

Inelastic electron-tunneling study of barriers grown on aluminum*

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Inelastic electron tunneling has been used to systematically study the techniques used to grow barriers on aluminum films when preparing aluminum-barrier-lead junctions. The hydroxyl and hydrocarbon content of a barrier was found to depend upon the method of preparation as well as the materials used. The spectra for barriers grown either in an oxygen-helium or water-vapor glow discharge were found to contain OH but not CH bands, while the spectra for those grown thermally either in oxygen or water contained both OH and CH bands. Barriers formed by pipetting water onto aluminum had a spectrum which contained OH and CH bands. The effect of using a glow discharge technique was examined by exposing several barriers to an argon glow discharge before depositing the lead electrode. The argon discharge treatment was found to remove all traces of CH bands from the spectra for these barriers. Finally, The problem of choosing a background spectrum when doing spectroscopic studies of doped junctions was examined. Several barriers were prepared by pipetting a few drops of an aqueous glycine solution onto freshly evaporated aluminum. The spectra for the doped barriers were found to contain OH bands similar to the OH bands for an oxygen-helium discharge grown barrier, and CH similar to those for a barrier grown by pipetting water.

I. INTRODUCTION

The pioneering inelastic tunneling experiments of Jaklevic and Lambe¹ on aluminum-barrier-lead tunnel junctions demonstrated that a tunneling electron will excite the vibrational modes of molecular impurities in the barrier. They showed that the inelastic interaction opens a new channel for tunneling which is detected as an increase in the conductance of the junction. The tunneling curve d^2I/dV^2 vs V was shown to reflect the vibrational spectrum of molecules in the barrier.

Since this work there have been many reports of hydroxyl and hydrocarbon impurities in the barriers of similar systems.²⁻⁹ In many of these studies the impurities were introduced unintentionally while the barrier was being formed.²⁻⁵ More recently, studies have been done on barriers intentionally doped with a wide variety of organic molecules.^{3,5,9} The goal of these recent papers has been to establish inelastic tunneling as a spectroscopic tool similar to infrared absorption or Raman scattering.

This work presents a systematic examination of the techniques often used to grow barriers on aluminum films. The results of this work show that the hydroxyl and hydrocarbon content of a barrier depends upon the method of preparation as well as on the materials used. The effect of using a glow discharge was examined by exposing barriers to an argon glow discharge. Finally, the problem of choosing a background spectrum when doing spectroscopic studies was examined. Aluminum-barrier-lead junctions were studied exclusively because most of the earlier work was done on them. The junction preparation details a description of the measurement techniques, and the

data reduction techniques are given in Sec. II. The results are presented and discussed in Sec. III, and a summary is presented in Sec. IV.

II. EXPERIMENTAL

Since we were interested in examining hydrocarbon impurities in the junctions, the system was thoroughly cleaned before starting these experiments, and every precaution was taken to keep it clean. In particular, care was taken to eliminate backstreaming of oil from the mechanical forepump. The bell jar was always roughed out by zeolite sorption pumps. Backstreaming through the diffusion pump was controlled by using a zeolite trap between the forepump and the diffusion pump, and a continuously replenished liquid-nitrogen cold trap between the diffusion pump and the bell jar.

The junctions were prepared by evaporating an aluminum¹⁰ electrode, growing a barrier on it, and then evaporating a lead¹¹ counter electrode. Barriers were grown thermally, by a glow discharge, or by pipetting pure water¹² or an aqueous solution of an organic substance onto the aluminum. The system was equipped with several evaporation sources and facilities for introducing the gases necessary for growing barriers. Thus, only the pipetting procedure involved venting the bell jar to room air while preparing a junction. Each of the barrier preparation techniques described below was tested several times, and in all we examined more than 30 junctions.

