



Surface Characterization of Adamantylethyltrichlorosilane (AdSi) Coatings on Aluminum

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ARL-TR-2020

July 1999

19990813 065

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ARL-TR-2020

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Abstract

Surface characterization techniques were used to evaluate adamantylethyltrichlorosilane (AdSi) as a potential coating to provide surface protection or as an initiator for diamond-like thin films. FT-IR and FT-Raman results indicate that, after formation and heating, the coating system has developed a cross-linked siloxane network. Quartz crystal microbalance and contact angle measurements were used to monitor the adsorption rates and the effect coverage of AdSi on oxidized aluminum (Al) surfaces. A concentration-dependent adsorption rate from hexane and ethanol/acetic acid solutions was observed. It was also evident that multilayer formation was occurring, probably due to the highly reactive chlorosilane functional groups.

Acknowledgments

Funding for this project was received from the U.S. Army Research Laboratory's (ARL) Directors Research Initiative. Drs. Brian J. Kennedy and Larry Seger were National Research Council Postdoctoral Research Associates during this work. Sara Jensen was an intern through the George Washington University Science and Engineering Applied Science Apprentice Program.

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1. Introduction

Adamantylethyltrichlorosilane (AdSi) was chosen as a candidate to provide surface protection and scratch resistance for aluminum (Al) and polymeric materials. Siloxane-based compounds are well known for their ability to provide antiwetting properties and for their use in primer applications for metal protection [1]. Another potential application for an adamantyl-type coating is to initiate diamond-like thin films on polymeric materials such as polycarbonate [2]. Considering the potential applications, AdSi was characterized on Al surfaces. This work represents the first characterization of an adamantyl-based organic thin film. Previous applications using AdSi focused on the development of adamantyl-modified silica gel for reversed-phase separation in high-performance liquid chromatography (HPLC) [3, 4].

Potential thin-film applications include semiconductors, sensors, corrosion protection, and friction reduction [5]. Candidates for the protection of Al surfaces include thin films based on alkanolic acids [6] or alkylsiloxanes [7, 8, 9] that readily react with the metal surface through specific functional groups. In comparison to weak adsorption properties of alkanolic acids with oxidized metals [10], the high reactivity of alkyltrichlorosilanes with oxidized metals [11] makes them an ideal candidate for surface protection. An advantage of alkylsiloxanes is that they undergo cross-linking through intermolecular condensation of -SiOH groups to form a network of $(\text{Si-O-Si})_n$ units bound to the underlying metal structure. Additional gains can be met by modifying the coating terminal tail group in order to customize coating characteristics for specific applications. For example, fluorosiloxanes and fluoropolymers are being investigated as coatings for naval vessels [1, 12, 13]. The fluoropolymers are highly inert and provide a low surface energy coating that resists marine fouling.

Surface characterization techniques can be used to develop a basic understanding of the reaction and stability of AdSi on metallic and polymeric surfaces. FT-IR and FT-Raman techniques are routinely used to determine the chemical structures of coatings on various surfaces. Quartz crystal microgravimetry (QCM) and contact angle measurements are also used to understand adsorption kinetics and effective surface coverage, respectively. Combining the

analysis from these techniques enables a basic understanding of the surface protection capabilities of AdSi to be developed.

2. Experimental

For FT-IR studies, glass microscope slides were cleaned and then coated with ~100 nm of aluminum in a vacuum evaporator (10^{-6} torr). After exposure to atmospheric conditions, the slides were stored in an ethanol solution containing 0.1% acetic acid (HAc). This process maintains surface cleanliness until the coating is applied. For the coating application process, the Al samples were dried in an oven at 50° C before being immersed in sample solutions of adamantylethyltrichlorosilane (AdSi) (Gelest) dissolved in ethanol (Aldrich, HPLC grade) adjusted to pH 4.0 (~0.1% acetic acid). These solutions were stable for several weeks. Pure AdSi rapidly reacts with humid air to form a solid, cross-linked siloxane material, so precautions were used to minimize exposure of pure AdSi to moisture and to atmospheric conditions prior to solvent exposure. Surface preparation techniques were compared using solutions of AdSi in hexane vs. those in ethanol/HAc. Comparisons of solvent conditions for coating formation were made using FT-IR and QCM. Surfaces prepared in hexane and ethanol/HAc provided identical spectral characteristics. Therefore, any spectra presented herein represent results from surfaces prepared in ethanol/HAc. Spectrally, surfaces were evaluated as a function of analyte concentration and immersion times (from minutes to hours). The coating integrity was also evaluated as a function of thermal exposure by storing the surfaces in an oven maintained at 120 and 200° C.

