AN IETS (inelastic electron tunneling spectroscopy) study of surface reactions.

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AN IETS STUDY OF SURFACE REACTIONS APPLICABLE TO ADHESION

by

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Inelastic electron tunneling spectroscopy (IETS) has been used to study two classes of adhesion promoting compounds adsorbed on alumina: trialkoxysilanes and phosphonic acids. It has been shown that both types of compounds can condense directly with hydroxyl groups on the surface.
Condensation is through the alkoxy groups in the case of the silanes and through the hydroxyl groups in the case of the acids. The silanes can further condense to form surface siloxanes. The absence of bands characteristic of the phosphoryl group in the spectra of the acids is indicative of resonance bond formation followed by ionic bonding to the surface.
I. INTRODUCTION

In many instances, metal surfaces undergo several chemical pretreatment processes prior to adhesive bonding. The purpose of these processes is to enhance certain desirable characteristics of the completed structure such as bond strength and durability. Although the effects of certain pretreatments have been well characterized empirically, the surface chemistry is not always well understood. Insight into the chemical nature of the pretreated metal surface is therefore of interest. An experimental technique which is ideally suited for studying the way in which chemical compounds are adsorbed onto metal oxide surfaces is inelastic electron tunneling spectroscopy (IETS). This technique relies on the existence of the oxide layer, is non-destructive, and provides vibrational mode information about chemical species adsorbed onto the metal oxide, thus making it appropriate for investigating chemical reactions associated with adhesion.

This paper will describe the technique of IETS, discuss its advantages and limitations as applied to surface reaction studies, and provide specific examples of how the technique has been used to study the chemisorption of silane coupling compounds and phosphonic acid hydration inhibitors on alumina. These compounds are known to
improve the strength and long-term durability of bonded aluminum structures, and are therefore of great importance in the area of applied adhesion science.

II. PRINCIPLES OF IETS

IETS is a solid state energy loss spectroscopy which utilizes a metal/insulator/metal (MI/I/M2) tunnel junction as illustrated in Figure 1a. By applying a negative bias to the base electrode, M1, electrons will tunnel from M1 into the counter electrode, M2, and thus produce a tunneling current which is dependent upon both the thickness of the tunneling barrier and the bias voltage. An energy diagram of the system is illustrated in Figure 1b, where $\Phi$ is the work function of the metal, $\varepsilon_F$ is the Fermi energy, and $eV$ is the energy of the electron which tunnels from the Fermi level of M1 to a vacant state in M2. Also illustrated within the barrier in Figure 1a is a classical oscillator depicting a molecule adsorbed on the surface of the metal oxide. When the energy of the tunneling electron is less than the vibrational energy of the adsorbed molecule, $\hbar \nu_m$, the electron will tunnel elastically, i.e., without energy loss. By increasing the bias voltage, the energy of the electron is increased. When the electron energy is equal to the
vibrational energy of the adsorbed molecule, it can excite the vibrational mode of the molecule, thereby losing energy and tunneling inelastically. The onset of this new tunneling mode results in a slight change in the current-voltage characteristic of the tunnel junction (Fig. 2a). Superimposing a small ac modulation voltage on top of the dc bias and using harmonic detection to obtain the second derivative of the I-V curve gives rise to a peak whenever the condition $eV_m = \hbar \nu_m$ is met (Fig. 2b). Recording this as a function of the applied bias voltage results in a spectrum with peaks corresponding to the modes of vibration of the adsorbed molecule. Excellent reviews of the theoretical and experimental aspects of IETS are available in the literature.\textsuperscript{1,2}

III. ADVANTAGES AND LIMITATIONS OF IETS

A tunneling electron perturbs the uniformity of the electric field at the site of an adsorbed molecule to such an extent that both Raman and infrared active modes appear in the tunneling spectra with comparable intensities, and the usual spectroscopic selection rules are relaxed. One useful guideline, when properly applied, is that dipole moments parallel to the tunneling electron’s motion interact more strongly with the electron than do those
perpendicular to its motion. Combining this knowledge with that of the vibrational modes can provide valuable insight into the orientation of molecules with respect to the oxide surface.

The spectral range of IETS extends from 300 cm\(^{-1}\) to 4000 cm\(^{-1}\), which includes all molecular vibrations. IETS is extremely sensitive to minute quantities of adsorbate on the oxide surface, and even with the recent advances in FT-IR, IETS remains the most sensitive surface analysis technique. In fact, since the tunneling current decreases exponentially with increasing barrier thickness, adsorbate coverage of several monolayers is unsuitable for IETS.

