

Inelastic electron tunneling spectroscopy of silane coupling agents adsorbed on alumina

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Inelastic electron tunneling spectroscopy (IETS) has been used to obtain vibrational spectra of alkoxyxilanes adsorbed on aluminum oxide. The spectra reveal that: (1) monoalkoxyxilanes are not adsorbed whereas trialkoxyxilanes are readily adsorbed, (2) the reaction mechanism of triethoxyxilanes and trimethoxyxilanes is the same, and (3) the reaction mechanism under anhydrous conditions utilizes surface OH or OD groups present on alumina. These results support the hypothesis that the alkoxy groups exchange with OH groups on the surface to form siloxane bonds, and that these bonds are stabilized with trialkoxyxilanes. For monoalkoxyxilanes, either the bonds do not form so readily, or they are not stabilized by further condensation of the adsorbed species. Instead, the monoalkoxyxilanes appear to catalyze further oxidation of the alumina surface.

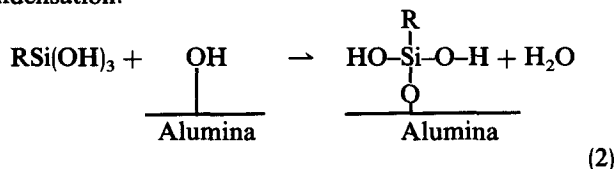
INTRODUCTION

Coupling agents are defined¹ as compounds that improve the chemical resistance to degradation of bonds across the interface between two dissimilar materials. They are thought to chemically link surface molecules of one material with those of the other. Organofunctional trialkoxyxilanes are commonly used to bond organic polymers to inorganic mineral surfaces in this way. They have the chemical structure RSiX_3 where R is an organofunctional group and X is a hydrolyzable alkoxy group. Small amounts of these compounds at the interface between a mineral filler and an organic polymer have a profound effect on the strength of the composite.² Hence, an understanding of these coupling reactions is fundamental to the study of the adhesion of organic polymers to inorganic substrates. The generally accepted theory^{3,4} of the coupling mechanism of organofunctional silanes is that the silicon atom forms a stable link between an organofunctional group on the one hand and readily hydrolyzable alkoxy groups on the other. For example, triethoxyxilanes, $\text{RSi}(\text{OEt})_3$, are believed to react by hydrolysis of one or more of the ethoxy groups to form silanols which then condense (polymerize) to form siloxanes, or react directly with OH groups on the mineral surface. Stepwise, the reaction would be as follows:

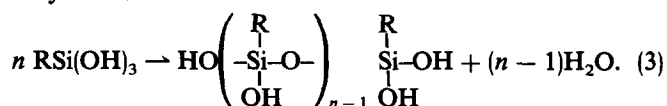
Hydrolysis:



Condensation:



Polymerization:



Although analogous reactions on glass surfaces have been studied by FT-IR spectroscopy, the evidence for direct

condensation with OH groups on glass is rather slender. The evidence for condensation with OH groups on metal surfaces is even weaker. Thus, the mechanism of interaction of silanes with alumina must be considered quite debatable. Research has therefore been carried out using a number of different silanes deposited on oxidized aluminum surfaces, and examining the reaction products using the experimental technique of inelastic electron tunneling spectroscopy (IETS).

IETS is a method for obtaining vibrational spectra of adsorbed molecules. It provides a sensitive means of gaining information on the interface region of metal-insulator-metal tunnel junctions.⁵⁻⁸ By doping the interface of a tunnel junction with the coupling agent of interest, one obtains the vibrational spectrum of one monolayer, or less, adsorbed at the interface. Spectra thus obtained are similar to IR and Raman spectra, and analysis is primarily by comparison with IR and Raman spectra.

Several IETS studies of silane compounds on alumina have been reported previously,⁹⁻¹² but the reaction mechanisms, if any, were not ascertained. By comparing spectra obtained by different workers, using the same or similar compounds, we are now able to see similarities and differences between slightly different experimental techniques and between different coupling compounds. Some conclusions on the mechanism of reaction are then presented.

