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Application of Inelastic Electron Tunneling to the Study of Adhesion

Abstract

The problem of devising meaningful and reliable methods for nondestructive evaluation of adhesively bonded joints has been the subject of considerable effort for many years. It remains an important and unsolved problem. The use of conventional NOT methods involving ultrasonics is not entirely satisfactory because the thickness of a bond line is small compared with typical acoustic wavelengths and, perhaps more importantly, because the strength and service life of an adhesive bond is dependent on its chemical as well as mechanical properties. That is, an adhesive bond that is mechanically perfect may fail because of chemical degradation initiated at the adhesive/adhered interface.

Keywords

nondestructive testing, nondestructive evaluation

Disciplines

Materials Science and Engineering | Structures and Materials

APPLICATION OF INELASTIC ELECTRON TUNNELING TO THE
STUDY OF ADHESION

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The problem of devising meaningful and reliable methods for nondestructive evaluation of adhesively bonded joints has been the subject of considerable effort for many years. It remains an important and unsolved problem. The use of conventional NDT methods involving ultrasonics is not entirely satisfactory because the thickness of a bond line is small compared with typical acoustic wavelengths and, perhaps more importantly, because the strength and service life of an adhesive bond is dependent on its chemical as well as mechanical properties. That is, an adhesive bond that is mechanically perfect may fail because of chemical degradation initiated at the adhesive/adhered interface.

Figure 1 is a schematic of a typical metal/adhesive bond. Any metal employed in a practical situation will have a thin oxide layer on its surface and consequently any adhesively bonded metal joint will involve an oxide/polymeric interface.

The dashed line in Fig. 1 represents a typical fracture line (or fracture surface) which occurs in failure. It is well known that the fracture line is very rarely limited to the glue line^{1,4} (adhesive/oxide interface). The final morphology of a fracture line and the position of the initial crack may be only weakly related if at all. Once a critical sized crack is formed the development of the line is usually determined by the mechanical properties of the component materials.

In addition to mechanical mechanisms of failure such as large stress concentrations associated with voids and residual stress, chemical and physico-chemical mechanisms associated with interface phenomena are frequently involved in the initiation of bond failure.

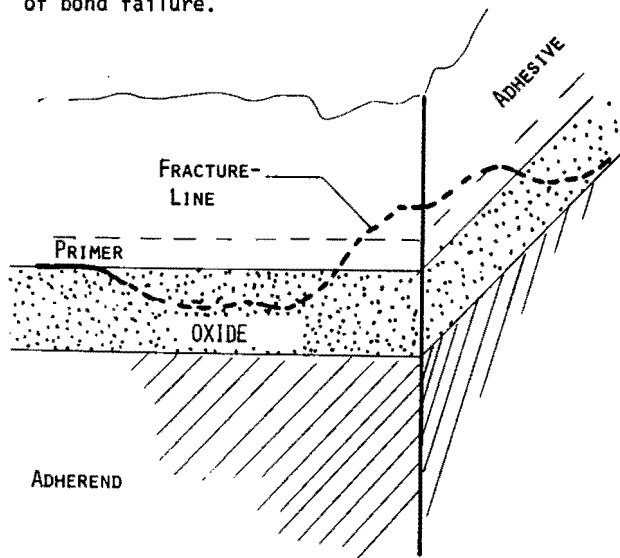


Figure 1. Schematic of adhesive bond joint

An interface consists of an organic or polymeric substance in intimate contact with a non-stoichiometric metal oxide. Many of the metal oxides are excellent catalysts. The oxides of many common metals such as Al, Mn, Cr, Fe, Ni or Zn are well known for their ability to catalyze reactions in organics. TiO₂ is an excellent catalyst and its action in oxidizing a polymeric binder is well known to be the cause of "chalking" of paints³. Black and Blomquist⁴ reported that adhesive joints employing phenolic and epoxy resins were critically degraded by the metal adherend when heated in air due to catalytic oxidation of the adhesive. Such effects were observed for numerous common metals. The results of Black and Blomquist are illustrated in Table 1:

TABLE 1

EFFECT OF HEATING IN AIR ON PHENOLIC/EPOXY BONDS BETWEEN DIFFERENT METALS

Metal	Shear Strength (bars)	
	before	heating after
Al	122	65
Mn	118	72
Cr	112	63
Fe	99	38
Ni	111	47
Zn	127	78
Cu	96	0
Ag	146	80
Ce	130	82

The role of H₂O in degrading an adhesive bond is not understood in detail but its action in accelerating detrimental chemical reactions is well documented².

