

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE Technical Papers		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER 2303	
				5e. TASK NUMBER m1A3	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				8. PERFORMING ORGANIZATION REPORT	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
20030110 072					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT A	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Leilani Richardson
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) (661) 275-5015

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

13 separate items enclosed

V DTS

13030/AB

MEMORANDUM FOR PRS (In-House/Contractor Publication)

FROM: PROI (TI) (STINFO)

8 September 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY99-0179
Gonzalez, R.I.; Phillips, S.H.; Hoflund, G.B., "In-Situ Oxygen-Atom Erosion Study of a Polyhedral
Oligomeric Silsesquioxane (POSS)-Siloxane Copolymer Using a Novel Hyperthermal Oxygen Atom
Source and analysis by X-ray Photoelectron Spectroscopy."

Journal of Spacecraft & Rockets

(Statement A)

**In-Situ Oxygen-Atom Erosion Study of a Polyhedral
Oligomeric Silsesquioxane (POSS)-Siloxane Copolymer
Using a Novel Hyperthermal Oxygen Atom Source and
Analysis by X-ray Photoelectron Spectroscopy**

**Rene I. Gonzalez and Shawn H. Phillips
Air Force Research Laboratory
Edwards AFB, CA 93524**

**Gar B. Hoflund
Department of Chemical Engineering
University of Florida
Gainesville, FL 32611**

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

ABSTRACT

The surface of a film of a polyhedral oligomeric silsesquioxane (POSS)-siloxane copolymer has been characterized in-situ using X-ray photoelectron spectroscopy (XPS) before and after exposure to incremental fluences of oxygen atoms produced by a novel hyperthermal oxygen atom source. The data indicate that the atomic oxygen initially attacks the cyclohexyl groups that surround the POSS cage resulting in the formation and desorption of CO₂ from the surface. The carbon concentration in the near surface region is reduced from 64.1 at% for the as-entered surface to 13.5 at% following 63 hrs of O-atom exposure at a flux of 10¹⁴ O-atoms/cm²-s. The oxygen and silicon concentrations are increased with incremental exposures to the O-atom flux but the rates of increase slow with increased exposure. The oxygen concentration increases from 18.1 at% for the as-entered sample to 54.0 at% following the 63 hr exposure, and the silicon concentration increases from 17.8 to 32.5 at% after 63 hrs. The data reveal the formation of a silica layer on the surface which serves as a protective barrier preventing further degradation of the polymer underneath with increased exposure to the O-atom flux.

Close up
space

be consistent -
either hr or hrs

INTRODUCTION

The aggressive conditions present in low Earth orbit (LEO) at altitudes ranging from 200 to 700 km in the ionosphere reduce the longevity of organic materials used in the construction of space vehicles, thereby restricting the number of space-certified materials. The predominant environmental species in LEO responsible for this material degradation is atomic oxygen (AO) (1-4). AO is formed by the dissociation of molecular oxygen by ultraviolet radiation from the sun, resulting in a λ AO concentration of approximately 10^8 atoms/cm³. The reverse reaction in which an oxygen molecule forms from AO does not have a high reaction rate because it requires a teratomic collision. The third O atom is required to carry away the energy released by formation of O₂. For this reason the predominant species in LEO is AO. The actual flux of $\sim 10^{15}$ atoms/cm²-s impinging on a spacecraft is high due to orbiting speeds of approximately 8 km/s. At these relative speeds AO particles collide with a kinetic energy of ~ 5 eV (5-8). The effect of AO on spacecraft material degradation has been studied on space exposed materials [STS missions and NASA Long Duration Exposure Facility (LDEF)] (9-11) and in simulation facilities (12-14). In these studies the samples were analyzed by X-ray photoelectron spectroscopy (XPS) but only after exposing the AO-treated samples to air. Recent studies have shown that exposure to air chemically alters the reactive surfaces formed during AO exposure (15,16). Therefore, in-situ AO erosion studies of polymers must be performed to avoid artifacts induced by air exposure.

In this study a thin film of polyhedral oligomeric silsesquioxane (POSS)-siloxane copolymer has been characterized in-situ using XPS before and after incremental exposures to the flux produced by a novel electron stimulated desorption (ESD) atomic oxygen source (17). POSS molecules are hybrid inorganic/organic structures synthesized from the self-condensation reactions of alkyl-trichlorosilanes. Over the last seven years, Lichtenhan ^{et al.} ~~and coworkers~~ have focused on incorporating POSS frameworks into traditional polymer systems via copolymerization, grafting and blending processes. (18)

Need to reference this at this sentence.

define on first usage

They have reported on

Significant property enhancements ~~have been reported~~ for these hybrid polymers including increased use temperature, increased toughness, decreased flammability and increased oxidation resistance (18). These property enhancements are attributed to the nano-level interaction of the POSS framework with the polymer matrix. Traditionally, silica fillers have been used in polymer applications requiring alterations in physical and mechanical properties such as tensile strength, abrasion and fatigue resistance. In addition to numerous property enhancements, POSS polymers are lighter weight (~1.2 to 1.5 g/ml) while silica fillers have much higher densities (~2.4 ^{to} 2.6 g/ml) (19). Unlike silica fillers, POSS frameworks can be easily functionalized for polymer compatibility without significantly affecting processing conditions. Compared to silica fillers, POSS hybrid polymers are able to impart similar property enhancements, including many not possible utilizing filler technology. Previous studies have also shown that Si-O systems exhibit a superior resistance to AO degradation due in part to their oxophilicity and high bond strength (~8 eV) (20). However, pure siloxane systems have displayed many disadvantages for space applications, including the generation of volatile cyclic species when exposed to AO that can recondense on optical surfaces (21). This present study details the results obtained from exposing a POSS-polydimethylsiloxane (PDMS) film to a simulated LEO environment. Specifically, it describes the formation of a protective silica layer with exposure to an O-atom flux. This layer serves as a protective barrier preventing further degradation of the underlying polymer with increased AO exposure.

} be consid.
either
use
hyphen
(no space
around it
~2.4-2.6
or use
the word
"to")

O-Atom Source Characteristics

The ESD source used in this study (Model OA10, Atom Sources, Inc.) is ultrahigh vacuum (UHV) compatible, operates with the sample at room temperature and produces a high-purity, hyperthermal, O-atom flux greater than 10^{15} atoms $\text{cm}^{-2} \text{s}^{-1}$ at a distance of 5 cm from the sample surface with an O atom: O^+ ratio of about 10^8 . These sources are superior to plasma sources in that they produce hyperthermal, ground-state O

atoms and operate at UHV pressures ($\sim 10^{-9}$ torr) with negligible amounts of other species, including contaminants and UV radiation. Because of the high reactivity of atoms, this O-atom source and a similar H-atom source have been used in numerous surface studies (22-27). The operational concept of the hyperthermal oxygen atom generator is shown in Fig. 1. Ultrahigh purity molecular O_2 dissociatively adsorbs on a metallic Ag alloy membrane at the high-pressure side and permeates at elevated temperature ($\sim 400^\circ C$) to the UHV side. There the adsorbed atoms are struck by a directed flux of primary electrons, which results in ESD of O atoms forming a continuous flux. Many processes have to function in series at sufficiently high rates for the system to work, including dissociative adsorption of the molecular gas on the metal surface, permeation of atoms through the membrane, and formation of the neutral flux by ESD. Based on the measured ion energy distribution and mass spectrometric experiments, the neutral energy distribution is believed to have a maximum at about 5 eV with a full width at half maximum of about 3.6 eV (28).

