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Electron-energy-loss-spectroscopy studies of thermally generated defects in pure and lithium-doped MgO(100) films on Mo(100)

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Thermally generated defects in ultrathin MgO films on Mo(100) have been investigated using high-resolution electron-energy-loss spectroscopy (HREELS) in the 0–9-eV spectral region. The results indicate that the MgO films are thermally stable and nearly free from defects up to a temperature of 1100 K, above which defects in MgO are generated. The three distinct loss features observed at 1.15, 3.58, and 5.33 eV are due to electronic transitions associated with surface F centers, F aggregates, and F (or F^+) centers, respectively. The addition of lithium into the MgO films produces $[Li^+O^-]$ centers and promotes the production of F-type defects upon high-temperature treatment. The formation of the $[Li^+O^+]$ centers is likely a consequence of the substitution of Li^+ for Mg^{2+} in the magnesium oxide lattice. The present studies have demonstrated the capabilities of HREELS for studies of electronic transitions associated with a variety of defects in the near surface region.

I. INTRODUCTION

Investigations of the defect solid state of alkaline-earth oxides have been actively pursued for several decades. These alkaline-earth oxide crystals are face-centered cubic, the anions and cations being situated at the corners of two interpenetrating cubic sublattices. The electronic and geometrical configurations of defects in these crystals are then relatively easy to study due to their simple rock-salt structure. Accordingly, a variety of defects have been proposed and classified into several categories,[1] such as F- and V-type centers. Studies of these defect centers (color centers) have been stimulated recently by the discovery of new oxide catalysts which are promoted by deliberately adding impurities. These catalysts often exhibit superior activity and selectivity over their unpromoted counterparts. Li-doped MgO catalysts, for example, have been reported to promote the oxidative coupling of methane to ethane and ethylene through a methyl radical intermediate.[2] The $[Li^+O^-]$ centers, which are believed to be responsible for the methane activation step,[2] can be produced by heating the Li-doped MgO specimens to high temperatures, followed by rapidly quenching in liquid nitrogen.[3]

As part of an effort to understand the role of a variety of defects in the partial oxidation of methane to ethane and ethylene over Li-promoted MgO catalysts, we have recently carried out a high-resolution electron-energy-loss-spectroscopy (HREELS) study of color centers thermally generated in pure and Li-doped MgO films. This study demonstrates the capabilities of HREELS for studies of electronic transitions associated with a variety of defects in the near-surface region.

Pure and Li-doped MgO films were synthesized under well-controlled conditions by depositing Mg and codepositing Mg and Li, respectively, onto a refractory metal surface in an oxygen environment. Our previous studies have shown the merits of this approach for the preparation of highly ordered, stoichiometric MgO films.[4] By making an ultrathin, well-characterized MgO film on a metal substrate, surface charging associated with the insulating properties of the oxide material is circumvented during charged-particle measurements. Second, the MgO films synthesized under well-controlled ultrahigh-vacuum (UHV) conditions are ultrapure and thus the interpretation of spectral features is straightforward without complications due to the presence of impurities typically found in bulk single crystals. It has been shown[5] that the magnetic and optical properties of intrinsic defects of MgO have been obscured often because of these impurities. Finally, because HREELS is performed using an electron beam with a low primary energy at a sample current on the order of 10^{-10} A, potential electron-beam-induced damage is avoided. The nature of the defects in the MgO films can then be explored using this nondestructive method without electron irradiation damage effects.

II. EXPERIMENTAL DETAILS

The studies were carried out in an UHV system, described elsewhere,[6] with capabilities for HREELS, Auger electron spectroscopy, low-energy electron diffraction (LEED), and temperature programmed desorption (TPD), and for sample heating and cooling. The crystal cleaning procedure has also been published previously.[4]

The HREELS measurements were carried out in the scattering compartment of a two-tiered chamber. The primary energy of the electron beam of the spectrometer (LK-2000, Larry Kesmodel Technologies) can be varied in the 0–250-eV range. The ultimate energy resolution [full width at half maximum (FWHM) of the elastic peak] of the HREELS instrument is 0.005 eV. However, in order to optimize the signal intensity, the spectra were acquired at an energy resolution of 0.030 eV, which produced an elastic peak count rate of $\sim 10^6$ Hz.