Spectral analysis of surfaces was performed using a nitrogen-purged ATI Mattson Research Series 1 FTIR Spectrometer with a reflection absorption accessory at a 75° angle of incidence (Harrick, Refractor Plus). Solids and liquids were sealed between NaCl windows to acquire absorption spectra. The detector was a liquid nitrogen-cooled, mercury-cadmium-telluride detector. The resolution for pure solid and liquid samples was 1 cm^{-1} , and for surface analysis, the resolution was 4 cm^{-1} . Acquisitions were obtained using 1024 scans. A reference slide was prepared identically to the AdSi-treated slides and stored in ethanol until use.

FT-Raman was used for comparative analysis of liquid AdSi and to obtain additional spectral information in the low-frequency region. The Bomem DA-8.02 FT-Raman instrumentation has been described previously [14]. This consisted of a Bomem FT-Raman system using a 300-mW, Nd:YAG laser operating at 1.06 μm . The liquid sample was sealed in a glass vial to prevent reaction of the chlorosilane groups with atmospheric moisture.

Quartz crystal microgravimetry (QCM) analysis was performed to evaluate the concentration-dependent adsorption kinetics. A locally assembled QCM system used AT-cut quartz crystals that operated at 6 MHz. These were coated with 100 nm of Al with an active diameter of 6.35 mm (McCoy Crystals). A basic requirement for QCM studies was the use of nonpolar solvents. Therefore, all QCM adsorption studies involved the use of dry hexane with AdSi concentrations ranging from 2.5 to 0.025 mM. The solvent chamber was temperature regulated at 22° C.

Contact angle measurements were performed using an Advanced Surface Technologies, Inc., Model VCA 2500, contact angle measurement apparatus. The probe liquid was a single drop of triple-distilled water. A droplet was formed at the end of a hypodermic needle and was carefully lowered until the drop touched the surface of the substrate. At this point, a video image of the drop was recorded and contact angles were measured. Reported values represent 10 replicates of different droplets on the same sample. Readings were reproducible to within 2° for each sample.

3. Results and Discussion

The FT-IR absorption spectra for AdSi in the solid and liquid forms are shown in Figure 1. Figure 2 shows the FT-Raman spectrum for liquid AdSi. FT-Raman analysis of the solid phase was not possible due to a strong luminescence from the solid form. In the high-frequency region, detailed in Figure 3, the distinct peaks are primarily due to the C-H stretching modes from adamantane [15] convoluted with C-H stretching bands from the ethyl chain [16] located between the adamantane group and the Si group. The high-frequency and low-frequency assignments are summarized in Table 1.