Barriers were grown by running a glow discharge in either a 40%-oxygen¹³ 60%-helium¹³ mixture, or a water-vapor atmosphere. Typically, the discharge was run for 15 min at 500 V with a pressure between 200 and 250 μ m. Much high-

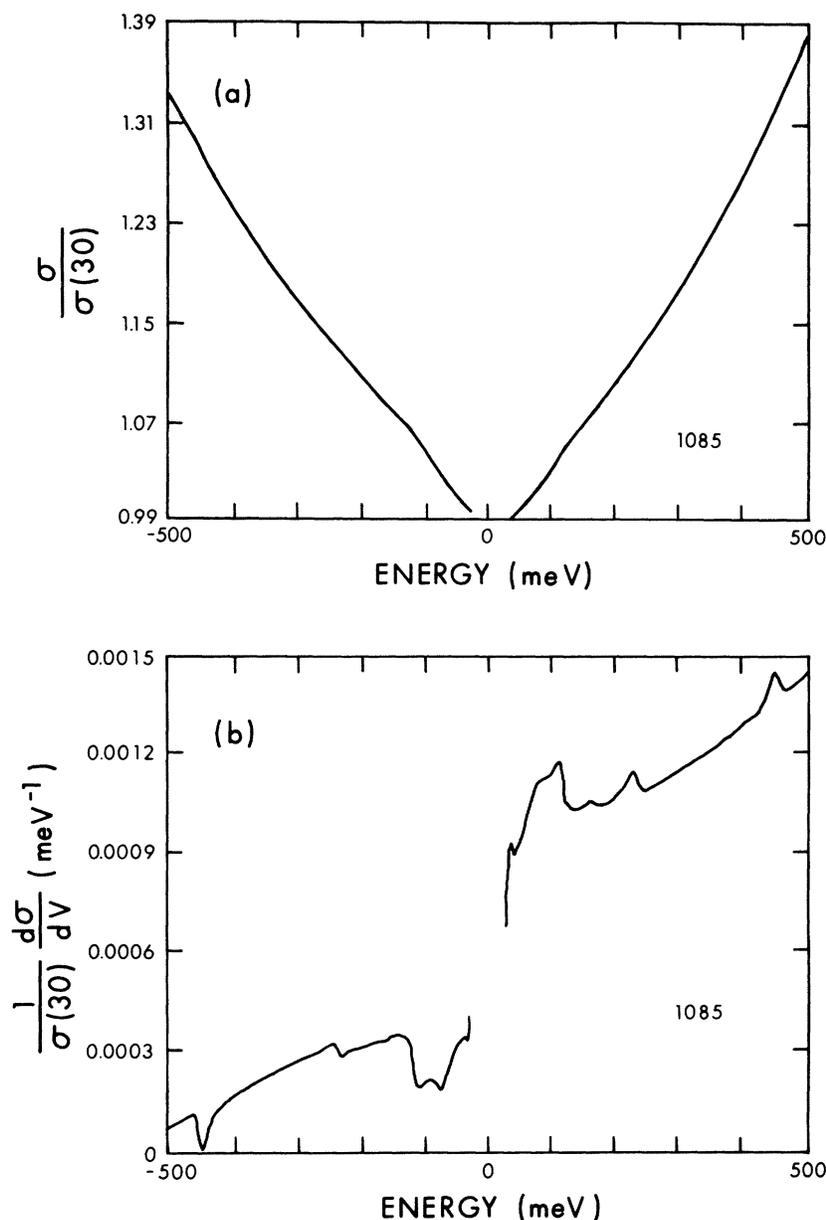


FIG. 1. Conductance (a) and its derivative (b) for a junction whose barrier was grown in a water-vapor glow discharge.

er pressures and longer times were required to grow barriers thermally. For these samples the substrates were heated in the bell jar to 300 °C in either $\frac{1}{2}$ atmosphere of oxygen for 16 h, or 10-Torr pressure of water for 2 h. All the above procedures were carried out without venting the bell jar to room air. On the other hand, the pipetting procedure described below involved venting the system. After removing the aluminum film from the bell jar a few drops of water or an aqueous solution of an organic substance would be pipetted onto it. The exposure times which varied from 10 to 120 sec were controlled by using a stream of helium gas to blow off any excess

solution.

