CHEMISTRY of MATERIALS

VOLUME 5, NUMBER 3 MARCH 1993

Communications

Surface Raman Scattering of Self-Assembled Monolayers of (3-Mercaptopropyl)trimethoxysilane on Silver: Orientational Effects of Hydrolysis and Condensation Reactions

Wade R. Thompson and Jeanne E. Pemberton*

Department of Chemistry, University of Arizona
Tucson, Arizona 85721

Received June 24, 1992
Revised Manuscript Received December 17, 1992

Organosilanes such as (3-mercaptopropyl)trimethoxysilane (3MPT) are used to promote a variety of desirable interfacial properties such as chemical durability, alkali resistance, electrical conduction, insulation, surface protection, and adhesion.[1-7] As the name implies, 3MPT is comprised of two important functional groups. The thiol tail is able to form a covalent bond to a variety of metals through the sulfur atom, and the methoxysilane head group is capable of undergoing hydrolysis and condensation reactions. Hydrolysis and condensation reactions of alkoxide solutions result in the formation of a gelled metal oxide network. This process is commonly referred to as sol–gel synthesis.[8-10]

The two functional groups of 3MPT allow it to be used as a molecular adhesive between two materials.[5,6] The surface orientation of the molecules and the functional groups is an important aspect of the ability of the molecules to promote adhesion. However, only a limited amount of research has been done to investigate how these molecules interact at the metal surfaces they are used to modify.

Vibrational spectroscopy is a powerful tool for characterizing organosilane systems, particularly alkane-containing organosilanes, because of the sensitivity of vibrational modes to conformation within the alkane chain. Vibrational spectroscopy of organosilanes on metal surfaces, in the past, has primarily been limited to experiments using reflection–absorption infrared spectroscopy.[11-13] Recent work in this laboratory has shown that Raman spectroscopy is also a useful vibrational technique for qualitative evaluation of surface orientation and conformational order in molecular monolayers formed from alkanethiols on metal surfaces.[14-16] This approach was used in this study to qualitatively determine these characteristics of a monolayer of 3MPT adsorbed onto Ag surfaces and characterize the resulting layer after subsequent hydrolysis and condensation of the monolayer film. This report represents the first application of Raman spectroscopy to the characterization of such reactions on metal surfaces.

Raman spectra were acquired on self-assembled monolayers of 3MPT adsorbed on smooth, polycrystalline Ag surfaces prepared by mechanical polishing with 0.3-μm

---

* Author to whom correspondence should be addressed.

(1) Arkles, B. *Chemtech* **1977**, *12*, 766.
(2) Plueddemann, E. P. *Silane Coupling Agents*; Plenum Press: New York, 1991.
(3) Walker, P. J. *Adhesion Sci. Technol.* **1991**, *5*, 279.
(4) Wasserman, S. R.; Biebuyck, H.; Whitesides, G. M. *J. Mater. Res.* **1989**, *4*, 886.
(5) McGee, J. B. U.S. Patent 4,315,970 1982.
(6) Goss, C. A.; Charych, D. H.; Majda, M. *Anal. Chem.* **1991**, *63*, 85.
(7) Allara, D. L.; Nuzzo, R. G. U.S. Patent 4,690,715 1987.
(8) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1987**, *11*, 663.
(9) Schmidt, J. *J. Non-Cryst. Solids* **1988**, *100*, 51.
(10) Sakka, S. *Treatise on Materials Science and Technology*; Academic Press: New York, 1982; Vol. 22, p 129.
(11) Boerio, F. J.; Schoenlein, L. H.; Greivenkamp, J. E. *J. Appl. Polym. Sci.* **1978**, *22*, 203.
(12) Boerio, F. J.; Armogan, L.; Cheng, S. Y. *J. Colloid Interface Sci.* **1980**, *73*, 416.
(13) Sabatani, E.; Rubinstein, I.; Maoz, R.; Sagiv, J. *J. Electroanal. Chem.* **1987**, *219*, 365.
(14) Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 2824.
(15) Pemberton, J. E.; Bryant, M. A.; Sobocinski, R. L.; Joa, S. L. *J. Phys. Chem.* **1992**, *96*, 3776.
(16) Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991**, *112*, 546.

