Inelastic electron tunneling spectroscopy, or IETS, provides an extremely sensitive method for monitoring the chemical and physical state of a molecular substance adsorbed onto an oxide surface. Inelastic tunneling data directly reflect the molecular vibrational frequencies of the first monolayer of adsorbed molecules and changes in the vibrational spectrum can be correlated with changes in the chemical state of the molecule/oxide interface. 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 sulfope (DPS) and tetraglycicydyl 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. The effects of water permeation may be studied using D2O as a tracer. The vibrational modes of D2O are easily distinguished from those of water which may be present as a contaminant. If the exchange reaction D2O + H2O + DHO + BCR occurs, it would be easily detected in the IETS spectrum. Initial experiments performed by simply immersing the tunnel junction into liquid D2O for several hours were unsuccessful because severe corrosion of the tunnel junction resulted. Experiments employing aluminum/aluminum oxide/adhesive/gold thin film junction for the study of H2O permeation are in progress. Further studies are planned to monitor the effects of heat treatment on the adhesive components and mixture.

Introduction

The objective of this program is to assess the feasibility of utilizing Inelastic Electron Tunneling Spectroscopy, or IETS, to monitor the chemical state of an adhesive/adherend interface of the type encountered in the adhesive bonding of aluminum components. The goal of the project is to determine what changes occur at an adhesive bondline during thermal curing and in bond degradation resulting from hydrothermal aging. Through such studies we hope to determine some of the important mechanisms of adhesive bond failure. IETS provides an extremely sensitive method for monitoring the chemical and physical state of a molecular substance adsorbed onto an oxide surface. Inelastic tunneling data directly 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. Since aluminum and other metals used in adhesive bonds have an oxide covering, the molecule/oxide interface geometry in inelastic tunnel junctions closely approximates that found in real adhesive systems. The method of IETS is not directly applicable as an "on-line" NDE technique but specific information concerning the mechanisms of bonding and bond degradation is needed in order to devise more meaningful NDE procedures.

We have carried out IETS experiments on the components of the high performance commercial adhesive, Hercules 3501. This epoxy system consists of two molecular components; diamino diphenyl sulfope (DPS) and tetraglycicydyl 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 low frequency vibrational modes and may be associated with the formation of hydrogen bonding of the NH2 groups to the oxide layer.

The effects of water permeation are being studied. D2O is being used as a tag molecule since it has vibrational modes which are easily distinguished from those of H2O. Using a new and exciting technique called external doping, molecules of H2O and D2O can be introduced into or removed from an already fabricated tunnel junction.

Experimental Results

Figure 1 shows a schematic of a typical adhesive bond between two pieces of aluminum metal. The adhesive is in contact with the aluminum oxide rather than the metal since an oxide quickly forms an aluminum when it is exposed to air or cleaned with etching solutions prior to bonding. In commercial applications the oxide thickness is typically 100 to 200 angstroms. There is a fantastic need for information regarding the microscopic interface between the adhesive and the oxide. It is difficult, however, to obtain the information using conventional methods. Ultrasonic techniques give critically needed information about the bulk properties of the adhesive but give little information about the interface region. The wavelengths in ultrasonic studies are considerably longer than the several angstroms associated with the thickness of the interface layer.
The chemical nature of the interface is very important to the integrity and service life of a bond. The dashed line in Fig. 1 shows a typical fracture line. Most of the fracture line surface is not at the interface; however, it often happens that the fracture line originates at the interface region. Black and Blomquist have studied several metal adhesive systems and find that when they are exposed to a heat treatment the shear strength decreases significantly, often by more than a factor of two. They concluded that the primary reason for this decrease in shear strength is due to catalytic action at the bondline.

Hydrothermal aging is believed to be one of the most important causes for bond failure in service. Studies have been done on the bulk properties in order to determine 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 fact that an adhesive interface consists of a molecular layer bonded to an oxide suggests the possibility of inelastic electron tunneling spectroscopy as a useful tool. Our programs in both IETS and adhesives are relatively new and, as a consequence, most of the information presented is preliminary. The high performance Hercules 3501 epoxy system, distributed by Hercules, Inc., was chosen for study during the third year.

The two molecules which form the epoxy system are shown in Fig. 2. The upper one is tetraglycidyl 4,4' diaminodiphenyl methane (DPM). It has four identical arms, each with an epoxy ring. The other molecule shown is diphenyl silane (DPS) which is the curative for the DPM epoxy molecule. The molecules are not planar. The atoms in the DPS molecule lie in two planes whose intersection is a line in the plane defined by the two oxygens and the sulphur. The DPM molecules are even more 3-dimensional. They form dimers relatively easily even at room temperature. Spectra must therefore be interpreted with an awareness of the fact that one or more of the arms may be joined to other molecules.

