulated to ensure that the cutting by-products are removed from the spark area. The tool consisted of a continuously fed fine Cu wire.

The sample slices were collected, and one chosen and mounted onto a head that attaches to the goniometer. It was reoriented with Laué diffraction as described earlier. The head was removed from the goniometer and mounted on a hand jib for polishing. The crystal was hand polished with decreasing Alumina powder, sizes beginning at 30 μm and ending at 0.05 μm, to obtain a mirror finish with a minimum of scratches and pits. The sample was then electrochemically polished at room temperature to remove the first few layers of material from the surface to insure that the surface was free of any damage due to mechanical polishing. The electrochemical solution used was 350 ml of ortho-phosphoric acid and 625 ml of ethyl alcohol at room temperature with a stainless steel cathode. A cathode voltage of 1-2 V and initial current density of 5 mA/cm² was used. The solution was continuously stirred using a magnetic stirrer to ensure uniform reactivity for the whole surface. The current and time was also
adjusted for the proper rate of electrochemical reaction to obtain a mirror surface. The sample was immediately rinsed successively with distilled water, ethanol and a mixture of 1 volume part ethanol to 1 volume part acetone,\textsuperscript{9} to quickly stop the chemical reaction. The sample was then mounted on a X, Y, Z, rotation vacuum manipulator with an isolated thoriated tungsten wire fixed behind it as a filament for heating. For measuring the temperature of the sample, a W-5\% Re / W-26\% Re thermocouple was spot welded to the holder very close to the sample. The thermocouple wires were not spot welded directly on the sample to avoid damage to the crystal since Mg is very soft and easily damaged. In the Ultra High Vacuum (UHV) system, the sample was further cleaned using cycles of Ar\textsuperscript{+} ion sputtering at 500 eV for a half hour followed by annealing to 125 °C for 10 - 20 minutes. Longer sputtering times would have resulted in a roughening of the surface as evidenced by a haze developing over the mirror finish. Higher annealing temperature would have lead to Mg evaporation which also causes roughening. After about 25 such cycles, sharp LEED patterns from the clean Mg (0001) sample were obtained. After the initial cleaning, the sample was prepared on a daily basis with 6 - 12 of above cleaning cycles to remove the oxide and surface contaminants.

3.2 Instrumentation

3.2.1 LEED/ESDIAD

This instrument that was constructed is a modification of the design first developed at the National Institute of Standards and Technology by Madey \textit{et al.}\textsuperscript{18} and has a total acceptance angle of about 60 °. The arrangement in Fig. 2 shows an electron gun that delivers a focused beam of electrons to the sample which is centered on the LEED/ESDIAD optics. In the LEED mode, the elastically scattered beam passes through the two hemispherical and one flat grids,
Fig. 2: LEED/ESDIAD Optics with the experimental setup.
and collides with the front surface of the first microchannel plate (MCP). In the ESDIAD mode, the grids are biased in such a way as to allow positively charged ions desorbing from the sample to pass through and impinge on the MCP. The MCP are thin (~1 mm thick) electron multipliers that each provide a gain of ~$10^3$. Two plates are used in tandem to provide a gain of ~$10^6$ so that single ions or electrons ejected from the sample surface can be observed. The output electrons from the plates are accelerated to the phosphor screen which provides a visible output. This is viewed with a high resolution CCD video camera and the image is stored in a Macintosh Computer by a matching frame grabber LG-3 from Scion Corporation using Scion-Image 1.54 software as the driver. To improve the picture quality, 50 one second images were averaged for each LEED/ESDIAD image.

Total ESD ion yields were obtained by using the detector in the ESDIAD mode and integrating all pixels in the observed intensity using the Scion-Image 1.54 software. The ESD ion yields were normalized to the incident electron beam current measured by a Keithly electrometer attached to the sample.

3.2.1.1 LEED/ESDIAD optics head

The head is shown in Fig. 3 with its individual components. It was mounted by means of stainless steel standoffs on a 8" Conflat flange that had the proper electrical feedthroughs welded into it. The insulating material was Macor and the grids of 50 wires per inch were 0.001" stainless steel. The stainless steel mounting pieces were machined in the Physics Department machine shop at Louisiana State University and the grids were made in the Surface Science
GRID, MCP ASSEMBLY

Fig. 3: LEED/ESDIAD optics head
Division machine shop at the National Institute of Standards and Technology.
The phosphor screens were made in the laboratory and the process is detailed in
sec. 3.2.1.4. All components were cleaned before assembling and installing in
vacuum as discussed in sec 3.2.1.2 and sec 3.2.1.3.

3.2.1.2 Cleaning Macor and Stainless steel

A solution of nitric acid 1:3 water by volume was prepared and the
relevant parts immersed in it for 5-7 minutes. They were rinsed in distilled water
in the ultrasonic cleaner for 5 to 10 minutes, rinsed in warm tap water for 1 hour
while turning every 20 minutes or so, rinsed again in 3-4 changes of distilled
water and finally air dried.

3.2.1.3 Cleaning Beryllium Copper (used as the electrical contacts) 35

The Beryllium Copper pieces were first briefly immersed in 5% by weight
HCl solution and then immerse for 30 seconds in 10% by weight NaOH solution
at room temperature. They were then rinsed in running tap water and distilled
water, and air dried.

