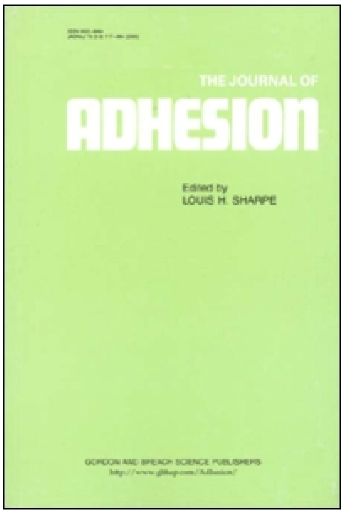

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article White, H. W. , Godwin, L. M. and Wolfram, T.(1978) 'A New Method for the Study of Adhesion: Application of Inelastic Electron Tunneling Spectroscopy', The Journal of Adhesion, 9: 3, 237 — 249

To link to this Article: DOI: 10.1080/00218467808075117

URL: http://dx.doi.org/10.1080/00218467808075117

J. *Adhesion*, 1978, Vol. 9, pp. 237–249

Printed in Scotland

A New Method for the Study of Adhesion: Application of Inelastic Electron Tunneling Spectroscopy†

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(*Received December 19, 1977*)
In Final Form March 15, 1978

Inelastic electron tunneling spectroscopy provides an incredibly sensitive and versatile method of detecting and identifying molecular species adsorbed on the surface of a metal oxide. IETS spectra have been measured on the components of the commercial adhesive, Hercules 3501. This epoxy system consists of two molecular components; diamino diphenyl sulfone (DPS) and tetraglycidycl 4,4′ diamino diphenyl methane (DPM). IETS spectra of the individual components and of the epoxy mixture adsorbed on aluminum oxide have been obtained and the vibrational modes and frequencies assigned by comparison with computer calculations and existing infrared optical spectra.

INTRODUCTION

A reliable metal adhesive joint must be resistant to both cohesive and adhesive failure. Cohesive failure involves initiation and propagation of cracks in the adhesive layer; whereas, adhesive failure involves initiation and propagation at the adhesive/adherend interface. Studies using ultrasonics, electron microscopy and other techniques have provided critically important information on the bulk properties and, to a lesser extent on the nature of the adhesive/metal oxide interface. The main reason that it has been difficult to characterize the adhesive/oxide interface is due to its small thickness which is of the order of 10 to 100 Å.

Inelastic electron tunneling spectroscopy (IETS) can play an important role in obtaining information about the interface by providing an extremely sensitive method for monitoring the chemical and physical state of a molecular substance adsorbed onto an oxide surface. Inelastic tunneling data directly

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† Supported in part by ARPA/AFML Contract No. F33615-74-C-5180.

reflect the molecular vibrational frequencies of the first monolayer of adsorbed molecules. Changes in the vibrational spectrum can be correlated with changes in the chemical state of the molecule/oxide interface. IETS does not follow the selection rules of either infrared or Raman active modes; both of these types of modes are present in IETS spectra.

Black and Blomquist[1] have studied several metal adhesive systems and find that exposure to a heat treatment decreases shear strength significantly, often by more than a factor of two. It was their conclusion that the primary reason for this decrease in shear strength was due to catalytic action at the bondline. The fracture lines associated with failure often originate in the adhesive/adherend interface region (i.e., bondline), as depicted by the dashed line in Figure 1 which is the schematic of a typical adhesive bond with aluminum components. IETS is a particularly useful tool for monitoring the chemical state of an interface of the type encountered in the adhesive bonding of such components.

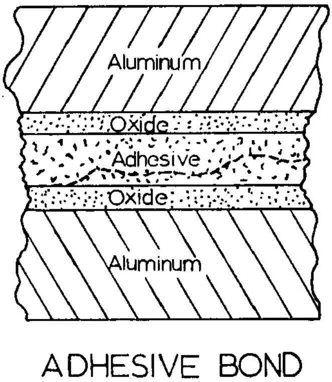


FIGURE 1 Schematic of a typical adhesive bond with aluminum components. The dashed line represents a fracture surface.