Some of the barriers prepared by the thermal-oxygen technique and some of those prepared by the water pipetting technique were exposed to an argon¹³ glow discharge before depositing the lead counter electrode. The argon discharge was run at 500 V for various times at 100- μ m pressure.

The barrier growth parameters, and electrode widths (0.2–0.8 mm) were chosen to provide junctions with resistances between 50 to 100 Ω . Junctions with resistances below 50 Ω often broke down at high biases while those above 1000 Ω were discarded because they had a poor signal-to-noise ratio.

The junctions were mounted in a holder having gold pressure contacts. This enabled quick mounting and cooling to liquid-nitrogen or -helium temperatures. All measurements were done with the junctions immersed in liquid helium at atmospheric pressure.

Harmonic detection techniques were used with a constant current bridge and a computer controlled data acquisition system,¹⁴ to measure and digitally record dV/dI and d^2V/dI^2 for the junctions. The computer was used to generate 2500 calibrated values of the dynamic conductance $\sigma = dI/dV$ and $d\sigma/dV$ for each sweep. Two sweeps were run for each junction, one from -500 to -30 meV, and one from 30 to 500 meV. By not recording in the region between ± 30 meV we avoided the lead phonons and the superconducting energy gap of the lead whose signals would have swamped the hydroxyl and hydrocarbon signals of interest to us. Thus, the dynamic range of the system was adjusted to optimize the features of interest, the inelastic effects in the barrier.

Shown in Figs. 1(a) and 1(b) are the curves of $\sigma(V)$ and $d\sigma(V)/dV$ for a typical junction. The asymmetry in $\sigma(V)$ is due to the differences in the electrode work functions and to some barrier properties. The inelastic tunneling structure which should be an even function of the bias is not visible in $\sigma(V)$, but shows up clearly as peaks in $d\sigma(V)/dV$. In Fig. 1(b) the inelastic structure for negative biases is seen to differ in size from the structure for positive biases. Thus, it is more convenient to display the inelastic tunneling by plotting the even conductance $\sigma_e = \frac{1}{2}[\sigma(+V) + \sigma(-V)]$ and its derivative $d\sigma_e/dV = \frac{1}{2}[d\sigma(+V)/dV - d\sigma(-V)/dV]$.

In order to compare the various junctions having different conductances it is convenient to normalize the data at some specific conductance. A useful value is the zero-bias conductance, but since we used superconducting lead we have normalized our data at 30 meV where the conductance only differs by (1 to 3)% from that at zero bias. Thus, our data are presented with $\sigma_e(V)/\sigma(30)$ or $[1/\sigma(30)] \times d\sigma_e(V)/dV$ as ordinates.

III. RESULTS

Inelastic tunneling via hydroxyl ions and hydrocarbon molecules has been observed in many studies of barriers grown on aluminum. The results shown below indicate that the particular bands which are observed depend not only on the materials used but also on the method of barrier preparation. A summary of the preparation techniques used is listed in the Appendix. So the reader may appreciate the similarities and differences between the various types of barriers, all the junctions except the glycine doped ones, are plotted

on a common scale in Figs. 2(a) and 2(b). In order to discuss them in more detail they are replotted in Figs. 3–5.

The curves for barriers prepared by an oxygen-helium glow discharge (1035), thermally in oxygen (1120), and thermally in oxygen followed by an argon glow discharge (1180) are shown in Fig. 3. These curves lie on top of each other in Fig. 2(b) so they have been vertically offset in Fig. 3. The peak near 36 meV is due to longitudinal phonons¹⁵ in the aluminum electrode. It is found in all our junctions and will not be discussed since our interest is in the barrier modes. Between 30 - and 250 -meV junctions 1120 and 1180 are identical to each other. Their only structure is the prominent peak near 115 meV which has been identified as due to an alumina hydrate^{1,2} bending mode. Junction 1035 is very similar except that the 115 -meV peak is about 20% larger, and its second harmonic is found near 230 meV. Junction 1035 also has a shoulder around 77 meV which is due to an OH bending mode.² All three curves have a peak near 450 meV which is due to an OH stretching mode.¹ Only junction 1120 which was prepared thermally in oxygen shows a hydrocarbon CH stretching mode near 360 meV.¹