EXPERIMENTAL

Preparation of the POSS-PDMS copolymer

The POSS siloxane copolymer used in this study shown in Fig. 2a was synthesized using a method similar to that described by Lichtenhan et al. (29-30). ^{Five} 5.00 g (4.54 mmol) of the diol-silsesquioxane monomer shown in Fig. 2b was dissolved in 10 ml of THF in a 50 ml flask to which 1.98 g (4.54 mmol) of bis(dimethylamino)polydimethylsiloxane (approximately 4.9 silanes per oligomer, $M_w=435.5$ g/mol) was added with an additional 15 ml of THF. The reaction was stirred and heated to $65^\circ C$ under nitrogen for 48 hrs. The polymer was then precipitated into 350 ml of methanol, stirred for 2 hrs, filtered and air dried for 12 hrs. To end cap the polymer with trimethylsilane, it was dissolved in 25 ml of THF with an excess of *N,N*-

Define
first
usage

Spelling
not the
word
in
sentence

(dimethylamino)trimethylsilane and reacted at 65°C under nitrogen for another 48 hrs. The polymer was again precipitated into 350 ml of methanol. After decanting the solvent, fresh methanol with dilute HCl was added to neutralize any excess amine. The solution was again decanted and the remaining white solid ^{was} dried under vacuum for 2 hrs, producing a yield of 6.27 g (95% theoretical yield). Molecular weights were determined from multi-angle laser light scattering measurements obtained from a DAWN-F detector (Wyatt Technologies) equipped with a GPC column, $M_n = 62,000$, $M_w = 118,000$, degree of polymerization = 43. Analysis of the ^{29}Si NMR data gives a degree of polymerization of 38 and shows on average 4.8 SiOMe₂ groups per repeat unit. ^{29}Si NMR 7.2 ppm (singlet, Me₃Si -endgroups, 2.0) – 21.5 ppm (multiplet, Me₂Si-O, 184) – 66.39, - 68.13, - 68.20, -69.51 ppm (4 singlets, POSS, 305.6).

space

define first usage

Preparation of thin films by solvent casting

Thin films of the trimethylsilane terminated PDMS POSS were made by dissolving 100 mg of the coarse powder in 15-20 mL of THF, solvent casting onto 1 cm x 1 cm aluminum substrates and drying at room temperature for 24 hrs. The aluminum substrates were prepared and cleaned with soap and water, DI water followed by ultrasonic cleaning in acetone, trichloroethylene, acetone and ethanol respectively.

Surface Characterization

A solvent casted PDMS-POSS film was wiped with isopropanol and inserted into the UHV chamber (base pressure $<10^{-10}$ torr). XPS was performed using a double-pass cylindrical mirror analyzer (DPCMA) (PHI Model 25-270AR). XPS survey spectra were taken in the retarding mode with a pass energy of 50 eV, and high-resolution XPS spectra were taken with a pass energy of 25 eV using Mg K α X-rays (PHI Model 04-151 x-ray source). Data collection was accomplished using a computer interfaced, digital pulse-counting circuit (31) followed by smoothing with digital-filtering techniques (32).

when are refs
29 & 30 listed?
Did I miss
them?
Somehow?

Prefer
to
spell out
first
word of
sentence

The sample was tilted 30 deg off the axis of the DPCMA, and the DPCMA accepted electrons emitted into a cone 42.6 6 deg off the DPCMA axis.

verb?

XPS spectra were first obtained from the as-entered, solvent-cleaned sample. The sample was then transferred into an adjoining UHV chamber that houses the ESD O-atom source via a magnetically coupled rotary/linear manipulator. There the surface was exposed to a hyperthermal O flux and re-examined without air exposure after total exposure times of 2 hrs, 24.6 hrs, and 63 hrs. The approximate normal distance between the sample face and source in this study was 15 cm, at which distance the flux was about 2.0×10^{13} atoms/cm²-s for the instrument settings used. The sample was maintained at room temperature during the-atom exposures with a slight temperature increase to 50°C due to exposure to the X-ray source during XPS data collection. The substrate temperature was determined using a chrome-alumel thermocouple. After the 63-hr AO exposure, the sample was exposed to air (room temperature, ~22°C, relative humidity ~ $\hat{A}O$ %) for 4.75 hrs and again examined using XPS.

need to separate it?
Labels would help

RESULTS AND DISCUSSION

XPS survey spectra obtained from an as-received, solvent-wiped POSS-PDMS surface before and after the \hat{A} 2, \hat{A} 24.6 and \hat{A} 63-hr O-atom exposure are shown in Fig. \hat{A} 3 a to \hat{A} 3 d, respectively. Spectrum e in Fig. 3 was taken after the 4.75-hr air exposure following the \hat{A} 63-hr O-atom treatment. The peak assignments shown in Fig. 4 pertain to all five spectra. The predominant peaks apparent in these spectra include the C 1s, O 1s, Si 2p, Si 2s, O 2s and O Auger peaks. Significant changes in relative peak heights are observed for the C, O, and Si features following the O-atom exposures. An estimate of the near surface composition has been calculated from the peak heights in the survey spectra by assuming that this region is homogeneous and using published atomic sensitivity factors (33). The compositions determined in this manner are presented in Table 1 for the as-entered, O-exposed and air exposed surfaces. The O 1s-to-Si 2p atomic ratio is 1.01 for

this is really only 1 figure?

was here also Fig 4

also Figs 4 & 6?

goes after Fig, not before what is Table 1?

the as-entered sample, and it is increased to 1.84 and then reduced to 1.66 and remains at 1.66 after the 2-, 24.6- and 63-hr O-atom exposures, respectively. After the 4.75-hr air exposure, the O 1s-to-Si 2p atomic ratio increases to 2.00. These increases in the O 1s-to-Si 2p atomic ratio resulting from exposure to the O-atom flux is characteristic of the formation of SiO₂ and is consistent with the high resolution spectra that follow. A significant reduction in the C 1s peak is observed as a result of the incremental exposures to the O-atom flux. The near-surface C concentration decreases from 64.1 at% for the as-entered sample to 13.5 at% after the 63-hr exposure. This decrease in C is due to the reaction of C in the near-surface region with O to form CO₂. A slight increase in the carbon contribution to 18.1 at% is observed after exposing to air for 4.75 hrs probably due to the adsorption of C-containing molecules from the air. Hydrogen in the POSS would also react with the AO to form water which would desorb.

single increase (is) or multiple increase (are) ?

