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Inelastic electron-tunneling study of MgO barriers

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A detailed study of MgO under a variety of preparation conditions has been carried out by inelastic electron-tunneling spectroscopy on Mg-MgO-Pb junctions. Surface vibrational modes play an important part in the observed spectra. The strong peak at 83 meV can be associated with the excitation of longitudinal-optical surface modes while two smaller maxima at 54 and 69 meV are attributable to a mixture of longitudinal- and transverse-optical surface modes. Some barriers were implanted with low-energy hydrogen ions creating magnesium hydride at the Mg-MgO interface. Hydrogen, either as magnesium hydride or substitutional H^- in the MgO lattice, was observed as an intense broad band near 124 meV in the inelastic tunneling spectrum. The catalytic action of water and hydrogen in the oxide growth process and their effect on the barrier height and roughness are also discussed.

I. INTRODUCTION

Inelastic electron-tunneling spectroscopy (IETS) is carried out by measuring the conductance $\sigma = dI/dV$ and its derivative $d\sigma/dV$ as a function of bias (corresponding to the energy range of interest) on metal-insulator-metal junctions. Peaks in $d\sigma/dV$ as a function of electron energy, eV, reflect the vibrational spectrum of molecules in the barrier. Chemical species incorporated in the barrier or adsorbed on the junction electrodes may thus be studied by IETS. In practice, the oxides of aluminum and magnesium have insulating properties good enough to withstand the application of bias voltages of the order of 1 V across thin barriers (~ 10 Å). Of these, aluminum oxide is by far the easiest to prepare, hence most of the published tunneling spectra are of Al-oxide—Pb junctions.[1] Early IETS studies of undoped MgO were carried out by Adler[2] and Klein *et al.*[3] A detailed review of IETS in doped MgO has been given by Walmsley and Nelson.[4] The lack of reproducibility (compared with aluminum oxide) in the IETS of undoped MgO junctions, produced in different laboratories, is one of the reasons that led the authors to study this oxide under various preparation techniques. The other consideration is that MgO is proving to be a very useful material for fabricating refractory metal Josephson junctions.[5]

This paper deals with (i) investigations of the influence of different preparation methods on the tunneling spectra, (ii) analyses of these spectra, specifically of the MgO phonons and the role played by water and hydrogen molecules present during and after oxide growth, (iii) the observation on magnesium hydride and deuteride modes on samples with ion-implanted hydrogen and deuterium, and (iv) a study of the different barrier heights produced by the various preparation techniques.

II. EXPERIMENT

A. Preparation methods

Mg-MgO-Pb tunnel junctions were prepared in an evaporator operating in the low 10^{-5}-Pa (10^{-7}-Torr) range. Two specially constructed liquid-nitrogen traps were used to prevent contamination, decrease water vapor, and improve vacuum. One of the cold traps (a Meissner trap) located within the bell jar had a large active surface area and enabled us to lower the residual gas pressure to below 2.7×10^{-6} Pa (2×10^{-8} Torr). Residual gas analyses were performed with a UTI model 100C quadrupole mass spectrometer. Junctions were prepared on fire-polished Pyrex substrates. After the deposition of silver contacts, a Mg layer (0.2 mm wide, 200 nm thick) was evaporated at a rate of 2 nm/s using a tubular covered boat. Scanning electron microscopy and electrical resistance measurements indicate that our Mg films are composed of crystallites having an average size of 10 nm. The ensuing oxidation was carried out using two types of procedures, characterized as wet or dry. Dry junctions were prepared with the Meissner trap activated about 10 min prior to magnesium evaporation. The presence of this large (10^4 cm^2) cold (77 K) surface situated near the substrates during preparation enabled us to reach very low partial pressures of water vapor. Although the amount of water vapor present is hard to estimate, a comparison of the time required to oxidize magnesium in the two situations indicates that the pressure was in the low 10^{-7}-Pa (10^{-9}-Torr) range. Besides water vapor, the residual gases comprised small amounts of molecular H_2 (<5 vol %), CO (8 vol %), and N + CO (15 vol %). In the wet method the cold trap in the bell jar was not activated and the partial pressure of water vapor was about 1.3×10^{-5} Pa (1×10^{-7} Torr).