We have never observed CH peaks in our glow discharge prepared barriers while they do occur in the thermally prepared ones. The differences may be either the shorter exposure time, 15 min at 200 μ m pressure for a glow discharge preparation versus 16 h at $\frac{1}{2}$ atm for a thermal preparation, or that the glow discharge may be sputtering hydrocarbon molecules off the oxide, or it may be breaking the CH bonds. To help clarify the picture, some barriers made using the thermal oxygen technique were exposed to an argon glow discharge. Junction 1180 illustrates that the result is a spectrum identical to that for junction 1120 but lacking the CH stretch. This indicates that using a discharge influences the barrier content.

These assumptions were tested further by examining several junctions prepared with water. Shown in Fig. 4 are junction 1085 which was prepared by exposing an aluminum film to a water vapor glow discharge, and junction 1047 which was prepared by pipetting water onto aluminum. The spectrum for junction 1085 has a distinct OH bending band near 77 meV and a distinct aluminum hydrate band near 115 meV. It also has a strong alumina hydrate second harmonic near 230 meV and a band near 162 meV which we tentatively identify as a second harmonic of the OH bending band near 77 meV. The justification for this is that we have only observed the peak near 162 meV along with a strong peak near 77 meV.

Comparison shows that the alumina hydrate peak near 230 meV and the OH bending band near