High-resolution XPS C 1s, O 1s and Si 2p obtained from the as-received, solvent-wiped surface before and after the 2-, 24- and 63-hr O-atom exposures are shown in spectra a-d of Figs. 4, 5 and 6 respectively. Spectrum e was obtained after the 4.75-hr air exposure following the 63 hr O-atom exposure. Variations in peak shapes and positions are observed between the nonexposed, O-atom-exposed, and air-exposed surfaces, indicating that the chemical species distribution is altered by exposure to the O-atom flux and then to air.

The C 1s peak shown in Fig. 4a, is centered at 285.2 eV indicating that the predominant form of carbon present for the as-entered sample is in the form of a fully substituted hydrocarbon, i.e. the cyclohexyl groups on the POSS cage. (34) In spectra b-d, the C 1s peak becomes broader and the peak center shifts to lower binding energy (BE) with increasing exposure to the O-atom flux. After the 63-hr exposure, the C 1s has a BE of 284.4 eV. This value is characteristic of methyl groups on the PDMS chain (34). The fact that these changes coincide with a decrease in the total carbon concentration in the near surface region from 64.1 to 13.5 at% implies that the cyclohexyl groups are being

include first comma or remove comma after 4a

removed selectively and leaving the methyl groups. This is due to the relative size of the POSS cage (1.5 nm) compared to the PDMS chain as shown in ^{Fig.} figure 2. Small shoulders are visible on the high BE side of the C 1s peak in spectra b, c and d. These probably are due to species such as alcohols, formaldehydes (BE ~286.0 to 287.7 eV) and organic acids (BE ~287.5) which form by reaction with the O-atom flux. Exposure to air (spectrum e) produces an increase in the shoulder near 285.0 eV. The O-atom exposure results in reactive surface sites which apparently adsorb hydrocarbons from the air. This observation is consistent with an increase in the C concentration after the air exposure as shown in Table 1.

Why
spec
Figure
out
now?

The O 1s spectra obtained from the sample after the various treatments are shown in Fig. 5. These peaks are broad indicating that various chemical states of oxygen are present. After the 2^{hr} exposure to the O-atom flux, the contribution from oxygen is significantly increased from 18.1 to 38.0 at%, and then increases further to 47.6 and 54.0 at% after the 24^{hr} and 63^{hr} exposures respectively. However, the peak shapes and positions do not change much with treatment indicating that the O-containing species have closely spaced O 1s BEs. A previous XPS study of PDMS has shown that the oxygen in the PDMS chain has a BE of 532.0 eV (34) while SiO₂ has a BE of between 532.5 eV. (35)

The Si 2p peaks obtained from the sample after the various treatments are shown in Fig. 6. Similar to the O 1s peak, the Si 2p peak for the as-entered sample (spectrum a) is broad[^] indicating the presence of several chemical states of silicon. This peak is centered at a BE of 102.7 eV which corresponds to RSiO_{1.5} in the POSS cage. However, spectra b, c and d reveal the formation of a SiO₂ layer with incremental exposures to the O-atom flux. The fact that little difference is observed in the spectra obtained after the 24-hr and 63-hr exposures indicates that this silica layer forms a protective barrier on the surface which prevents further degradation of the polymer with longer exposure to the O-atom flux. The 5-eV AO is not energetic enough to penetrate more than one or two

atomic layers into the polymer while XPS probes as deeply as 30 or more atomic layers beneath the surface. The significant compositional changes observed indicate that most of the near-surface region examined by XPS is altered by the AO exposure. The chemical reactions which form CO_2 and H_2O are exothermic so the local surface temperature may be relatively high. This fact and the fact that the AO induces a chemically induced driving force result in diffusion of subsurface C and H to the surface where they react with the AO. This mechanism is responsible for the subsurface compositional alterations observed using XPS.

CONCLUSION

The surface of a film of a polyhedral oligomeric silsesquioxane-siloxane copolymer has been characterized in-situ using XPS before and after exposure to different fluences of oxygen atoms produced by a novel hyperthermal oxygen atom source.

The XPS data indicate that exposure to the O-atom flux reduces the carbon content on the surface from 64.1 to 13.5 at% after a 63-hr exposure to an O-atom flux of 10^{14} atoms/cm².

s. The oxygen and silicon concentrations in the near-surface region determined using XPS increases with increasing exposure to the O flux. The oxygen-to-silicon ratio increases from 1.01 for the as-entered sample to 1.66 after 63 hrs of O-atom exposure; and after exposure to air this ratio increases to 2.00. High resolution XPS data suggest that the atomic oxygen initially attacks the cyclohexyl groups on the POSS cage forming CO_2 which desorbs. Increased exposure to the O-atom flux results in the formation of a silica layer on the surface which acts a protective barrier preventing further degradation of the underlying polymer. Exposure to air results in the adsorption of hydrocarbon species on the surface.

new paragraph?

don't break

Break into a summary section and a conclusion section

← summarize results

← tell what it means

ACKNOWLEDGMENT

The authors appreciate the efforts of Dr. Tim Haddad with regard to polymer synthesis and technical advice from Dr. Kevin Chaffee.

Table 1 Near-surface composition determined from XPS data obtained from the as-entered, solvent cleaned, O-atom and air-exposed POSS-PDMS sample

Surface	Composition, at%		
	O	C	Si
Sample Treatment			
As entered, solvent cleaned	18.1	64.1	17.8
2-h O-atom exposure	38.0	41.3	20.7
24-h O-atom exposure	47.6	23.7	28.6
63-h O-atom exposure	54.0	13.5	32.5
4.75-h air exposure following 63-h O-atom exposure	54.6	18.1	27.3