EXPERIMENTAL

Only experimental details that are pertinent for the comparison of this work with that of others will be described. Excellent reviews of the theory and experimental methods of IETS are available in the literature.^{6,7,13}

The metal-insulator-metal tunnel junctions were prepared by evaporating a 1 mm wide strip of aluminum onto a 9×18 mm glass microscope cover slide, at pressures of 5×10^{-7} Torr or less. In some cases the surface of the aluminum layer was oxidized by an oxygen glow discharge at 500 V dc and 15 mA, whereas in others an oxide layer was formed by exposing the strip to air. In all cases the oxidized aluminum was liquid-phase doped by applying a drop of the

silane, diluted in pure acetone, or an acetone and water mixture, onto the oxide surface and immediately spinning the substrate to remove the excess liquid. The substrate was then returned to the vacuum evaporator for depositing three equally spaced lead counterelectrodes. The completed junctions were clamped in a sample holder, where electrical contact was made by pressure welding the electrodes to indium coated brass screws to which electrical leads were connected. Junctions having resistances in the range 100 to 1000 Ω were found to be most suitable for measurements. They were cooled to 4.2 K by immersion in a liquid helium storage dewar. A bias voltage in the range 40 to 500 mV was applied across the junctions, and d^2I/dV^2 vs V was obtained by modulating the bias voltage with a 17 mV ac signal at 500 Hz and using lock-in detection to recover the second harmonic signal at 1000 Hz. Spectra were recorded using a Tracor Northern TN-1710 signal averager.

All silanes were obtained from Petrarch Systems and used as received, except for dilution with acetone, water, or mixtures.

RESULTS AND DISCUSSION

It was found that good spectra of silanes on alumina surfaces—those containing large and well defined peaks—were obtained only when traces of water were present. Usually this is no problem since water vapor appears as a residual gas in vacuum systems which are not pumped to pressures lower than 10^{-8} Torr. Note that a peak due to the OH stretch mode appears at 3620 cm^{-1} in the spectrum of an undoped junction that was not removed from the vacuum chamber during fabrication, Fig. 1.

The amount of OH on the surface can be increased by adding hydrogen gas along with the oxygen during the glow discharge for oxidizing aluminum. This effect was verified

by adding deuterium instead of hydrogen.¹⁴ The OD stretch peak then appeared at 2671 cm^{-1} . Since the silane spectra obtained depended on the conditions of oxidation as well as upon the presence of water, care will be taken to point out the exact conditions under which each junction was prepared.

Two types of silane compound were studied—trialkoxysilanes and monoalkoxysilanes. If the interaction with alumina is through exchange, condensation, or hydrogen bonding involving silane or silanol groups, then both compounds should react.

TRIALKOXYSILANES

The simplest of the trialkoxysilanes is triethoxysilane which has a hydrogen atom instead of the usual organofunctional group. For this compound, the only possible mode of reaction with alumina is via the ethoxy group.

Figures 2 and 3 illustrate how oxidation and techniques of doping affect the spectra obtained from the same compound. In both cases the dopant is triethoxysilane. For Fig. 2 the aluminum was oxidized by exposure to air and the dopant consisted of 10 μl of triethoxysilane dissolved in 3 ml solution of a mixture of equal parts of acetone and water. For Fig. 3, the oxide was formed by glow discharge at 100 mA for 30 s in a mixture of O_2 and D_2 at 0.5 Torr initial pressure. This process produces both an OD peak at 2671 cm^{-1} and an OH peak at 3620 cm^{-1} . The dopant in this case was 10 μl of triethoxysilane dissolved in 4 ml of 99.5% pure acetone. The noticeable differences in these two spectra are: (1) greater detail in the CH stretching modes at 2920 cm^{-1} in Fig. 3, (2) the absence of both the OD peak at 2671 cm^{-1} and an OH peak at 3620 cm^{-1} in Fig. 3, and (3) the presence of a large OH peak in Fig. 2. These differences are attributed to the following features. (1) The greater detail in the CH stretch modes in Fig. 3 suggests that a more uniform or structured oxide layer