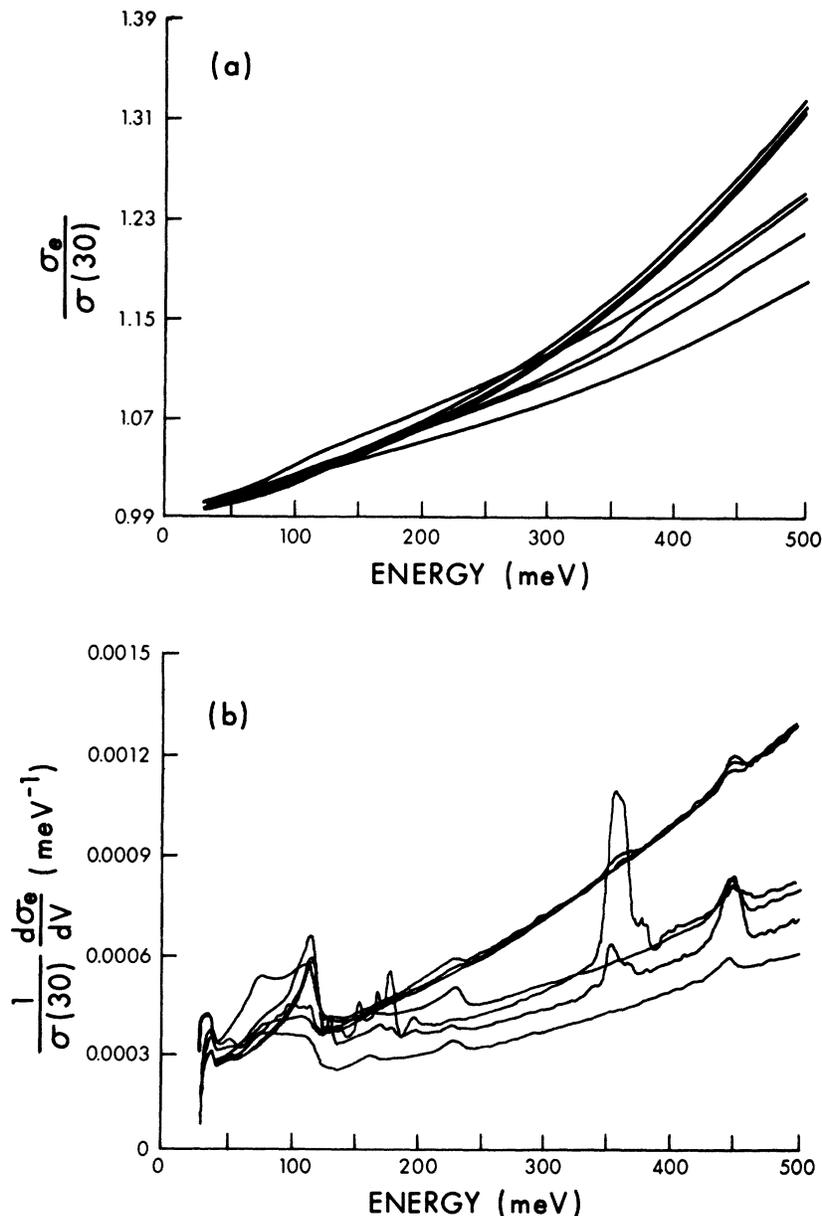


FIG. 2. Normalized even part of the conductance (a) and normalized derivative of the even part (b) for all but the glycine-doped barriers.

77 meV increase in amplitude in the sequence 1120, 1035, and 1085. A careful measurement shows that the alumina hydrate peak shifts from 116.2 meV for 1120 to 114.2 meV for 1035 to 112.7 meV for 1085. The implication is that the hydrate structure is slightly different for each of these junctions. The average oxygen-hydrogen bond strength must decrease to account for the downward shift of the peak. This weaker average bond strength allows larger amplitude vibrations, which means that anharmonic terms in the potential become more important and thus second harmonic peaks become visible.

The spectra for junctions such as 1047, which were prepared by pipetting water onto an aluminum base film, are considerably different from those shown so far. These junctions have a low-intensity plateau in the region between 77 and 115 meV rather than the distinct peaks of junction 1085. Even though there is no distinct alumina hydrate near 115 meV, its harmonic is found near 230 meV. The OH stretching band around 450 meV is more intense for this junction than for the others shown in Figs. 3 or 4. The CH stretching band near 360 meV and the CH bending bands near¹ 172 meV and¹ 179 meV clearly indicate the presence of hy-

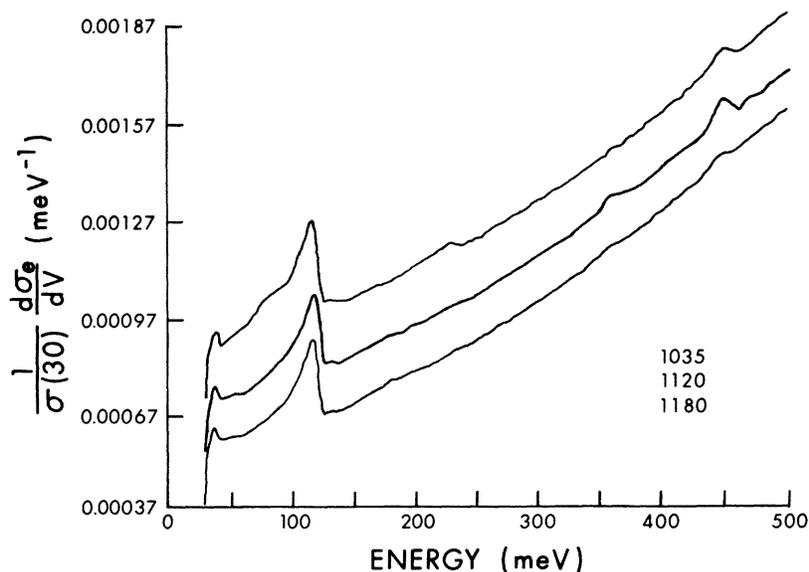


FIG. 3. 1035, oxygen-helium glow discharge barrier, curve vertically offset one full unit; 1120, barrier grown thermally in oxygen, curve vertically offset $\frac{1}{2}$ unit; 1180, barrier grown thermally in oxygen then exposed to an argon-glow discharge.

drocarbon contamination. The impurities causing the bands near 131 and 198 meV have not been identified. We interpret the lack of a strong alumina hydrate band to mean that these barriers are more amorphous than those prepared by a glow discharge. In this case the hydroxyl ions have a wider range of bonding strengths to the aluminum ions giving rise to a wider range of energies. This assumption is compatible with the problems we had in making junctions by pipetting pure water onto an aluminum film. Several of these samples resulted in junctions which were unstable at various bias voltages. By applying a 1.5-V bias across the barrier for about a minute at 4 K the insta-

bilities could be moved to a higher energy band with a different band width, while the junction resistance remained unchanged.