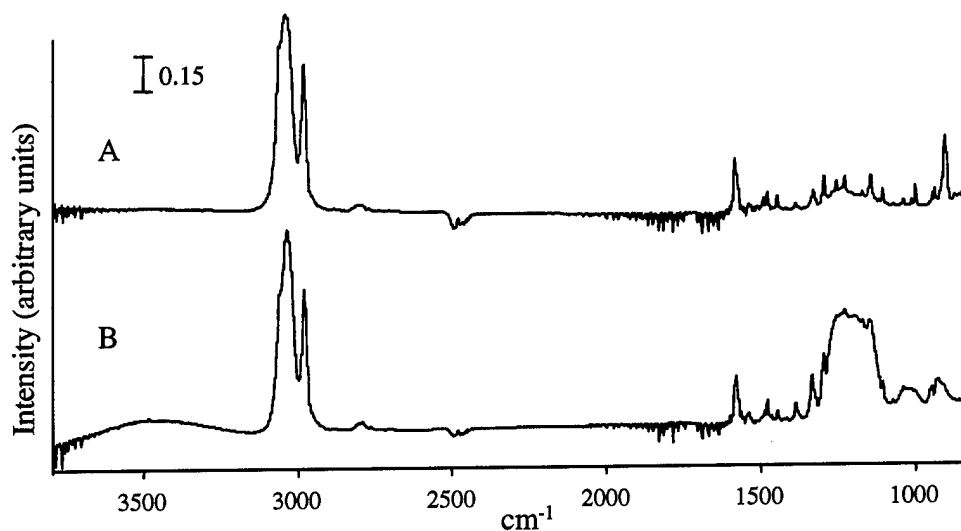


Figure 1. FT-IR Spectra for Adamantylethyltrichlorosilane (AdSi) Using 1 cm^{-1} Resolution. The Liquid Sample (A) was Sealed Between Two NaCl Plates. The Solid Sample (B) was Obtained After Brief Exposure to Atmospheric Lab Conditions and Drying.

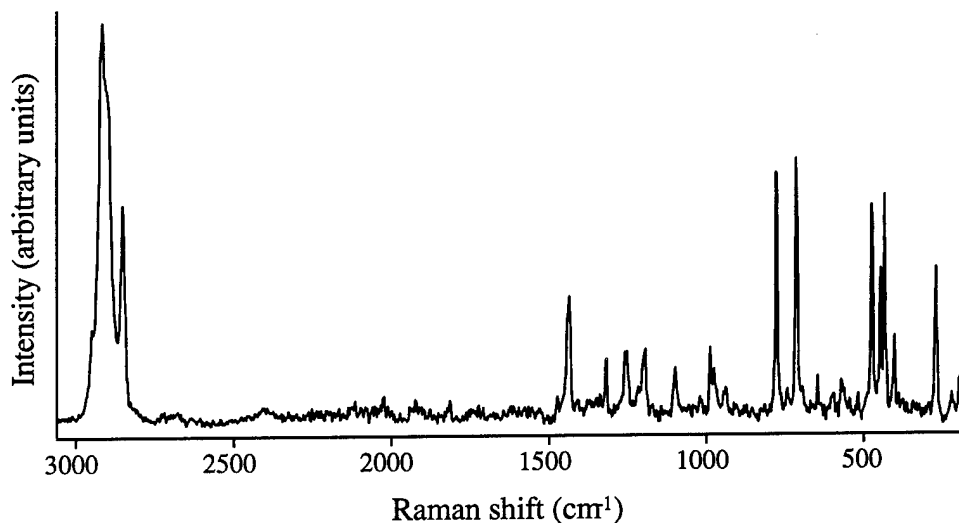


Figure 2. FT-Raman Spectrum of Liquid Phase AdSi Using 1 cm^{-1} Resolution.

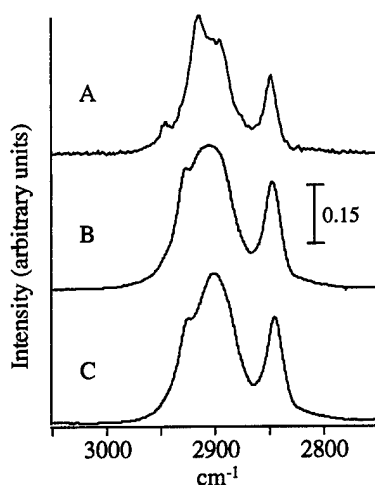


Figure 3. Comparison of the $\nu(\text{C-H})$ Stretching Region Using FT-Raman (A, Liquid) and FT-IR (B, Liquid; C, Solid) With 1 cm^{-1} Resolution.

Table 1. Characteristic Vibrational Modes (cm^{-1}) for AdSi as Shown in Figures 1–5

