Characterization of surface defects on MgO thin films by ultraviolet photoelectron and metastable impact electron spectroscopies

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Metastable impact electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy are used in this study to investigate low-defect and defective MgO(100) thin films. Unlike low-defect films, defective films exhibit a new spectroscopic feature located ~2 eV above the top of valence band. Exposing the defective film to oxygen quenches the emission of electrons from F centers created on the surface and in the subsurface regions. Extended defects, unseen in the MIES spectra of the clean surface, are detectable using NO titration. MIES and thermal programmed desorption indicate that at ~100 K NO adsorbs dissociatively on defects, forming N_2O. Only a small fraction of the MgO surface becomes covered with N_2O at ~100 K for the low-defect MgO film indicating that N_2O molecules preferentially adsorb on the extended defects. The saturation coverage of N_2O increases appreciably for the defective sample. © 2000 American Institute of Physics.

I. INTRODUCTION

Understanding defects at oxide surfaces is key to a molecular level description of the properties of supported catalysts and gas sensing devices. Furthermore, defect induced conductivity in transistor gate oxides has become a major challenge in the further miniaturization of various microelectronic devices. Despite their obvious crucial role in determining the physical and chemical properties of oxides, surface defects have received less attention compared to their bulk counterparts. The primary contributing factors are the inherent difficulties encountered in addressing the key issues, both experimentally and theoretically. Experimentally, the relatively low density of surface defects and sample charging typically encountered limit the application of most modern surface science analytical methods. Theoretically, addressing the lower symmetry of the surface and the structural reorganization imposed by defects together with the scarcity of reliable quantitative experimental data require enhanced computational power to reliably model defects at surfaces.

Many experimental difficulties can be overcome by utilizing ultrathin oxide films rather than bulk crystals. Films as thin as a few monolayers (ML) can be probed by electron spectroscopic probes due to facile dissipation of the induced charge by electron tunneling to/from the underlying metallic substrate. The basic similarities of the physical and chemical properties of thin films and bulk samples have been demonstrated (see, for example, Ref. 4).

Using this thin film methodology, in this study, we address the nature of near-surface defects by comparing electronic spectra from freshly prepared, low-defect surfaces with defective ones. MgO was chosen because it has been thoroughly characterized both theoretically and experimen-

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sorbates (see Ref. 13). In this study MIES is used for the detection and study of surface defects on MgO(100) thin films.

The near-surface electronic structure of MgO(100) thin films and cleaved crystals has been studied with HREELS, MIES, UPS, and XPS as well as theoretically. The MgO(100) band gap has been shown to be reduced at the surface to ~6.7 eV and the MgO(100) work function measured to be ~2.7 eV. Therefore, since no unoccupied levels are in resonance with the He*2s state, the Auger de-excitation (AD) mechanism dominates electron emission. Under these conditions, both UPS and MIES, in principle, yield identical features in the surface density of states (SDOS) yet complement one another in that each has unique selection rules and sampling depths.

MgO appears to be remarkably stable toward the formation of point defects and relatively few efforts to probe defective samples with MIES/UPS have been reported. However, significant theoretical efforts have been undertaken to investigate both point and extended defects on MgO surfaces. These studies predict that surface defects, e.g., F+ and F centers, should manifest themselves in UPS spectra as deep occupied levels in the band gap approximately 2 eV above the top of the O(2p) valence band.

In this article we demonstrate the suitability of MIES as a tool for characterizing surface defects. With MIES, the role of surface defects in the low temperature dissociative adsorption of NO is elucidated.

II. EXPERIMENT

The experiments were carried out in an ultrahigh vacuum (UHV) chamber (base pressure ~3×10^-10 Torr) equipped with MIES/UPS, Auger electron spectroscopy (AES), UPS, and low energy electron diffraction (LEED). The sample was mounted on a Ta wire loop in thermal contact with a liquid nitrogen (LN) cryostat, allowing the sample to be cooled to 90 K or heated to 1500 K during film preparation, treatment, or analysis. A differentially pumped quadrupole mass spectrometer (UTI) was used for the temperature programmed desorption (TPD) experiments.

