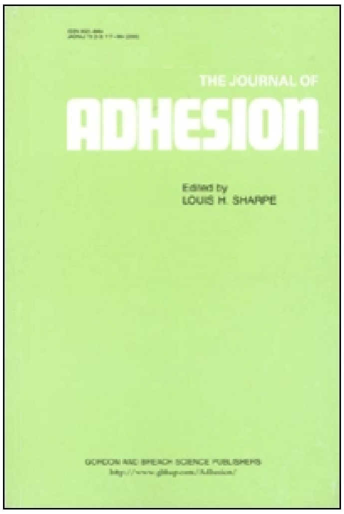

**The Journal of Adhesion**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

# Adsorption of Model Adhesive Compounds onto Plasma-Polymerized Silica-Like Films

R. H. Turner[a]; F. J. Boerio[a]
[a] Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, Ohio, USA

**To cite this Article** Turner, R. H. and Boerio, F. J.(2001) 'Adsorption of Model Adhesive Compounds onto Plasma-Polymerized Silica-Like Films', The Journal of Adhesion, 77: 3, 251 — 273
**To link to this Article: DOI:** 10.1080/00218460108030740
**URL:** http://dx.doi.org/10.1080/00218460108030740

The Journal of Adhesion, 77: 251–273, 2001
Copyright © 2001 Taylor & Francis
0021-8464/01 $12.00 + .00

# Adsorption of Model Adhesive Compounds onto Plasma-Polymerized Silica-Like Films

R. H. TURNER and F. J. BOERIO

*Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, Ohio, USA*

*(Received 13 December 2000; in final form 21 August 2001)*

Plasma-polymerized silica-like primer films on aluminum substrates were prepared and exposed to diethanolamine (DEA), a model adhesive compound, from dilute solution. Reflection-absorption infrared (RAIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to investigate the chemical interactions between the adsorbed compound and the substrate. RAIR spectroscopy showed significant changes in the structural chemistry of the silica-like films after exposure to ethanol with and without DEA. Although no evidence of adsorption was observed in the infrared spectra, XPS indicated that a small amount of model compound did adsorb onto the surface of the silica-like film. The N(1s) photoelectron spectra of the adsorbate showed two components; one was typical of the bulk amine, and the other indicated that the amine group of the adsorbed model adhesive had chemically interacted with the substrate. The adsorbate/substrate interaction strength was also examined by heating the sample in ultra-high vacuum (UHV) and observing the temperature at which desorption occurred. The sample was heated to 250°C for several hours and no desorption was detected. It was concluded that protonation of the amine group had occurred forming a quaternary ammonium ion. It was also likely that bonding between the alcohol functionality and the silica surface added to the adsorption strength.

*Keywords*: Plasma-polymerized primers; Silica-like films; Model epoxy adhesives; Interface; RAIR; XPS

---

Address correspondence to F. J. Boerio, Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH 45221, USA. E-mail: fboerio@uceng.edu

## 1. INTRODUCTION

Structural adhesive bonding of aluminum components is an important process in the manufacture of aircraft and automobiles. Bonded structural components are stronger and stiffer than conventional components because adhesive bonding distributes forces over a large area of contact compared with the relatively small areas created by spot welding or mechanical fasteners. Because of the gain in strength and stiffness, less structural material is necessary for adhesively-bonded components. This results in a weight savings that is crucial to aircraft and for improving the mileage of automobiles. However, aluminum surfaces must be pretreated before bonding in order to prevent corrosion and failure at the aluminum/adhesive interface. Currently, acid etching and acid anodization are used to pretreat aluminum surfaces for adhesive bonding, and these processes consume vast amounts of clean water and produce toxic chemical waste. The need for a more environmentally-compatible pretreatment is clear.

One environmentally safe alternative to aqueous chemical pretreatments is to plasma etch the aluminum and then deposit a plasma-polymerized film that acts as an adhesive primer. Plasma-polymerized silica-like films have been determined to be effective primers for obtaining durable bonds between epoxy adhesives and aluminum substrates [1–3]. These silica-like films exhibit excellent adhesion to aluminum substrates and prevent corrosion at the adhesive/substrate interface. Although adhesion and durability for joints prepared with silica-like films is comparable with conventional pretreatments, failure analysis of durability specimens showed that failure occurred between the epoxy adhesive and the silica-like film [1].