Ultrathin MgO films were synthesized in an UHV environment by evaporating Mg onto a clean Mo(100) surface in the presence of oxygen. The procedure for the MgO film preparation and the detailed studies regarding characterization of the films have been presented elsewhere.[4,6] Our LEED and surface spectroscopic studies have shown that the MgO films, prepared under optimum oxidation conditions, grow epitaxially in the 200–600-K substrate temperature range and have essentially a one-to-one stoichiometry. The stoichiometric films are nearly free from defects, as indicated by our electron-energy-loss spectra which follow.

Li-doped MgO films were prepared under UHV conditions by codepositing Mg and Li onto Mo(100) in 2×10^{-7} Torr of oxygen. Magnesium deposition was performed via evaporation of a high-purity ribbon tightly wrapped around a tungsten filament. Lithium atoms were deposited onto the surface from a SAES source. The two metal dosers were mounted close together inside a cylindrical tantalum cage located approximately 3 cm away from the specimen during the evaporation. The flux of Mg and Li evaporation was directly monitored by a mass spectrometer which was mounted in line with the metal sources. Film stoichiometry was adjusted by tuning the relative evaporation flux of Mg and Li. Our LEED studies showed that the rocksalt structure of MgO is preserved upon doping as the Li content was varied from 0 to 15 at. %.

III. RESULTS

The evolution of defects in pure MgO films as a function of annealing temperature T has been examined using HREELS. Figure 1 gives a set of HREELS spectra acquired subsequent to annealing in 5×10^{-7} Torr of oxygen to the indicated temperatures. The films were grown on a room-temperature substrate and the spectra were collected at a substrate temperature of 80 K using an electron beam with a primary energy E_p of 15 eV. The spectra exhibit a prominent loss feature at 6.3 eV below $T=1000$ K. This feature is believed to be a surface-related interband transition associated with surface atoms of fivefold coordination[7] since its energy is considerably less than the 7.8-eV band gap of MgO.[8] Previous work[7] has shown that this peak is enhanced at low primary energies and at grazing incidence, indicating that it originates from the surface. The sharp loss features at energies near the elastic peak are due to excitations of the surface optical phonon and its multiple losses.

Two shoulders appeared at ~1.1 and ~5.3 eV within the bulk band-gap region upon annealing to $T\geq1200$ K. The high loss energy feature became better resolved with increasing T. At $T\simeq1400$ K, a new peak was apparent at 3.6 eV. This third feature appears at lower annealing temperatures and is more intense, as shown in Fig. 2, where the spectra were acquired using an electron beam

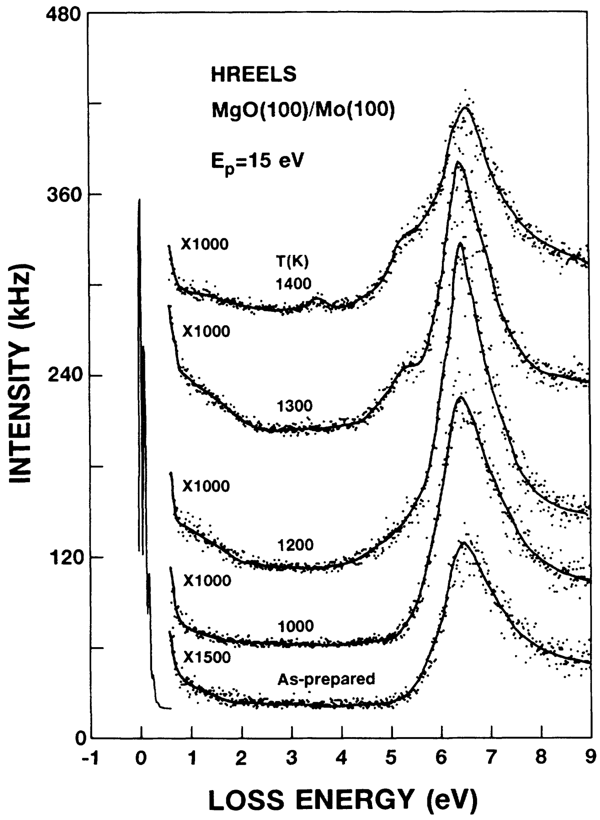

FIG. 1. HREELS spectra of an ~20 monolayer MgO film acquired subsequent to annealing in 5×10^{-7} Torr of oxygen for 1 min to the temperatures indicated. The data were collected in the specular direction using an electron beam with $E_p=15$ eV at a substrate temperature of 80 K.