For the MIES/UPS studies, a cold-cathode discharge source, which is described elsewhere, was employed. Briefly, the source provides both ultraviolet photons [He(I) hν = 21.2 eV] and He* 2S/2P metastable atoms with thermal kinetic energy. In the beam the relative abundance of He atoms in the triplet state (E* = 19.8 eV) versus the singlet state (20.6 eV) was determined by He*-Ar impact to be 7:1. However, no spectral features attributed to target excitation with the singlet helium were found, most likely due to efficient singlet to triplet conversion at the surface. The total intensity of the metastable beam was on the order of 10^9 atoms/s at the sample, allowing collection of MIES and UPS spectra in ~90 s. Approximately 30 cm in front of the sample the metastable/ photon beam was modulated with a mechanical chopper allowing the MIES and UPS spectra to be acquired in two counting channels simultaneously using a time-of-flight separation method. The incident angle of the photon/metastable beams and the angle to the axis of the analyzer were 45° with respect to the surface normal. A double pass cylindrical mirror analyzer (CMA) (PHI 15-255G) was used in constant pass energy mode for MIES/UPS and XPS spectral acquisition. To enhance the detection efficiency near zero kinetic energy, the sample was biased ~45 V with respect to ground. This procedure permits the monitoring of the work function (WF) change and has been shown to have no influence on the MIES/UPS spectra.

The binding energies in the spectra have been referenced to E F, corresponding to those electrons emitted from the Fermi level of the Mo(100) substrate.

As discussed previously, a significant influence of surface defects on the properties of pure and doped oxide thin films is anticipated. Therefore, to elucidate the role of defects, the preparation of ‘low-defect’ and ‘defect-rich’ samples is essential. MgO films, ~10 ML in thickness (determined via AES), were grown by depositing Mg in 1×10^-6 Torr O2 onto a Mo(100) surface held at 550 K. Mg was evaporated at a rate of ~0.15 ML/min from a high purity Mg ribbon wrapped around a W filament. As shown in previous studies, MgO films on Mo(100) prepared under these conditions grow epitaxially, and have electronic and chemical properties comparable to those of MgO single crystals. In order to ensure the stoichiometry of the MgO surface and to minimize the density of defects, the low-defect films were annealed to 750 K in a 5×10^-7 Torr O2 background for 30 min with a gradual (~20 min) heating and cooling cycle. The LEED pattern exhibited a 1×1 structure, however, the diffusiveness of the spots suggested the presence of a mosaic structure reported in previous SPALEED studies and in scanning tunneling microscopy (STM) images. The annealed films exhibited stability to multiple thermal (300 K→90 K→800 K→300 K) cycles, and with time.

Since Ar+ ion bombardment appears to be ineffective in defect creation as shown by UPS of MgO(100), three alternative methods for defect formation were evaluated: electron bombardment, thermal quenching, and the addition of alkali metal.

For electron bombardment, electron stimulated desorption of oxygen is the major process by which surface vacancies are created. Variations of the electron energy from 500 eV to 3 keV and exposure up to 5×10^-3 C/cm² were carried out, similar to previous studies of defect formation on oxide surfaces.

Thermal generation of defects in ultrathin MgO films on Mo(100) has been investigated. It was shown that clean MgO thin films are thermally stable and nearly free from defects up to 1100 K, above which a detectable quantity of near-surface F centers is generated. To create nonequilibrium surface defects, the rate of quenching must be faster than the diffusional relaxation of the vacancies. Therefore the sample was first annealed to 1100 K for approximately 1 min and then quenched to ~100 K. The temperature gradient between the sample and the LN cryostat provided the maximal cooling rate possible (more than 6 K/s between 1100 and 800 K in the present design).