Hydrothermal aging is believed to be one of the most important causes for bond failure in service. IETS can provide a unique method for studying how water which permeates a bond contributes to its degradation. The role of the water at the interface is considered to be very important but to date there have been no good means of studying its effect. The effects of water permeation can be studied using H_2O, or by using D_2O as a tracer so that it can be distinguished from H_2O already present in a tunnel junction as a contaminant.

We have carried out IETS experiments on the components of the commercial adhesive, Hercules 3501. This epoxy system consists of two molecular components; diamino diphenyl sulfone (DPS) and tetraglycidycl 4,4′diamino diphenyl methane (DPM). IETS spectra of the individual components and of the epoxy mixture adsorbed on aluminum oxide have been obtained and the vibrational modes and frequencies assigned by comparison with computer calculations and existing infrared optical spectra. Some evidence for an aging effect has been observed for the adsorbed DPS. This effect appears as a dramatic change in the low frequency vibrational modes and may be associated with the formation of hydrogen bonds or the polymerization of the DPS. Further studies of this effect are in progress.

DESCRIPTION OF IETS

Inelastic electron tunneling spectroscopy provides an incredibly sensitive and versatile method of detecting and identifying molecular species adsorbed on the surface of a metal oxide.

The phenomena of inelastic electron tunneling was discovered by Jaklevic and Lambe in 1966.[2, 3] In the last few years the enormous potential of IETS as a diagnostic tool has begun to be realized. Applications include studies of molecular adsorption,[4, 5] identification of trace substances[6] and biological molecules,[7, 8] studies of radiation damage to biological molecules,[9] and studies of catalytic particles.[10] A review of IETS has been given recently by Hansma.[11]

IETS involves the tunneling of electrons through the passivating oxide layer of a metal/metal oxide/metal thin film junction. A typical tunnel junction is fabricated by evaporation of a thin metallic film such as aluminum onto a glass or ceramic substrate. The film is then oxidized to form an oxide layer 20 to 30 Å in thickness. A molecular substance to be studied is then deposited onto the oxide by one of a varity of "doping" techniques. In the usual case the molecular layer is 5 to 25 Å in thickness. Finally, a second metallic film (often lead) is deposited over the molecular layer forming a thin film junction as shown in Figure 2.

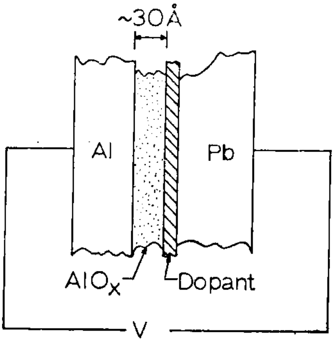


FIGURE 2 Schematic cross section of an aluminum/aluminum oxide/dopant/lead tunnel junction showing the application of a bias voltage *V*.

A variable bias is applied across the junction terminals and the current is measured. Since the oxide layer is an excellent insulator only a small current of the order of milliamperes flows across the junction. This current is due to electrons which tunnel (in the quantum mechanical sense) through the insulating oxide barrier. A schematic of the tunneling process is given in Figure 3. Figure 3a illustrates the *elastic* tunneling process in which an electron tunnels through the oxide barrier from an occupied state below the Fermi level in the aluminum to an unoccupied electron state above the Fermi level of the lead film. Electrons which tunnel without loss of energy contribute to the elastic tunneling current. Figure 3b illustrates an *inelastic* tunneling process. In this case the tunneling electron interacts with a molecule adsorbed on the oxide and excites one of the characteristic vibrational modes of the molecule. If the molecular vibrational frequency is ν_m then the energy lost by the tunneling electron is $h\nu_m$. It is evident from the diagram that the threshold bias for such an inelastic tunneling event is $eV_{\text{threshold}} = h\nu_m$. There is a different threshold voltage for each vibrational mode of the molecules on the oxide.

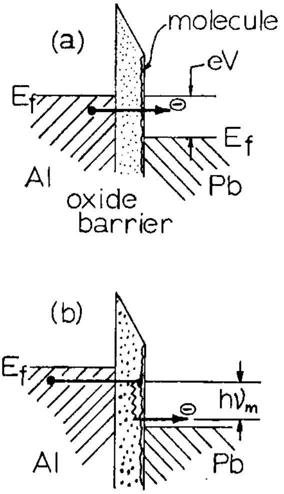


FIGURE 3 The tunneling process associated with elastic tunneling is shown in Figure (a). Figure (b) shows the process for inelastic electron tunneling.