3.2.1.4 Phosphor Screens

The phosphor must be sensitive to low energy electrons (less than 500
eV), exhibit no outgassing under UHV conditions and be dust free. In order to
satisfy these requirements, the following method was developed.

The screen is made with p-1 phosphor, also known as zinc silicate
phosphor (from Electronic Space Products International), and is coated on a
transparent (75 %) metal coated glass screen using a variation of the method used
by Carr and Chaban. 36 The metal coating provides a conducting pathway to
eliminate charging problems when electrons hit the screen.
An air brush or a very small spray gun, a few drops of concentrated phosphoric acid, acetone, methanol, ethanol, distilled water and an oven was needed to make the phosphor screens. The surface of the metal coated screen was cleaned for about 10 minutes each with acetone, then methanol, then ethanol and finally distilled water. A solution to fix the phosphor on to the screen was made consisting of 5-6 drops of concentrated phosphoric acid and 25 ml of acetone. Part of this solution was introduced into the jar of the air brush. Under a chemical hood the solution was sprayed on to the metal coated side of the glass screen in an uniform manner starting from one end of the glass and finishing at the other. Then a small amount of the phosphor powder was shaken on to the wet surface and the screen was tapped until the powder coated the entire surface. The screen was inverted and the loose powder was tapped off. At this point the phosphor was not thick enough to be 100% efficient, so a shake and bake method was used. The phosphor coated screen was re-sprayed and the process was repeated. After about two to three such coatings, it was possible to obtain a thick, uniform coating of phosphor on the screen. The screen was then baked at 200°C in air for two hours in the oven to dry it. This method has been successful in providing a thick, uniformly coated phosphor screen with the phosphor well fixed to the screen and very low out gassing under UHV conditions.

3.2.2 STM

This system was commercially manufactured by Park Scientific Instruments. It is an Auto Probe VP 900 model mounted in a UHV chamber and used in the STM mode. The tip was fabricated from 0.02" diameter Pt/Ir wire by cutting in air using a sharp wire cutter and then installed in the instrument without further preparation. The system was operated at a base pressure of 5x10^-11 torr. The sample was cleaned as described in sec 3.1 and LEED was used to confirm
the cleanliness and order of the sample. Prior to each data run, the tip was cleaned in vacuum by field emission in the following manner. A potential of about +100 V was applied to the tip with the sample held at ground. The tip was manually brought up to a spot near the edge of the sample until an emission current of about 1-5 mA was observed. This position was maintained for about 1-2 minutes after which the tip was pulled back. It was repositioned toward the center of the sample using the X motion. The system is equipped with an auto approach mode, to bring the tip up to the sample without crashing the tip into it.

The STM was operated with two different scan area sizes. The large scan area (a 0.5 mm to 10 µm square) was the low resolution mode and the small scan area (a 40 Å to 0.5 µm square) was the high resolution mode. Initial scans were taken in the low resolution mode to locate an area that was reasonably flat. When such an area was found and appeared to be relatively uniform, the instrument was switched to the high resolution mode. The time lapse between completion of the sample cleaning and the first scan in the high resolution mode was about an hour.

3.2.3 Exposure Procedure

Oxygen was exposed to the Mg(0001) sample simply by filling the UHV chamber with a known pressure of 99.998% pure research grade oxygen. Exposures were measured as chamber pressure multiplied by time where the pressure was measured with an uncorrected ion gauge. Exposures throughout the paper is given in terms of Langmuir, L (1 x 10^-6 torr·sec).

3.2.3.1 LEED/ESDIAD

The oxidation was performed by filling the chamber with an oxygen pressure of 1.8 x 10^-8 torr for exposures up to 14 L, 3.6 x 10^-8 torr for exposures from 14-30 L, 1.8 x 10^-7 torr for exposures from 30-40 L, and 3.6 x 10^-7 torr for
exposures from 40-200 L. There are no reported pressure effects at these low pressures. 9-12 Exposures were done sequentially with times of one minute for each exposure step.

3.2.3.2 STM

The oxidation was performed by filling the chamber with an oxygen pressure of 3.6x10^{-9} torr for exposures up to 1.0 L, 1.8x10^{-8} torr for exposures up to 10 L and 1.8x10^{-7} torr for exposures up to 40 L, again sequentially for a time of one minute for each exposure step. Since the tip effectively shadows at least a 50 mm x 50 mm area of the sample directly under it when it is maintaining a tunneling current, the exposures were made by backing the tip away from the sample. The tip was retracted under computer control by about 1 mm by simply turning off the Z feedback in the high resolution mode. After the desired exposure the feedback was turned on and the software controlled the tip approach to the sample to re-establish a tunneling current. The X and Y positions were manually adjusted slightly to center the scan to the original position to compensate for the small lateral drift. The entire procedure to obtain an image after each exposure required 5-10 minutes and, in general, three successive images were obtained for each exposure.
CHAPTER 4: RESULTS

4.1 ESDIAD

Fig. 4 gives the observed ESDIAD patterns as a function of exposure. The brightness level and contrast level were set equal in all images in Fig. 4 so that comparison between images is possible. The electron gun energy was 340 eV. The ion yield as a function of exposure is shown in Fig. 5 and is normalized to the beam current measured at the sample. We see in Fig. 4.A and 4.B that there is only background ion emission at exposures of less than 8 L. Fig. 5 shows that the ion yield starts to increase monotonically by 12 L and increases substantially at 20 L. At this exposure, Fig. 4.C shows an aggregation of counts at the center of the ESDIAD pattern. Subsequently, at larger oxygen exposures, ion yield steadily increases until 100 L where it begins to saturate as shown in Fig. 5. There is no substantial difference in either the shape or intensity of the ESDIAD pattern between 100 L and 200 L, indicating that saturation is essentially complete by 100 L.