Oxidation of the magnesium was performed in three different ways. (1) Plasma oxidation consisting of a glow discharge of 27 Pa (200 mTorr) of ultrapure oxygen. During this type of preparation the ion current was 13 mA and the voltage 430—460 V for 20 to 50 min. No barriers could be obtained by this technique using the dry method, even after 4 h (a similar technique with aluminum provides an oxide suitable for tunneling in less than 2 min). Hence, all plasma oxidation was carried out using the wet technique.

(2) Ion-gun oxidation in which a small saddle-field ion

gun was used to confine the glow discharge to a small region in the vicinity of the junction, the accelerating voltage was kept very low and the ion current was small (<0.3 mA). The dynamic pressure of oxygen was 1.5×10^{-3} Pa (1.1×10^{-5} Torr) while oxidation time equaled 5 min. The Meissner trap was always active (dry method) during gun oxidation. Again, no junctions could be produced unless the gun was flushed with hydrogen prior to oxidation.

(3) Thermal oxidation in air for 5 to 10 min at temperatures ranging from 80 to 110 °C. Despite the simplicity of this last method, it can result in barrier contamination due to impurities present in the air. This method is nonetheless of interest, as most of the data in the literature[4] was obtained on junctions whose barriers were prepared this way. Following oxidation, two cross strips of lead 0.6 mm wide and 200 nm thick were evaporated (at 2 nm/s) to form the cover electrodes. The completed junctions were removed from the vacuum system, mounted on sample holders, and within minutes were stored in liquid nitrogen.

Since one of our interests was the role of H_2O and H_2 molecules adsorbed on magnesium surfaces before oxidation, we subjected the samples to a variety of treatments. We applied two types of hydrogen treatments to the Mg films prior to oxidation. In the first case the Mg was bombarded by hydrogen ions from a saddle-field ion gun for 4 to 6 min before oxidation. The ion current was 0.3 mA and dynamic H pressure 1.1×10^{-3} Pa (8.5×10^{-6} Torr). In the other case fresh Mg films were subjected to a flow of molecular hydrogen for 15 min to 1 h at pressures up to 33.2 Pa (250 mTorr). Similar treatment was also carried out using deuterium. It was found that those Mg films which were not hydrogen or deuterium pretreated could not be oxidized to provide a tunneling barrier if the Meissner trap had been activated prior to oxidation. It should be noted that Al films can be oxidized even if the trap is activated prior to oxidation and evaporation of the Al film[6] in the same vacuum system under the same conditions (see Sec. III). This suggests that water vapor is very influential in oxide formation. In order to control the amount of water adsorbed on the Mg surface, the following technique was employed. The Mg base layer was plasma oxidized for 5 min prior to activating the Meissner trap (wet method). With the trap activated the partly oxidized surface is cleaned in an argon glow discharge for 5 to 16 min and then plasma oxidized for 45 to 50 min. In this paper we discuss results obtained on junctions prepared by wet, dry, gun, and thermal oxidation of the Mg base layer, with and without hydrogen and deuterium treatment of the surface.

B. Measurements

Measurements of σ and $d\sigma/dV$ were performed using an updated version of a bridge and computerized data-acquisition system described elsewhere[7,8]. The measurements were carried out over the range ±500 mV but avoiding the region ±30 mV dominated by the quasiparticle tunneling effects in superconducting Pb. The modulation amplitude was from 3 to 5 mV peak to peak at 500 Hz. The data σ and $d\sigma/dV$ were all calibrated, recorded, and analyzed by an on-line computer system similar to the one described by Adler.[8] This system also enabled us to calculate barrier parameters using the methods of Simmons[9] and Brinkman, Dynes, and Rowell.[10] The procedure gives barrier heights on both sides of the barrier as well as its approximate thickness. For ease of comparison among various junctions the spectra presented in this paper are given in terms of the logarithmic derivative $(1/\sigma)(d\sigma/dV)$.