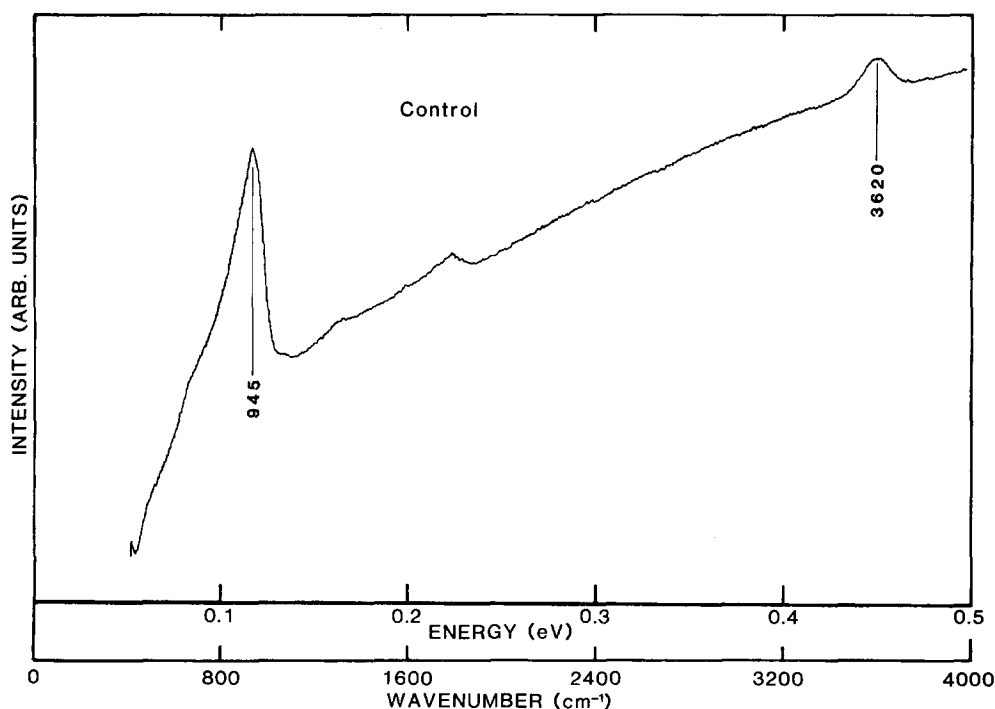


FIG. 1. IETS results for an undoped Al/AIO/Pb junction. Peaks at 945 and 3620 cm^{-1} are attributed to AIO and OH vibrational modes, respectively.

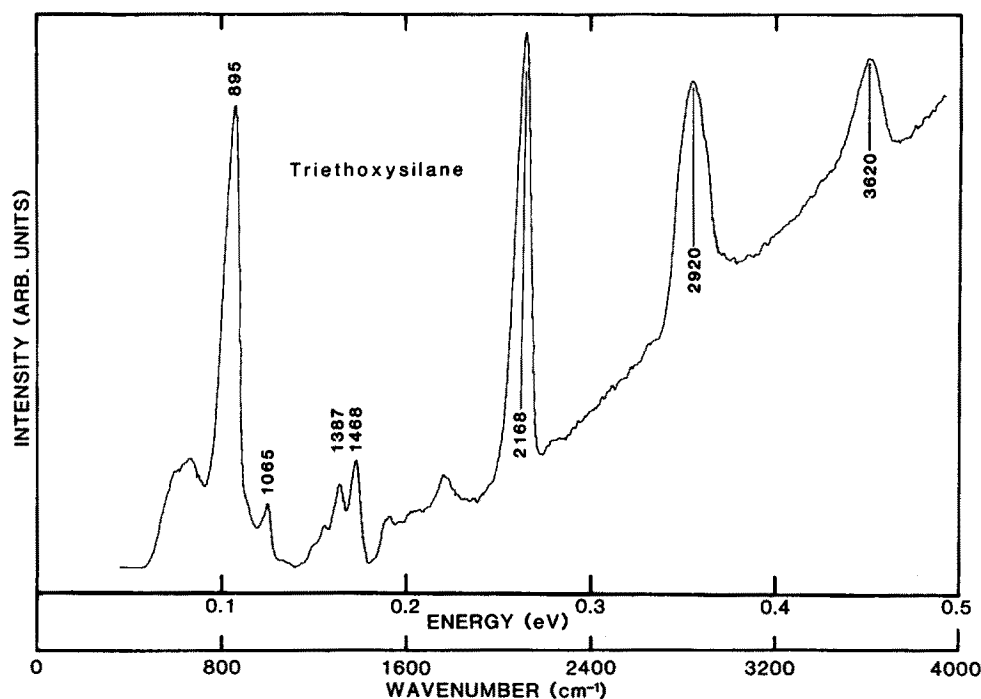


FIG. 2. IETS results for an AlOH surface doped with triethoxysilane in acetone and water. Peaks at 895 and 2168 cm^{-1} are characteristic of SiH bending and stretch modes. The broad peak at 2920 cm^{-1} is attributed to unresolved CH_3 stretching modes, and those at 1387 and 1468 cm^{-1} to the sym. and asym. deformation modes of CH_3 .