It has been shown that the addition of Li to MgO films promotes the production of F-type centers on the surface and in the subsurface region upon high temperature...
III. RESULTS AND DISCUSSION

A. Point defect formation

In Fig. 1 the low energy part of MIES and UPS spectra acquired sequentially on a thin MgO film are presented: A MIES as prepared, B and C MIES and UPS after electron bombardment, and D MIES after O₂ exposure. For the sake of clarity, the total MgO spectrum B is shown in the inset. The as-prepared film shows the usual O(2p) derived valence band structure with a band gap of ~6.7 eV, free of any structure within the band gap. However, spectrum B demonstrates the appearance of a new weak F-center feature at ~2 eV upon electron bombardment in both the MIES and UPS spectra. The new band is stable with time under UHV conditions, but disappears immediately upon exposure to a few langmuirs (L) of oxygen. Noteworthy is the absence of any appreciable intensity at the Fermi edge for the new structure, indicating its nonmetallic character. Given the extreme surface sensitivity of MIES, the simultaneous appearance of the new structure in both the MIES and UPS spectra suggests that surface and subsurface states are responsible for the electron emission. It should be noted that this induced band in the MIES/UPS spectra was observed for all three methods of defect creation. However, the weak intensity of this feature in the band gap does not allow quantitative assessment of the subtle differences among the preparation procedures, i.e., which is superior. Therefore, for the sake of reproducibility all further results for defective surfaces were obtained with thermally quenched samples.

We assign these new bands observed in the MIES/UPS spectra to Auger de-excitation from newly created F centers or F aggregates. A number of factors favor this conclusion.

(i) For the as-prepared films this band is well below detection limits. This is true as well for all previously reported UPS, MIES, EELS, and EPR results on thin films, powders, and single crystals, indicating that steps, kinks, and grain boundaries do not contribute to the features in the band gap. Instead, such imperfections contribute primarily to the broadening of the O(2p) band and to the narrowing of the band gap. 17,18

(ii) The new feature’s energy position and shape are independent of the treatment procedure used for defect formation, in agreement with previous HREELS results utilizing the identical preparation techniques. 9

(iii) It is known from electron stimulated desorption studies of MgO that oxygen ions and neutrals are preferentially desorbed, leaving oxygen vacancies on the surface. 30

(iv) Oxygen interacts strongly with the annealed surface, eliminating the new feature from the MIES spectrum.

(v) Finally, the energy position of the new feature coincides with the theoretical prediction for surface F centers. 23,31

In view of recent studies on the initial stages of Mg doping of MgO, the possibility that the new feature corresponds to the formation of small nonmetallic Mg clusters should be considered. Indeed, the position of the feature designated as “F” closely matches that observed for small Mg clusters. 25,31 Furthermore, electron induced metal cluster and metallic island formation on alkali halide thin films has recently been reported. 29 However, it is unlikely that either of these gives rise to the F feature since the appearance of small metal aggregates under electron bombardment requires (i) significant efficiency for oxygen vacancy formation and (ii) a relatively high surface mobility of the created F centers at the given temperature. Neither of these conditions is found in the present study, i.e., the electron bombardment was carried out at low (~100 K) temperatures and the primary beam intensities were <0.3 μA.

The UPS spectra exhibit an identical feature, implying a significant density of subsurface defects. This conclusion is in agreement with previous HREELS data showing an enhancement of defect related energy loss features with increasing sampling depth. 9 The surface concentration of the
new defects can be estimated to be on the order of $10^{12}$ per cm$^2$ from the relative intensities of the O(2$p$) and F features in the MIES spectrum, matching closely the reported nucleation density of small Mg clusters (presumably associated with F centers) on MgO.\(^{25}\)