Junction 1127 is shown in Fig. 5 to illustrate the effect of a glow discharge upon a barrier which was prepared in the same way as junction 1047. This junction, like 1047, has a broad plateau between 77 and 115 meV. The second harmonics of the 77-meV OH band and 115-meV alumina hydrate are clearly visible at the appropriate energies. There are no signs of any CH bands implying that the argon discharge has either sputtered the hydrocarbon molecules from the barrier, or broken the CH bonds. The same mechanism

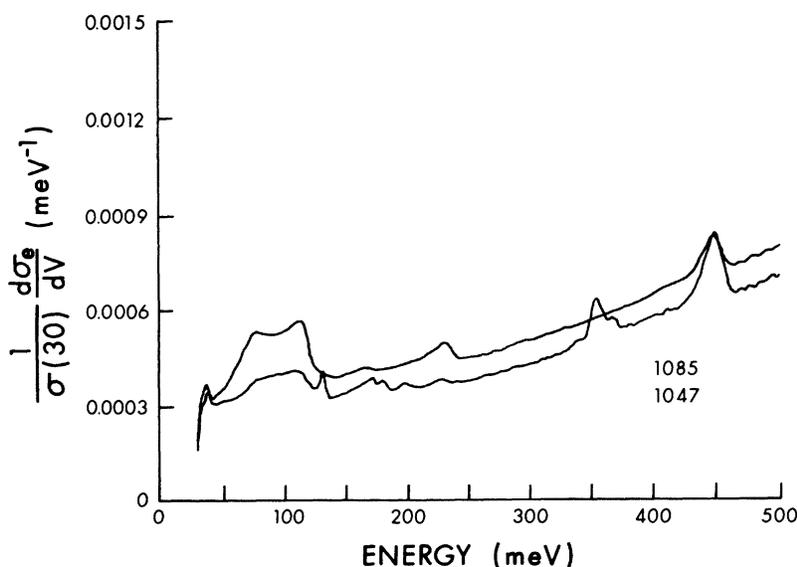


FIG. 4. 1085, barrier grown in water-vapor glow discharge; 1047, barrier grown by pipetting water.

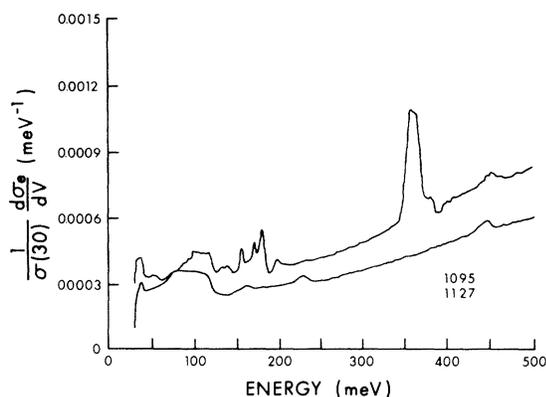


FIG. 5. 1127, barrier grown by pipetting water then exposed to an argon glow discharge. 1095, barrier grown thermally in water vapor.

must also be responsible for the decrease in the intensity of the 450-meV OH stretching band.

Junction 1095 which is also shown in Fig. 5 was prepared thermally in water vapor. The presence of the CH stretching peak near 360 meV further illustrates that the water contains hydrocarbons. Comparison of this junction with junction 1085, which was prepared by water glow discharge, and with junction 1047, which was prepared by the water pipetting technique, demonstrates that the spectrum depends upon preparation technique.

Solutions containing organic molecules were also used to grow barriers on aluminum films. For these junctions the tunneling spectrum consists of bands from the organic molecule superimposed on a background composed of the bands discussed above. To examine the problem of identifying which bands are due to the organic doping, we have studied several junctions prepared with aqueous glycine¹⁶ solutions. The solution used to prepare junction 1065, which is shown in Fig. 6(a), contained ten times more glycine than that used to prepare 1066 which is also shown there. For comparison, junctions 1035 and 1047, which were discussed earlier, are shown in Fig. 6(b).