is formed. This result is in agreement with that of Werrett,¹⁵ who reported a similar improvement when the oxide layer is formed by a glow discharge, and by Hansma¹⁷ who pointed out the importance of the method of oxidation in structural analysis of adsorbed species. On the other hand, by comparing Figs. 2 and 3 with the IETS spectrum of the same silane obtained by Brewis *et al.*,² the method of applying the silane—from the vapor or as a liquid, diluted with acetone—has no significant effect on the spectrum obtained. (2) The absence of OD and OH peaks in Fig. 3 suggests that chemis-

orption of the silane has taken place by condensation at all available sites on the alumina surface. On the other hand, when water was added with the silane, Fig. 2, residual OH groups are found. Thus, it does not appear that the silane must hydrolyze before reaction with the surface, Eq. (1). Instead, it appears that direct condensation of the silane can take place. Furukawa *et al.*¹¹ observed changes in the spectra of adsorbed trimethoxysilanes when water was added subsequently by vapor infusion. Presumably, the adsorbed silane can undergo later hydrolysis. However, it does not seem to

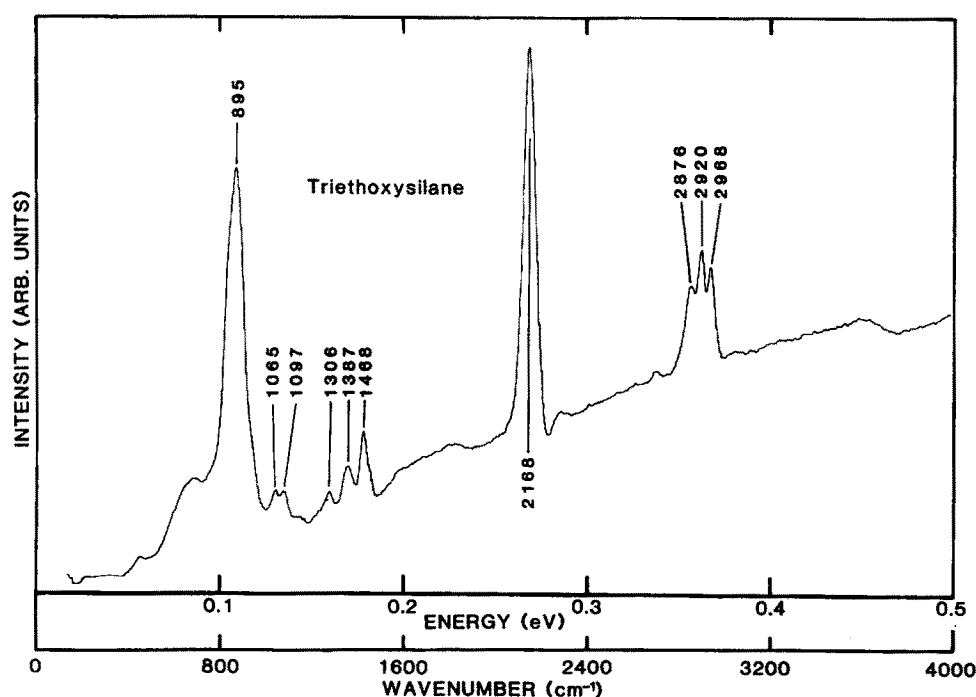


FIG. 3. IETS results for an AlOH + A-10D surface doped with triethoxysilane in pure acetone. In comparison with the spectrum shown in Fig. 1, the CH_3 peaks are well resolved and the OH peak absent. The weak peaks at 1065 and 1097 cm^{-1} are attributed to the asym. vibrational mode of Si-O-Si.