0897-4756/93/2805-0241$04.00/0

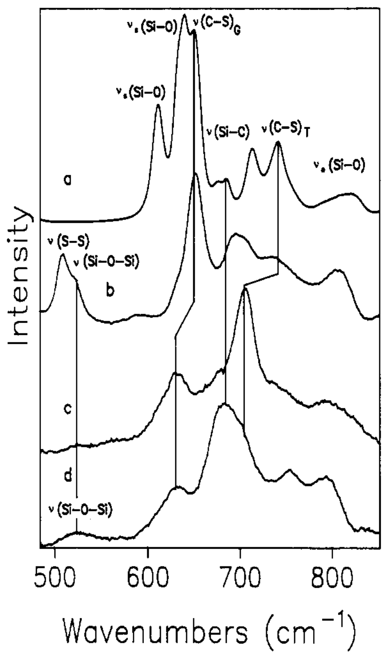

Figure 1. Raman spectra in ν(C–S) region of (a) bulk liquid 3MPT, (b) bulk 3MPT gel, (c) 3MPT adsorbed to Ag before hydrolysis and condensation reactions, and (d) 3MPT adsorbed to Ag after hydrolysis and condensation reactions.

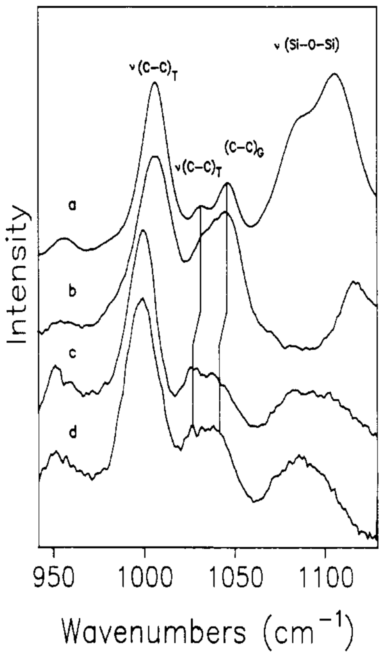

Figure 2. Raman spectra in ν(C–C) region of (a) bulk liquid 3MPT, (b) bulk 3MPT gel, (c) 3MPT adsorbed to Ag before hydrolysis and condensation reactions, and (d) 3MPT adsorbed to Ag after hydrolysis and condensation reactions.

alumina. These films were formed by immersion of the Ag surfaces in 1–20 mM 3MPT/100% ethanol solutions for times ranging from 3–6 h. After film formation, the surfaces were rinsed with 100% ethanol and allowed to air dry. Hydrolysis of the 3MPT films was accomplished by immersion in a pH 1 aqueous solution for 24 h. Hydrolysis of bulk 3MPT to a gelled solid was accomplished by mixing 3.0 mL 3MPT and 10.0 mL of 50/50 v/v water/methanol and allowing gelation overnight. Excess methanol and water were removed by heating the resulting gel at 110 °C for 24 h. Spectra of the adsorbed molecules were obtained using 100 mW of 514.5-nm Ar^+ laser radiation on a spectrometer system described previously.[14–16]

In solution, alkane-containing molecules are capable of existing in a variety of conformations resulting in considerable disorder. This disorder is indicated by the presence of gauche (G) conformations in the alkane chain. In the presence of G conformations, these molecules are unable to pack uniformly. More uniform packing is facilitated if the alkane chains in the molecules exist in an all-trans (T) conformation.

Figure 1shows Raman spectra in the ν(C–S) region for bulk liquid 3MPT, gelled bulk 3MPT, 3MPT adsorbed to Ag before hydrolysis and condensation, and 3MPT adsorbed to Ag after hydrolysis and condensation. In the bulk spectrum in Figure 1a, the relative intensity of the $\nu(C–S)_G$ at 649 cm^{-1} is greater than the $\nu(C–S)_T$ at 742 cm^{-1}, indicating the prevalence of the G conformer. Similarly, the spectrum of the gelled solid, Figure 1b, shows considerable intensity in the $\nu(C–S)_G$ indicating disorder in this system as well. When 3MPT adsorbs to the Ag surface, both ν(C–S) vibrations shift to lower frequencies as shown in Figure 1c. This decrease is the result of the thiolate bonding between the sulfur and the Ag surface.[16,17] Moreover, although strict quantitation of disorder from the Raman intensities for the G and T conformers on the surface is not yet possible, the relative intensities of the ν(C–S) G and T bands of adsorbed 3MPT suggest that the T conformation is more prevalent. This observation implies that the 3MPT molecules self-assemble into an organized layer on the Ag surface. If multilayer film formation were occurring, one would expect to see evidence of S–H vibrations (2573 cm^{-1}) or S–S bond formation (510 cm^{-1}).[16,18] Both vibrations are evident in the spectrum of the hydrolyzed solid, but neither appears in the Raman spectrum of the surface film.