In over-all shape, 1065 is similar to 1035 and 1066 is similar to 1047, but both 1065 and 1066 contain more bands than 1035 and 1047 together. A detailed examination shows that 1065 contains peaks near 115 and 230 meV which are identical to the alumina hydrate peak and its second harmonic found in 1035. 1065 also contains hydrocarbon peaks near 172, 179, and 360 meV just as 1047 does, but in 1065 they are much larger. Neither junction 1035 nor junction 1047 has a spectra which adequately describes the background for these solutions. Junction 1035 lacks the hydrocarbon contamination from the water, while

1047 lacks the alumina hydrate peaks. The alumina hydrate peaks are the harder ones to deal with because it is not known how much alumina hydrate will be produced by a solution. Note, for example, that junction 1066 has a much smaller peak near 115 meV. On the other hand, the hydrocarbon peaks in 1047 could be subtracted from those in 1065 or 1066 since the same water was used for all these junctions. Thus, a great deal of care must be used in analyzing the tunneling spectrum of doped junctions.

IV. SUMMARY

Three observations can be made as a result of the data presented in this paper. The first is that the techniques used to grow a barrier on aluminum is as important as the materials used in determining the barrier content. The dependence upon technique is best illustrated by comparing the hydroxyl and hydrocarbon bands in the tunneling curves of barriers grown with water. The glow discharge junctions had distinct OH bands but no CH ones, while the other techniques showed fewer distinct OH peaks and intense CH peaks. The technique used was much less important for barriers grown in oxygen.

The second observation is that a glow discharge can be used to remove hydrocarbon peaks from tunneling curves. The glow discharge may be breaking CH bonds and leaving isolated carbon and hydrogen atoms or it may be sputtering the hydrocarbons off the barrier. One of the implications of this observation is that drastic precautions need not be taken to eliminate hydrocarbons from a vacuum system in order to produce barriers which show no inelastic processes involving hydrocarbons. Since the conclusion of these experiments we have reduced our precautions and have continued to make hydrocarbon free junctions with a glow discharge.

Finally, we examined the problems of choosing a background spectrum when doing spectroscopic studies on doped barriers. The background spectra for barriers grown by pipetting aqueous solutions onto aluminum may contain hydroxyl and hydrocarbon bands. The hydrocarbon part can be found by looking at the spectrum for barriers grown by water alone. Barriers grown by water do not have alumina hydrate peaks like barriers grown in a glow discharge, but the solutions being studied may produce them. Indeed, the glycine solutions reported in this paper have peaks near 115 and 230 meV which are similar to the alumina hydrate peaks found for an oxygen-helium glow discharge grown barrier. Thus, care must be used when identifying peaks in a spectroscopic experiment. The background spectra cannot be