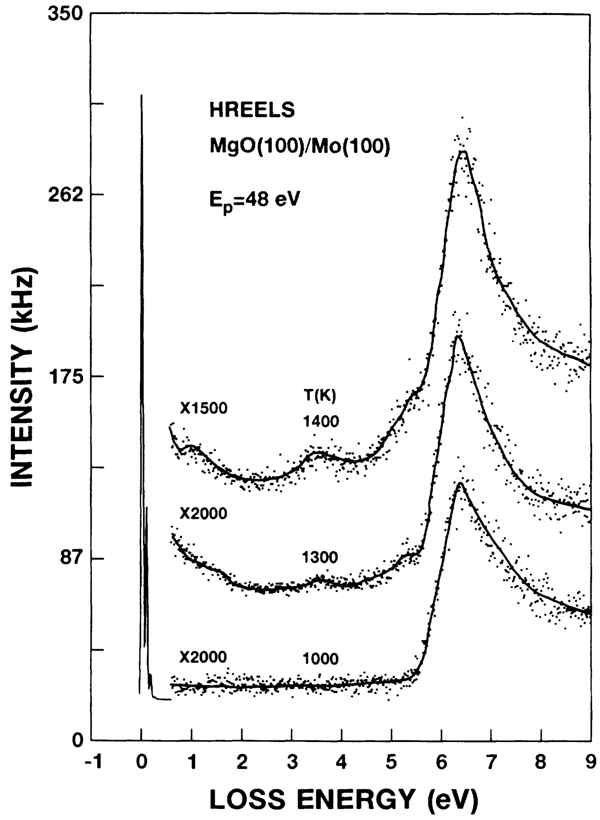

FIG. 2. HREELS spectra of an ~20 monolayer MgO film acquired subsequent to annealing in 5×10^{-7} Torr of oxygen for 1 min to the temperatures indicated. The data were collected in the specular direction using an electron beam with $E_p=48$ eV at a substrate temperature of 80 K.

with a high primary energy of 48 eV. These spectral features occurring after a high-temperature treatment of the specimens can be explained as arising from defect states of MgO. To demonstrate these loss features clearly, the difference spectra with reference to those acquired at $T=1000$ K were taken in the 0.5–6.0-eV spectral region, as shown in Fig. 3. Figure 4 displays different HREELS spectra acquired subsequent to heating freshly prepared MgO films in a hydrogen environment for 1 h.

Further heating of the specimen resulted in complete desorption of the MgO film, as indicated in our TPD spectra (Fig. 5). The detailed studies regarding TPD spectra as a function of background pressure of oxygen during film synthesis have been presented elsewhere.[4] It is noteworthy from Fig. 5 that the oxide desorption peak has a shape characteristic of zero-order desorption. Therefore, the heat of sublimation ΔH_{MgO} of the MgO films can be obtained from Arrhenius plots of the leading-edge desorption rate,[9] yielding $\Delta H_{\mathrm{MgO}}=146$ kcal/mol. This value is consistent with that reported previously for bulk MgO.[10] The small shoulder whose peak desorption temperature lies below the desorption maximum in Fig. 5 is interpreted as arising from defects in the MgO films corresponding to incompletely coordinated MgO.[4]