4.2 LEED

Fig. 6 shows the observed LEED patterns as a function of exposure. The brightness level and contrast level were again set equal in all images in Fig. 6 to facilitate comparison between images. The electron beam energy was held constant at 72 eV for the patterns shown. The clean surface shown in Fig. 6.A produces sharp bright diffraction spots. As the oxidation progresses, Fig. 6.C shows that the LEED pattern almost disappears by 8 L and but appears at higher exposures, 13 L, where a more diffuse LEED pattern is observed(Fig. 6.D). From this point, the intensity slowly decreases to that observed at saturation(200 L, Fig. 6.F).
Fig. 4: ESDIAD patterns and total angular distribution: A. clean surface; B. at 8-12 L exposure; C. at 20 L exposure and ~ 2°; D. at 40 L exposure and ~ 8°; E. at 100 L exposure and ~ 12°; F. at 200 L exposure and ~ 15°.
Fig. 5: ESD Angle Integrated Positive Ion Yield in the oxidation of Mg(0001).
Fig. 6: LEED pictures:
A. clean surface
B. at 6 L exposure
C. at 8 L exposure
D. at 13 L exposure
E. at 20 L exposure
F. at 200 L exposure.
4.3 STM

The STM study shows atom movement along step edges (called fuzzy edges or frizzies\textsuperscript{37}), large scale terrace movement and three distinct features associated with the oxidation process. We have used the descriptive terms of dots, bumps and protrusions to describe the three oxidation features. The brightness and contrast level has again been set equal in all images in Fig. 7, 9 and 10 and also those in Fig. 8, 11 to 17 so that comparison between images are possible. The vertical streaks in the images are probably due to the tip picking up a Mg or O atom from the surface in scanning from top to bottom of the image and redepositing it in the later part of the scan line.

Note that the clean surface as observed by the STM has been exposed to background gas for about 1-2 hours, the time needed for the preparations necessary to obtain the first scan. This means that the clean surface that is observed has experienced a \( \sim 0.4 \) L exposure to the background gas which consists of mainly H\(_2\).

4.3.1 Fuzzy edges

The fuzzy edges are always observed on the clean sample and at exposures of oxygen less than 0.2 L. These fuzzy edges are basically Mg atoms at the step edges which are moved by the tip. i.e. atoms are very mobile at the step edge and simply move out of the way when the tip gets too close\textsuperscript{37}. This effect can be observed in Fig. 7 where the fuzziness of the step edge is dragged in the direction of the scanning tip which, in this case, is from right to left. With increasing oxygen exposure, the entire surface stabilizes by about 0.4 L starting with the pinning of the step edges presumably by oxygen atoms.
4.3.2 Terrace movement

For the clean surface and exposures less than 1 L, we observe large scale motion of Mg atoms on the sample. The motion takes two form, rearrangement of the top layer of atoms, i.e., transport of groups of atoms within one terrace and transfer of atoms from second to the top layer. Fig. 8.A and 8.B are consecutive scans taken at 1 L exposure showing such rearrangement of the surface. The top terraces are 2.6 Å in thickness, which corresponds to the known layer separation of 2.6 Å for Mg(0001). Also in Fig. 8 the middle arrow points to a terrace consisting of a monolayer of Mg, pinned to the terrace below a point where two steps are located. We call this a pinned double step.

4.3.3 Dots

The dots that are visible are atomic in size and ~0.1Å high. They are visible only when viewed at high z magnification with a light source near the viewing angle. The pair of images Fig 9.A and 9.B shows two consecutive scans of the "clean" surface. They show that the atoms rearrange between scans. This movement is most probably induced by the tip itself in scanning across the surface. Fig. 10.A to 10.C are images of Mg(0001) surface at 0.4 L, 0.6 L and 1 L oxygen exposure respectively. These images show that the number of dots increases linearly with oxygen exposure. The number of dots in a typical 37.2 Å square area is 119, 175 and 279 for the 0.4 L, 0.6 L and 1 L oxygen exposure, respectively. We assume from this one to one correspondence that the dots are due to the presence of oxygen atoms. They could be oxygen atoms themselves either on or a directly below the surface or Mg atoms displaced from the top layer by oxygen which has taken its place in the lattice or by Mg atoms being pushed up by the subsurface oxygen atoms. In any case, the dots are correlated with the presence of oxygen and are highly mobile.
Fig. 7: STM image of a clean surface with fuzzy edges
Fig. 8: A and B are consecutive STM scans at 1L exposure. By comparing A and B, the arrows show the terrace movement.
Fig. 9: A and B are consecutive scans of the "clean" surface

(Fig. con'd.)
Fig. 10: STM images show the increase of dots with oxygen exposure
A. at 0.4 L; B. at 0.6 L; C. at 1 L.