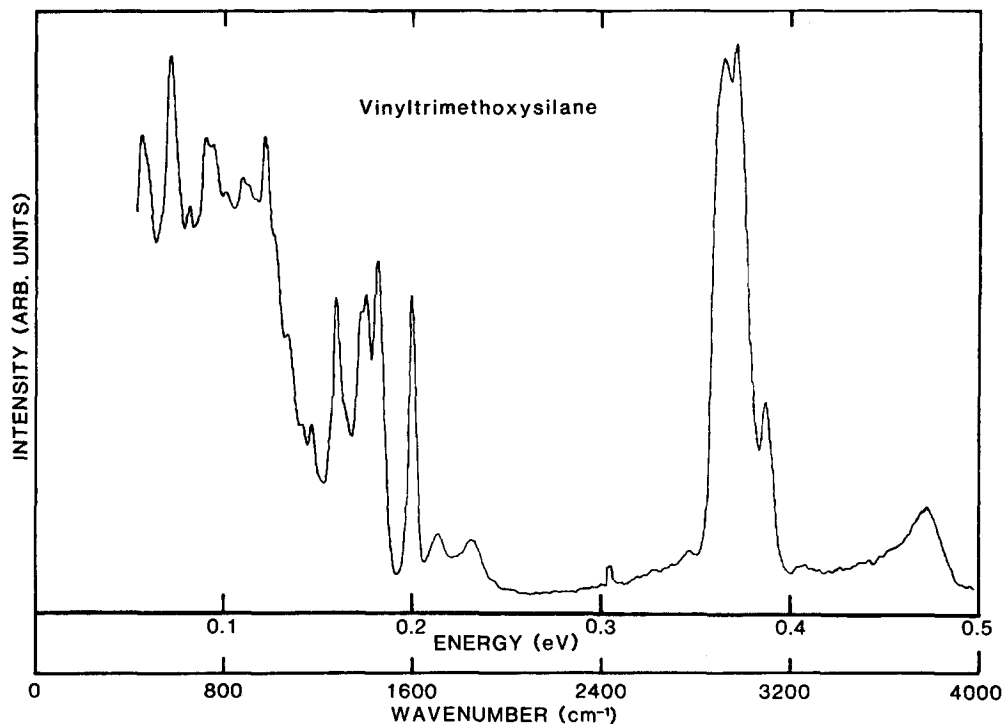


FIG. 4. IETS results for an AlOH surface doped with vinyltrimethoxysilane in water. The vinyl group on silicon has four characteristic peaks; the out-of-plane hydrogen deformation mode at 550 cm^{-1} , the Si-vinyl str. at 976 cm^{-1} , the C=C str. at 1600 cm^{-1} , and the vinyl CH str. at 3040 cm^{-1} .

be a necessary step before chemisorption.

A less obvious difference between the spectra in Figs. 2 and 3 is a small single peak at 1065 cm^{-1} in Fig. 2 which appears as a doublet with peaks at 1065 and 1097 cm^{-1} in Fig. 3. These peaks may be due to the asymmetric stretching mode of Si-O-Si. The infrared band for this mode usually appears around 1060 cm^{-1} for alkyl-substituted disiloxanes, and splits into two or more overlapping peaks as the siloxane chain becomes longer.¹⁶ This suggests that more polymer-

ization of the silane has taken place in Fig. 3. The weak peak at 445 cm^{-1} is in the proper region to correspond to the symmetric Si-O-Si mode. As will be pointed out later, these peaks were also observed in other trialkoxy compounds.

Figures 4 and 5 are spectra obtained with vinyltrimethoxysilane and vinyltriethoxysilane. These compounds were diluted with water before being applied to the alumina, which accounts for the OH peak at 3620 cm^{-1} . There are two important details to note in comparing these spectra: (a)

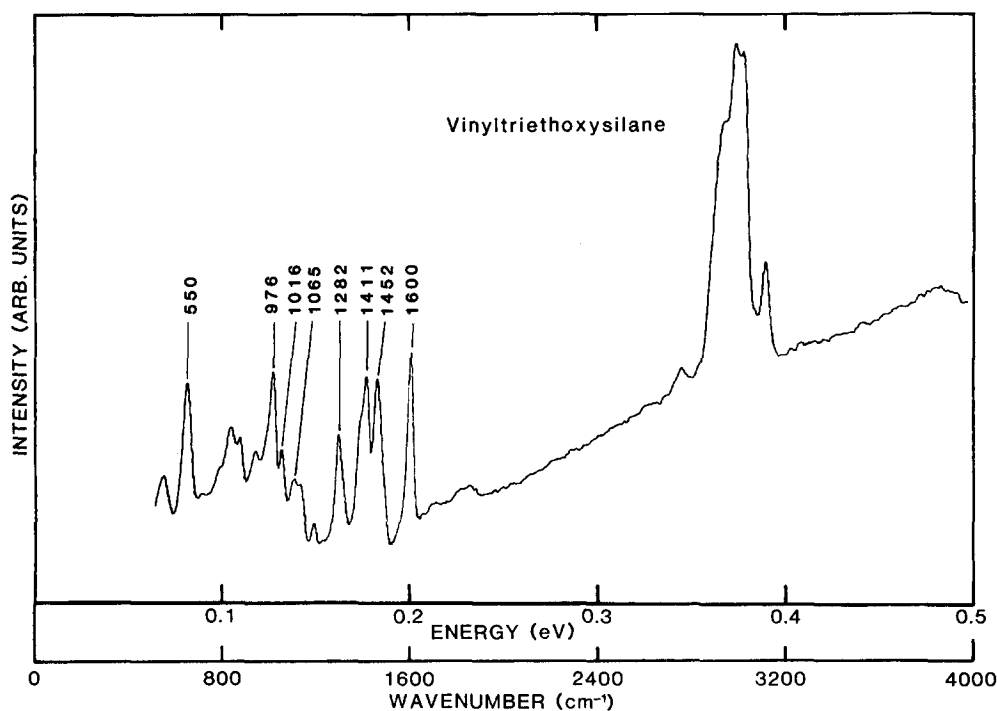


FIG. 5. IETS results for an AlOH surface doped with vinyltriethoxysilane in water. By comparison with Fig. 4, the salient features of vinyltrimethoxy and vinyltriethoxysilane are identical.