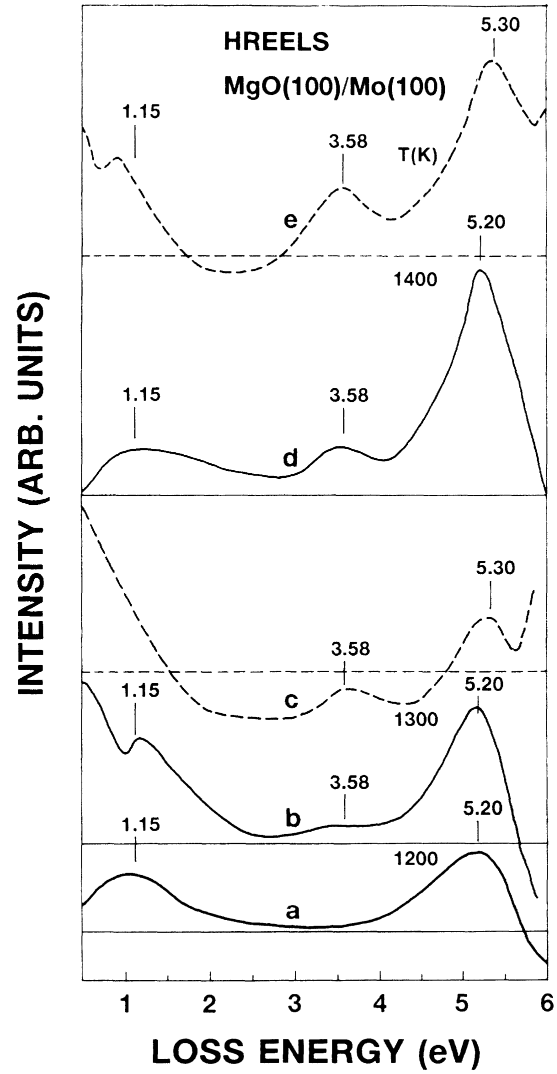

FIG. 3. The difference spectra of HREELS obtained from Figs. 1 and 2 with reference to those acquired at an annealing temperature of 1000 K. *a*, $T=1200$ K; *b* and *c*, $T=1300$ K; *d* and *e*, $T=1400$ K. The solid and dashed curves represent the spectra acquired using an electron beam with $E_p=15$ and 48 eV, respectively.

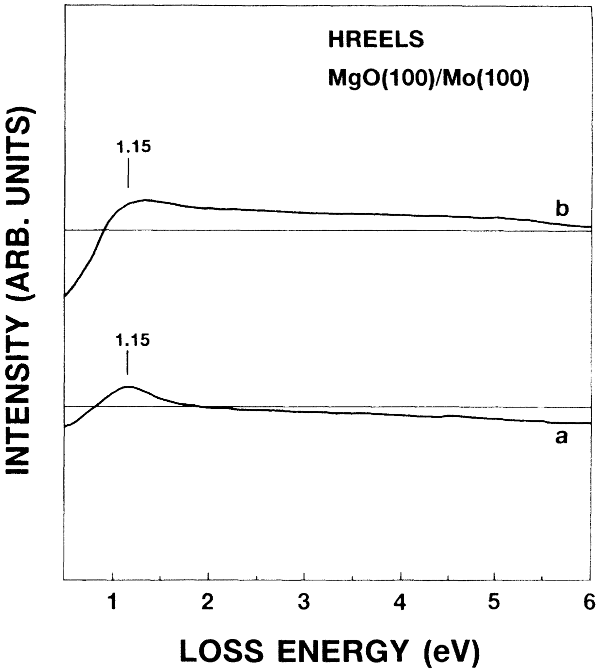

FIG. 4. The difference spectra of HREELS, acquired subsequent to a reduction of MgO films by heating in a hydrogen environment for 1 h, with reference to those acquired before reduction. *a*, $T=800$ K, 1×10^{-6} Torr of hydrogen, and *b*, $T=900$ K, 1×10^{-6} Torr of hydrogen.

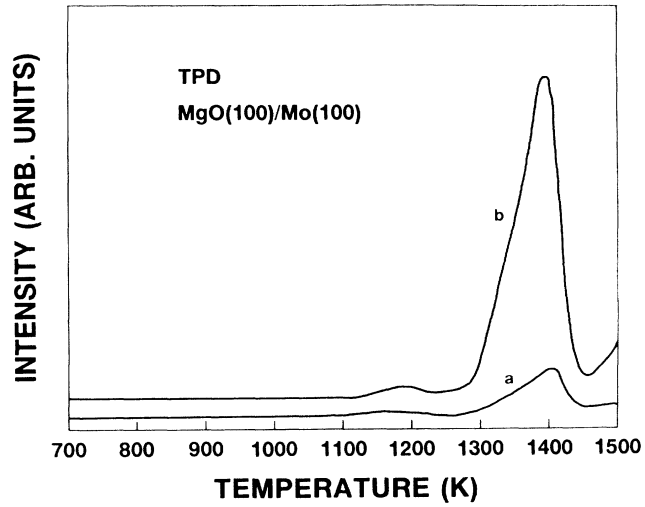

FIG. 5. TPD spectra of an ~14 monolayer MgO film on Mo(100). The spectra were obtained at a linear heating rate of 7 K/s using a quadrupole mass spectrometer at *a*, $m/e=16$ and *b*, $m/e=24$.