Peak width in IETS is governed by two parameters: thermal and modulation broadening. Thermal broadening is a result of the distribution of electron energies about the Fermi level at finite temperatures. This contribution to the peak width is minimized by cooling the completed tunnel junction to 4.2 K prior to data collection. Modulation broadening is proportional to the amplitude of the applied ac modulation voltage, and is minimized by choosing the optimum ac voltage which still allows for reasonable signal to noise ratio. A typical modulation voltage of 1.5 eV (1 eV = 8.065 cm\(^{-1}\)) results in
resolution of the order of 25 cm\(^{-1}\) with the tunnel junction temperature maintained at 4.2 K.

The most serious limitation of IETS is that it can only be done with devices consisting of metal/insulator/metal tunnel junctions. The most common system is aluminum/aluminum-oxide/lead (Al/Al-O/Pb), which is exactly the system of practical interest when investigating the reaction mechanisms involved in the adhesive bonding of aluminum structures. It has been shown that the top electrode does not significantly alter the surface chemistry of the oxide layer, and that the positions of the vibrational modes of adsorbed molecules are the same as those observed in IR spectroscopy to within the limits of uncertainty due to resolution.\(^3\)

IV. SAMPLE PREPARATION

The metal/insulator/metal tunnel junctions are fabricated by evaporating three narrow aluminum strips onto a smooth glass substrate at pressures of 3\(\times\)10\(^{-7}\) Torr or less in a vacuum evaporator. A glow discharge is then used to oxidize the aluminum surface to form a tunneling barrier of about 20 Å thickness. A monolayer or less of the compound of interest is then adsorbed as a dopant on the oxide. This is done outside the vacuum chamber by
liquid-phase doping, with the compound of interest being
diluted to a concentration of about 0.1% by weight in a
solvent. The excess liquid is removed from the surface by
rapidly spinning the substrate in a mechanical spinner.
The substrate is then returned to the evaporator, where
lead electrodes are applied, thus making three devices
available for measurements. The completed devices are
inserted into an edge connector sample holder which is
lowered into a liquid helium storage Dewar for four-point
probe measurements. Devices having junction resistances
of about 200 ohms are ideal for our spectrometer.

V. SILANE COUPLING COMPOUNDS

Organofunctional silanes are often used as coupling
compounds in the bonding of polymers to alumina or silica.
This terminology has arisen because the alkoxy groups are
thought to react with the mineral surface while the
organofunctional groups react with the adhesive to form a
coupling bond between the two, thus improving the adhesior
of the bonded structure. A schematic representation of the
aluminum oxide surface is shown in Figure 3, and some
possible mechanisms by which triethoxysilane adsorbs on
alumina are illustrated in Figure 4. Analysis, in terms
of the observed vibrational bands in IET spectra, has been used in an attempt to discern which, if any, of these possible mechanisms is most likely.\textsuperscript{5,6}

The spectrum of an undoped Al/Al-O/Pb tunnel junction is displayed in Figure 5. This spectrum will be superimposed as a background on all other spectra to be discussed. The broad band at 940 cm\textsuperscript{-1} is due to the vibrational modes of aluminum oxide, the weak band at 1855 cm\textsuperscript{-1} is attributed to aluminum hydride, and the band at 3600 cm\textsuperscript{-1} arises from the stretching vibrations of surface hydroxyl groups.

The spectrum of triethoxysilane adsorbed on alumina is displayed in Figure 6. In this particular case the aluminum surface was oxidized by a dc glow discharge in an atmosphere consisting of both oxygen and deuterium. This process is known to produce both hydroxyl and deuterated hydroxyl groups on the surface, resulting in an OH band at 3600 cm\textsuperscript{-1} and an OD band at 2661 cm\textsuperscript{-1} in the undoped junction.\textsuperscript{7} The tunnel junction was liquid doped in this case with 10\textsuperscript{-3} ml of triethoxysilane in 4 ml of acetone. The purpose of these procedures was to assure that the silane was anhydrous before reacting with the surface, and
to discern the role of the surface hydroxyl groups in the reaction. The absence of the OH and OD bands in this spectrum suggest that chemisorption of the silane has taken place by condensation at all available hydroxyl sites on the surface.