REFERENCES

1. Koontz, S. L., Leger, L. J., Rickman, S.L., Hakes, C. L., Bui, D. T., Hunton D. E., and Cross, J. B., "EOIM-III Mass Spectroscopy and Polymer Chemistry: STS46, July-August 1991," *Journal of Spacecraft and Rockets*, Vol. 32, No. 3, 1995, pp. 473-478.
2. Cross, J. B., Koontz, S. L., and Hunton, D. E., "Flight Mass-Spectrometer Calibration in a High-Velocity Atomic-Oxygen Beam," *Journal of Spacecraft and Rockets*, Vol. 32, 1995, pp. 496-501.
3. Jursa, A. E. (ed.), "Handbook of Geophysics and the Space Environment," Air Force Geophysics Lab., U. S. Air Force (National Technical Information Service), 1985, Chap. 14, pp. 14-39.
4. Hedin, A. E., "Revised Thermospheric Model Based on Mass Spectrometer and Incoherent Scatter Data: MSIS-83," *Journal of Geophysical Research*, Vol. 88, 1983, pp. 10170-10188.
5. Reddy, M. R., "Review Effect of Low Earth Orbit Atomic Oxygen on Spacecraft Materials," *Journal of Materials Science*, Vol. 30, 1995, pp. 281-286.
6. Packirisamy, S., Schwan, D., and Litt, M. H., "Review Atomic Oxygen Resistant Coatings for Low Earth Orbit Space Structures," *Journal of Materials Science*, Vol. 30, No. 2, 1995, pp. 308-320.
7. Koontz, S. L., Albyn, K., and Leger, L. J., "EOIM-III Mass Spectroscopy and Polymer Chemistry: STS46, July-August 1991," *Journal of Spacecraft and Rockets*, Vol. 28, 1991, pp. 315-323.
8. Reddy, M. R., Srinivasamurthy, N., and Agrawal, B. L., "Effect of the Low-Earth-Orbit Atomic Oxygen Environment on Solar-Array Materials," *ESA Journal*, Vol. 16, 1992, pp. 193-208.

9. Koontz, S. L., Albyn, K., Leger, L. J., Hunton, D. E. , Cross, J. B., and Hakes, C. J., "EOIM-III Mass Spectroscopy and Polymer Chemistry: STS46, July-August 1991," *Journal of Spacecraft and Rockets*, Vol. 32, No. 3, 1995, pp.483-495.
10. deGroth, K. K., and Banks, B. A., "Atomic Oxygen Undercutting of LDEF Aluminized-Kapton Multilayer Insulation," 1st LDEF Post-Retrieval Symposium, Kissimee, FL, June 1991. *Need complete proceedings citation*
11. Banks, B. A., Rutledge, S. K., deGroth, K.K., Mirtich, M. J. Gebauer. L., Olle, R., and Hill, C. M., "The Implication of the LDEF Results on Space Freedom Power System Materials," 5th International Symposium on Materials in a Space Environment, Cannes-Madelieu, France, Sept. 1991.
12. Tennyson, R.C., "Atomic Oxygen Effects on Polymer-Based Materials, " *Canadian Journal of Physics*, Vol. 69, 1991, pp. 1190-1194.
13. Cazaubon, B., Paillous, A., Siffre, J., and Thomas, R., "Five Electron Volt Atomic Oxygen Pulsed Beam Characterization by Quadrapolar Mass Spectrometry," *Journal of Spacecraft and Rockets*, Vol. 33, No. 6, 1996, pp. 870-876.
14. deGroh, K. K., Terlep, J. A., and Dever, T. M., "Atomic Oxygen Durability of Solar Concetrator Materials for Space Station Freedom," NASA TM 105378, 1990.
15. Grossman, E., Lifshitz, Y., Wolan, J. T., Mount, C. K., and Hoflund, G. B., "In Situ Erosion Study of Kapton Using a Novel Hyperthermal Oxygen Atom Source," *Journal of Spacecraft and Rockets*, Vol. 35, No. 6, 1998, pp. 75-78.
16. Wolan, J. T., and Hoflund, G. B., "Chemical and Structural Alterations Induced at Kapton Surfaces by Air Exposure Following Atomic Oxygen or 1keV Ar+ Treatments," *Journal of Vacuum Science and Technology*, A 17(2), 1999, pp. 562-564.

italicize

17. Hoflund, G. B., and Weaver, J. F., "Performance Characteristics of a Hyperthermal Oxygen Atom Generator," *Measurement in Science and Technology*, Vol. 53, 1994, pp. 201-205.
18. (a) Mather, P. T., Jeon, H.G., Romo-Urbe, A., Haddad, T. S., Lichtenhan, J. D., "Mechanical Relaxation and Microstructure of Poly(norbornyl-POSS) Copolymers," *Macromolecules*, 1999, Vol. 32, pp. 1194;
- (b) Lee, A. and Lichtenhan, J. D., "Viscoelastic Responses of Polyhedral Oligosilsesquioxane Reinforced Epoxy Systems," *Macromolecules*, 1996, 31, 4970;
- (c) Haddad, T. S. and Lichtenhan, J. D., "Hybrid Organic-Inorganic Thermoplastics: Styryl-Based Polyhedral Oligomeric Silsesquioxane Polymers," *Macromolecules*, 1996, 29, 7302;
- (d) Haddad, T. S. and Lichtenhan, J. D., "Hybrid Styryl-Based Polyhedral Oligomeric Silsesquioxane (POSS) Polymers," *Mat. Res. Soc. Symp. Proc.*, 1996, 435, 25;
- (e) Lichtenhan, J. D., Noel, C. J., Bolf, A. G. and Ruth, P. N., "Thermoplastic Hybrid Materials: Polyhedral Oligomeric Silsesquioxane (POSS) Reagents, Linear Polymers, and Blends," *Mat. Res. Soc. Symp. Proc.*, 1996, 435, 3.
19. (a) Olsson, K., "An Improved Method to Prepare Octa-(alkylsilsesquioxanes) (RSi)8O12," *Arkiv För Kemi*, 1958, 13, 367;
- (b) Strong, A. B., *Fundamentals of Composites Manufacturing: Materials, Methods, and Applications*; Ploskona, C. A., Ed., Society of Manufacturing Engineers, Dearborn, Michigan, 1989.
20. (a) Taylor, G. H. and Wolf, T. M., "Oxygen Plasma Removal of Thin Polymer Films," *Polym. Eng. & Sci.*, 1980, 20, 1087;

book titles should be underlined unless the journal format states otherwise - how then do they differentiate from journal titles?