Combining the HREELS and TPD results, we conclude that the MgO films synthesized on a Mo(100) surface are thermally stable and nearly free from defects up to 1100 K, above which defects in MgO films are generated. At $T \simeq 1400$ K, a significant portion of the MgO films has desorbed as indicated by the HREELS and TPD spectra. The desorption of MgO films is complete at temperatures above ~ 1500 K.

Figure 6 shows typical Auger spectra acquired following the synthesis of the films. The spectrum of a pure MgO film exhibits two prominent features at 32.0 and 505.0 eV which arise from the $Mg^{2+}(L_{23}VV)$ and O^{2-} (KLL) Auger transitions,[6,11,12] respectively. Upon doping with 10 at. % Li (see spectrum *b*), the intensity of the $Mg^{2+}(L_{23}VV)$ Auger transition decreases relative to the $O^{2-}(KLL)$ Auger transition. Spectrum *c* displays Auger features of an ~ 10 monolayer Li_2O film.

Thin films prepared by codepositing Mg and Li onto a clean Mo(100) surface in an oxygen environment have been characterized using HREELS. Figure 7 represents a set of HREELS spectra acquired as a function of annealing temperature. The as-prepared films containing 10 at. % lithium exhibit HREELS spectra which are very similar to those of pure MgO films. Upon annealing to $T \geq 1000$ K, a distinct loss feature at ~ 1.6 eV emerges and saturates in intensity with an increase in T. Two additional loss features at 3.6 and 5.3 eV develop at $T \geq 1100$ K. These latter features have the same loss energies as those found for pure MgO films which have been annealed to high temperature. In Fig. 8, the intensities of these losses, together with those obtained from the pure MgO films, normalized to the respective elastic

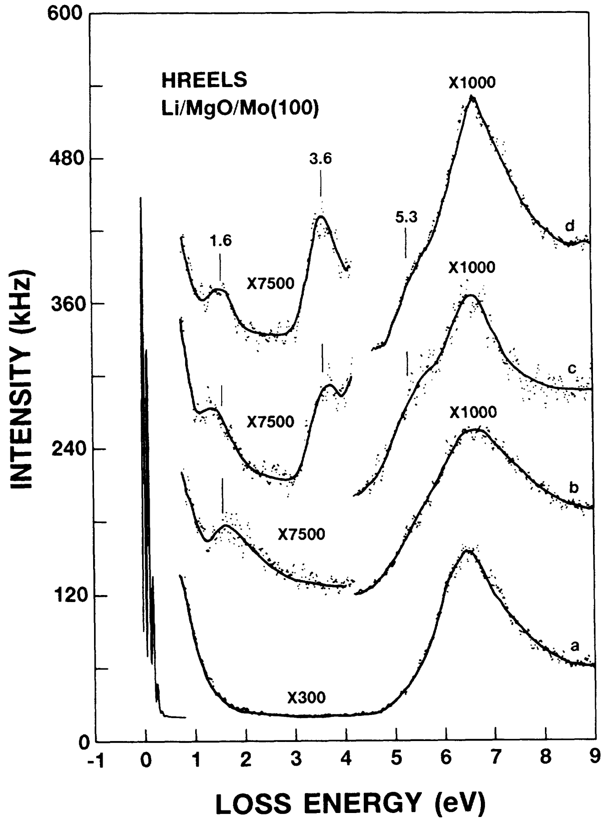

FIG. 7. HREELS spectra acquired subsequent to annealing a 10-at. % Li-doped MgO film in 5×10^{-7} Torr of oxygen to various temperatures: *a*, as-prepared at 300 K; *b*, 1000 K; *c*, 1200 K; *d*, 1300 K. The film thickness is 20 monolayers. The loss features marked at 1.6, 3.6, and 5.3 eV in the figure are attributed to $[Li^+O^-]$ centers, F aggregates, and F centers, respectively. The spectral data were collected using an electron beam with the primary energy of 15 eV at a sample temperature of 80 K.