III. RESULTS

A. Effects of preparation methods

Our experience shows that it is difficult to oxidize magnesium in the absence of water vapor. Even an oxygen plasma becomes an ineffective oxidation tool if the Meissner trap in the bell jar is activated prior to Mg evaporation, and no suitable barrier can be produced in several hours. Under identical conditions aluminum yields excellent barriers in 2 min.[6] Catalytic action of water is a unique feature of Mg oxidation.

Calibrated plots of the logarithmic derivative $(1/\sigma)(d\sigma/dV)$ versus voltage bias in the (0–500)-mV range are shown in Fig. 1 for different preparations. Details of the low-energy structures (0–210 mV) appear in Fig. 2. The influence of the various preparation methods on the general shape of the curves is evident. Tunneling

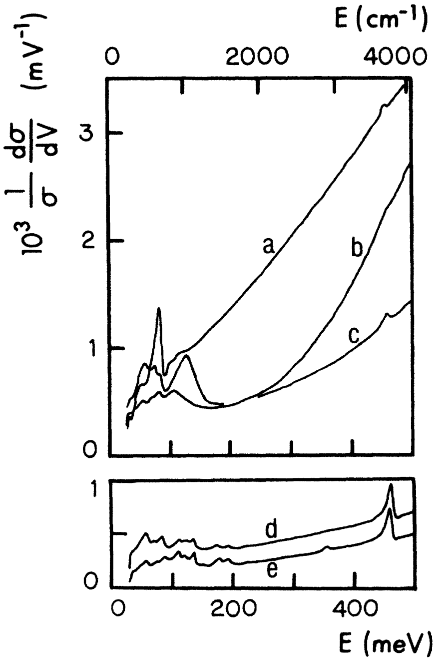

FIG. 1. Inelastic electron-tunneling spectra of typical Mg-MgO-Pb junctions: (*a*) gun oxide with hydrogen preflush of the gun, (*b*) plasma oxide with molecular hydrogen pretreatment of the Mg film, (*c*) plasma oxide with hydrogen ion pretreatment of the Mg film prior to oxidation (dry method), (*d*) wet method, and (*e*) thermal oxidation in air. Curves (*a*), (*b*), and (*c*) are dry junctions as described in the text.

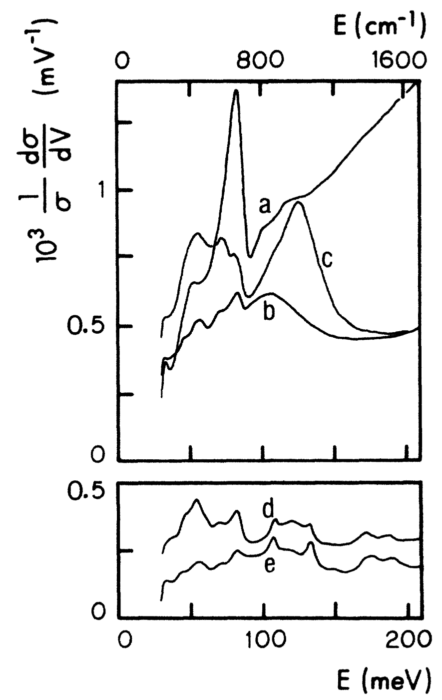

FIG. 2. Spectra highlighting details of the (0—200)-meV range. Curves are denoted as in Fig. 1.

spectra of junctions prepared by means of the dry method (curve *a* in Figs. 1 and 2) show a peak at 83 meV with a weaker peak on its low-energy side near 54 meV. At 454 meV there is a small maximum due to OH stretching modes.