### B. Titration with NO probe molecules

In general, low-defect oxide surfaces are known to be highly inert, whereas surfaces which are significantly defective, are reactive.\(^1\) Comparative studies of MIES and TPD following adsorption of NO molecules on low-defect and defective thin films were carried out in order to obtain information regarding the nature of surface and near-surface defects on the MgO films. NO was chosen to probe the defect adsorption sites since recent TPD experiments on a vacuum cleaved MgO(100) single crystal have shown exclusive adsorption of NO on surface defects at $T > 90$ K.\(^{32}\) No nitric oxide adsorption was detected at 300 K with either MIES/UPS or TPD in the present study, in agreement with previous MIES data.\(^{33}\) In Fig. 2(A) a sequence of MIES spectra of a low-defect MgO thin film at 90 K collected during NO exposure is presented. Figure 2(B) shows data for the same sample thermally quenched to create defects. Noticeable changes in the MgO(100) MIES spectra are apparent upon NO adsorption [Fig. 2(A)]. A $-0.6$ eV work function increase upon saturation of the NO coverage is consistent with charge transfer from MgO to the adsorbate.

New features labeled A, B, and C in Figs. 2(A) and 2(B) evolve during the NO exposure. There is an $\sim 25\%$ attenuation of the O(2$p$) intensity concomitant with the developments of the A, B, and C bands. These changes become more pronounced for the defective surface in Fig. 2(B), where at saturation coverage the newly developed features dominate the spectrum and the O(2$p$) intensity shows an 80% attenuation. In contrast, in Fig. 3 the UPS spectra sequence taken concurrently with the MIES data of the defective sample in Fig. 2(B) shows only minor changes during NO adsorption, indicating that for the defective sample, only a small fraction of the surface is covered with adsorbate. Due to uncertainties in the nature of the He$^*$—adsorbate interaction\(^{13}\) it is not possible to determine precisely the adsorbate coverage from the MIES spectra. However, recently the O(2$p$) intensity attenuation in MIES spectra and TPD following methanol adsorption on MgO has been used for coverage estimation.\(^{34}\) Based on these results the saturation coverage of NO is estimated to be $13 \pm 2\%$ and $35 \pm 5\%$ in Figs. 2(A) and 2(B), respectively. In Fig. 4 a MIES difference spectrum of MgO(100) saturated with NO is presented. Features A, B, and C are assigned to N$_2$O molecules. The energy position of the observed adsorbate bands matches energies corresponding to ionization of the 2$\pi$, 7$\sigma$, and 1$\pi$ states of N$_2$O in Fig. 4 (the gas phase spectrum\(^{35}\) was offset to take into account the polarization shift). The relative intensity of the peaks may be different from that of the gas phase due to preferential orientation of the molecules on the surface and to intrinsic variations in the AD process. In addition, artifacts of the subtraction procedure of the spectrum might contribute to the high/low energy shoulders, the relative intensity interplay, and the energy shift.

N$_2$O formation was also confirmed by TPD. In Fig. 5, TPD following NO adsorption on as-prepared and defective (see inset) MgO films are shown. In agreement with the spectral assignment, N$_2$O ions have the highest intensity, indicating that N$_2$O is the dominant species on the surface. The coincidence of the peak maxima of NO and N$_2$O and their relative abundance (NO$^+$ in the mass spectrum is $\sim 30\%$ of the N$_2$O$^+$ signal) is indicative of NO originating from N$_2$O cracking during ionization. Thus, there is evidence that NO
adsorbs dissociatively on MgO at 90 K. For the defective surface the total TPD signal is noticeably enhanced, consistent with the increased O(2p) attenuation in the MIES spectrum. Separate MIES/UPS and TPD measurements following N₂O adsorption on MgO were carried out to confirm the MIES assignment and to rule out the role of N₂O impurity in the NO gas.

Two major conclusions can be drawn from these experiments. First, defect sites are responsible for NO adsorption, and second, NO adsorbs dissociatively at 90 K. Indeed, for vacuum cleaved MgO(100) single crystals, TPD data exhibit a broad NO desorption feature at ∼100 K. This feature comprises approximately 1% of a monolayer and saturates at very low coverage. Since the same feature is observed in our TPD spectra and since there is a strong dependence of its intensity on the defect density on the MgO film, this desorption feature is assigned as corresponding to surface defect sites. The amount of newly produced F centers for defective films, which does not exceed 1% of the total amount of surface sites, cannot explain the relatively large N₂O saturation coverage for the as-prepared and defective films.