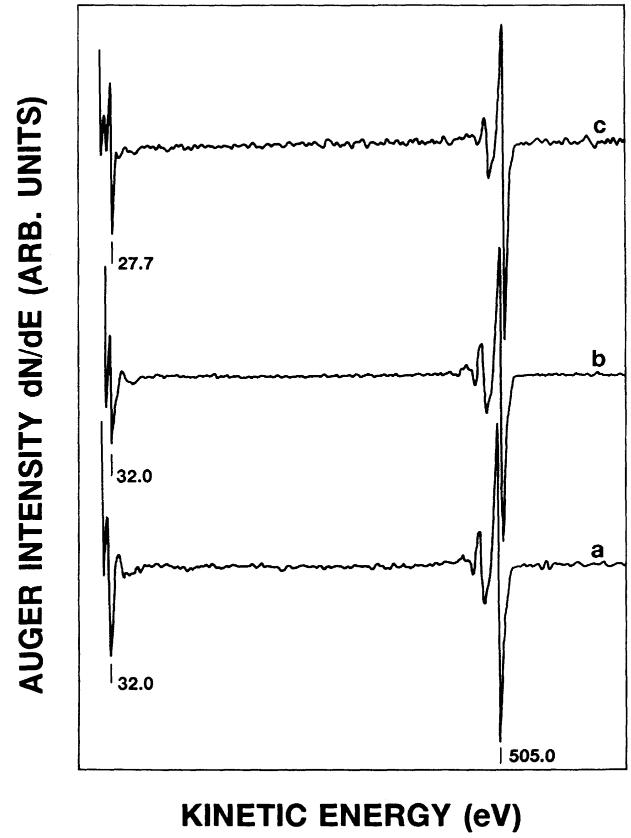

FIG. 6. Auger spectra obtained from *a*, a pure MgO film ($\sim$20 monolayers), *b*, a 10-at. % Li-doped MgO film ($\sim$20 monolayers), and *c*, a pure Li_2O film ($\sim$10 monolayers).

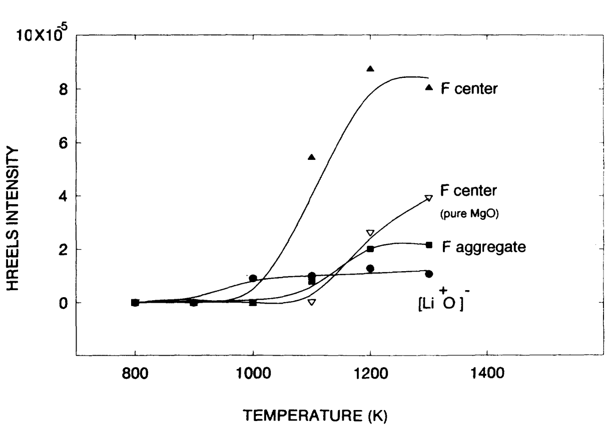

FIG. 8. HREELS intensities of the various defects normalized to the respective elastic peak vs annealing temperature. Open symbols represent the data obtained from pure MgO films. The Li content was 10 at. %.

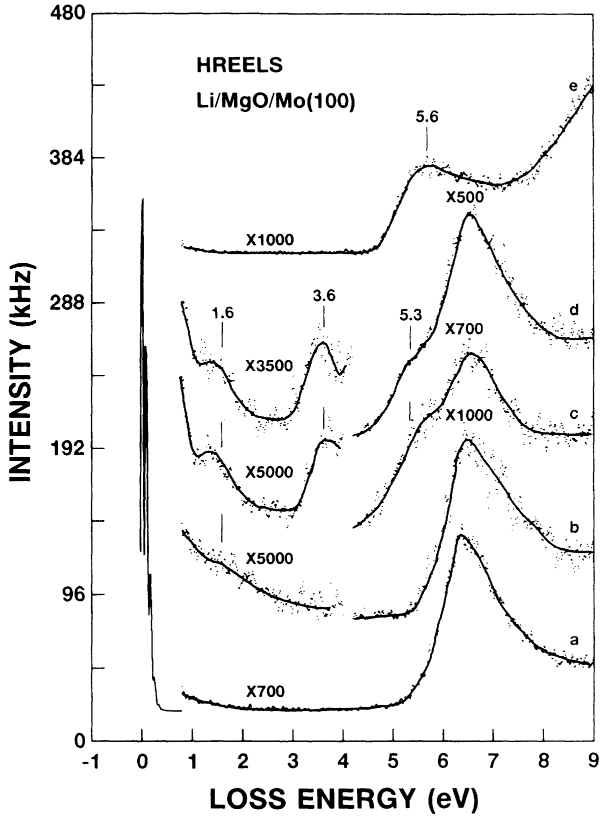

FIG. 9. HREELS spectra vs the Li concentration. *a*, a pure MgO film, $T=1000$ K; *b*, a 1.7-at.% Li-doped MgO film, $T=1200$ K; *c*, a 10-at.% Li-doped MgO film, $T=1200$ K; *d*, a 15-at.% Li-doped MgO film, $T=1200$ K; *e*, a pure Li_2O film, as prepared at 300 K. The film thickness is 20 monolayers. The spectral data were collected using an electron beam with the primary energy of 15 eV at a sample temperature of 80 K.

peak, are plotted as a function of annealing temperature.