Spectra of junctions pretreated with molecular hydrogen (curve *b* in Figs. 1 and 2) show a band extending from 30 to 150 meV with a broad maximum located near 108 meV. The two characteristic peaks at 83 and 54 meV appear on the low-energy shoulder of this band. The peak at 454 meV is very weak and is barely visible on the steep slope. Spectra obtained using deuterium in place of hydrogen are shown in Fig. 3 and appear similar to the spectra obtained with hydrogen. In order to distinguish between the spectra of the two isotopes of hydrogen the treatment was carried out in conjunction with the wet method. In this instance, the Meissner trap was activated soon after Mg evaporation (rather than before) allowing the adsorption of a small amount of water. The IET spectra show a somewhat better resolved structure (Fig. 4) but still the difference between H and D treated junctions is

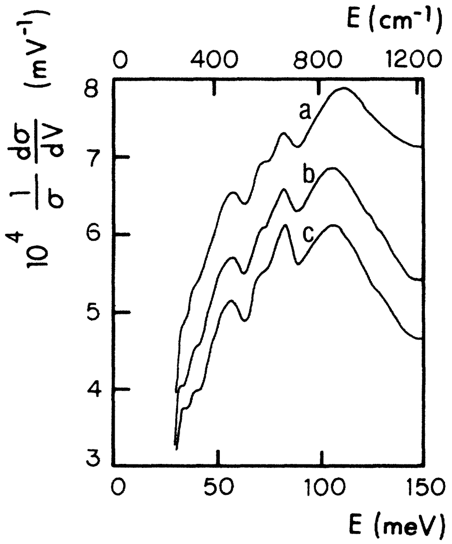

FIG. 3. Spectra of dry junctions treated with molecular hydrogen and deuterium. (*a*) deuterium treatment, 50 min, 33.2 Pa (250 mTorr), (*b*) hydrogen treatment, 15 min, 33.2 Pa, (*c*) hydrogen treatment, 50 min, 33.2 Pa.

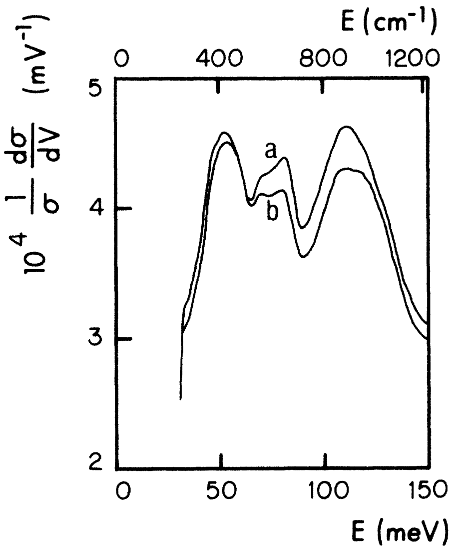

FIG. 4. Detailed spectra of typical Mg-MgO-Pb junctions prepared by the wet method and treated with molecular hydrogen or deuterium. (*a*) junction hydrogen treated for 60 min, 33.2 Pa (250 mTorr), (*b*) junction deuterium treated for 60 min, 33.2 Pa.

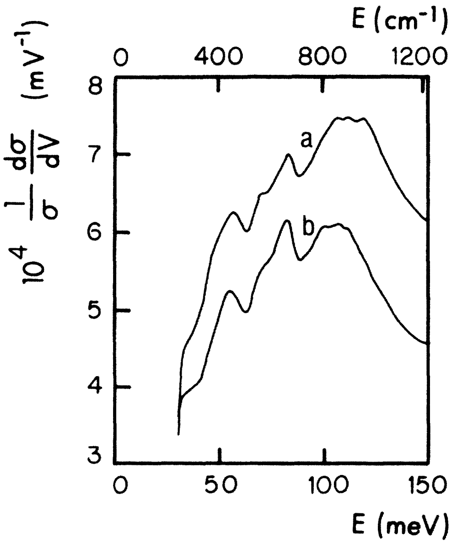

FIG. 5. Spectra of ion-bombarded and hydrogen-treated junctions. (*a*) argon ion bombardment for 12 min, (*b*) hydrogen treated for 50 min at 33.2 Pa (250 mTorr).

small. A more interesting result was obtained by bombarding a partially oxidized Mg strip with argon ions. This method yielded junctions whose spectra are similar to the molecular hydrogen-treated ones. The results are shown in Fig. 5.