The initiation of chemical degradation of an adhesive bond takes place at the microscopic interface between the metal oxide and the adhesive (or primer). We are concerned in our project with possible new measurement techniques for detecting and monitoring the chemical state of this microscopic interface. The technique of inelastic electron tunneling spectroscopy (on IETS) offers a potential tool of incredible sensitivity and great versatility for investigating, in situ, the chemical state of a metal oxide/adhesive interface. It should be made clear that at the present time it is not obvious how IETS can be employed as a

practical, "on-line", NDE tool. However, it seems clear that knowledge of the oxide/adhesive interface chemistry would be extremely valuable in developing new types of NDE measurements.

With this point of view we initiated, in January of this year, a small exploratory project to assess the feasibility of utilizing IETS to monitor the properties of an aluminum oxide/adhesive interface.

Inelastic Electron Tunneling Spectroscopy

In order to describe our progress a brief review of inelastic electron tunneling spectroscopy^{5,6} is needed. We are concerned with a metal/insulator/metal thin film junction as illustrated in Fig. 2. A typical tunnel-junction is fabricated by evaporation of a thin Al film onto a glass substrate. The film is oxidized to form an aluminum oxide layer 30 to 100 Å in thickness; similar to the natural oxide on any aluminum surface. A molecular substance such as an adhesive is then deposited on the oxide by a variety of "doping" techniques⁶. In most cases the molecular layer is 5 to 20 Å in thickness. Finally, a second metallic film (often Pb) is deposited over the molecular layer forming a four terminal thin film MIM junction as shown in Fig. 2.

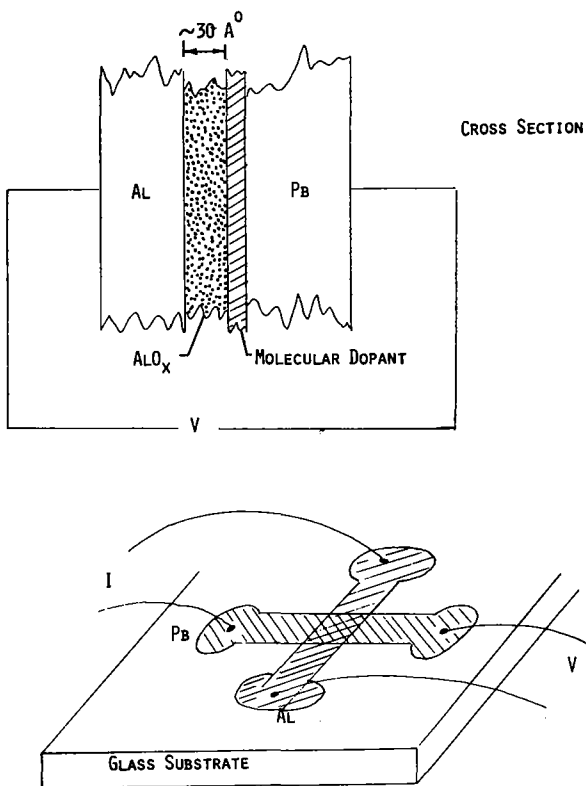


Figure 2. Schematic diagram of metal/insulator/metal junction.

A variable bias is applied across two of the junction terminals and the current is measured across the second two terminals. Since the oxide is a good insulator only a small current of the order of 5×10^{-3} amperes flows across the junction. This current is due principally to electrons which, in the quantum mechanical sense, tunnel through the oxide barrier. A schematic of the tunneling process is shown in Fig. 3. Fig. 3a illustrates the elastic electron tunneling process in which an electron tunnels through the insulating barrier from below the Fermi level of the Al film to an empty state above the Fermi level in the Pb film with no loss of energy. Fig. 3b illustrates the inelastic process. In this case the tunneling electron collides with one of the molecules on the oxide and excites one of the vibrational modes of the molecule having a characteristic energy $h\nu_m$ where ν_m is the vibrational frequency.