At a threshold voltage there is an abrupt change in the slope of the current–voltage characteristic of the tunnel junction. This change is illustrated in Figure 4a. The detection of this effect can be greatly enhanced by using electronic modulation methods to record the junction conductance $G = dI/dV$ and the second derivative d^2I/dV^2. An inelastic tunneling process changes the junction conductance by a percent or so as illustrated in Figure 4b. The effect in d^2I/dV^2 is very large as shown in Figure 4c since the only sharp structure in the conductance is due to inelastic tunneling. Experiments are almost always performed at liquid helium temperatures in order to eliminate thermal smearing of tunneling structure. The sensitivity of the technique is truly remarkable; a fraction of a monolayer or as few as 10^{10} molecules are easily studied.

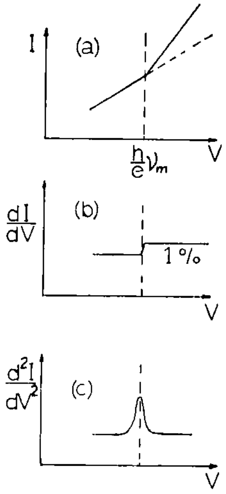


FIGURE 4 Figure (a) shows the increase in the tunneling current I at the voltage $V = h\nu_m/e$. Figures (b) and (c) show the changes in dI/dV and d^2I/dV^2, respectively.

The appearance of a d^2I/dV^2 versus V curve is very similar to an infrared absorption spectra in that peaks in the IETS and dips in the IR spectra correspond to the location of vibrational modes. There are significant differences, however. All the vibrational modes appear in an electron tunneling spectrum but only those vibration modes which have a dipole moment will be observed in an infrared spectrum. For example, some symmetric vibrational modes are observed in tunneling but not in infrared absorption. The reasons for differences in selection rules for electron tunneling are as follows:

1) The de Broglie wavelength of the tunneling electron is of the order of the molecular dimensions so that the dipole approximation is invalid.

2) The electron is a strongly interacting particle and polarizes the molecules,

3) The electron interacts through both the molecular dipole and the polarizability tensor.[3, 11]

IETS can be used to identify various interface molecular species by comparing the d^2I/dV^2 versus V curves with available infrared spectra. Experiments have been performed which show that it is possible to distinguish between physically adsorbed molecules and those which have reacted with the oxide layer.[12, 13] For example, the studies of phenol [12] using IETS show that it is adsorbed predominantly as $C_6H_5O^-$ and that hydroquinone is adsorbed principally as $C_6H_4(OH)O^-$ and in the di-ion form $C_6H_4O_2^{2-}$. Other IETS experiments show that organic acids react with the oxide to form surface complexes involving the aluminum cations.[13]

IETS can also be used to identify various hydroxyl ions and water present on and in a typical passivating oxide. Evidence of hydrogen bonding between surface hydroxyls has also been demonstrated.[12]

There is a strong orientational dependence of the intensity of vibrational modes which are observed by IETS. It has been theorized [11] that when the oscillating molecular dipole is oriented parallel to the oxide surface the corresponding IETS intensity will be weak and primarily due to "Raman" like vibrational modes. The intensity is expected to be large when the molecular dipole is perpendicular to the oxide surface due to strong excitation of "infrared" like modes. These orientational effects have been verified in a number of IETS experiments including studies of benzoic acid [11] and aromatics. Korman and Coleman [14] have used intensity data to deduce information about the orientation of a variety of adsorbed nitro substituted single aromatic ring compounds. They also were able to derive information about the chemisorption bonds of the aromatic series.