The cross-link reaction for the DPM and DPS molecules is shown in Fig. 3. 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 C6H5O-. The OH groups make this molecule very polar and 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. The aluminum electrode was first evaporated at 10^-6 Torr. A glow discharge was then used to form the oxide layer. A liquid doping technique was used to deposit approximately one monolayer of the molecules on the oxide. The process involves making a dilute solution of the molecular species to be studied, placing a drop of the solution on the electrode, and spinning off the excess. A lead counter electrode was then evaporated over the molecules.

The DPB resin was not easy to dissolve. Methyl ethyl ketone (mekol) worked best. These two solvents, and to a lesser extent chloroform, dissolved the OPS matrix.

Figure 4 is a block diagram of the spectrometer system. The junction is cooled to 4.2K. A DC bias across the junction is slowly swept from 50 to 500 millivolts. An AC 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 DC bias. The second harmonic signal is proportional to:

\[
\frac{d^2V}{dt^2}
\]

Peaks in this signal locate the energies of the vibrational modes as read from the bias voltage (energy) scale.

Figure 5 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 milli-electron volts (meV), which corresponds approximately to the wavenumber range 400 to 400 cm^-1. The OH stretch peak near 450 meV is observed in most IETS spectra. The CH stretch near 355 meV 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 Fig. 5. The measured locations, in meV, of the peaks are shown following the group assignment. 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.

Figure 5. Two spectra taken on a junction doped with the curative DPS.

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.

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 just 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 NH2 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 NH2 groups on the ends of the DPS molecule have chemisorbed to the oxide layer.

Figure 6 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 epoxy molecule dissolved in the THF. Again, there is a large CH stretch peak located at 355 meV. The third curve labeled "DPM, 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 NH2 stretch modes. CH 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.

Figure 7 shows a clean junction made in the presence of H2O vapor. Note the OH stretch at 355 meV. Curve B is the spectrum for a clean junction exposed to D2O vapor after fabrication. The peak at 327 meV is an OD stretch mode indicating that D2O penetrated into the junction. This new technique of external doping appears to be a very promising technique for studying the interaction of molecules with surfaces. Of particular interest to us is the diffusion of H2O and D2O into and out of tunnel junctions under the proper experimental conditions.

Figure 8 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. We are currently trying to improve spectral resolution and do some heat treatment and aging studies on the combined system.

At the First International Conference on Inelastic Electron Tunneling Spectroscopy held at the University of Missouri-Columbia during May 1977, Jeklevic and Gaerttner reported the observation of IETS spectra of molecules which had been introduced into completely fabricated tunnel junctions. Curve A in Fig. 7 shows a clean junction made in the presence of H2O vapor. Note the OH stretch at 450 meV. Curve B is the spectrum for a clean junction exposed to D2O vapor after fabrication. The peak at 327 meV is an OD stretch mode indicating that D2O penetrated into the junction. This new technique of external doping appears to be a very promising technique for studying the interaction of molecules with surfaces.

The curve labeled "DPM (D)" is a spectrum for DPM which had 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 D2O as tag molecules. The "DPM(D)" spectra 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 the other spectra. We must be cautious in our interpretation of this spectrum since some structural changes may have occurred during the deuteration process.
Our current activities are as follows:

1. Improve spectral quality. A signal averaging system is needed to eliminate the effects of low frequency noise. The resolution in our spectra could be enhanced considerably.

2. Investigate possible surface bonding mechanisms. The character of the bonding mechanisms for adhesive systems is not well known but is critical to an understanding of adhesive systems.

3. Effects of heat treatment and hydrothermal aging. The recent advances reported in the external doping technique are being tried.

Conclusions

IETS (inelastic electron tunneling spectroscopy) is not directly applicable as a practical NDE technique and it is not trivial to apply IETS to the determination of adhesive-interface properties. However, at the present time, it is the only method available which allows an in situ study of adhesive/oxide interface bonding.

The feasibility of applying IETS to study changes in the molecular properties of an adhesive adsorbed on oxide due to time, temperature and permeating water has been demonstrated.

IETS offers a technique which, in the very near future, will become the most important (if not the only) method for determining the interface physics and chemistry of adhesive bondlines.

Information obtained from IETS studies will add greatly to the understanding of non-mechanical adhesive bond failure. Such knowledge should help in devising appropriate NDE measurements.

Initial studies using IETS should be applied to adhesives of simple molecular structure before proceeding to more complex systems.

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