Vibrational mode	Liquid AdSi, FT-IR	Solid AdSi, FT-IR	Applied to Al_2O_3 , FT-IR	Liquid AdSi, FT-Raman
(Si-OH)	–	–	3400	–
($\text{R}_3\text{C-H}$)	–	–	–	2947
(CH_2) asymmetric stretch	2928	2925	2926	–
(CH_2) asymmetric stretch	2906	2902	2904	2916
(CH_2) _{FR} symmetric stretch	–	–	–	2902, 2897
(CH_2) symmetric stretch	2848	2846	2846	2849
CH_2 scissoring deformation	1453	1451	1451	1463
CH_2 wagging	1362, 1348, 1316	1361, 1347, 1315	1348	1316
C-C stretching	1256, 1200, 1166, 1126	1258, 1204, 1168	1256, 1203, 1168	1260, 1250, 1193
Si- CH_2 stretching	1098	–	–	998, 973
(-Si-O-Si-) _n	–	1000–1200	1020–1150	–
Si-OH stretching	910	911	–	–
C-C stretching	882, 870	869–900	~900	–
CH_2 rocking	814, 806	819	~800	–
Si-C	774, 712	798, 714	798, 714	777, 713
CCC deformation	–	–	–	405
Si- Cl_3	–	–	–	475, 434, 272
CH_2 rocking	–	–	–	447

For the liquid phase using FTIR, the high-frequency modes, primarily from absorption of the adamantyl group, are assigned to the CH₂ symmetric mode at 2847.6 cm⁻¹ and a CH₂ asymmetric stretching mode at 2906.3 cm⁻¹. Also evident in the detail of this region (Figure 3) is a shoulder at 2927.8 cm⁻¹ that can be attributed to the CH₂ asymmetric stretching mode from the alkyl chain. The FT-Raman spectrum provides better resolution of these bands, with similar band positions. In general, spectral shifts in the C-H stretching region between the solid and liquid states (Table 1) are indicative of the chemical interactions where a shift to lower frequencies is noted for solids [17].

The low-frequency region, summarized in Table 1 and shown in Figure 5, provides details about Si-O, Si-C, Si-Cl, and C-C stretching modes. The obvious difference between the liquid and solid FT-IR spectra is the broad band between 1000 and 1200 cm⁻¹ for the solid. This is attributed to the formation of a networked system of (Si-O-Si)_n groups following extensive cross-linking through silanization of Si-OH groups.

The low-frequency region also represents a combination of modes from the silane group, the ethyl chain, and the adamantyl group. For example, the adamantyl group alone contains vibrational modes at 796, 967, 1103, 1351, and 1448 cm⁻¹ [15]. Alkyltrichlorosilanes commonly contain vibrational modes near 700, 960, 1020, 1230, 1240, 1350, and 1425 cm⁻¹ [18, 19, 20]. Considering this overlap, the vibrational assignments in Table 1 are based on literature values for similar systems.

The FT-IR and FT-Raman spectra show the large peak near 1453 cm⁻¹ due to the CH₂ scissoring mode from the ethyl chain and adamantane. CH₂ wagging modes are evident between 1315 and 1362 cm⁻¹. Numerous C-C stretching and Si-CH₂ stretching modes occur between 973 and 1256 cm⁻¹. The FT-IR and FT-Raman spectra exhibit several peaks assigned to the ν (Si-C) gauche stretch near 714 cm⁻¹ and the ν (Si-C) trans stretch near 780 cm⁻¹ [21]. Further characterization in this region is complicated due to overlap of the adamantane spectral characteristics with the ν (C-C) modes from the alkyl chain. The distinct modes in the FT-Raman spectrum between 270-475 cm⁻¹ result from Si-Cl vibrational modes [22].

Figure 4 represents FT-IR grazing angle spectra for an aluminum slide treated with a solution of 2.5-mM AdSi in EtOH/HAc using 7-min soak times. An initial observation is that thin films of AdSi readily adsorb onto Al surfaces. Quartz crystal microbalance studies suggest that multilayers rapidly form on oxidized aluminum, an issue addressed later. The spectrum for AdSi adsorbed on oxidized Al has obvious features between 1020 and 1150 cm^{-1} that represent siloxane formation, $(\text{-Si-O-Si-})_n$, between adjacent monomer units. A spectral comparison of the liquid, the solid, and adsorbed states for a dried coating sample in the low-frequency region is highlighted in Figure 5. Compared to siloxane spectral features in the solid form ($\sim 1000\text{--}1200\text{ cm}^{-1}$), it is evident that siloxane formation in the coating appears incomplete. This infers that the coating coverage is not complete and that surface defects may exist.