Additional evidence for the formation of an organized monolayer in this system is found in the ν(C–C) region shown in Figure 2. This region also exhibits separate vibrations for G and T conformers that can be qualitatively interpreted in terms of disorder of the propyl chain. For the 3MPT solution and gelled solid, the intense $\nu(C–C)_G$ band suggests considerable disorder. However, when 3MPT is adsorbed to the Ag surface, the $\nu(C–C)_T$ bands increase in relative intensity, further suggesting that an organized layer is formed.

The ν(Si–O) vibrations also contain useful information about orientation of 3MPT on the Ag surface.[19–21] In bulk 3MPT, Figure 1a, the ν_s(Si–O) vibration appears as a doublet at 609 and 637 cm^{-1} as a result of the silicon atom being attached to the thiol chain. The ν_a(Si–O) stretch appears as a broad vibration centered at ca. 820 cm^{-1}.[20] When 3MPT adsorbs to the Ag surface, the ν_s(Si–O) band disappears, but the ν_a(Si–O) does not. This effect is most likely due to the surface orientation of the methoxy groups relative to the Ag surface. Surface selection rules dictate that vibrations more perpendicular to the surface are

---

(17) Joo, T. H.; Kim, K.; Kim, M. S. *J. Mol. Struct.* **1987**, *158*, 265.

(18) Dollish, F. R.; Fateley, W. G.; Bentley, F. F. *Characteristic Raman Frequencies of Organic Compounds*; John Wiley and Sons: New York, 1974.

(19) Smith, A. L. *Chemical, Biochemical and Industrial Applications of Infrared Spectroscopy*; John Wiley and Sons: New York, 1985.

(20) Koenig, J. L.; Shih, P.; Lagally, P. *Mater. Sci. Eng.* **1975**, *20*, 145.

(21) Lippert, J. L.; Melpolder, S. B.; Kelts, L. M. *J. Non-Cryst. Solids* **1988**, *104*, 139.

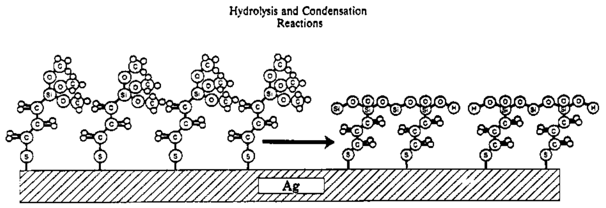

Figure 3. Schematic showing reorientation of film due to hydrolysis and condensation reactions of the methoxy groups.

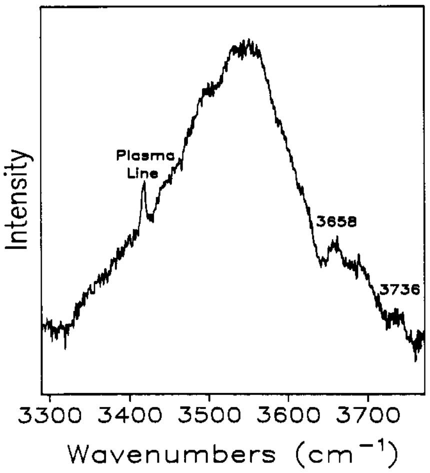

Figure 4. Raman spectra in ν(SiO–H) region of 3MPT adsorbed to Ag after hydrolysis and condensation reactions.

enhanced relative to vibrations parallel to the surface.[22,23] Based on these rules, the results suggest that the ν_s(Si–O) vibration is in a largely parallel orientation and the ν(C–S)$_T$ vibration is in a largely perpendicular orientation with respect to the surface normal.

When the adsorbed 3MPT layer undergoes hydrolysis and condensation reactions, the surface Raman spectra suggest that reorientation of the molecules occurs. This effect is shown schematically in Figure 3. The ν(C–S)$_T$ mode decreases considerably in intensity, while the ν(Si–C) vibration at 684 cm^{-1} increases in intensity. It is believed that upon hydrolysis and condensation, the molecules reorient to allow formation of a bridging Si–O–Si network. This seems to be accomplished by rotation of the molecule such that the C–S bond becomes more parallel to the surface as suggested by the decrease in the ν(C–S)$_T$ intensity. Such a rotation positions the Si–C bond more perpendicular to the surface with the other three oxygen corners of the silicon tetrahedron in a planar arrangement. In this planar array, the oxygen and silicon atoms form the expected Si–O–Si network, supported by the thiol chain, across the Ag surface. Evidence for the formation of the Si–O–Si network is the appearance of the 525-cm^{-1} band, which has previously been associated with the Si–O–Si vibration,[24] and the shift of the ν_a(Si–O) vibration to lower frequencies.[25] The reorientation due to the hydrolysis and condensation reactions does not significantly affect the orientation of the C–C bonds. The propyl chain remains largely in an all-trans orientation. As a result, little change is observed in the ν(C–C) region after reaction has occurred.