Junctions in which the Mg was implanted with hydrogen ions (from the ion gun) prior to oxidation appear in curve *c* of Figs. 1 and 2. These show a large new peak at 124 meV. Figure 6 shows the effects of hydrogen and deuterium implantation. One can see that the 124-meV peak has shifted to 88 meV in the deuterium-implanted samples.

The tunneling spectrum of a junction prepared by the wet method appears in curve *d* (Figs. 1 and 2). Three separate regions can be seen along with a strong OH stretching peak at 454 meV. The low-energy band has maxima at 54, 69, and 83 meV. The central region shows three maxima positioned at 108, 118, and 131 meV. Finally the high-energy band is the weakest with two peaks at about 172 and 185 meV. The spectra of junctions prepared by thermal oxidation in air at 110 °C are shown in curve *e* (Figs. 1 and 2); they exhibit three bands similar to those observed in the wet junctions but with differing relative intensities. The low-energy band is distinctly weaker than the other two, and much less developed than in wet junctions. The central band is the strongest with two well-separated maxima at 108 and 132 meV. The other parts of the spectrum are almost identical to that of the wet junctions. These thermally oxidized junctions also show a small peak near 360 meV due to organic vapors present in room air during oxidation. It is noteworthy that the noise level observed in wet junctions is much lower than in dry ones. The latter have particularly high-noise levels in the (200–400)-mV bias range: The noise level increases with increasing resistance. Quality spectra on dry junctions with resistances above 100 Ω were impossible to obtain even using time constants longer than 10 sec.

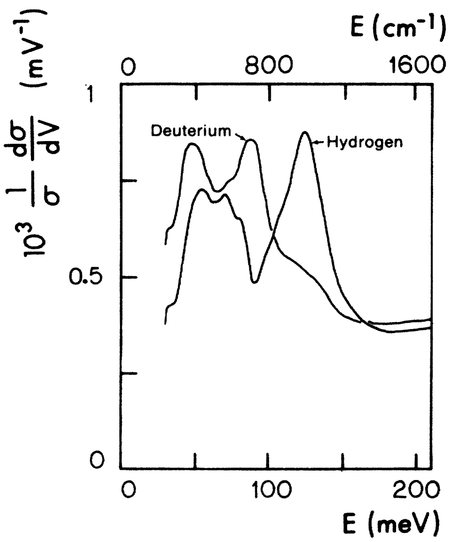

FIG. 6. Spectra of junctions in which the Mg was implanted with low-energy hydrogen and deuterium ions using a saddle-field ion gun prior to plasma oxidation (dry method).

TABLE I. Barrier heights calculated using a trapezoidal model.

Method of preparation	$F_1(V)$	$F_2(V)$
Clean metal work functions[a]	3.66	4.25
Gun oxidation gun preflushed with hydrogen	1.0–2.8	1.5–3.1
Molecular H (or D) treated Mg prior to oxidation	1.9–2.3	1.7–2.4
Argon-ion bombardment	1.7–2.3	2.3–2.5
Wet preparation	2.6–3.4	5.0–5.6
Thermal oxidation in air	2.2–2.4	5.5–6.5
Hydrogen or Deuterium ion treated Mg prior to oxidation	0.8–1.0	6.0–8.0

[a] *Handbook of Chemistry and Physics,* edited by R. C. Weast, M. J. Astle, and W. H. Beyer (Chemical Rubber Company, Cleveland, 1985).

B. Potential barrier parameters

The data were analyzed assuming a trapezoidal barrier of uniform thickness.[9,10] Real barriers differ significantly from this simplified model. First of all, the barrier shape is modified by charged defects in the oxide layer as well as by polar impurities adsorbed on the metal oxide interfaces. Image potentials are also important. Furthermore, real barriers are not uniform in thickness. We also expect the oxide layers to be quite rough, as will be discussed below. Despite these drawbacks, these trapezoidal barriers provide insight into barrier thickness and asymmetry so long as the numerical values of the barrier parameters are not taken too literally. Values obtained for these parameters are given in Table I. The barrier heights on the Mg and Pb side are denoted as F_1 and F_2, respectively. The calculated barrier thickness was only weakly dependent on the preparation method and in all cases was about 1 nm, probably a low estimate. The results may be subdivided into four groups. Junctions prepared using molecular H_2 (or D_2), gun oxidation, and Ar-ion bombardment had symmetric barriers ($F_1 \sim F_2$) with an average height of about 2 V. Barriers in wet junctions and those thermally oxidized are strongly asymmetric ($F \sim 1.5$–4 V) and much higher. Dry junctions have lower and less asymmetric barriers than the wet ones. Finally, hydrogen-ion-implanted junctions have both high and very asymmetric barriers.