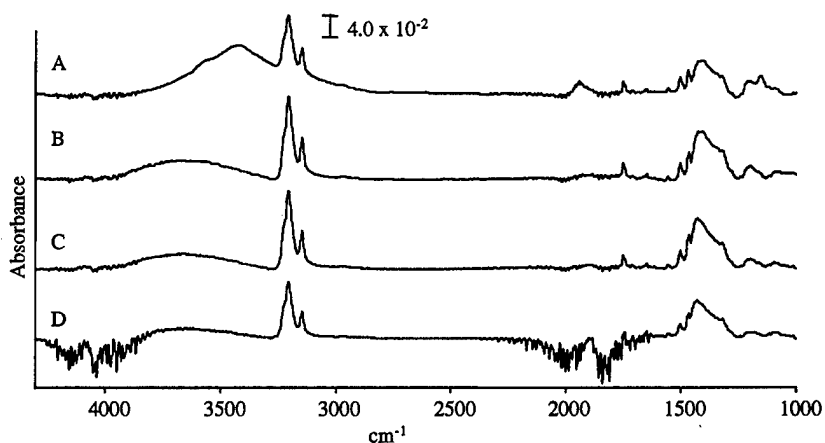


Figure 4. Self-Assembled Monolayer of AdSi Formed on Al From 2.5-mM AdSi in a 0.1% Acetic Acid/Ethanol Solution Using a 7-min Soak Time, 4 cm^{-1} Resolution. The Spectra Shown Were Air-Dried (A), Dried at 120° C for 15 min (B), Dried at 120° C Overnight (C), and Rinsed With Ethanol and Then Dried at 120° C for 30 min (D). The Absorbance Remains Stable Throughout, Although the Water Noise in D is More Evident Than in Spectra A–C.

Characterization of AdSi as a coating is made by comparing the spectra of the pure compounds and the FT-IR grazing angle spectra of AdSi on Al substrates (Figure 4). These results are also summarized in Table 1. Spectral comparisons of the liquid and solid forms vs. as a coating, such as that shown in Figure 5, provide insight regarding the chemical interactions of adsorbed species. For example, self-assembled monolayers (SAMs) formed from alkanethiols

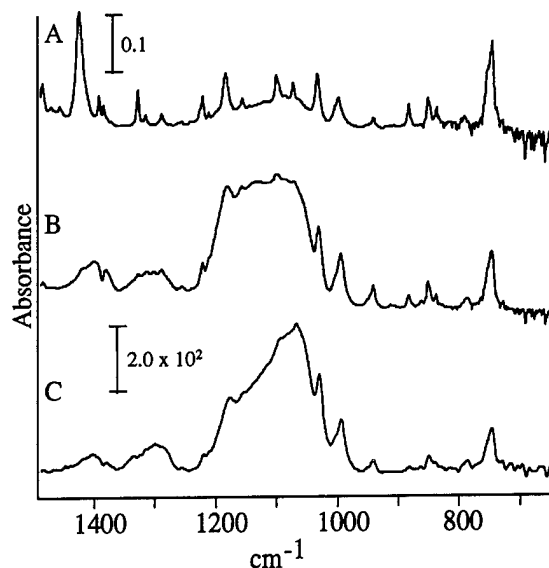


Figure 5. Low-Frequency Region of AdSi Spectra for a) Liquid, b) Solid, and c) on Al_2O_3 Surface After Oven Drying.

on silver surfaces studied by Bryant and Pemberton consistently reveal crystalline-like structures similar to the solid form of the pure compound [23]. These observations imply that the alkanethiol SAM coatings are rigidly and favorably bound to the surface and that the structures are more solid-like than liquid-like. Alkanethiols predominately establish this lower energy, crystalline-like state through van der Waals interactions of adjacent alkane chains.

Coatings based on trichlorosilanes are well known to rapidly adsorb and form multilayers. Observations described herein correlate with several proposed mechanisms used to describe the formation of monolayers and multilayers of alkylsiloxanes [7, 8, 9]. Upon heating to 120°C , surface-bound water and hydroxyl species are removed (Figure 4). Accordingly, the Si-Cl units have dissociated to form Si-OH, followed by cross-linking through intermolecular condensation between adjacent Si units. This latter point is observed through the increased intensity and broadening of the siloxane $(\text{Si-O-Si})_n$ bands between 1000 and 1200 cm^{-1} . Before network formation, the compounds are chemically adsorbed to the underlying Al_2O_3 structure through an Si-O linkage. Spectral characteristics in the high-frequency region between 2500 – 3600 cm^{-1} for monolayers formed from alkylsiloxanes are characterized by $\nu(\text{C-H})$ stretching modes and OH

stretching from physisorbed water and Si-OH. Figure 3 details these spectral characteristics for the liquid and solid samples, and Figure 4 shows the entire coating spectra under varying conditions. The predominant feature near 3400 cm^{-1} is due to absorbed water and to Si-OH groups that have not completely silanized.