In Fig. 6 the MIES O 2p and N₂O 2σ peak intensities as a function of the NO exposure are presented. The N₂O TPD dependence versus NO exposure is plotted in the inset of Fig. 5. The data clearly show that these features become saturated at varying coverages, depending upon the extent of the thermal quenching. Based on these saturation coverage data we conclude that the as-prepared films contain a significant density of extended defects, e.g., steps, kinks, and grain boundaries. The density of extended defects is increased following a thermal quench of the sample. These extended defects are responsible for the unusually large N₂O accumulation and control the adsorption kinetics. This conclusion is consistent with recent studies of thin MgO films by SPA-LEED and STM. In these studies it was shown that MgO films are routinely composed of small grains (∼50–100 Å). Unfortunately, there has been no systematic study of the morphology evolution of MgO upon annealing, alkali doping, or electron bombardment. However STM images of MgO films grown reactively at elevated substrate temperature (∼1100 K) indic-
Dissociative adsorption of NO has been observed on MgO surfaces. The open and closed symbols correspond to defective and as-prepared MgO thin films, respectively. MIES as coverages approach 1 ML. At these relatively high coverages, intermolecular interactions cause orientational transformations in the adsorbate layer that give rise to a variation in the molecular orbitals exposed to the surface. In this study, the total saturation coverage is far below a monolayer, but orientational changes still manifest themselves in the intensity interplay of peaks A, B, and C. This explanation is consistent with the proposed adsorption scheme, i.e., $N_2O$ molecules are adsorbed on defect sites close to steps or grain boundaries. In spite of the low overall coverage, the local adsorbate concentration can become sufficiently high to initiate orientation transitions.

The total area of the steps and grain boundaries could cover a reasonable fraction of the surface area and could be responsible for the relatively high saturation coverage.

From the observed saturation coverage, the adsorption and dissociation most likely take place on extended defects. However, due to the possible diffusion of the $N_2O$ molecules to surface imperfections, the role of the terrace point defects as sites for NO dissociation cannot be ruled out. Also worth noting is the low sticking coefficient for NO in comparison to that of methanol. A saturation coverage of NO (see Fig. 6) is achieved with an exposure of $\sim30$ L, an exposure almost an order of magnitude higher than the saturation exposure required for methanol.

Another noteworthy observation, apparent at high coverages (not shown here), is the interplay of the relative intensity of the 2$\pi$, 7$\sigma$, and 1$\pi$ states as a function of NO coverage. Indeed, relative intensity variations are common for MIES as coverages approach 1 ML. At these relatively high coverages, intermolecular interactions cause orientational transformations in the adsorbate layer that give rise to a variation in the molecular orbitals exposed to the surface. In this study, the total saturation coverage is far below a monolayer, but orientational changes still manifest themselves in the intensity interplay of peaks A, B, and C. This explanation is consistent with the proposed adsorption scheme, i.e., $N_2O$ molecules are adsorbed on defect sites close to steps or grain boundaries. In spite of the low overall coverage, the local adsorbate concentration can become sufficiently high to initiate orientation transitions.

### IV. SUMMARY

This comparative study of low-defect and high-defect MgO thin films demonstrates the ability of MIES to reveal spectroscopic information of surface defects on nonconducting materials. Only point defects produce a detectable surface state in the band gap of MgO. Although undetected in the MIES spectra of the clean surface, extended defects become detectable upon NO titration. Titration of the surface defects with NO molecules in conjunction with MIES reveals new information regarding the adsorption kinetics and chemical reactivity of defect sites. Based on MIES and TPD data, the low temperature dissociative adsorption of NO on MgO surfaces permits the detection of NO adsorption on MgO surfaces at low temperatures. This density is significantly higher following thermal quenching.

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