(Fig. con’d.)
4.3.4 Bumps

The second structures observed in the STM images are bumps 1.2 Å in height and with a circular base ~16-18 Å in diameter which first appear at 0.6 L exposure on the terrace planes. The bumps are fairly uniform in size and their number increases linearly with increased exposure. The number of bumps in the same ~37500 Å² area in the 1 L exposure (Fig. 8.A) and 2 L exposure (Fig. 11.A) are 5 and 10 respectively. Above 2 L exposure, the number of bumps stays the same but the size of the bumps increases. Fig. 11.B obtained at 4 L exposure shows the bumps have increased in thickness to 3.6 Å and in their base diameter to ~35 Å. At 6 L oxygen exposure shown in Fig. 12, they have grown in size to the base diameter of ~50 Å without any change in height. At 12 L with still no increase in height, the bumps coalesce to form a smooth surface with surface corrugation of ~ 1 Å(Fig. 13). Above 12 L, bumps of 1.2 Å height again appear but are fewer in number.

4.3.5 Protrusions

The third type of morphology associated with the oxidation of Mg(0001) is a tall structure which always initially appears at a double step pinning site as shown in Fig. 14 at 0.2 L. They are initially ~3.7 Å in height with a base diameter of 23 Å, and are elongated along the step edges. These features evolve into protrusions as shown in Fig. 11.A. An anomalous protrusion is observed in Fig. 11.B developing at a point where the top and the second layer terraces were initially pinned. The top terrace breaks away from the pinning site, and this site appears to be the seed for the protrusion. The normal protrusions become ~10 Å in height and 35 Å in base diameter by 2 L as shown in Fig. 11.A, and at larger exposures, grow laterally with the base diameter increasing to ~ 60 Å as shown in
Fig. 11: STM images showing growth of bumps; A. at 2 L exposure bumps are small and a normal protrusion shown by an arrow; B. at 4 L exposure bumps are large and a new protrusion shown by arrow. (Fig. con'd.)
Fig. 12: STM image at 6 L exposure showing the large bumps and the new protrusion is indicated by an arrow.
Fig. 13: STM image at 12 L exposure showing the coalescence of the bumps.
Fig. 14: STM image at 0.2 L exposure showing by arrow an oxidized pinning site that first appear on the edge of a terrace.
Fig. 12. The anomalous protrusion becomes 18-15 Å in height and base diameter 60-64 Å by 4 L as shown in Fig. 11.B, and at larger exposures, grows in size with the base diameter increasing to 70-73 Å as shown in Fig. 12. The only distinction between this and a normal protrusion is its rate of growth. Above 6 L, all the protrusions stop growing in size and new protrusions begin to appear and increase in number (Fig. 15, 16, and 17). These protrusions rapidly grow in size and are characterized by the numbers displayed in the Table.1 below. The area covered by the protrusions is measured by counting the number of protrusions in a 147 Å x 176 Å area of the top terrace and calculating the percentage of area.

Table 1: The dimensions and number of protrusions that appears after 12 L oxygen exposure

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Area covered by protrusions</th>
<th>Height of new protrusions</th>
<th>Base diameter of new protrusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 L</td>
<td>26 %</td>
<td>No new protrusions</td>
<td></td>
</tr>
<tr>
<td>14 L</td>
<td>42 %</td>
<td>~ 1 Å</td>
<td>~ 24 Å</td>
</tr>
<tr>
<td>20 L</td>
<td>55 %</td>
<td>~ 2.6 Å</td>
<td>~ 25 Å</td>
</tr>
<tr>
<td>40 L</td>
<td>87 %</td>
<td>~ 3.0 Å</td>
<td>~ 50 Å</td>
</tr>
</tbody>
</table>
Fig. 15: STM image at 14 L exposure.
Fig. 16: STM image at 20 L exposure showing the increasing number of protrusions.
Fig. 17: STM images at 40 L exposure: A. soon after exposure; B. 20-30 minutes after the exposure.

(Fig. con'd.)
CHAPTER 5: DISCUSSION

A chart summarizing the results is given in Fig. 18. It is obvious from this and previous work that the oxidation takes place in several stages. Each stage will be discussed separately.

5.1 The oxygen exposure range 0-1 L

ESDIAD and LEED data do not show any significant change in this range. In contrast, the STM images show profound changes and are a fountain of information in this range. These images give information about initial oxidation features, tip interaction and the stability of the surface.

In this exposure range, the Mg step edges which appear fuzzy on the clean surface become brighter and sharper with oxygen exposure. The fuzzy edges are due to the mobility of the Mg atoms along the edge. This has been observed previously in Cu(110), and is due to these metals having a low Debye temperature (318 K for Mg and 315 K for Cu) close to the room temperature, 300 K. Recall that the Debye temperature is a measure of the temperature above which all modes of the atomic cores of a solid are excited, and below which modes begin to freeze out, i.e., it can be interpreted as the "stiffness" of the crystal. The terrace movement and general instability of the surface shown in Fig. 8 are significant in this exposure range.