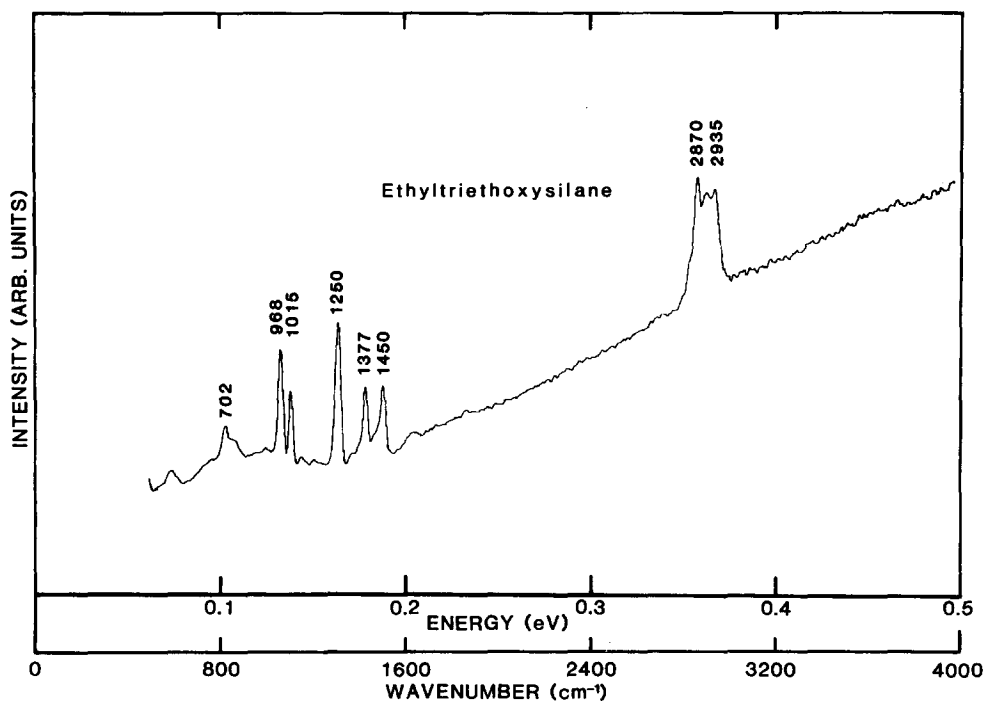


FIG. 6. IETS results for an AlOH surface doped with ethyltriethoxysilane in pure acetone. The prominent peaks are characteristic of SiC_2H_5 groups. Peaks at 1377 and 1450 cm^{-1} correspond to sym. and asym. CH_3 deformations, 1250 cm^{-1} to CH_2 wagging, and 1015 cm^{-1} to CH_3 rocking modes.

the relatively intense bands at 1600 cm^{-1} , due to $\text{C}=\text{C}$ stretching, and at 550 cm^{-1} corresponding to the $\text{Si}-\text{CH}=\text{CH}_2$ out-of-plane hydrogen deformation mode, and (b) the spectra are identical in that the same peaks appear in each, and the ratio of the heights for peaks associated with the vinyl group to those associated with the $\text{C}-\text{H}$ stretching in the 2900 cm^{-1} region is the same. From these observations we conclude that the vinyl group is unchanged and does not play an active role in the reaction of these compounds with the alumina surface, and the alkoxy groups are

completely hydrolyzed. Again, there are peaks at 1065 and 445 cm^{-1} corresponding to asymmetric and symmetric $\text{Si}-\text{O}-\text{Si}$ stretch motions.

The spectrum of ethyltriethoxysilane (Fig. 6) is identical to that reported by Brewis *et al.*¹² This again points out the reproducibility of spectra obtained by different investigators using slightly different techniques of applying the silane, i.e., liquid vs vapor phase doping. This compound was diluted with pure acetone, which accounts for the absence of an OH peak.