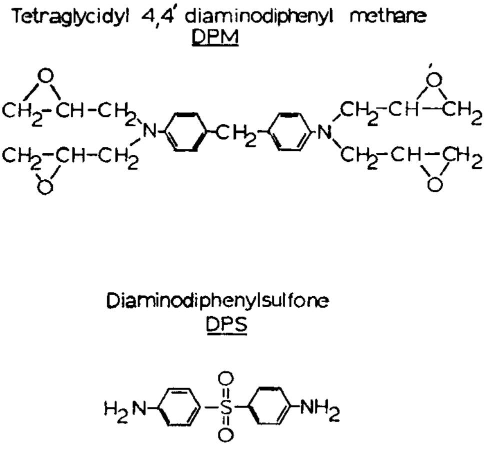
In summary, it is evident that the method of IETS is capable of detecting monolayer and sub-monolayer coverages of molecular species on an oxide film. The resolution and sensitivity of IETS are sufficient to distinguish between physically adsorbed molecules and molecular species formed by chemical reaction at the interface. Using knowledge of which modes are Raman or infrared active together with IETS peak positions and intensity data allows rather detailed information on the nature of adsorbed species to be determined. Finally, by use of various isotopes and chemically substituted side groups it is often possible to make definitive conclusions on the type of molecular species present.

Interpretation of IETS data is hampered by the fact that at the present time there is no theory which allows even the relative intensities of an IETS spectrum to be calculated. The calculation of d^2I/dV^2 versus V for a simple molecule is not an easy task and progress in this area has been slow. Some recent efforts on this problem have been presented.[15]

Specific considerations of how IETS experiments can be devised to study the adhesive bond formed between the adsorbed molecules and the aluminum oxide layer are presented in the next section.

EXPERIMENTAL PROCEDURE

The two molecules which form the epoxy system chosen for study are shown in Figure 5. The upper one is the epoxy tetraglycidycl 4,4′ diamino diphenyl methane (DPM), and the other is diamino diphenyl sulfone (DPS) which is the curative for the DPM. The molecular structure for both of these molecules and their cross-link molecule is complicated. The atoms for the DPS molecule lie in two planes whose intersection is a line in the plane defined by the two oxygens and the sulfur. A modified tetrahedral bond is formed about the oxygen by the two sulfur and two carbon atoms. The DPM molecules are even more 3-dimensional with four identical arms, each with an epoxy ring. These molecules also have an added disadvantage in that interpretation of their spectra must be done with the awareness that they form dimers relatively easily, even at room temperature.



Tetraglycidyl 4,4′ diaminodiphenyl methane
DPM

Diaminodiphenylsulfone
DPS

FIGURE 5 Schematics of the two molecules which form the epoxy resin (DPM) and curative (DPS) of Hercules 3501.

The cross-link reaction for the DPM and DPS molecules is shown in Figure 6. In the cross-linked molecule there is an OH group on each arm. The arms in the cross-linked structure link with other arms in a somewhat disorganized fashion. The result is a very 3-dimensional structure. The methane group and rings are incorporated into the matrix.

Bonding to the aluminum oxide probably occurs through the OH group, in much the same way in which phenol bonds to an aluminum oxide film, namely, as $C_6H_5O^-$.[12] The OH groups make this molecule very polar and

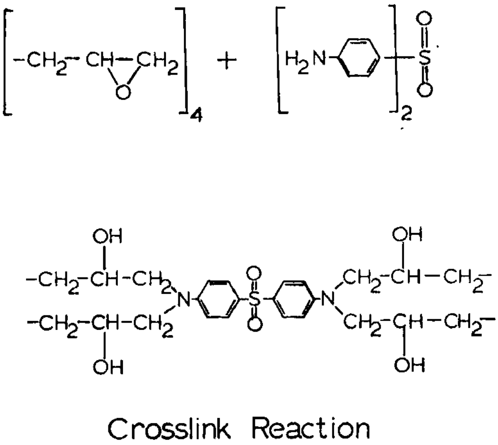


FIGURE 6 Schematic of the cross-linked reaction and molecule for Hercules 3501.

thereby susceptible to water permeation. The presence of water on the substrate could adversely affect the bonding properties.