Dots of 0.1 Å corrugation are observed in this region. By considering Fig. 9.A and 9.B it is apparent that these dots interact with the tip. A count of dots in a specific area in the images given in Fig. 10.A to 10.C, shows that they are directly proportional to oxygen exposure (sec 4.3.3). The dots do not show
Exposure | 0.0-0.6 L | 0.6-1.0 L | 1.0-2.0 L | 2.0-6.0 L | 8.0-15 L
--- | --- | --- | --- | --- | ---
ESDIAD | No pattern. | Pattern becomes diffuse and begins to fade. | Pattern disappears at 8 L and a diffuse MgO(111) 1x1 pattern begins to form at 13 L. |
LEED | Sharp Mg(0001) 1x1 pattern. | Pattern becomes diffuse and begins to fade. | Pattern disappears at 8 L and a diffuse MgO(111) 1x1 pattern begins to form at 13 L. |
STM Terraces | Observed fuzzy edges of terraces becomes brighter and sharper. Large scale atom transfer on and between terraces are observed. | The surface stabilizes, terrace edges become sharp and no large scale atom movements are observed. | Dots disappear. | No bumps observed. |
STM Dots | Dots of 0.1 A corrugation are observed to be directly proportional to the oxygen exposure in this range. | Dots disappear. | Base diameter increases to ~65 A. By 14 L, new protrusions of height ~1 Å and ~24 Å base diameter appear. |
STM Bumps | No bumps observed. | Bumps of 1.2 Å thickness and ~17 Å base diameter appear on the plane of the terraces. | The number increases and is directly proportional to the oxygen exposure. | At 12 L, the bumps coalesce to form a smooth surface with surface corrugation of ~1 Å. Above this exposure, new bumps of ~1.2 Å appear but are fewer in number. |
STM Protrusions | Seed protrusions appear at pinning sites. These are ~3.7 Å in height and 23 Å in base diameter elongated along the step edge. | Normal protrusions grow to ~10 Å in height and ~35 Å in base diameter. | Base diameter increases to ~65 Å. By 14 L, new protrusions of height ~1 Å and ~24 Å base diameter appear. |
XPS Ghijsen et al. | LBE peak is observed at the lowest exposure. HBE peak appears at 0.2 L. | O Is total intensity varied only slightly in this range. | O Is total intensity increases sharply by 2 L. |
HREELS Thiry et al. | Both peaks P1 and P2 are observed to be present from the initial exposure and increase in the same way. | The intensity of both peaks have an inflection point at 4 L at which point they increase more rapidly. |
AES Florstrom and Martinsson | The O(KLL) oxygen peak at 506 eV increases in intensity linearly until 2 L. | At 2 L the O(KLL) signal breaks upward with linear increase to 10 L. Two interfacial peaks appear at 2 L and become a maximum by 8 and 11 L respectively. |
EELS Florstrom and Martinsson | The loss peaks for the clean surface (7.2 eV) and the bulk (10.7 eV) plasmon decrease in intensity. | By 5 L a new loss peak is observed at 5.1 eV which coexisted at this exposure with reduced intensity 7.2 eV loss peak and became a maximum at 15 L. |
EELS Hayden et al. | The loss peaks for the clean surface (7.5 eV) and the bulk (10.8 eV) plasmon decrease in intensity. | Between 6-10 L the loss peaks at 4.9 eV and interband transitions peaks were observed. |

Fig. 18: A and B are the summary of the present and previously published work.
<table>
<thead>
<tr>
<th>Exposure</th>
<th>20-30 L</th>
<th>30-40 L</th>
<th>100 L</th>
<th>200 L</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ESDIAD</strong></td>
<td>More counts appear by 20 L but pattern is unclear.</td>
<td>Pattern begins to look elliptical and brightens by 40 L.</td>
<td>Pattern is bright, elliptical and grows large.</td>
<td>Pattern is not much different from what observed at 100 L except it is brighter and larger.</td>
</tr>
<tr>
<td><strong>LEED</strong></td>
<td>The diffuse MgO(111) 1x1 pattern begins to very slowly fade at 200 L.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>STM</strong></td>
<td>Bumps of ~1.2 Å exists throughout this exposure range but are very few in number.</td>
<td>No study done in this range.</td>
<td>No study done in this range.</td>
<td></td>
</tr>
<tr>
<td><strong>STM Protrusions</strong></td>
<td>By 20 L, 55% of the selected area is covered with new protrusions of ~2.6 Å in height and ~25 Å in base diameter.</td>
<td>By 40 L, 87% of the selected area is covered by protrusions of ~3.0 Å in height and ~50 Å in base diameter.</td>
<td>No study done in this range.</td>
<td></td>
</tr>
<tr>
<td><strong>XPS</strong></td>
<td>After initially increasing the ratio $I_{HBE}/I_{LBE}$ became a constant maximum value of 0.7 by 20 L. The increasing O 1s total intensity finally leveled off by 100-200 L.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>HREELS</strong></td>
<td>$P_1$ reaches a maximum by 20 L.</td>
<td>$P_1$ rapidly level off and saturates completely by 100 L.</td>
<td>$P_2$ saturates after 200 L.</td>
<td></td>
</tr>
<tr>
<td><strong>EELS</strong></td>
<td>By 25 L loss peaks at 16.5 and 22 eV are observed and they corresponds to loss peaks observed for the bulk MgO at 17 and 24 eV.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
bi-structure or an interval pattern. We conclude that these dots are oxygen atoms rather than undissociated O$_2$ or displaced Mg atoms and that they are sitting on or directly below the surface.