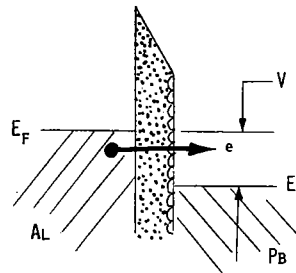


Figure 3a. Elastic tunneling

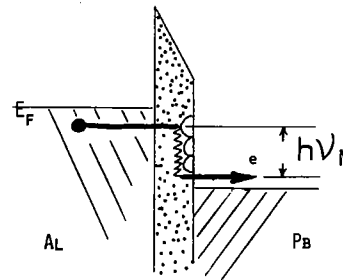


Figure 3b. Inelastic tunneling

An inelastic tunneling process produces an abrupt change in the slope of the current-voltage characteristic at an applied voltage equal to the vibrational frequency $h\nu_m$. The effect is shown schematically in Fig. 4a. The effect can be greatly enhanced in two ways. First, by making measurements at very low temperatures thermal smearing effects can be greatly reduced. Usually measurements are made at liquid helium temperatures so that the Pb film is superconducting. Second, by using electronic modulation methods the junction conductance $G = dI/dV$ and the second derivative

$\frac{d^2I}{dV^2}$ can be recorded. Structure due to excitation of molecular vibrational modes of the molecular layer are easily observed in d^2I/dV^2 versus V curves. The characteristic shapes of these curves are illustrated in Fig. 4b and c. The structure due to inelastic tunneling processes as seen in d^2I/dV^2 curves is remarkably similar to infrared absorption by the molecular substance. However, the tunneling method is different in several respects. First, the sensitivity to small quantities of material is fantastic: A monolayer of material on a junction with an area of 10^{-2} cm^2 is very easily detected. Second, all vibrational modes are detected by tunneling. That is, there are no selection rules and both infrared and Raman modes are seen in the same spectrum.

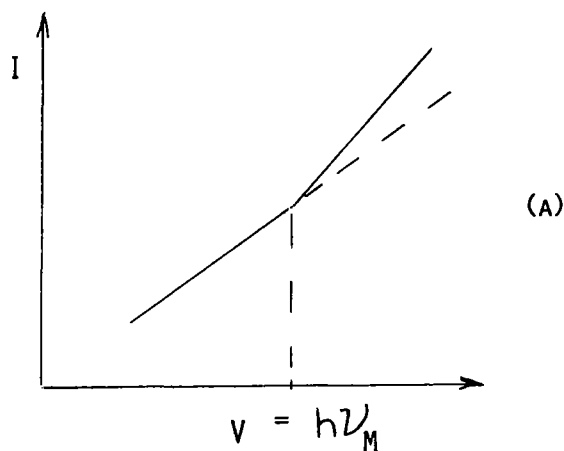


Figure 4a. Current-voltage curve characteristic of inelastic tunneling process

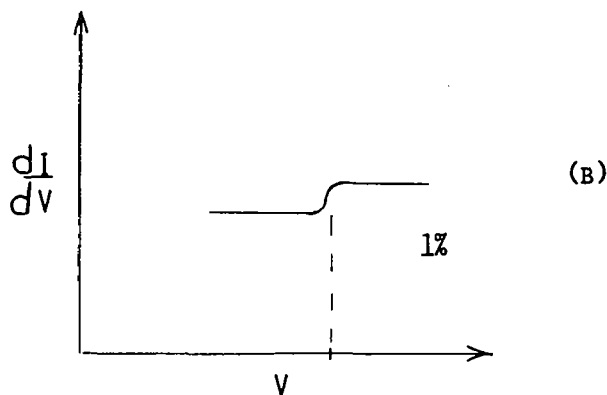


Figure 4b. First derivative of 4a.