- (b) Connell, J. W., Crivello, J. V. and Bi, D., "Effect of Low Earth Orbit Atomic Oxygen Exposure on Epoxy Functionalized Siloxanes," *J. App. Polym. Sci.*, 1995, 57, 1251.
21. Thorne, J. A. and Whipple, C. L., "Silicones in Outer Space," *The Effects of Space Environment on Materials*, Society of Aerospace Material and Process Engineers, North Hollywood, California, 1967, 2, 243.
22. Wolan, J. T., Mount, C. K., and Hoflund, G. B., "Chemical Reactions Induced by the Room-Temperature Interaction of Hyperthermal Atomic Hydrogen with the Native Oxide Layer on GaAs(001) Surfaces Studied by ISS and XPS," *Journal of Vacuum Science and Technology*, B, Vol. 16, 1998, pp. 1446-1449.
23. Epling, W. S., Mount C. K., and Hoflund, G. B., "Study of Polycrystalline Ni/Cr Alloy V. Hydrogen-Atom Exposure," *Thin Solid Films*, Vol. 304, 1997, pp. 273-277.
24. Hoflund, G. B., and Wolan, J. T., "Application of Novel O- and H-atom Sources in Molecular Beam Epitaxy," *Journal of Vacuum Science and Technology*, B, Vol. 16, 1998, pp. 1446-1449.
25. Wolan, J. T., and Hoflund, G. B., "Chemical Reactions Induced by the Room-Temperature Interaction of Hyperthermal Atomic Hydrogen with the Native Oxide Layer on InP(111) Surface Studies by ISS and XPS," *Journal of Vacuum Science and Technology*, A, Vol. 16, 1998, pp. 2546-2551.
26. Wolan, J. T., Mount, C. K., and Hoflund, G. B., "Room-Temperature Oxidation of a GaAs(001) Surface Induced by the Interaction of Hyperthermal Atomic Oxygen and Studied by X-ray Photoelectron Spectroscopy and Ion Scattering Spectroscopy," *Applied Physics Letters*, Vol. 72, 1998, pp. 1469-1471.
27. Epling, W. S., Mount, C. K., Hoflund, G. B., and Young, V. Y., "Chemical Alteration of Thin Alumina Films on Aluminum During Hydrogen Atom Exposures," *Applied Surface Science*, Vol 126, 1998, pp. 235-239.

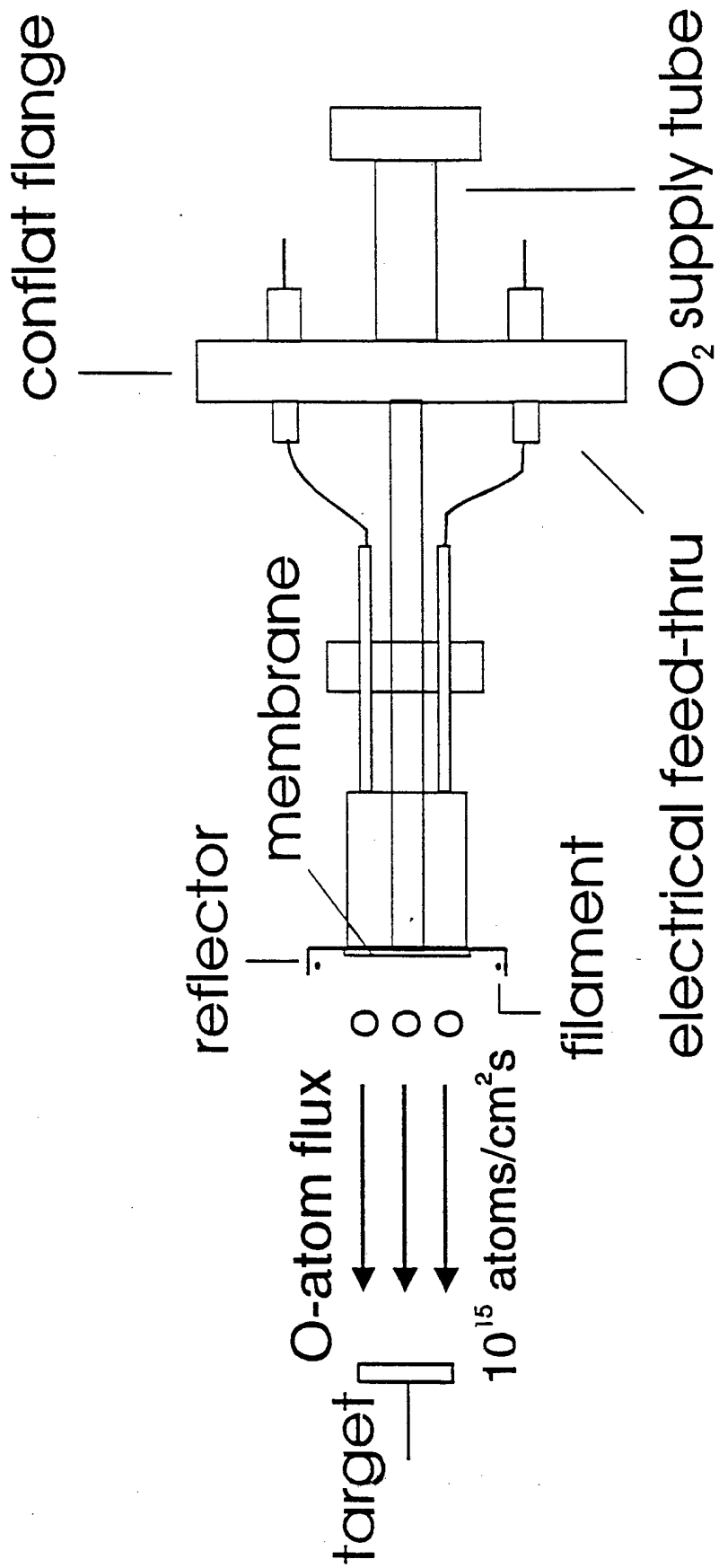
28. Corallo, G. R., Hoflund, G. B. and Outlaw, R. A., " An Energy Resolved Electron Stimulated Desorption (ESD) Study of Oxygen-Exposed Ag(110)," *Surface and Interface Analysis*, Vol. 12, 1988, pp. 185-190.
29. Lichtenhan, J. D., Feher, F., Gilman, J. W., Carter, J. and Vu, N., "Silsesquioxane-Siloxane Copolymers from Polyhedral Silsesquioxanes," *Macromolecules*, Vol. 26, 1993, pp. 2141-2142.
30. Gilman, J. W., Schlitzer, D. S. and Lichtenhan, J. D., "Low Earth Orbit Resistant Siloxane Copolymers," *Journal of Applied Polymer Science*, Vol. 60, 1996, pp. 591-596.
31. Gilbert, R. E., Cox, D. F., and Hoflund, G. B., "Computer-Interfaced Digital Pulse Counting Circuit," *Review of Scientific Instruments*, Vol. 53, 1982, pp. 1627-1630.
32. Savitzky, A., and Golay, M. J. E., "Smoothing and Differentiation of Data by Simplified Least-Squares Procedures," *Analytical Chemistry*, Vol. 36, 1964, pp. 1627-1630.
33. Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F., and Muilenberg, G. E. (eds.), *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corp., Eden Prairie, MN, 1979.
34. Beamson, G., and Briggs, D., *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*, Wiley, Chichester, England, UK, 1992, pp. 268-269.
35. Moulder, J. F., Stickle, W. F., Sobol, P. E., and Bomben, K. D., *Handbook of X-ray Photoelectron Spectroscopy*, Physical Electronics Inc., Eden Prarie, MN, 1995.