The 1.2 Å high bumps that appear on the terrace planes are probably due to atomic oxygen congregating around a nucleation site and incorporating into the Mg lattice below the surface.

This initial exposure range also shows the growth of protrusions that appear at ~0.2 L exposure and are elongated along the step edges. They are initiated at pinning sites and increase in height to 1 L exposure, as shown in Fig. 14 and Fig. 11.A. In the subsequent discussion of this and higher exposure ranges, they will be shown to be the signature of the true oxide.

The following observations identify the bumps as the incorporated oxygen and the protrusions as the ionic oxide. The protrusions appear at the very beginning of the oxidation at 0.2 L (the lowest exposure studied here) at pinning sites and the bumps appear above 0.6 L. The previous XPS work by Ghijsen et al.$^2$ observed the oxide forming with initial exposures and the incorporated oxygen forming only above 0.2 L exposure, which is consistent with the protrusions being the oxide and the bumps being the incorporated oxygen. Previous HREELS work by Thiry et al.$^{13}$ confirms the existence of the two kinds of oxygen at this exposure but they find both kinds to exist at the very beginning. This later observation is not seen in our result. Previous AES work by Flodstrom and Martinsson$^{12}$ gives a linear uptake curve for the oxygen. Previous ellipsometry work by Kötz et al.$^{11}$ is consistent with the picture of areas of distinct Mg and MgO properties in this range.
Experimental evidence for oxygen being incorporated below the surface is given by the following. Our ESDIAD data shows no ion yield in this range indicating that the oxygen is incorporated below the surface since ion desorption only occurs from the top most layer. The measurements by Hayden *et al.*\textsuperscript{10} show a sharply decreasing work function attributable to the incorporation of oxygen below the surface. Fig. 19 shows two possible subsurface sites distinguished by the fact that O in 19.B is directly above a Mg atom whereas in 19.A, it is not. This incorporation would result in lifting the Mg atoms above the surface and producing the bumps we observe. The layer separation of MgO(111) is 1.2 Å compared to the separation of 2.6 Å in Mg(0001). If one layer of oxygen has been incorporated below the top Mg layer, then bumps of ~1.2 Å would indicate a 1.9 Å layer separation for the incorporated oxygen (2.6 Å+1.2 Å(bump)=3.8 Å) for two layers of Mg and one layer of incorporated oxygen). This result, can be used to calculate that the height of the bumps is 3.6 Å if three oxygen layers are incorporated (3*3.8 Å=11.4 Å-(3*2.6 Å)=3.6 Å). The height measurements are consistent with the formation of 1 or 3 incorporated oxygen layers with a layer separation of 1.9 Å. Moreover, the lattice match between the close-packed atoms in the Mg(0001) (3.21 Å) and the Mg atoms in the MgO(111) face (2.98 Å) is close. As a result the strain to grow a MgO(111) type oxide with the same lattice constant as Mg(0001) surface is relatively small.\textsuperscript{12} The MgO(111) layer separation is 1.2 Å and therefore 1.9 Å result for the incorporated layer separation is constant with it.

Both incorporated oxygen and ionic oxide form in this range, the former appearing as bumps in the STM image, the latter, as protrusions. We suggest that the ionic oxide is more difficult to form since it requires a specific type of lattice
Fig. 19: Mg(0001) crystal shown\textsuperscript{38} in A and B with the two possible incorporation sites for oxygen. The dark small balls are Mg atoms and the larger white balls are the incorporated oxygen atoms. The two different sites are both threefold hollow sites. But directly below one site there is a substrate atom in the second layer and the other site has a vacancy directly below it.\textsuperscript{39}
defect, namely the pinned double step shown in Fig. 8. All the pinned double steps we observe lead to protrusions. The dots we observe could be precursors to the formation of the subsurface incorporated oxygen (the bumps), with their high mobility suggesting that they are oxygen atoms on top of the surface that have not yet penetrated to the subsurface bumps. It is possible that they are Mg atoms displaced from the top of the surface by oxygen atoms. The fact that this oxygen is not seen in ESD could be due to its not being in a maximum valency bond nor in a covalent bond that forms a repulsive state when excited by the incident electrons.

The lack of ESD from the protrusions is intriguing. This suggests that there is little or no oxide on their surfaces at this point in the oxidation process.

5.2 The oxygen exposure range 1-6 L

In this range, the dots disappear from the STM images and the bumps and protrusions grow in direct proportion to the oxygen exposure. By 4 L the height of the bumps increases to 3.6 Å. ESDIAD does not show any O+ ion desorption above the background level indicating that there is probably little or no MgO on the surface. By 6 L, the original LEED pattern is diffused and is fading in intensity. The broadening of spots and the increase in background is attributed to the bumps not being in registry with the substrate or with other bumps.