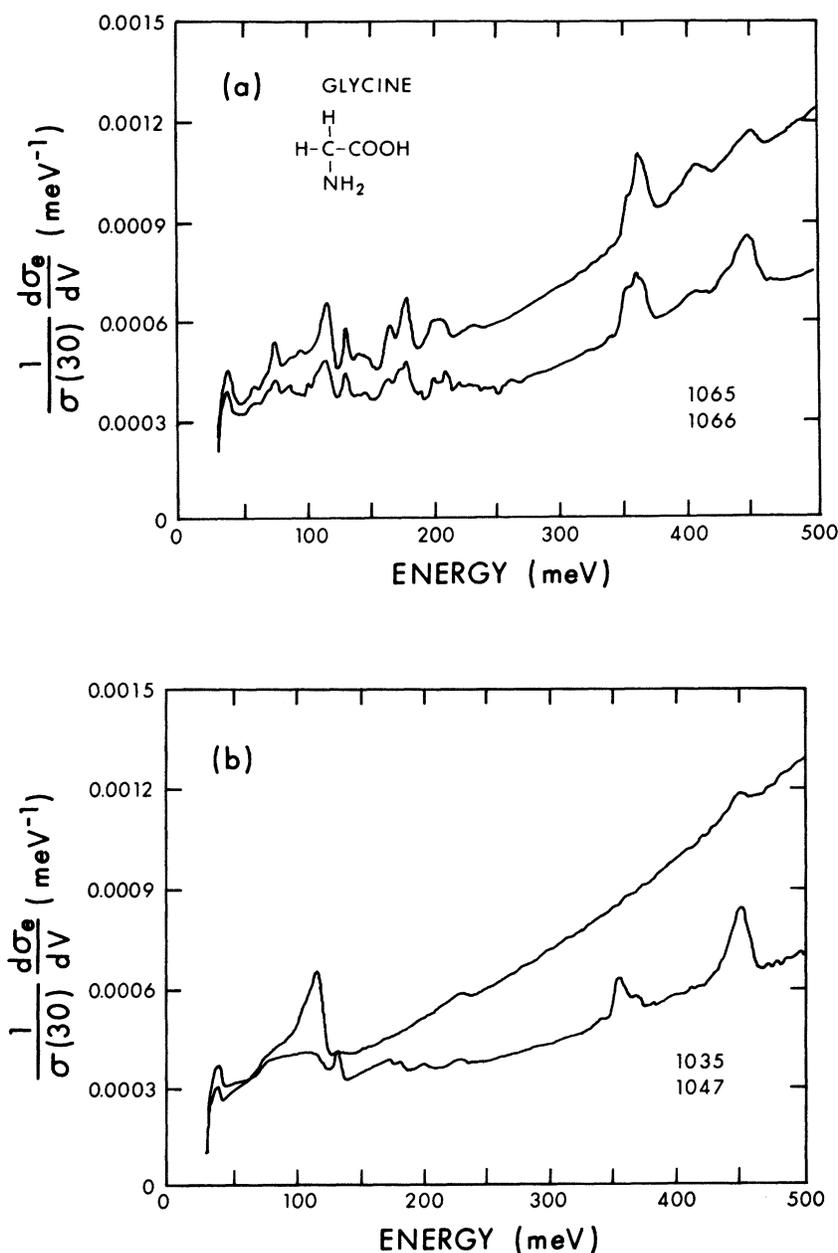


FIG. 6. (a) 1065 and 1066, barriers grown by pipetting glycine solutions onto fresh aluminum; (b) 1035, oxygen-helium glow discharge prepared barrier and 1047, barrier prepared by pipetting water onto fresh aluminum.

determined simply by looking at the spectra for water or that for a glow discharge prepared barrier.

The presence of the alumina hydrate structure in the glycine prepared barriers is of interest by itself. It suggests that the ions and electric field present at the barrier surface during its growth were similar to those present during an oxygen-helium glow discharge preparation. Miles and Smith first suggested this similarity in 1963,¹⁷ but the details of both processes are still uncertain.

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APPENDIX: SUMMARY OF PREPARATION TECHNIQUE

(1) 40%-oxygen-60%-helium glow discharge: 500 V, 15 min, 200- μm pressure, example 1035.

(2) Water-vapor glow discharge: 500 V, 15 min, 250- μ m pressure, example 1085.

(3) Thermal oxygen: 300 °C, 16 h, $\frac{1}{2}$ atm. example 1120.

(4) Thermal water: 300 °C, 2 h, 10-Torr pressure, example 1095.

(5) Pipet water: remove fresh aluminum film from bell jar, pipet water on for 60 sec, blow dry with helium gas, put back in the bell jar, example 1047.

(6) Pipet solution: same as (5) but used aqueous glycine for 20 sec, example 1065.

(7) Thermal oxygen plus argon glow-discharge: same as (3), but followed with an argon glow discharge, 500 V, 5 min, 100- μ m pressure, example 1180.

(8) Pipet water plus argon glow discharge: same as (5), but followed with an argon glow discharge, 500 V, 15 min, 100- μ m pressure, example 1127.

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