Spectra in the ν(Si–OH) region, shown in Figure 4, suggest that the Si–O–Si network contains a variety of Si–OH defects and adsorbed water, consistent with other observations of the surface chemistry of silica sol–gel systems.[26–29] The broad band between 3150 and 3550 cm^{-1} is assigned to water physisorbed to the surface. In addition, weak bands at ca. 3658 and 3736 cm^{-1} are observed that indicate the presence of several surface Si–OH environments. The band at 3658 cm^{-1} has been previously assigned to bridged (i.e., hydrogen-bonded) surface Si–OH groups,[26] and the small shoulder at 3736 cm^{-1} suggests the presence of isolated (i.e., not hydrogen-bonded) surface Si–OH groups.[26] Thus, ample qualitative evidence exists for the presence of distinct Si–OH groups on the surface of these monolayers. Unfortunately, surface Raman spectroscopy is not a good quantitative tool rendering quantification of the different Si–OH populations impossible from the information at hand.

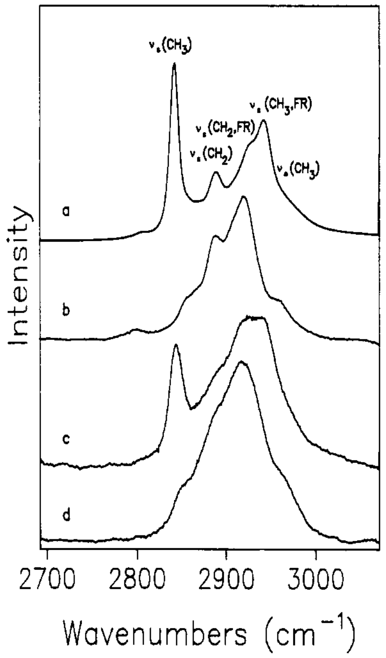

Figure 5. Raman spectra in ν(C–H) region of (a) bulk liquid 3MPT, (b) bulk 3MPT gel, (c) 3MPT adsorbed to Ag before hydrolysis and condensation reactions, and (d) 3MPT adsorbed to Ag after hydrolysis and condensation reactions.

The vibrational spectra in the ν(C–H) region shown in Figure 5 confirm that the methoxy groups of the 3MPT react in the hydrolysis reaction. Before 3MPT is hydrolyzed, the ν_s(CH$_3$) and ν_s(CH$_3$) Fermi resonance bands of the methoxy groups at ca. 2840 and 2941 cm^{-1}, respectively, are very intense. When the solution and adsorbed molecules undergo hydrolysis and condensation reactions, both of these bands almost totally disappear. The remaining ν(C–H) vibrations are associated with the CH$_2$ units of the propyl chain. These data further support the premise that sol–gel chemistry is occurring at the methoxy groups on the silicon atom.

In summary, the results presented here suggest that 3MPT adsorbs to the Ag surface as the thiolate forming

---

[22] Moskovits, M.; Suh, J. S. *J. Phys. Chem.* **1984**, *88*, 5526.

[23] Moskovits, M.; DiLella, D. P.; Maynard, K. *Langmuir* **1988**, *41*, 67.

[24] Ishida, H.; Chiang, C.; Koenig, J. *Polymer* **1982**, *23*, 251.

[25] Zerda, T. W.; Artaki, I.; Jonas, J. *J. Non-Cryst. Solids* **1986**, *81*, 365.

[26] Bertoluzza, A.; Fagnano, C.; Morelli, M. A.; Guglielmi, M.; Scarinici, G.; Maliavski, N. *J. Raman Spectrosc.* **1988**, *19*, 297.

[27] Morrow, B. A.; McFarlan, A. J. *J. Non-Cryst. Solids* **1990**, *120*, 61.

[28] Orcel, G.; Phalippou, J.; Hench, L. L. *J. Non-Cryst. Solids* **1988**, *88*, 114.

[29] McDonald, R. S. *J. Phys. Chem.* **1958**, *62*, 1168.

an ordered monolayer film. When the methoxy groups of the monolayer are hydrolyzed, the Raman spectra suggest that the molecules reorient on the metal surface, producing an Si–O–Si network containing Si–OH defects. This novel approach of adsorbing the organosilane to a metal surface may provide a useful substrate on which to grow a layer of SiO_2 using sol–gel chemistry techniques. This surface chemistry is currently being pursued and will be reported at a later date.

Acknowledgment. The authors are grateful for support of this work by the National Science Foundation (CHE-9023678 and CHE-9121469).