Our STM data also show that the dots are no longer observed on the surface, indicating that the oxygen can more readily be incorporated below the surface or that Mg atoms are attracted to one of the observed features on the surface. The gross movement of atoms on the terraces and fuzziness of the step edges have also ended indicating that the oxygen has stabilized and stiffened the lattice.
Good agreement is found between the present result and the work of Hayden et al.\textsuperscript{10} and Kötz et al.\textsuperscript{11}. From their model, assuming a mixture of areas with Mg/MgO properties, they find a layer thickness of 4 Å in this range. This is consistent with our STM images showing unreacted Mg, MgO (protrusions) and incorporated oxygen (bumps). But the coalescing 3.6 Å bumps indicate a layer thickness \(\sim 11\ \text{Å} (1.9\ \text{Å} \times 6)\).

Flodstrom and Martinsson's\textsuperscript{12} interpretation of their data in terms of a subsurface incorporated oxygen is consistent with our STM images which show a growth in only of the number of bumps (incorporated oxygen). Above 2 L they observed an increase in the rate of oxygen uptake and estimated a thickness of 3.6 Å of what they presumed is an oxide layer. Again our data is consistent with this picture where we see the bumps grow to a height of 3.6 Å. However, this is a growth of the incorporated oxygen rather than the oxide and the coalescence of the bumps at 12 L produce a layer of \(\sim 11\ \text{Å} (1.9\ \text{Å} \times 6)\). Their AES data show an increase in the oxide growth which is consistent with our observations of the growth of the protrusions.

Our STM data also explain the HREELS work of Thiry et al.\textsuperscript{13} They find the intensities of both incorporated and oxide peaks have an inflection point at 4 L after which they start to increase rapidly in intensity. They explained this by stating that a monolayer of surface oxide is formed at this 4 L exposure. Our data shows, however, that this is due to the growth of both the protrusions and the bumps after 4 L.

5.3 The oxygen exposure range 6-15 L

The oxidation continues with the 3.6 Å high bumps growing in area only and the initiation of new protrusions. At this exposure the ESDIAD data do not show any distinct ion pattern but the ion yield curve increases showing that some
O⁺ ions begin to desorb. The LEED pattern is more diffuse and fades completely at 8 L and reappears by 13 L exposure. This behavior is, in general, consistent with the previous LEED studies¹⁰,¹² but not in exact detail.

Our STM data show a large number of bumps of 3.6 Å height growing laterally on the surface at 6 L. By 12 L they coalesce to form a complete layer on the surface whose corrugation is measured to be less than 1 Å. This is consistent with LEED pattern fading away and reappearing. We assume that the LEED pattern at low exposures arises only from the unreacted Mg metal surface and that the bumps are not in registry with the substrate so they do not contribute to the LEED. The 1x1 LEED later becomes diffuse as the metal islands shrink and reduces the coherence length. The pattern is re-established once the bumps coalesce and establish a long range order and coherence.

By 14 L new protrusions are observed on the surface in our STM data. Work function measurements of Hayden et al.¹⁰ show a minimum at 12 L followed by a slow rise to a stable plateau. The increase in work function following the minimum is attributed by them to the formation of epitaxial growth of areas of MgO which is consistent with our observed growth of new protrusions on the surface. Moreover, the ESD ion desorption yield starts at near 12 L and increases rapidly at 15 L giving credence to the presumption that these protrusions are ionic.

The model used by Kötz et al.¹¹ in the 6-12 L range suggests that the thickness of the adsorbing mixed layer drops from 4 to 1.5 Å. This is consistent with our results which show that coalescence of bumps take place at 12 L and that
the surface roughness reduces to around 1 Å on the terrace planes. Since the incorporated oxygen is now a continuous layer on the terraces, it would not be detectable in their measurements.

Flodstrom and Martinsson\textsuperscript{12} also found in the 2-10 L oxygen exposure range, islands of MgO to be three layers thick (3.6 Å) and that by 10 L exposure these islands grow to completely cover the surface. This is consistent with our study except that the layers are not MgO but incorporated oxygen.