In order to improve the durability of the adhesive/primer interface, it is necessary to characterize the chemical interactions between the epoxy adhesive and the plasma-polymerized primer film. Unfortunately, adhesive/substrate interfaces are inaccessible for analysis because they are buried and very thin. In addition, interfacial failure surfaces generated by durability tests are too contaminated for exacting chemical analysis. However, a few specialized techniques are available for characterizing the chemistry at the adhesive/substrate interface.

One approach for accessing buried interfaces is to bring the interface within the detection depth of a surface analysis technique. This can be done by sputtering away the material on top of an interface with an ion beam while analyzing with a suitable technique, such as X-ray photoelectron spectroscopy (XPS). Although this method can give an accurate elemental depth profile, the ion beam will alter the molecular structure at the interface. Another technique for studying the chemical interactions at the adhesive/substrate interface is to apply a very thin layer of adhesive to a substrate and then examine the interface with an appropriate analysis technique such as reflection-absorption infrared (RAIR) spectroscopy or XPS. This technique suffers from the fact that the relatively weak spectroscopic signals from the interfacial species cannot be discriminated from signals that come from the bulk overlayer. However, the contribution of the signal from the interface will increase as the thickness of the bulk overlayer is decreased, and several specimens with decreasing film thickness must be carefully compared.

Another method by which the adhesive/substrate interface can be studied is to adsorb a low molecular weight material that models the chemical properties of the adhesive onto the substrate [4–6]. Low molecular weight amine alcohols accurately model the chemical functionality of commercial amine-cured epoxy resins. Figure 1A shows the chemical reaction between an epoxide resin molecule and an amine-curing agent and the resulting network, which has both secondary amine ($(R^1)_2$-NH) and alcohol ($R^2$-OH) functionalities. Figure 1B shows a dialcohol amine model adhesive with the same overall chemical functionality as the amine-cured epoxy resin. Studies with adhesive resins and curing agents have not shown any evidence for strong substrate/adsorbate interactions involving the epoxy or aromatic groups [7]. However, most studies have shown that the main chemical interactions between amine-curing adhesives and inorganic substrates are due to the amine and hydroxyl functional groups of the adhesive [8, 9].

Affrossman and MacDonald used XPS and static secondary ion mass spectroscopy (SIMS) to determine the chemical interactions between amine and amine alcohol model epoxy compounds and oxidized aluminum substrates [4]. They showed that, depending on the acidity of the aluminum oxide, amine alcohols reacted with the substrate by hydrogen bonding with the alcohol (OH) or the amine (NH) functionality.

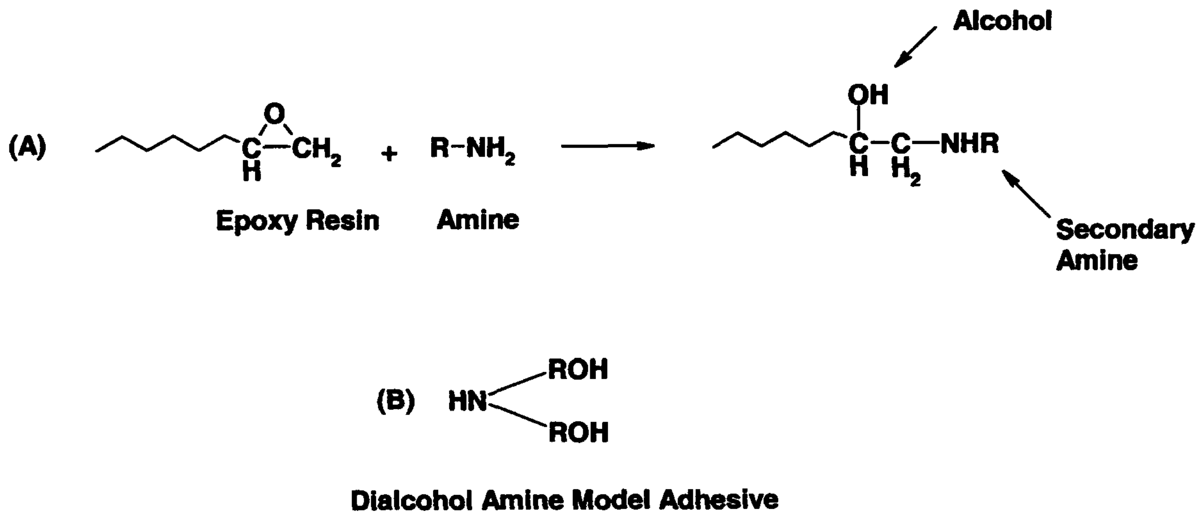

FIGURE 1 Diagram showing (A) the chemical reaction between an epoxy resin and an amine curing agent and (B) a dialcohol amine model adhesive.