IV. DISCUSSION

A. Spectral features below 90 mV

Structure below 30 meV is due primarily to quasiparticle tunneling in Pb and is dominated by the lead phonons, and to a much lesser extent, by Mg phonons, and will not be discussed here. Two maxima, located at 54 and 83 meV, are present in the spectra of all junctions independent of their fabrication method. In wet as well as thermally oxidized junctions, there is a third maximum located at 69 meV. In this spectral region, one can expect the inelastic tunneling of electrons to be accompanied by the emission of bulk and surface phonons in the MgO layer. The excitation of bending modes of hydroxyls present in the bulk oxide or adsorbed on the oxide surface is also possible. The peak at 54 meV dominates this region in the wet junctions but is reduced to a smaller shoulder on the 83-meV peak in the dry and gun-oxidized junctions. Annealing experiments[11] indicate that in wet junctions the intensity of this peak increases with time while remaining unchanged in junctions with only small concentrations of OH. This indicates that there are two different peaks near the 54-meV structure. One of these peaks is due to OH bending modes (also visible in aluminum oxide junctions) and increases with annealing time at room temperature, while the other (unaffected by annealing) may be associated with MgO phonons. Spectra showing these bands in wet and dry junctions are displayed in Fig. 7. The background to the spectra were subtracted using the method devised by Magno and Adler.[12] The curves in Fig. 7 are scaled to produce the same peak intensity at 83 meV for both wet and dry junctions. Assuming the OH bending modes are present primarily in wet junctions, we associate the structures at 54, 69, and 83 meV with MgO phonons. The phonon density of states for MgO has been obtained from neutron scattering data by the use of a shell and breathing-shell models,[13] and more recently by the use of a bond-bending force model.[14] Those results differ considerably from our experimental data both in peak position and relative intensity. Therefore, we conclude that the very thin MgO layers in our tunnel junctions have their phonon spectra grossly modified by the surface modes. Verification of this hypothesis is found in the work of Rieder and Horl[15,16] who studied the role of the surface vibrations on MgO microcrystals. The problem of surface vibrations in MgO crystals also received much theoretical attention. Calculations have been made on the surface-phonon density of states in MgO microcrystals[17] and on a 15-layer slab both with and without lattice relaxation being taken into account.[17–20]

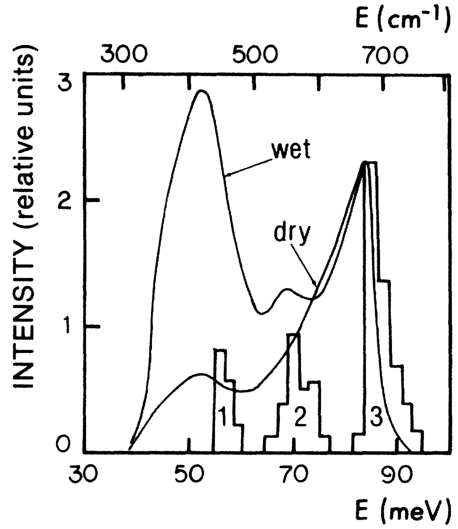

FIG. 7. Low-energy spectra of wet and dry junctions normalized to give equal peak intensities at 83 meV after subtraction of the background (see text). 1, 2, and 3 are histograms of the excess surface phonon density of states calculated by Chen and de Wette (Ref. 18).