5.4 The oxygen exposure range 20-40 L

The ESD ion yield curve shows a sharp rise in this range with an upward inflection point at 20 L and continues to increase until saturation. A well defined ESDIAD pattern shows the ion emission in a very broad range of azimuthal angles for the desorption. This is consistent with O\textsuperscript{+} ion desorption from the protrusions which would give a broad cone of emission. Consider the STM data in Fig. 16 which show the new protrusions appearing on the surface by 20 L. The height and base measurements of these protrusions tabulated in Table 1 in sec 4.3.5, indicate that from 12 L to 14 L there is an increase in the number of protrusions with dimensions of \(\sim 1\) Å height and \(\sim 24\) Å in base diameter. From 14 L to 20 L they continue to increase in height with no appreciable base diameter growth (\(\sim 2.6\) Å in height and \(\sim 25\) Å base diameter) and in the range 20 L to 40 L the protrusions grow mostly in base diameter and little in height (\(\sim 3\) Å height and \(\sim 50\) Å in base diameter) to finally cover the surface. The growth of the protrusions in area is consistent with the upward inflection point observed in the ESD ion yield at 20 L. The correlation of the ESD intensity and the area of the protrusions reinforce our assumption that the protrusions are the ionic oxide. These results are consistent with the EELS data of Flodstrom and Martinsson which show the thickness of the oxide increases to form bulk-like MgO by 25 L.
An interesting dynamic feature is observed in this exposure range. At 40 L exposure, Fig. 17 gives the STM images taken 30 minutes apart. In the initial scan taken immediately after the completion of the oxygen exposure the sample has more bumps and fewer protrusions (Fig. 17.A). These protrusions can be quantified by measuring the area they occupy in a specific region of the surface. It is found that in Fig. 17.A the protrusions cover ~38% of the area while Fig. 17.B taken 30 minutes later shows the protrusions covering 87% of the area. This clearly shows that the bumps are unstable and a conversion occurs from bumps to the more stable protrusion indicating that the bumps act as precursors to the thickening of the oxide observed at this oxygen exposure range supporting our presumption that the bumps are the incorporate oxygen and the protrusions are ionic. Moreover Ghijsen et al.\textsuperscript{2} showed by progressively heating a sample exposed to oxygen that the incorporated oxygen at higher temperature converts to the more stable ionic oxide consistent with the above picture.

Thiry et al.\textsuperscript{13}, observed a similar kind of behavior in a HREELS study where the incorporated oxygen turned into the ionic oxide after 30 minutes without further oxygen exposure. Previous work by J. Wintterlin et al.\textsuperscript{40} and Behm\textsuperscript{41} on oxygen adsorbates on Al(111) investigated by STM has also observed protrusion like features at the edges of terraces at high oxygen exposure when their AES revealed the onset of oxide formation. They concluded that these protrusions along the step edges are the ionic oxide.
CHAPTER 6 : CONCLUSION

The STM images show that the clean Mg(0001) surface is very unstable, and large scale atom transport on or between terraces with loosely bound Mg atoms at the step edges that move to the side as the tip scans the surface (fuzzy edges). We assume the oxygen dissociates as it adsorbs on the surface. The dissociated oxygen is loosely bonded to the surface and is highly mobile. It is not possible from the STM data to determine if the oxygen is on or below the surface. The dots observed at low exposures could be Mg displaced from the top layer by oxygen or Mg atoms which have slightly moved upward by oxygen in the plane below. In any case, the atoms are correlated with oxygen dose and are highly mobile under the influence of the tip.

Oxide formation is first observed at low exposure in the form of protrusions at pinned double step sites. This is a very specific type of defect and it apparently lowers the potential barrier for oxide formation. These defects are not the source of the primary oxidation process which occurs at higher exposures. The surface is, however, stabilized by this oxide as the large scale atom movement and fuzzy edges are no longer observed. This is reasonable since the Mg-O ionic bond is stronger than Mg-Mg metal bond.

With further exposure, oxygen penetrates the surface forming bumps (incorporated oxygen) 1.2 Å in height. Our observations are consistent with the oxygen initially forming a single layer underneath the top layer of Mg. This process is random with no order in the location of the initial bumps and continues up to 2 L exposure. The fading of the LEED pattern indicate that the top layer of Mg atoms are randomly moved out by their crystallographic locations by the oxygen below. Above 2 L, the random formation of bumps stops with additional
oxygen attaching itself to bumps that are present rather than forming new bumps. Apparently oxygen is incorporated much easier at a site that has already been strained by the presence of one or several oxygen atoms, i.e., there appears to be less strain associated with two or more atoms that are in neighboring sites than those in isolated sites. By 4 L these bumps have grown in thickness to 3.6 Å due to the formation of what we believe to be three layers of oxygen atoms interspersed with the Mg layers. Curiously we do not observe a bump height, that would correspond to two layers of oxygen and no bumps larger than three layers of oxygen. This would indicate that the one and three layer configurations are more stable than two or four or larger layer configurations. With further oxygen exposure, the oxygen still preferentially attaches to existing bumps causing the bumps to grow in area but not in height. The lack of a LEED pattern in this range indicates that the bumps are not in registry with the substrate Mg atoms in the lattice. By 12 L, the bumps have coalesced to completely cover the surface at which point the entire surface of the terraces is in registry as shown by the reemergence of the LEED pattern. Our techniques are not capable of determining the thickness of the coalesced incorporated layer at this point and can not say if the thickness reduces indicating oxide formation.

As the oxygen exposure increases a new set of protrusions begin to form on top of the coalesced incorporated oxygen layer. Correlations in growth with the growth of the XPS and EELS peaks tells us the new protrusions are the ionic oxide and they are the significant contribution to the overall oxide growth. The exact process of oxide formation is unknown but our data indicate it is a dynamical process. The bump like features formed when this partially oxidized surface is exposed to oxygen convert with time to tall protrusions which are identified as the ionic oxide. The XPS and ESD data shows that the oxide is
forming at the surface and the incorporated oxygen layer remains intact. This suggests a process in which the incorporated oxygen layers act as a strained lattice to promote the formation of the surface oxide layer.
REFERENCES


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Anura Upul Goonewardene was born on December 2, 1962, in Colombo, Sri Lanka to Keerthi and Felicia Goonewardene. He was raised in Colombo and graduated from High School at Royal College, in April 1981.

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