Kelber and Brow employed a similar approach to determine epoxy/metal-oxide interactions, using thin films of an amine alcohol applied from dilute solutions [5]. Using XPS, they observed a very strong adsorption and a chemical interaction between the amine group of the adsorbed model compound and aluminum metal-oxide substrates that were pretreated in various ways. In addition, they characterized the interaction strength by observing the temperature at which adsorbate desorbed from the substrates when heated in UHV.

Abel *et al.* also used an amine alcohol model epoxy adhesive to determine the chemical reactions that occur between an epoxy adhesive and aluminum substrates that were pretreated with a silane coupling agent [6]. They characterized the chemical interactions by using XPS and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). Several types of chemical interactions were observed, including covalent bonding of the model compound to the silane primer and bonding of the alcohol functionality to the aluminum oxide surface through alkoxide bonds.

Dillingham and Boerio examined epoxy/aluminum failure surfaces in XPS and showed that amine protonation occurred at the epoxy/aluminum interface but not in the bulk of the epoxy [10]. They attributed the amine protonation to acidic sites on the surface of the aluminum substrate. The evidence from this work supports the use of an amine-like model compound in order to study the adhesive/substrate interfaces of real-world adhesive joints.

The goal of this research was to determine the chemical interactions at the interface between amine-cured epoxy adhesives and plasma-polymerized silica-like films by using an appropriate model adhesive compound. Diethanolamine (DEA) was chosen as a dialcohol amine adsorbate since it is a small molecule, soluble in ethanol, and accurately models the chemistry of an amine-cured epoxy network. Using XPS and RAIR, the chemical interactions between the DEA adsorbate and plasma-polymerized silica-like primer films were monitored.

## 2. EXPERIMENTAL

Substrates were prepared by evaporating pure aluminum (99.9%) onto clean glass microscope slides. The substrates were then etched in an oxygen plasma and coated with plasma-polymerized silica-like films using a microwave-coupled plasma reactor shown in Figure 2. The plasma reactor used a pulsed microwave power source, 2.45 GHz, to drive a plasma confined to a stainless steel vessel. Several access ports shown on the vessel were modified to enable the necessary etching, carrier, and deposition gases to be introduced into the reactor. Other ports provided rotary motion for the sample stage, vacuum, and a quartz window feed-through for microwave power.

Substrates were plasma etched for 5 minutes at 500 mTorr using 5 standard cubic centimeters per minute (SCCM) of argon and 45 SCCM of oxygen. Silica-like films were deposited onto the substrates by plasma polymerization. The deposition was carried out for 3 minutes at 500 mTorr using a mixture of argon, oxygen, and hexamethyldisiloxane (HMDSO) monomer at flow rates of 5, 45, and 0.2 SCCM, respectively. Pulsed microwave power at 200 Watts, using a pulse width of 1.5 ms, was used for plasma etching and deposition.

DEA solutions were prepared from 0.05 wt% of diethanolamine (99% pure) in ethanol (HPLC grade). A substrate was exposed to the DEA solution by covering the substrate surface with approximately 1 ml of solution and allowing it to dry. After drying, the specimen was rigorously rinsed in pure ethanol and blown dry with compressed argon. As a control, another substrate was exposed to pure ethanol by the same method, and then rinsed in pure ethanol before blowing it dry with argon.

The thickness of the silica-like films was determined after deposition, using a variable angle spectroscopic ellipsometer (VASE) from J. A. Woollam. Optical parameters $\Delta$ and $\Psi$ were collected from 300 to 1000 nm at 10 nm intervals and for 60–75° angles of incidence at 5° intervals. A computer program, WVASE32, was used to fit a mathematical model to the experimental data and to determine the thickness of the silica-like films. The model used optical constants ($n$ and $k$) that were measured from a bare aluminum-coated glass substrate and taken from thermally grown amorphous $SiO_2$ [11].