Comparison of these calculations with our experimental data leads to the conclusion that besides the surface phonons, lattice relaxation must play an important part. To interpret our results we turn to the calculations of Chen and de Wette[19] for a relaxed 15-layer (001) slab of MgO (this is the most probable orientation of the oxide grown on randomly oriented crystallites[21]). They used a rigid-shell model assuming the effective charges of the surface ions and their polarizabilities to be the same as those of the bulk. Relaxation changes only the short-range repulsive interactions between the lattice ions, described by Born-Mayer potentials. The short-range interaction is the result of the electron-shell overlap of neighboring ions. Change in the overlap causes a displacement of the shell with respect to an ion core, thus creating a dipole moment. Because of the slab symmetry, the only nonvanishing components are perpendicular to the surface. The polarization of the unrelaxed ions is assumed to be zero. By taking into account the short-range interactions and the polarization of the unrelaxed ions, Chen and de Wette were able to calculate the total potential energy of the relaxed slab and in turn the difference in potential energy between a relaxed and unrelaxed slab. This difference is a function of ionic polarization and relaxing displacements of the cations and anions. Assuming three relaxed layers on each side of the slab, they minimize the energy difference and calculate values for the ion displacements and dipole moments in each layer. The above describes their solution of the static part of the problem.

The dynamic part of the problem is approached using a dynamic matrix method and solving the eigenvalue problem for a reduced surface Brillouin zone. These solutions are extremely complicated, as they present the surface-phonon density of states in terms of the difference between the total and bulk densities of state. To facilitate a comparison with the experiment, Chen and de Wette presented their final results in the form of a histogram of this excess surface-phonon density of states. Figure 7 shows three sets of surface modes designated 1, 2, and 3, the small contribution due to bulk phonons being omitted for the sake of clarity. The strong mode with a maximum at 83 meV (histogram 3 in Fig. 7) is associated with the longitudinal optical-surface mode. Two weaker bands (histograms 1 and 2) were ascribed to mixed longitudinal and transverse surface vibrations. The bulk phonons at 54 meV are not shown in Fig. 7. It is not clear that the bulk phonons play a substantial role in the very thin tunneling oxide layers present in these junctions. It must be pointed out that in spite of the good agreement between the histograms and our data, the theoretical results do not consider some of the boundary conditions which occur in tunnel junctions. Only one of the oxide layer surfaces is able to relax (the surface at the MgO-Pb interface). Our MgO layer is probably not a single crystal slab. For many years the existence of maxima in the excess surface-phonon density of states remained unexplained, and it was suggested by Rieder[22] that the surface hydroxyls were responsible for obscuring the neutron scattering experiments described in Refs. 15 and 16 and creating this peak. Our results show that this is not the case and that the observed peaks may indeed be due to the surface-phonon density of states of MgO.

B. Spectral features above 90 meV

Experiments in which the freshly evaporated Mg layer was treated with ion-implanted hydrogen (or deuterium) suggest that the broad band with a maximum near 124 meV (curve *c* in Fig. 2) is due to excitations in magnesium hydride. This hypothesis is partially corroborated by ir absorption results on powered MgH_2 with strong intermolecular hydrogen bonds.[23] We have further confirmed the identification with magnesium hydride by repeating the experiment with deuterium (Fig. 6) in which the 124-meV peak is found to be shifted to 88 meV as expected.

Another possibility is that the 124-meV peak is due to substitutional H^- ions in MgO. Such $MgO:H^-$ vibrations have been observed by Gonzalez, Chen, and Mostoller[24] in the region between 1000 and 1100 cm^{-1}.

Of the other peaks, the structure near 132 meV, prominent in both the wet and thermally oxidized junctions is probably due to the excitation of a C-H out-of-plane bending mode, and has been studied in detail.[12] This mode, often found in tunnel junctions, probably arises when formic acid is created from the reaction of water vapor with the oxides of carbon and is subsequently chemisorbed on the surface. Hydrogen and carbon oxides are always available to produce formic acid in small quantities.