both
titles -
see previous
note

FIGURE CAPTIONS

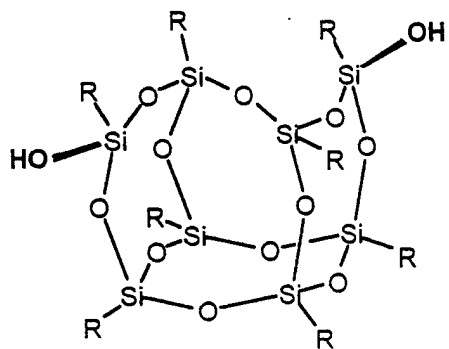
- Figure 1** Schematic diagram of the atom source.
- Figure 2** Synthetic scheme for synthesis of the POSS-PDMS (polydimethylsiloxane) copolymer used in this
- Figure 3** XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film after insertion into the vacuum system (a), after 2 hr (b), 24 hr (c), and 63 hrs exposure to the hyperthermal O-atom flux (d), and 4.75 hr air exposure following the 63 hr O-atom exposure (e).
- Figure 4** XPS C 1s spectra obtained from a solvent-cleaned, POSS-PDMS film after insertion into the vacuum system (a), after 2 hr (b), 24 hr (c), and 63 hrs exposure to the hyperthermal O-atom flux (d), and 4.75 hr air exposure following the 63 hr O-atom exposure (e).
- Figure 5** XPS O 1s spectra obtained from a solvent-cleaned, POSS-PDMS film after insertion into the vacuum system (a), after 2 hr (b), 24 hr (c), and 63 hrs exposure to the hyperthermal O-atom flux (d), and 4.75 hr air exposure following the 63 hr O-atom exposure (e).
- Figure 6** XPS Si 2p spectra obtained from a solvent-cleaned, POSS-PDMS film after insertion into the vacuum system (a), after 2 hr (b), 24 hr (c), and 63 hrs exposure to the hyperthermal O-atom flux (d), and 4.75 hr air exposure following the 63 hr O-atom exposure (e).

Where
are
these?

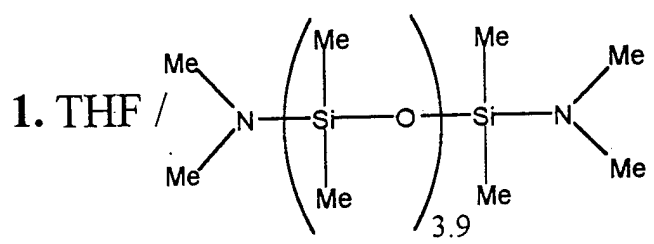


Need to include figure numbers - they are referred to in text that way

Fg 1?



R = cyclohexyl



2. Work up reaction in MeOH

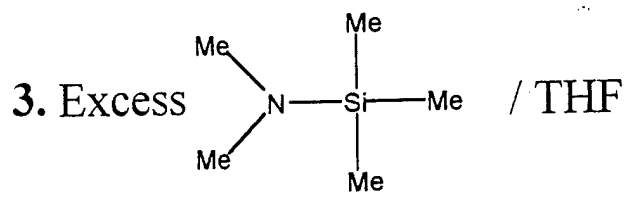


Fig 2a
?