Aluminum/aluminum oxide/dopant/lead tunnel junctions were fabricated where "dopant" refers to the molecules on which IETS spectra are to be obtained. First, the aluminum electrode was evaporated at 10^{-6} Torr, followed by the growth of an oxide layer using glow discharge in a partial pressure of oxygen. Approximately one monolayer of the sample molecule was deposited on the oxide by placing one drop of a dilute solution of the molecule to be studied on the electrode, and spinning off the excess. The solution concentration is varied until the proper resistance for the junction is obtained, but it is usually in the range 0.1 to 1.0 mg per ml. A lead counter electrode was then evaporated over the molecules, again at 10^{-6} Torr.

Ideally a solvent with a simple molecular structure is used to dissolve the sample molecules to avoid complicating the spectrum with the vibrational modes of the solvent molecules. However, the DPM resin was not easy to dissolve. Methyl ethyl ketone (mekol) and tetrahydrofuran (THF) worked best, neither of which is as simple in structure as would have been desired. These two solvents, and to a lesser extent chloroform, dissolved the DPS curative.

Figure 7 is a block diagram of the spectrometer system. The junction is cooled to 4.2 K. A d.c. bias across the junction is slowly swept from 50 to 500 millivolts. An a.c. signal of 1000 Hz and approximately 1 millivolt (rms) is applied continuously. The amplitude of the second harmonic signal as generated by the tunnel junction is recorded on an XY recorder as a function of the d.c. bias. The second harmonic signal is proportional to d^2V/dI^2. Peaks in this signal locate the energies of the vibrational modes as read from the bias voltage (energy) scale.

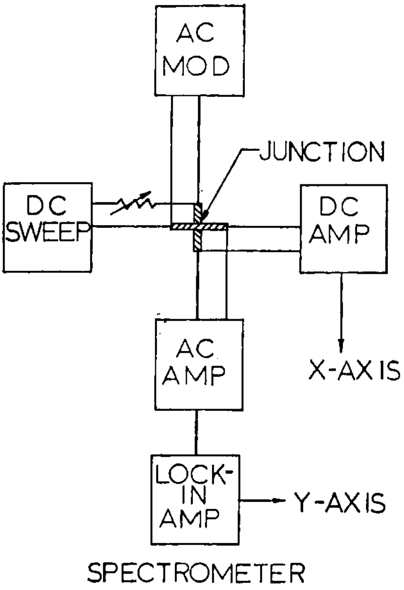


FIGURE 7 Block diagram of the important components of the IETS spectrometer used for the measurements.

RESULTS

Spectra were first obtained on each of the molecules, then for the two molecules placed together on the same junction. This work is to be followed by studying the effects of heat treatment and hydrothermal aging on the observed spectra. Figure 8 shows two curves, A and B, taken on a junction doped with DPS using mekol as a solvent. The energy range is from about 50 to 500 millielectronvolts (meV), which corresponds approximately to the wavenumber range 400 to 4000 cm^{-1} (1 meV = 8.066 cm^{-1}). The OH stretch peak near 450 meV is observed in most IETS spectra. The CH stretch near 355 is found in all hydrocarbon spectra. The lower energy peaks for the DPS molecule were assigned by comparison with IR, other IETS data, and with normal mode frequencies calculated using literature values for the force constants. Both atomic motions and frequencies were obtained from the normal mode calculations. If an observed peak was more than 3 meV from a calculated vibrational energy a question mark was placed after its assignment label in Figure 8. The measured locations in meV are shown following the group assignment. The S=O bend at 197 is close to the calculated value of 196 meV; however, the assignment is not certain since DPM in Figure 9

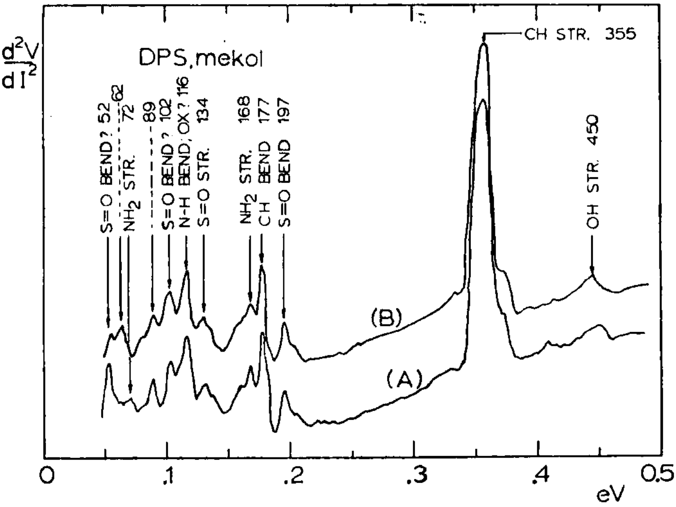


FIGURE 8 Two IETS spectra, A and B, taken on a junction doped with DPS using mekol as a solvent.