In the coating spectra (Figure 4), it is evident that water is initially physisorbed within the multilayer system. After both brief and extended drying periods at 120°C , the intensity of this large absorption decreases and is then similar to that observed with a solid sample. As a measure of thermal and solvent stability, temperature exposures to 200°C and storage of surfaces in ethanol were made. Such extreme temperature exposures and soaking the AdSi-coated Al substrates in ethanol do not significantly reduce the intensity of any spectral features, particularly the -OH mode near 3400 cm^{-1} . These results suggest that the silanization process to form $(\text{Si-O-Si})_n$ siloxane groups is not complete and that Si-OH groups remain. Evidence for the formation of a networked siloxane system will be discussed later in this report. The remaining features are straightforwardly assigned to $\nu(\text{CH}_2)$ and $\nu(\text{CH})$ vibrational modes from adamantyl and ethyl groups.

• **QCM and Contact Angle Measurements.** The concentration dependence for AdSi adsorption onto Al was evaluated in situ using QCM and ex situ using FT-IR. QCM also provides semi-quantitative information related to the adsorption kinetics. Figure 6 represents the spectral differences for coating Al with various concentrations of AdSi in EtOH/HAc. The samples were immersed for 7 min, then heated at 120°C for 30 min prior to FT-IR spectral analysis. A concentration dependence is noted for the adsorption process during these short exposure times. However, the QCM analysis in Figure 7 more accurately portrays the concentration-dependent adsorption kinetics for AdSi in hexane.

For the QCM experiments, the final concentrations of AdSi in hexane were rapidly adjusted to be 2.5, 1.0, 0.25, and 0.025 mM. The AT-cut, Al-coated crystals operated at 6 MHz were thoroughly washed in organic solvent prior to soaking in hexane. A stable frequency was monitored before each concentration injection. The QCM plots are shown in Figure 7.

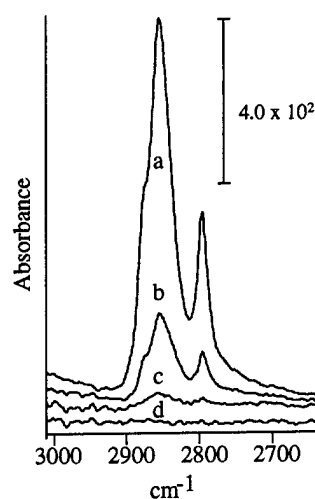


Figure 6. FT-IR Spectral Comparison for Coating AdSi Onto Al in EtOH With 0.1% Acetic Acid. AdSi Concentration: a) 2.5, b) 1.0, c) 0.25, and d) 0.025 mM. Soak Times Were 7 min.