The evolution of defect features observed in HREELS has also been examined as a function of film stoichiometry. The pure MgO films exhibit no loss features within the bulk band-gap region following an annealing up to $T=1100$ K, whereas three distinct peaks at 1.6, 3.6, and 5.3 eV occur upon annealing the Li-doped MgO films to $T \geq 1100$ K. The intensities of these loss features are dependent on Li concentration. Included in Fig. 9(e) is the spectrum of a pure Li_2O film which shows a loss peak at 5.6 eV.

IV. DISCUSSION

A. Defects thermally generated in pure MgO films

It is noteworthy that the ~5-eV loss feature in Fig. 3 increases in intensity as E_p is decreased from 48 to 15 eV. This suggests that this feature originates from the bulk since the electron mean free path at $E_p=15$ eV is considerably longer than at $E_p=48$ eV. That is, 48-eV electrons are much more surface sensitive than are 15-eV electrons. Nevertheless, the overall surface-sensitive nature of the employed technique indicates that the species giving rise to this transition is in the near-surface region. The FWHM of this peak also varies from 0.93 eV at $E_p=15$ eV to 0.76 eV at $E_p=50$ eV. In early optical-absorption studies, a band at 4.90 eV in neutron-irradiated crystals[13,14] has been identified as an F^+ center (an oxygen vacancy with one electron trapped). Work on additive-colored MgO (by heating the crystal to a high temperature in the vapor of Mg) and high-energy electron-irradiated crystals suggests that the F-defect (an oxygen vacancy containing two electrons) feature also occurs at this energy.[15–17] Theoretical calculations indeed predict that the absorption bands due to F and F^+ centers should occur at almost the same excitation energy.[18] Chen, Williams, and Sibley[19] were able to decompose the F/F^+ excitation features at room temperature into an F^+ contribution centered at 4.90 eV and an F contribution at 5.01 eV with a half-width of 0.77 eV.

Accordingly, the 5.33-eV peak observed in our experiments can be attributed to an F center. However, the broadening of this peak at the low-energy side of the spectra acquired at $E_p=15$ eV implies that some F^+ centers also exist in the films. Because of the absence of transition-metal impurities in our MgO films, excessive charge in an F^+ center cannot be compensated by multivalency transition-metal ions. The requirement of charge compensation due to the production of F^+ centers in the MgO films can be achieved, however, by inducing an image charge in the metallic (Mo) substrate.

The 3.58-eV loss is likewise attributed to F aggregate centers since an identical peak observed in optical-absorption measurements is believed to be due to the association of vacancies.[14,20] An appealing model for this aggregate has been tentatively proposed to consist of nearest-neighbor anion and cation vacancies.[21,22] Electron-spin resonance (ESR) and optical-absorption results[13,14] have shown that the concentration of F^+ centers in MgO single crystals subjected to neutron irradiation saturates with increasing neutron dose. It was therefore suggested that the production of F/F^+ aggregate centers was responsible for this maximum F^+ center density.

The existence of an F_s^+ center (a surface oxygen vacancy containing one electron) was initially proposed in optical measurements of fine powder samples of MgO using the diffuse reflectance technique.[23] A feature at 2.05 eV was attributed to this F_s^+ center. Utilizing EELS under well-controlled UHV conditions, Henrich, Dresselhaus, and Zeiger[7] have observed a loss peak on single-crystal MgO at 2.3 eV, whose size varied with the specimen and with surface treatment.