RAIR spectra were obtained after plasma polymerization and after DEA/ethanol exposure using a Nicolet Magna 760 FTIR and a grazing angle accessory set at a grazing angle of 85°. X-ray photoelectron spectra were obtained using a Physical Electronics model 5300 XPS. Spectra were acquired using magnesium $K_\alpha$ radiation at

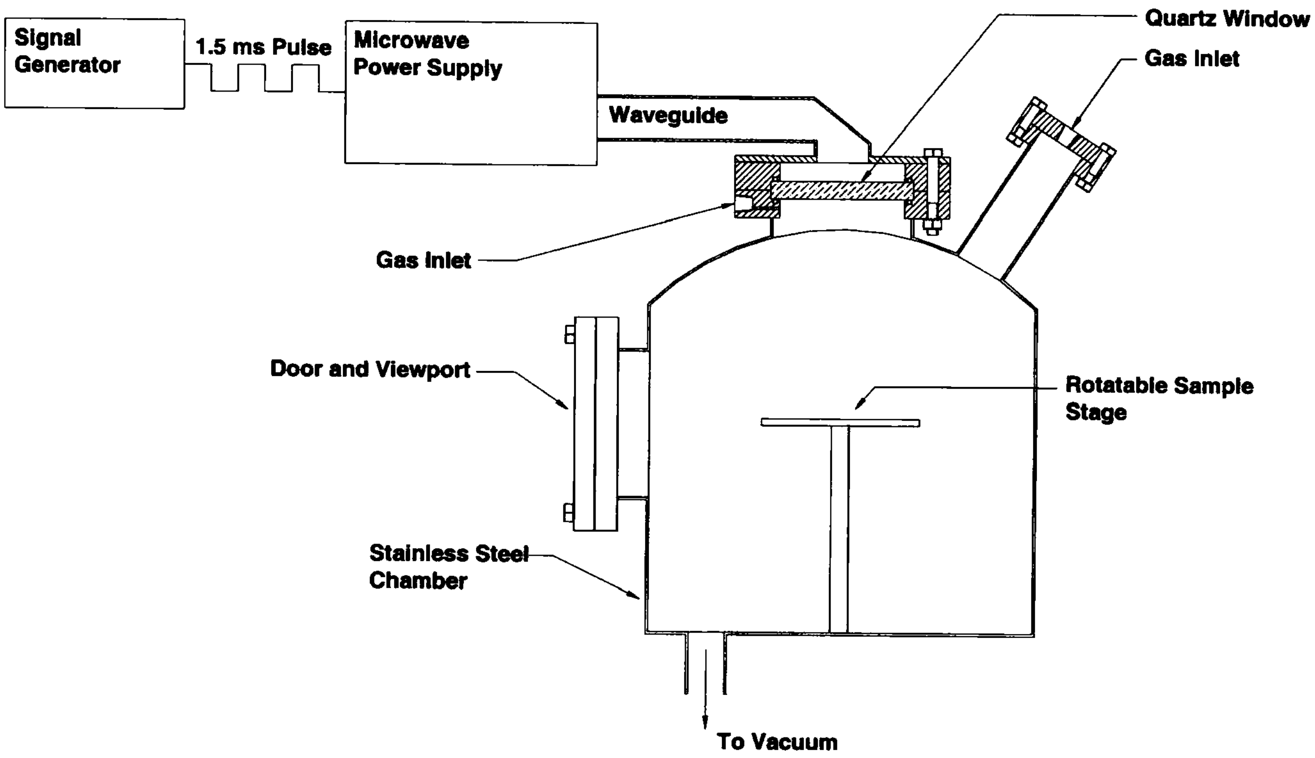

FIGURE 2 Diagram of the microwave plasma reactor.

300 watts. Survey and high-resolution spectra were acquired using 89.45 and 35.75 eV pass energies, respectively. To increase the surface sensitivity, the spectra were acquired at a 15° take-off angle. The effects of sample charging were eliminated by correcting the observed spectra to yield a C(1s) binding energy for saturated hydrocarbons equal to 284.6 eV. Samples were heated by transferring them onto a temperature-controlled stage in a turbo-pumped UHV chamber (*ca.* $5 \times 10^{-8}$ Torr) attached to the XPS. As a check, the control specimen was analyzed for contaminants before and after heating at 200°C for 1 hour.