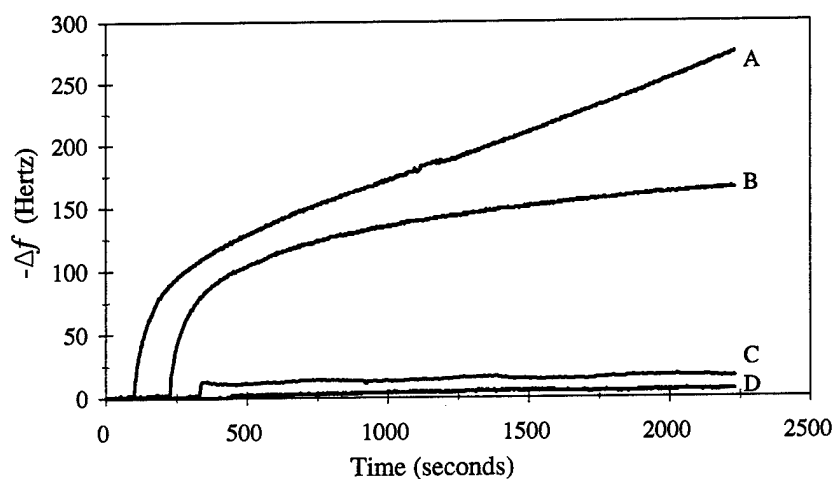


Figure 7. Concentration Dependence of AdSi Adsorption Onto Al as Studied Through QCM. The AdSi Was Applied to Hexane at Concentrations of a) 2.5 mM, b) 0.25 mM, c) 0.025 mM, and d) 0.0025 mM. The Injection of AdSi Was Staggered by ca. 100 s for Subsequent Exposures in Order to Maintain Clarity Between Separate Lines.

Although only semi-quantitative results can be obtained from the QCM method used in this work, it is possible to make inferences based upon the results. A similar trend is observed for the FT-IR spectra using EtOH and the QCM data using hexane. The frequency change and the

absorbance intensity both increase with increasing concentration. The QCM trends shown at each concentration continue to be observed for over 12 hr. At the low concentrations, below 0.25 mM, it is evident that submonolayer formation results. In contrast, the higher concentrations rapidly and continuously form multiple layers of AdSi on Al. These observations allow conclusions to be drawn regarding multilayer formation.

The adsorption of octadecanoic acid monolayers onto Al has been shown [6]. For comparison to the AdSi system, the adsorption of octadecanoic acid onto Al QCM crystals described herein yielded a monolayer system with a frequency change of ca. 60 Hz. Similar observations have been made for octadecanethiol monolayers on Au-coated crystals [24]. The octadecanethiol and octadecanoic acid systems are well known to form highly ordered, well-packed monolayer systems. Assuming a poorer packing density for the bulky adamantyl compound, it is expected that a smaller frequency change would be observed for monolayer coverage. As shown in Figure 7, it is evident that large frequency changes are being measured. For the 0.025-mM adsorption plot, the Δf is ca. 15 Hz, a value smaller than anticipated for monolayer coverage. However, at the higher concentrations, the Δf values continue to increase and are assumed to represent multilayer formation.

The contact angle for a drop of water on the Al QCM crystals was 81° for blank Al and 92° for AdSi-coated Al using a dried surface. Upon heating the surface at 200° C for 15 min, the contact angles remain unchanged. The small difference between blank Al and the AdSi-coated Al implies several possibilities. The coating may not uniformly cover the underlying metal substrate. This would lead to the development of surface roughness features. Another possibility is that during the multilayer formation process silanol groups protruding away from the surface are exposed to the liquid drop. With -OH groups exposed to the contact water, the surface would be expected to be more easily wetted, as the results suggest.

The results presented herein are in agreement with proposed mechanisms for siloxane adsorption [7, 8, 9]. An example of this mechanism for AdSi is depicted in Figure 8. In nonaqueous environments (e.g., hexane) the trichlorosilanes react with surface hydroxyl groups

to form interfacial siloxane bonds [25]. Surface-bound water is also presumed to be available to drive the surface-to-chlorosilane reaction [26]. A by-product of this reaction is the formation of HCl and H₂O. As a by-product, this water would be further available to allow multilayer formation, as observed through QCM. Condensation of the adsorbed species through heating to 120° C drives the silanization between adjacent SiOH (or SiCl) units, therefore forming a networked surface multilayer. Also noted in Figure 4 is that the surface heating process removes surface-bound water to a limiting extent.

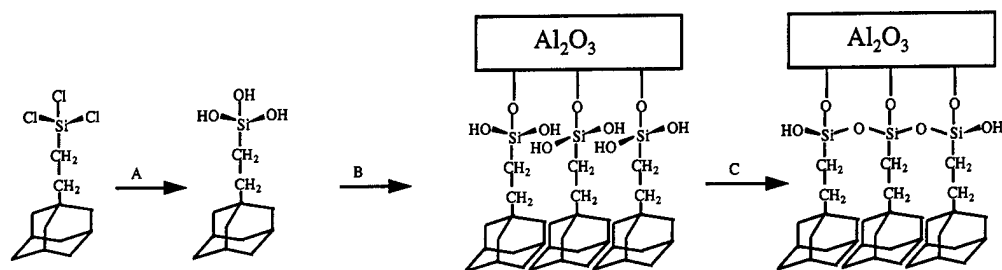


Figure 8. Mechanism for the Absorption of AdSi Onto Al₂O₃. A) Represents the Solution Preparation of AdSi in EtOH/0.1% HAc, B) Is the Immersion of the Al-Coated Glass Slide Into the Solution, and C) Is the Thermal Annealing Process That Facilitates Silanization, Thus Providing a More Durable Surface Coating.