These authors tentatively attributed this loss to a surface F center. An alternative assignment of this loss feature has been proposed more recently by Underhill and Gallon,[24] based on the thermal decay of the peak and complimentary theoretical studies. These workers suggested that this loss could be assigned to a surface V^- center (a surface cation vacancy with a hole trapped on an adjacent oxygen anion). Indeed earlier optical studies[25] have shown that the formation of the V^- centers gives rise to an optical-absorption band at 2.3 eV. However, in the work of Underhill and Gallon, the growth of this feature was induced by electron bombardment. An MgO crystal subjected to such an intense electron irradiation might very well contain a variety of defects, such as defect aggregates.[14] These defects could not be differentiated due to the poor energy resolution (~ 1 eV) of the spectrometer used in their experiments. In the present studies, no loss features were observed in the 2.0–3.0-eV region. The 1.15-eV peak likely corresponds to a transition associated with surface F centers. Further support for this assignment is the presence of bulk F/F^+ centers in the MgO films that have been subjected to treatment at high temperature.

The assignment of the 1.15-eV loss to a surface F center is further supported by the evidence obtained in our hydrogen reduction experiments. Figure 4 shows HREELS spectra acquired subsequent to heating the MgO films in a hydrogen environment for 1 h. Reduction of MgO films by hydrogen induces a new peak at 1.15 eV. This peak, which is identical to the one observed in MgO films after a high-temperature treatment, can be interpreted as arising from a surface F center due to the removal of a surface lattice oxygen by hydrogen.

B. Defects in lithium-doped MgO films

Centers of the type $[M^+O^-]$ in single crystals of alkaline-earth oxides have been studied previously by Abraham and co-workers[3] using ESR and optical-absorption spectroscopy. These authors have shown that the formation of $[\mathrm{Li^+O^-}]$ center gives rise to a characteristic resonance at $g_\perp = 2.054$ and $g_\parallel = 2.0043$ in ESR spectra and to a characteristic absorption feature with a maximum at 1.8 eV in optical spectra. The loss feature observed at ~ 1.6 eV therefore strongly indicates the presence of $[\mathrm{Li^+O^-}]$ centers in our MgO films.

Abraham and co-workers[3] have previously proposed a model in which the lithium impurities in as-grown MgO crystals were considered to be present primarily in precipitates (probably in the oxide form of Li_2O) with some soluble Li^+ ions randomly distributed in the crystal. Upon high temperature or extensive electron irradiation treatment, each precipitate generates a microgalaxy of substitutional Li^+ ions surrounding the precipitate, giving rise to a cloud of stable $[\mathrm{Li^+O^-}]$ centers. In the present studies, the formation of these centers generated by high-temperature annealing may be explained using this model. It follows then that the diffusion of Li^+ from the precipitates to form a $[\mathrm{Li^+O^-}]$ center reaches thermal equilibrium above 1000 K since the $[\mathrm{Li^+O^-}]$ HREELS intensity remains essentially constant in the 1000–1300-K temperature region (see Fig. 8). On the other hand, the production of F-type defects has been found to increase as the annealing temperature is increased from 1100 to 1200 K. Our thermal desorption studies have shown that pure Li_2O films desorb above 1000 K with a peak maximum temperature at ~ 1250 K. The increase in the production of defects of F type at high temperature is likely a consequence of the desorption of Li_2O that leads to the generation of oxygen vacancies in the bulk of MgO.

The presence of Li in MgO also increases the formation of F-type defects, an increase that is likely a consequence of the substitution of Li^+ for Mg^{2+} in the magnesium oxide lattice. Figure 8 clearly shows the difference between promoted and unpromoted MgO films in the production of F defects. This promotion is also evident in Fig. 9 in which the concentration of F-type defects in MgO is found to increase with an increase in the Li content.

V. CONCLUSIONS

In conclusion, three types of defects thermally generated in pure MgO films on Mo(100) have been identified using HREELS in the 0–9-eV spectral region. The HREELS and TPD results indicate that the MgO films are thermally stable and nearly free from defects up to 1100 K, above which defects in MgO develop. The loss features occurring at 1.15, 3.58, and 5.33 eV are attributed to surface F centers, F aggregates, and F (or F^+) centers, respectively. The desorption of the MgO films is complete at ~ 1500 K. The addition of Li into the MgO films gives rise to a loss feature at ~ 1.6 eV which is attributed to the $[\mathrm{Li^+O^-}]$ center. The production of F-type defects was found to be increased due to the presence of lithium. This promotion is likely a consequence of the substitution of Li^+ for Mg^{2+} in the MgO lattice and the loss of Li precipitates upon high-temperature annealing. The present studies have demonstrated the capabilities of HREELS for the study of electronic transitions associated with a variety of defects.

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