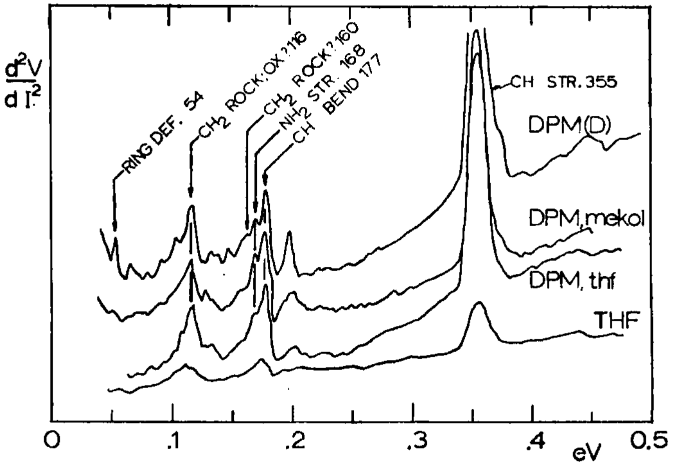


FIGURE 9 IETS spectra for four separate junctions. The lower curve is for a junction doped with the solvent THF, the junctions for the two middle curves were doped with DPM dissolved in THF and mekol, and the upper curve is for a deuterated DPM junction.

also shows a peak near 197. The CH band at 177, the NH_2 stretch at 168 and the S=O stretch at 134 meV agree well with calculated vibrational energies and other data. The peak at 116 meV could be either a NH bend or an oxide phonon. Many doped junctions and nearly all undoped junctions show the presence of an oxide phonon at 117; however, the calculated vibrational energy for the NH bend is 115 meV. The peak at 102 meV was tentatively identified as an S=O bend since this group had a calculated frequency near 98 meV. The assignment at 52 meV was made in the same manner except that the S=O motion had a calculated frequency of 48 meV.

Until now the features discussed have been the same for both spectra A and B. In the energy range 55 to 75 meV the spectra are different. Spectrum A was taken on the junction soon after preparation. Spectrum B was taken nine days later, during which time the junction had been stored in a clean, dry atmosphere. The junction resistance remained constant at 1500 ohms. Spectrum A shows a small peak at 72 meV which is within 2 meV of the value of the normal mode energy calculated for an NH_2 stretch in DPS. Spectrum B shows no evidence for a peak at 72 meV but shows a new distinct peak at 62 meV. An aging effect has occurred. There is very little evidence in the literature of any polymerization occurring inside of a tunnel junction, but there is evidence for chemisorption. We speculate that the NH_2 groups on the ends of the DPS molecule have chemisorbed to the oxide layer.

Figure 9 shows the spectra of four separate junctions. The lower curve is the spectrum for a junction doped with only the solvent THF. It serves as a background spectrum. Both THF and mekol spectra show a small peak near 174 meV which is undoubtedly due to CH bend modes and a small peak near 117 meV which is probably due to an oxide phonon. The second curve from the bottom, labeled "DPM, THF" is for the DPM opoxy molecule dissolved in the THF. Again, there is a large CH stretch peak located at

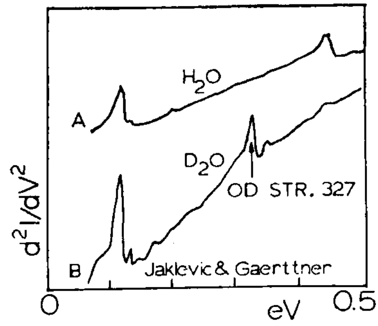


FIGURE 10 A portion of the figure from the work of Jaklevic and Gaerttner which illustrates the diffusion and detection of D_2O into a tunnel junction after fabrication.