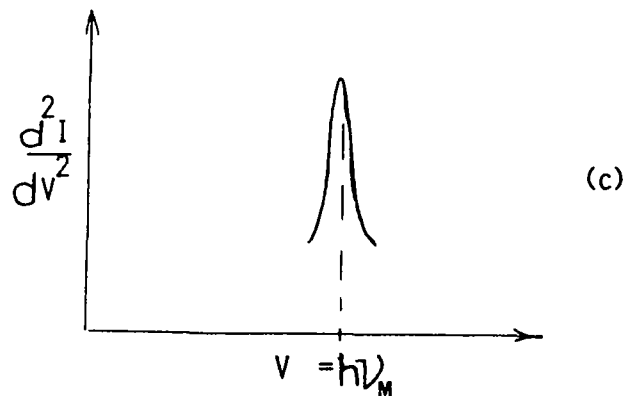


Figure 4c. Second derivative of 4b.

As an example of IETS we show in Fig. 5 the tunneling spectrum of the organic compound phenylalanine. The upper panel is the tunneling spectrum obtained by Simonsen and Coleman⁶ and the lower panel is the infrared transmittance reported by Nugol Mull.⁷ A large number of characteristic vibrational modes are easily identified and the IETS spectrum is quite similar to the IR spectrum. The IETS spectrum can be used to monitor the chemical state of the molecular layer. It is this property that is the basis of employing IETS for the study of an oxide/adhesive interface.

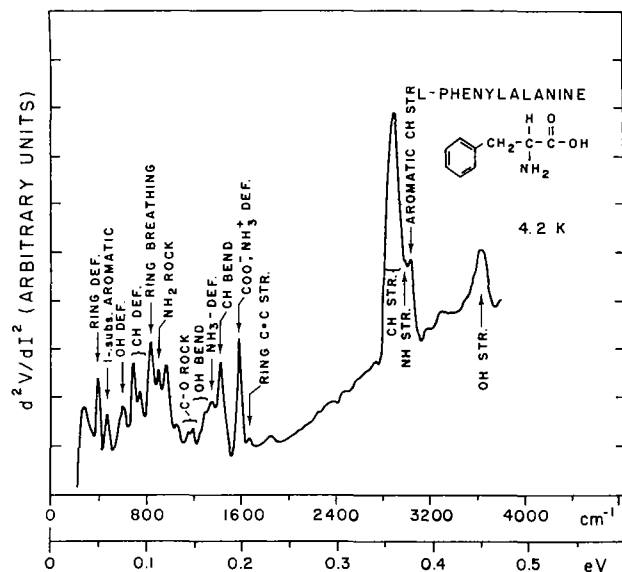


Figure 5. Tunneling spectrum of organic compound phenylalanine.

Application of IETS to Adhesives

The purpose of our project is to assess the feasibility of utilizing IETS as a tool for the study of the chemical state of a metal oxide/adhesive interface. Our immediate objectives are to determine if measurable changes in the tunneling spectrum can be correlated with processes involved in adhesive setting, curing, and degradation.