## 3. RESULTS AND DISCUSSION

### 3.1. Infrared Results

Ellipsometry measurements indicated a film thickness of 29.6 nm ± 0.2 nm. Figure 3 shows the RAIR spectrum of the as-deposited silica-like film. The spectrum shows characteristic peaks typical of inorganic silica-like material. The broad band around 3350 $cm^{-1}$ was due to the O-H stretching of hydrogen-bonded silanol (SiO-H) groups. The broadness of this band was due to the wide distribution of hydrogen-bonding environments of the silanol groups. The shoulder near 3650 $cm^{-1}$ was due to O-H stretching of isolated SiO-H groups [12]. The strongest absorption band in the spectrum had a peak at 1225 $cm^{-1}$ and was due to asymmetric stretching of Si-O-Si bonds. The peak at 950 $cm^{-1}$ was due to Si-O stretching in Si-OH groups. Finally, the peaks at 800 and 490 $cm^{-1}$ were due to Si-O-Si bending and rocking vibrations, respectively.

Significant chemical changes in the silica-like films occurred after exposure to ethanol and the DEA solution. Figure 4 shows the RAIR spectra for the silica-like film as deposited (A), after ethanol exposure and ethanol rinse (B), and after exposure to the DEA solution and ethanol rinse (C). When the spectra of the control specimens, (A) and/or (B), were subtracted from the sample spectrum, (C), additional peaks of small amplitude were not observed, and therefore the subtraction spectra are not presented here. In addition, infrared absorption bands due to the amine group of the model compound, N-H

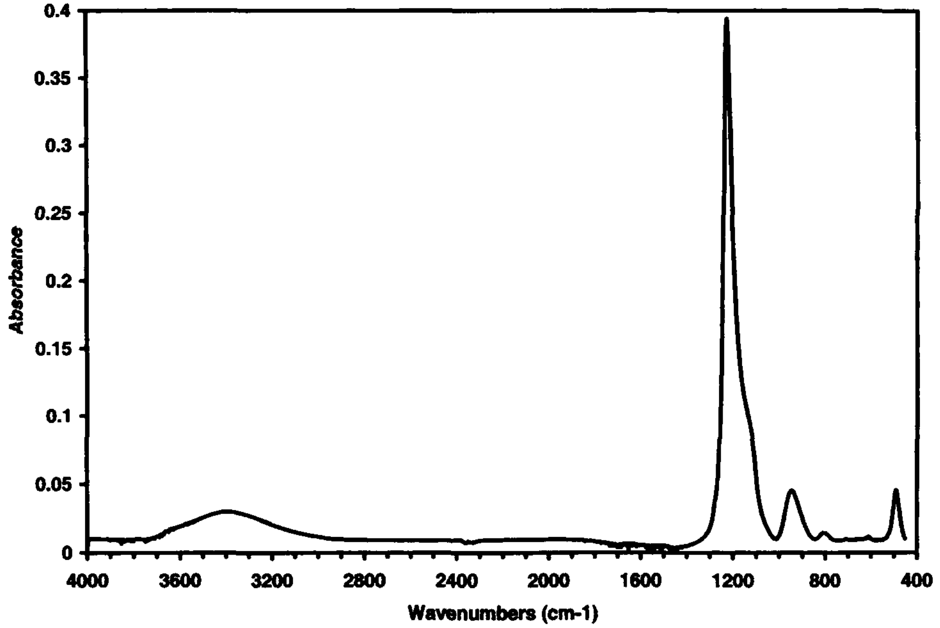

FIGURE 3 RAIR spectrum of a 30 nm plasma-polymerized silica-like film deposited with pulsed microwave power at 200 Watts for 3 minutes at 500 mTorr using 5, 45, and 0.2 SCCM argon, oxygen, and HMDSO, respectively.