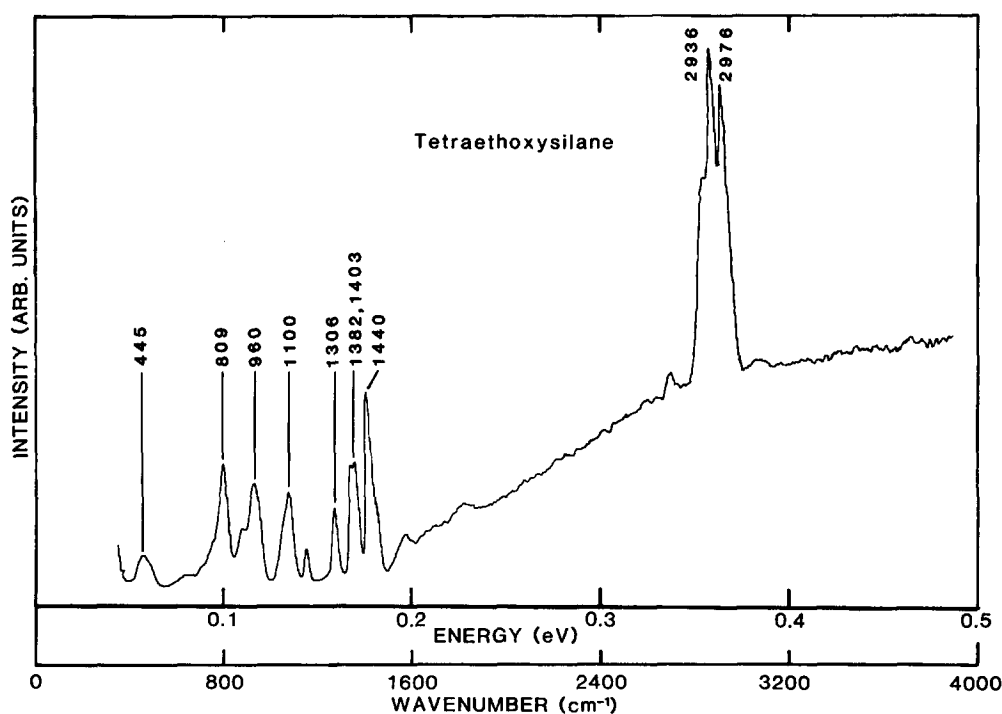


FIG. 7. IETS results for an AlOH surface doped with tetraethoxysilane in pure acetone. Other than the peaks characteristic of C_2H_5 groups, there are peaks attributed to unhydrolyzed OEt groups as evidenced by the sym. and asym. stretching frequencies of $\text{Si}-\text{O}-\text{C}$ at 960 and 1100 cm^{-1} .

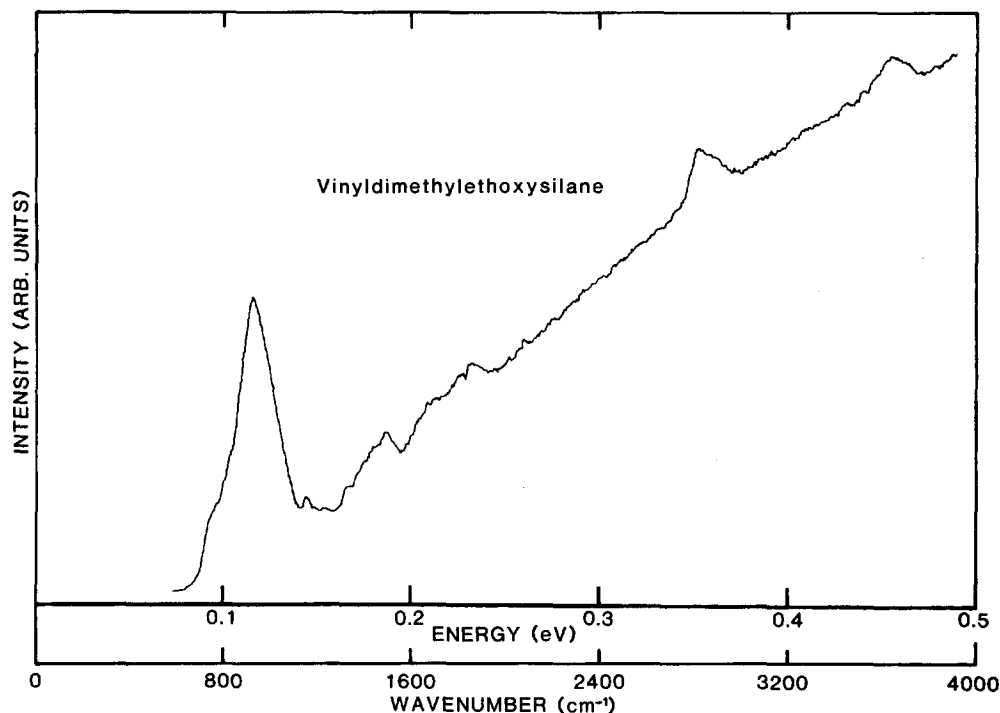


FIG. 8. IETS results for an AlOH surface doped with vinyl dimethylethoxysilane. The primary difference between this spectrum and that shown in Fig. 1 is a slight trace of hydrocarbon contamination evidenced by the weak broadband at 2950 cm^{-1} .