The weak bands at 1065 cm\(^{-1}\) and 1097 cm\(^{-1}\) have been attributed to the asymmetric stretching modes of Si-O-Si, which suggest that polymerization of the silane has taken place. Similar results were also obtained with anhydrous vinyltriethoxysilane and vinyltrimethoxysilane. Together, these results suggest that trialkoxysilanes can condense directly with surface hydroxyl groups on alumina to form siloxane interfacial bonds, and these bonds may be stabilized by condensation between chemisorbed silane molecules to form siloxane oligomers.

Although no conclusive evidence for any of the bonding mechanisms in Figure 4 was observed, results of this investigation support either covalent or ionic bonding. However, in the chemisorption of phosphonic acids on alumina, IETS has provided strong evidence for the existence of ionic bonding.
VI. PHOSPHONIC ACID HYDRATION INHIBITORS

It has been shown that the presence or intrusion of water into the bondline area is a major cause of bond failure in adhesively bonded aluminum structures. Therefore, the identification of chemical compounds which dehydrate the surfaces prior to bonding, and which also make the completed structure resistant to subsequent water intrusion has received great attention. Phosphonic acid and several alkylphosphonic acids have exhibited these desirable characteristics, and have therefore been described as hydration inhibitors.

There are several proposed mechanisms of how these acids react with the surface of aluminum oxide, some of which closely parallel those illustrated in Figure 4 for triethoxysilane. The mechanism most generally accepted is that of condensation via the hydroxyl groups of the acid with those on the surface to form covalent P-O-Al bonds. IETS has been utilized to investigate the validity of such mechanisms, and combined with other analysis techniques, has provided valuable insight into the surface chemistry of these acids when adsorbed on alumina.

The IET spectrum of phosphonic acid adsorbed on
alumina is presented in Figure 7. The intense peaks at 1034 cm$^{-1}$ and 2428 cm$^{-1}$ are attributed to the bending and stretching modes of the P-H bond respectively, and the remaining features have also been assigned. The most interesting aspect of this spectrum is the lack of any bands associated with the phosphoryl group, which is known from IR absorption studies to have a characteristically strong stretching mode in the vicinity of 1200 cm$^{-1}$. The IET spectra of several alkylphosphonic acids also lacked these bands.

The absence of the P=O bands in these spectra suggests that the phosphoryl groups no longer exist as independent entities in the adsorbed acids. This can be accounted for by the formation of a resonance bond between the phosphoryl oxygen and adjacent hydroxyl oxygens upon condensation with surface hydroxyls. The acid becomes an anion which interacts ionically with the surface. In this way the surface is dehydrated, and the alkyl group is unaltered, thus accounting for the known hydration inhibiting effects of these acids on bonded aluminum structures.
VII. CONCLUSIONS

From this work it can be concluded that both trialkoxysilanes and phosphonic acids can condense directly on alumina. For the silanes the condensation product will be an alcohol, and the adsorbed silane can polymerize by subsequent condensation to form surface siloxanes. In the case of phosphonic acids, the condensation product is water. The deprotonated hydroxyl then appears to form a resonance anion with the phosphoryl group and bond ionically to available aluminum sites on the surface. The absence of any bands in the spectra corresponding to the phosphoryl group makes covalent bonding less likely. The case for ionic bonding of the silanes is weaker because the expected position (approx. 1000 cm\(^{-1}\)) of the band associated with the Si-O-Al covalent bond is always obscured by other bands, and its presence or absence cannot be determined.
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FIGURE CAPTIONS

Fig. 1 a) Schematic representation of an IETS tunnel junction and b) associated energy level diagram.

Fig. 2 a) I-V curve of an IETS tunnel junction showing change in slope at onset of inelastic tunneling and b) its second derivative.

Fig. 3 Idealized representation of the surface of aluminum oxide.

Fig. 4 Possible bonding mechanisms of triethoxysilane to aluminum oxide.

Fig. 5 IET spectrum of an undoped Al/Al-O/Pb tunnel junction.

Fig. 6 IET spectrum of triethoxysilane adsorbed on alumina (Ref. 6).

Fig. 7 IET spectrum of phosphonic acid adsorbed on alumina.
Figure 1
Figure 2
Possible Bonding Mechanisms

- Covalent Bonding
- Ionic Bonding
- Hydrogen Bonding
- Interstitial Insertion

*Figure 4*
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<td>Dr. Y. Gupta</td>
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<td>Department of Physics</td>
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<td>Pullman, WA 99163</td>
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<td>Director</td>
<td>Naval Research Laboratory</td>
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<td>Administrative Contracting Officer</td>
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