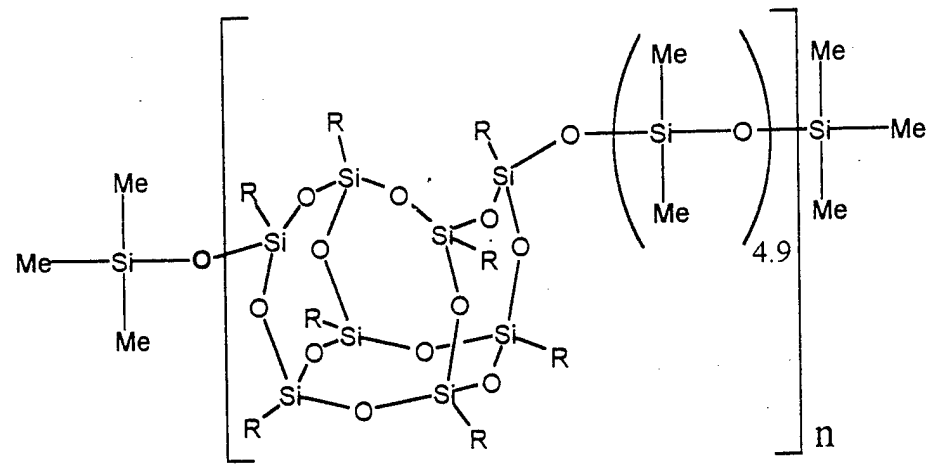
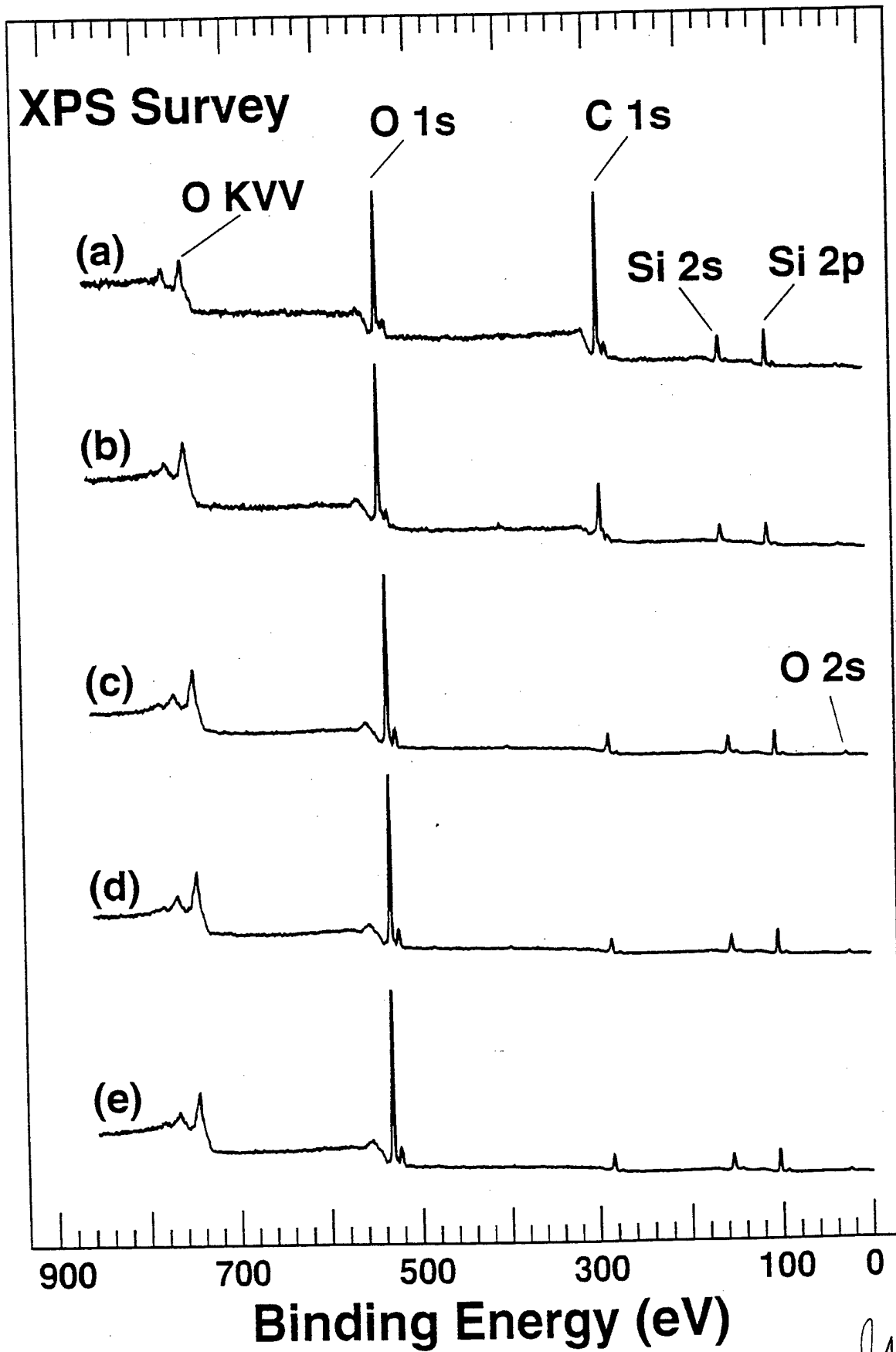
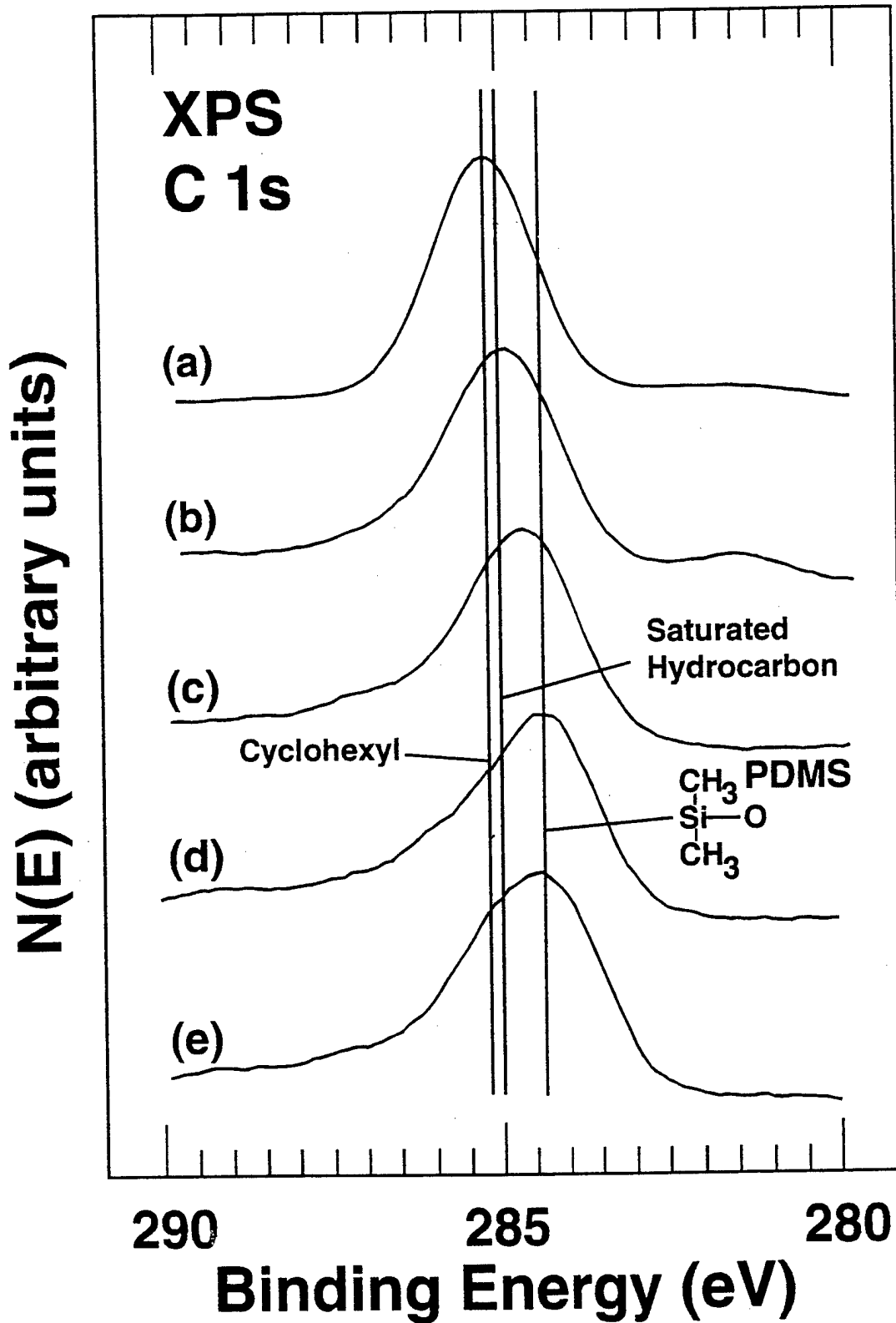


Fig 2b
?

N(E) (arbitrary units)