An application limitation is observed during the QCM studies in hexane. After the initial deposition period, the Al-coated QCM crystal appears to corrode under the presence of AdSi during exposures of 12 or more hours. It may be that the HCl by-product is readily diluted into the EtOH/HAc solution as opposed to its poor solubility in a nonpolar hexane solution. In the case of a nonpolar solvent, the HCl may become localized within the adsorbate structure with surface-bound water. An acidic condition such as this would subsequently cause corrosion of the metal material. For comparison, a similar analysis was performed in dry hexane using a N₂ purge yielding an adsorption identical to a nonpurged system. It was anticipated that a N₂ purge would provide a drier hexane solution and facilitate HCl gas removal. Instead, the HCl appears to remain confined to the metal-coating interfacial region leading to corrosion of the thin Al layer in a manner similar to that without N₂. Intense drying of the Al-coated QCM crystals immediately prior to use did not prevent this corrosion.

The durability of the AdSi coating system applied to Al-coated glass slides was also addressed. After thermal curing at 120° C, ethanol and H₂O soaks for 30 min or more did not affect the coating integrity as observed through FT-IR signal intensities. Also, long-term heating (>15 hr) at 200° C only led to ca. 15% decrease in signal intensity. Samples exposed to ambient laboratory conditions also proved stable for exposure periods in excess of 8 months. These initial simple tests indicate that the coating durability is good and is in agreement with a basic requirement for use as a corrosion inhibitor or primer. Additional applications of AdSi on polymeric substrates (e.g., polycarbonate) as an adhesion promoter or diamond-like thin film initiator are being investigated.

The evidence contained herein suggests that multilayer adsorption occurs. As a coating for corrosion protection, the benefits of a multilayer system can be realized. However, to be used as a diamond-like film for scratch protection applications on polycarbonate a multilayer system may inhibit the transparency. Considering this, an application-dependent concentration and immersion time would have to be determined for specific goals.

4. Conclusion

Coatings using AdSi formed very rapidly from a variety of organic solutions onto oxide surfaces. In this work, the adsorption of AdSi on aluminum surfaces was investigated for potential corrosion inhibitor applications. AdSi rapidly coated Al surfaces containing native oxide species and readily cross-linked to form a networked alkylsiloxane compound that was chemically bound to the underlying metal surface. The cross-linked coating was durable to short periods of heat and solvent treatments and was stable under long-term exposure to atmospheric conditions.

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE July 1999		3. REPORT TYPE AND DATES COVERED Final, Dec 97 - May 99
4. TITLE AND SUBTITLE Surface Characterization of Adamantylethyltrichlorosilane (AdSi) Coatings on Aluminum				5. FUNDING NUMBERS 1L162618AH80
6. AUTHOR(S) Brian J. Kennedy, Sara Jensen, Larry Seger, and Robert A. Fifer				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRL-WM-BD Aberdeen Proving Ground, MD 21005-5066				8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-2020
9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)				10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.				12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) Surface characterization techniques were used to evaluate adamantylethyltrichlorosilane (AdSi) as a potential coating to provide surface protection or as an initiator for diamond-like thin films. FT-IR and FT-Raman results indicate that, after formation and heating, the coating system has developed a cross-linked siloxane network. Quartz crystal microbalance and contact angle measurements were used to monitor the adsorption rates and the effect coverage of AdSi on oxidized aluminum (Al) surfaces. A concentration-dependent adsorption rate from hexane and ethanol/acetic acid solutions was observed. It was also evident that multilayer formation was occurring, probably due to the highly reactive chlorosilane functional groups.				
14. SUBJECT TERMS coatings, aluminum, siloxanes, surface protection				15. NUMBER OF PAGES 23
				16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UNCLASSIFIED	

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