Experiments were also carried out using tetraethoxysilane as the dopant, applied in the same way, Fig. 7. Since this compound has no organofunctional group, its spectrum contains only those peaks due to either unhydrolyzed ethoxy groups, or those resulting from hydrolysis and reaction with alumina. Again there is a relatively strong peak at 1100 cm^{-1} , corresponding to the asymmetric Si-O-Si stretch mode, and a much weaker peak at 445 cm^{-1} , corresponding to the symmetric Si-O-Si stretch. However, there is a relatively strong peak at 809 cm^{-1} , which corresponds to the symmetric Si-O-C stretch, and one would therefore expect the asymmetric Si-O-C stretch to appear at 1100 cm^{-1} , as a doublet.¹⁸ The relatively strong peak at 1100 cm^{-1} could well be due to a combination of both the Si-O-Si and Si-O-C asymmetric stretch.

From the analysis of these spectra obtained when alumina is treated with trialkoxysilanes and tetraethoxysilane, it is concluded that the organofunctional groups do not play an active role in the reaction of these compounds with the surface. On the other hand, the alkoxy groups do play an active role but hydrolysis of the alkoxy groups to form silanols is not a necessary precursor step in the reaction. The number of alkoxy groups required for a silane to bond with alumina is not known. In principle, one should be sufficient. As a test of this hypothesis, several junctions were doped with monoalkoxysilanes.

ALKOXY-SILANES

To rule out the possibility that silanes react with alumina via the organofunctional groups, and answer the question of the number of alkoxy groups required if the reaction is via the alkoxy group, samples were prepared using monoalkoxysilanes. The compounds vinyl dimethylethoxysilane

and dimethylethoxysilane were chosen because each contain readily identifiable bonds: the carbon-carbon double bond in the vinyl group and the Si-H bond in the dimethylethoxysilane. For the trialkoxysilanes, these bonds produce prominent peaks at 1600 and 2186 cm^{-1} , respectively (see Figs. 2-5), and one would expect the same to be the case for monoalkoxysilanes.

Figure 8 is a representative spectrum for these compounds when the junction is doped with the pure compound without dilution. The result is rather surprising—these compounds are not chemisorbed on alumina. In all cases, however, the junction resistance is rather high ($R > 1\text{ k}\Omega$) after doping. In general, the junction resistance increases from one to two orders of magnitude after applying a monoalkoxysilane. This result suggests that the monoalkoxysilanes promote the oxidation of aluminum but do not themselves bond to the surface.

Several attempts were made to promote the reaction of dimethylethoxysilane with alumina: (1) heating the substrate to 100°C after doping, (2) adding acetic acid and water to the silane and heating the substrate after doping,³ and (3) adding propylamine and water to the silane and heating the substrate after doping.³ None of these variations in procedure led to the appearance of an Si-H peak in the spectra. Thus, no adsorption of dimethylethoxysilane seems to occur.

CONCLUSIONS

The following conclusions are obtained: (1) trialkoxysilanes are adsorbed on the surface of oxidized aluminum whereas monoalkoxysilanes are not, (2) the spectra of triethoxy and trimethoxysilanes are the same, therefore: (a) chemisorption is independent of the type of alkoxy group, and (b) complete hydrolysis had occurred under the doping con-

ditions used, (3) surface OH or OD groups participate in the reaction when anhydrous silanes are added to the alumina, and (4) in this case, siloxane bonds are formed at the surface.

All of these results suggest the following hypotheses: Trialkoxysilanes can condense directly with OH groups on an alumina surface to form siloxane interfacial bonds. Such bonds are probably stabilized subsequently by condensation between chemisorbed silane molecules to form siloxane oligomers. On the other hand, monoalkoxysilanes appear to be unable to bond to an alumina surface, either because their reactivity is intrinsically lower or because they are not able to condense further to form a nonvolatile polysiloxane layer *in situ*. Their intrinsic reactivity will, of course, be reduced because they have fewer reactive sites per molecule. Nevertheless, they clearly act as catalysts for further oxidation of the aluminum surface, as evidenced by the rapid increase in junction resistance on doping the substrate with them.

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