355 meV. The third curve labeled "DMP, mekol" shows essentially the same features as the second. The peak at 177 meV is probably a CH bend. The peak at 168 meV is probably due to NH_2 stretch modes. CH_2 rock modes are expected to be observed near 116 meV; however, the peak at that location could be due, at least in part, to an oxide phonon expected near 117 meV.

The curve labeled "DPM(D)" is a spectrum for DPM which has been deuterated by an exchange reaction before placing in the junction. One of the goals of this project is to study the role of water at the interface of an adhesive bond. Water can be diffused into a junction and its presence can be monitored by using D_2O as tag molecules. The "DPM(D)" spectrum was taken to provide information on the size and location of peaks associated with a deuterated DPM molecule. The spectrum has peaks not observed in other spectra. We must be cautious in our interpretation of this spectrum since some structural changes may have occurred during the deuteration process.

Jaklevic and Gaerttner have reported the observation of IETS spectra of molecules which were introduced into completely fabricated tunnel junctions.[16] Figure 10 is a portion of their Figure 1 and illustrates the appearance of the D_2O. Curve A shows a clean junction made in the presence of H_2O vapor. Note the OH stretch at 450 meV. Curve B is the spectrum for a clean junction exposed to D_2O vapor after fabrication. The peak at 327 meV is an OD stretch mode indicating that D_2O penetrated into the junction. This new technique of external doping appears to be a very promising technique for studying the interaction of adhesive molecules with surfaces. Of particular interest to us is the diffusion of H_2O and D_2O into and out of tunnel junctions under the proper experimental conditions.

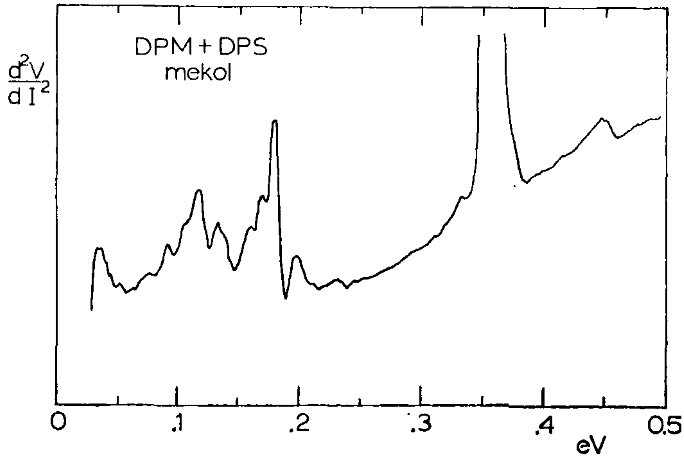


FIGURE 11 IETS spectrum for a junction containing both DPS and DPM molecules.

Figure 11 shows the spectrum for a junction containing both DPS and DPM molecules. The features are similar to those in spectrum A of the DPS molecule. One reason for this similarity may be due to the fact that the signature for the DPS molecule was always much stronger than that for the DPM molecule. Obtaining good noise-free junctions was considerably more difficult for the DPM molecule than for the smaller DPS.

SUMMARY

IETS is a useful tool for the study of molecular adhesion to an oxide. It is one of the most important methods available for determining the interface physics and chemistry of adhesive bondlines. Its usefulness is greatly enhanced by the fact that *in situ* studies can be made.

Spectra have been obtained on the components and mixture of the high performance, two component epoxy Hercules 3501. The vibrational modes were identified by comparison with infrared and Raman data, and with computer calculations using force constant information. Evidence for an aging effect was found in the DPS component.

It is suggested that initial studies using IETS should be applied to adhesives of simple molecular structure before proceeding to more complex systems.

Acknowledgements

The authors express their appreciation to D. O. Thompson for suggestion of the problem, to D. Kaelble, W. D. Bascom, R. C. Jaklevic and J. Lambe for helpful discussions, and to H. Kim for providing a program for calculation of vibrational mode frequencies. We thank P. K. Hansma for help in designing the spectrometer system.

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