C. Barrier parameters

The shape of the potential barrier in junctions depends strongly on OH dipole concentrations on the surface of the oxide layer. This fact is well established in Al-oxide—Pb junctions.[25,26] In those junctions the barrier height on the base electrode side was usually much lower than that of the cover electrode side. The difference in barrier heights can be several volts. In aluminum-based junctions[26] even a small surface coverage (about 20%) by OH dipoles with the hydrogen pointing away from the oxide surface is enough to raise the barrier height by about several volts. The same probably occurs in the Mg-MgO-Pb junctions of this study. It may also be responsible for lowering Mg barrier height in the specimens containing OH dipoles near the Mg layer.

Referring to Table I it is clear that for both the wet and thermally oxidized junctions, which also show strong OH stretching modes at 454 meV, the Pb barrier height is increased (above the clean Pb work function) due to the polarization at the oxide-Pb interface. The lowering of barrier height at the Mg interface is probably due to subsurface oxygen as found in aluminum—aluminum oxide junctions.[26–28] This subsurface oxygen along with Mg produces an outward-pointing dipole which serves to reduce the Mg work function with oxygen adsorption. The actual reduction in barrier height depends on the net surface polarization established between the competing subsurface O-Mg and supersurface Mg-O dipoles. This reduction is most pronounced in the dry and hydrogen-implanted junctions.

Hydroxyls have yet another important role in the magnesium oxidation processes. The difficulties experienced in attempting to produce oxide barriers on Mg surfaces using an oxygen plasma in the absence of water vapor suggest that water acts as a catalyst in the oxidation process by lowering the Mg work function. It is known that Mg oxidation starts from low work-function patches.[28,29] Comparison of OH stretch peak intensities in wet junctions (assumed to be due to a full monolayer coverage) with those dry junctions indicates that a minimum surface coverage of about 10% is required to make oxides by plasma oxidation. Thus in dry junctions, the average distance between OH sites, and hence between oxidation centers, is of the order of the final oxide thickness. This implies that the resulting oxide layers are probably very nonuniform in thickness. This roughness of the oxide layer is probably responsible for the lower potential barrier heights found in the junctions with low hydride or hydroxyl concentrations. It is the low average barrier heights of the dry junctions which is responsible for the steepness of the background in Figs. 1 and 2. The thin spots in the oxide layer may also be the cause of the higher noise levels observed in the dry junctions.

Oxide nonuniformities cause local thermal instabilities and enable the junction current to heat the Pb counterelectrode above its superconducting critical temperature and give rise to the observed noise. This type of noise has been studied in Al-oxide—Pb junctions.[30]

V. SUMMARY

A surface coverage of about 10% of adsorbed water is required to obtain a continuous film of MgO suitable for tunneling barriers produced by the plasma oxidation of magnesium in a pure oxygen plasma. At lower coverages the augmented distance between nucleation sites of the oxide produces MgO films of nonuniform thickness for layers from 1 to 2 nm. These Mg-MgO-Pb junctions prepared by the dry method have generally higher noise levels and lower barriers than those made by the wet procedure or with a thermal oxide. The latter have more asymmetric barriers. Additional OH dipoles present at the MgO-Pb interface in both wet and thermally oxidized junctions serve to raise the barrier height at the Pb side of these junctions.

Junctions prepared with hydrogen-ion implantation also have very low noise levels. In these junctions the presence of magnesium hydride seems to produce more uniform oxide barriers.

Interpretation of the inelastic electron-tunneling spectra lead to the conclusion that the oxide layer in Mg-MgO-Pb junctions may be regarded as a mosaic of (001) slabs uniformly inwardly relaxed (decreasing lattice constant near the surface due to unbalanced ionic bonding forces). The peak near 82 meV may be due to the excitation of longitudinal-optical surface modes polarized in the sagittal plane. The peaks near 54 and 69 meV are due to these longitudinal phonons mixed with transverse-optical surface modes of the same polarization. In the wet junctions the large 54-meV peak is due to bending modes of O-H adsorbed on the MgO surface.

Finally we established that magnesium hydride can be produced by low-energy ion bombardment of fresh magnesium surfaces. The molecular vibrations of magnesium hydride give rise to a band centered at 124 meV and magnesium deuteride at 88 meV.

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