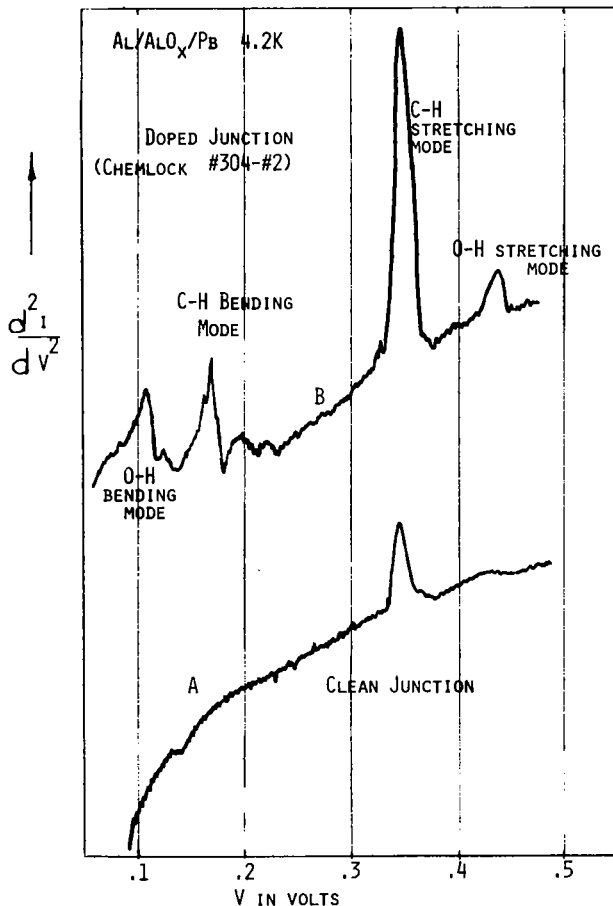


Figure 7. Inelastic tunneling spectra for (A) a clean junction and (B) a junction with epoxy contamination.

In Fig. 7 we show inelastic tunneling spectra obtained on two different junctions. Curve A is for a "clean" junction which was not doped with a molecular material. There is very little structure in the d^2I/dV^2 curve. The shoulder at about .15 V is due to the O-H stretching mode. These structures are associated with residual contamination on the junction acquired during the formation of the oxide in the vacuum system. Curve B is for a junction doped with one component of a commercial epoxy adhesive, "Chemlock 304." Several vibrational modes associated with the adhesive component are clearly evident. The most intense modes are the C-H stretching and bending modes. The O-H stretching and bending modes are also very intense.

The data presented in Fig. 8 is our first attempt to observe inelastic tunneling with the adhesive dopant. There are many other vibrational modes evident in the data but considerable improvement in the signal to noise must be accomplished before the data can be used quantitatively. A number of improvements in the fabrication and signal processing are currently being implemented.

Experiments are underway to look at the spectrum of the other component of Chemlock and at the mixed epoxy itself. Following this we shall attempt

to monitor changes in the epoxy due to thermal setting and degradation of the adhesive due to water and/or heating in a gaseous environment. An assessment of the feasibility of using IETS to study the chemical state at an aluminum oxide/adhesive interface should be completed in the next few months.

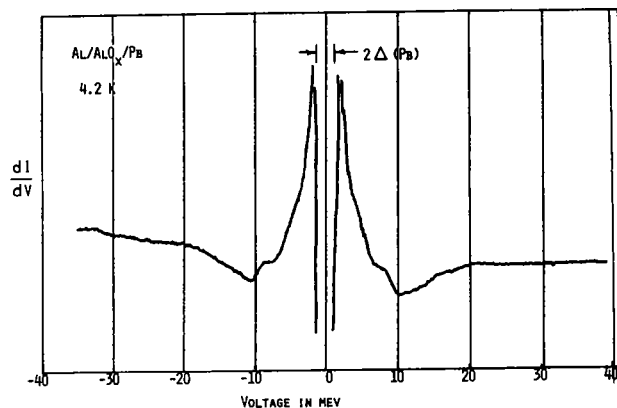


Figure 8. First attempt to observe inelastic tunneling spectra with an added dopant in the junction.

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DISCUSSION

PROF. MAX WILLIAMS (University of Pittsburgh): We have time for any questions of points of fact. We won't have time for discussion of the paper, but are there any questions as points of fact?

DR. BILL BASCOM (Naval Research Laboratory): Can you distinguish between a hydroxyl of water and hydroxyl bonded to aluminum?

PROF. WILLIAMS: I think I must ask you to just reply either yes or no or maybe.

PROF. WOLFRAM: I suspect the answer is maybe.

PROF. WILLIAMS: I saw one other question of fact back here.

DR. G. GARDNER (Southwest Research Institute): At what temperature are these measurements?

PROF. WOLFRAM: Pardon?

DR. GARDNER: At what temperature are these measurements?

PROF. WOLFRAM: These measurements that you saw were performed at liquid helium temperatures. The technique itself does not require superconductivity. You increase your sensitivity or your resolution by going to low temperature. It also impedes any further chemical processes, so you can take a picture of it, then warm it back up, and then go back down and freeze in your particular chemical state. It doesn't really require superconductivity; it does require low temperatures to get resolution.

PROF. WILLIAMS: Thank you very much, Dr. Wolfram, particularly for meeting your shortened time for presentation.