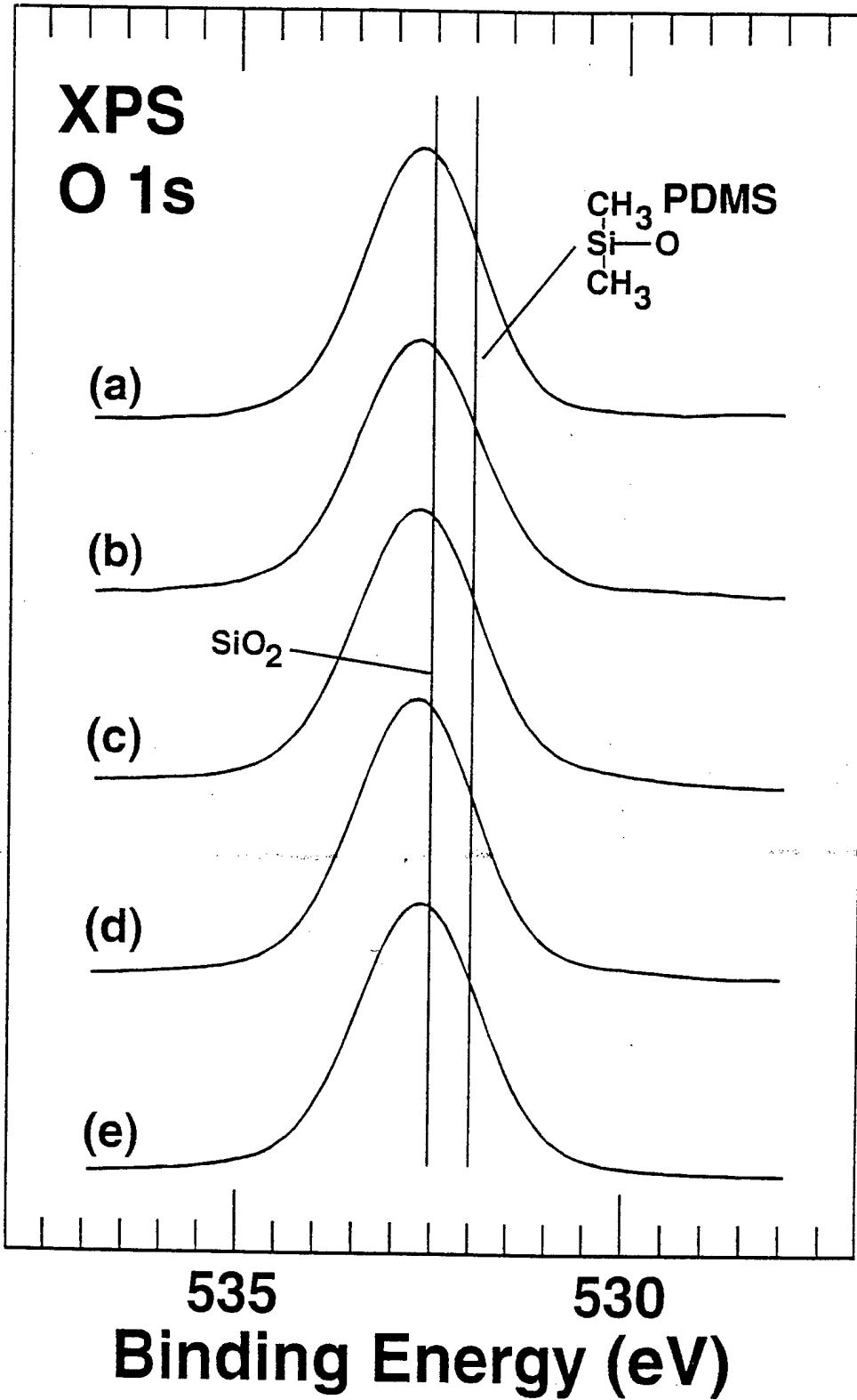


James
is this 3a



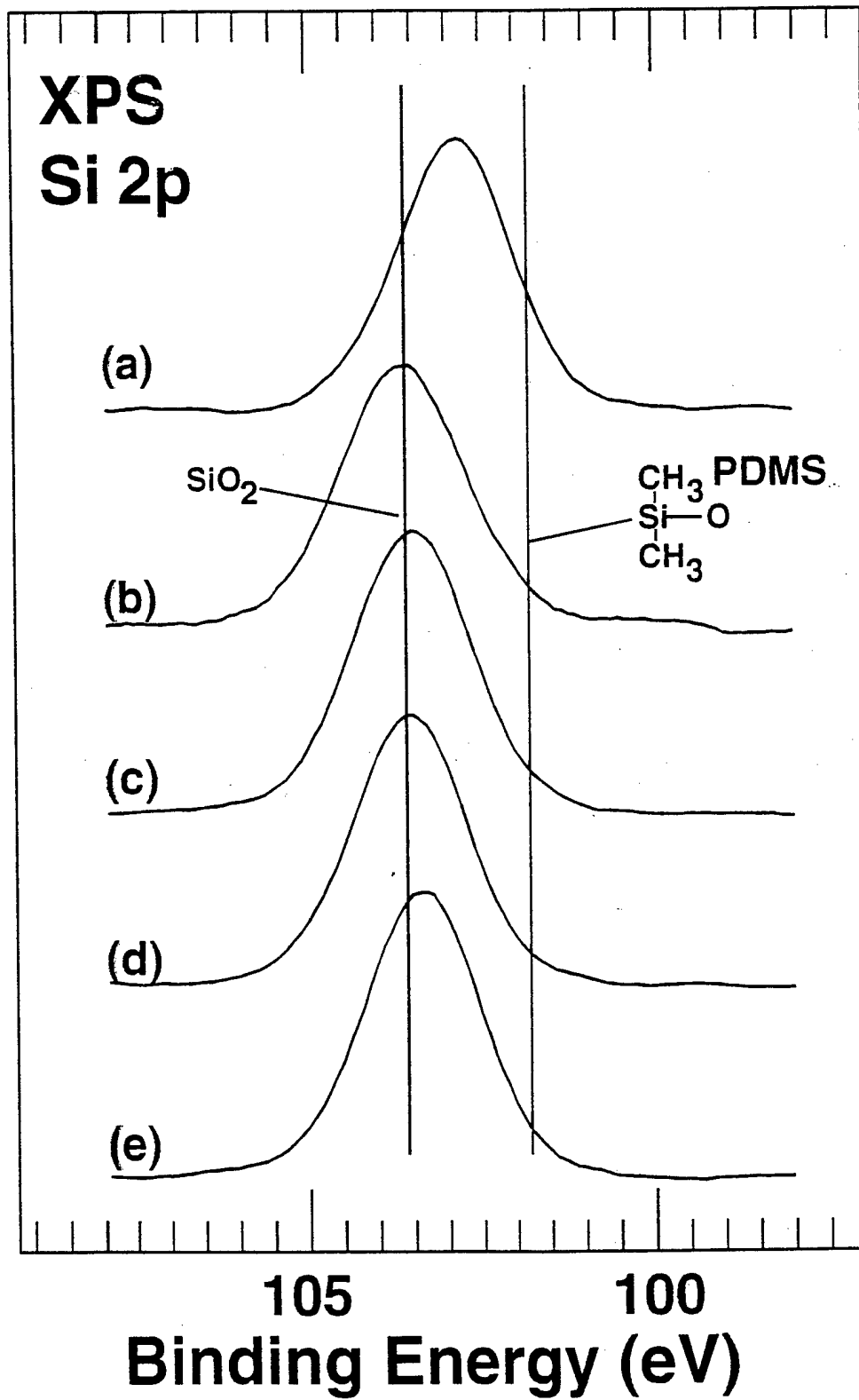
3b?

N(E) (arbitrary units)



3c?

N(E) (arbitrary units)



3d?