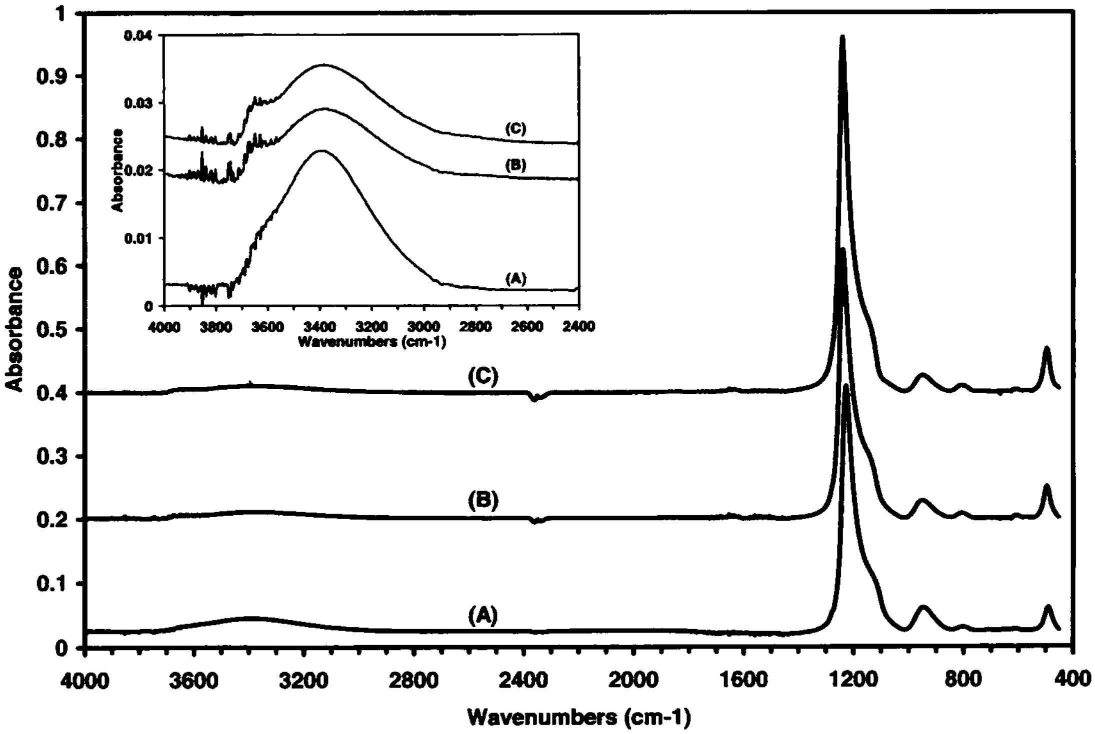

FIGURE 4 RAIR spectra for the silica-like films (A) as deposited, (B) after exposure to ethanol, and (C) after exposure to DEA in ethanol. The inset shows an expanded view of the 2600–4000 cm $^{-1}$ region.

or N-C stretching, were not detected using RAIR. Because the control specimen showed the same structural changes as the specimen exposed to the DEA solution, the changes in the silica-like films were attributed to the ethanol.

The inset in Figure 4 shows the 2600–4000 $cm^{-1}$ region and a decrease in the hydrogen-bonded O-H band at 3350 $cm^{-1}$ was observed for the specimens exposed to ethanol and the DEA solution. Also, a decrease in the intensity of the Si-OH band at 950 $cm^{-1}$ was observed due to the decrease in hydroxyl concentration. Accompanying increases in the Si-O-Si stretching, bending, and rocking bands at 1225, 800, and 490 $cm^{-1}$, respectively, indicated that Si-O-Si bonds were formed. Silanol (Si-OH) groups will undergo a reversible condensation reaction to form siloxane (Si-O-Si) bonds in silica-like materials as shown by the reaction given below [13, 14]:

$$2SiOH \longleftrightarrow SiOSi + H_2O.$$

For this study, the direction of the reaction was likely driven to condensation by the hygroscopic nature of the ethanol and DEA solutions. Parada *et al.* observed hydroxylation, the reverse reaction, for silica-like films exposed to water vapor [15].

Figure 5 shows the 1000–1400 $cm^{-1}$ region of the RAIR spectra for the silica-like film, as deposited (A), after ethanol exposure and ethanol rinse (B), and after exposure to the DEA solution and ethanol rinse (C). After exposure to the DEA and ethanol solutions, the Si-O-Si stretching band near 1225 $cm^{-1}$ shifted to 1238 $cm^{-1}$. The frequency of the Si-O-Si stretching band depends on the Si-O-Si bond angle, which is representative of stresses within silica and silica-like materials. A lower Si-O-Si stretching frequency indicated a high Si-O-Si bonding angle, and upon exposure to the ethanol and DEA solutions the bond angle increased. Fitch *et al.* observed that relaxation of intrinsic stresses within amorphous $SiO_2$ films was accompanied by an increase in the Si-O-Si stretching frequency, which indicated an increase in the Si-O-Si bond angle [16].

### 3.2. XPS Results

Figure 6 shows the survey spectra for the silica-like film as deposited (A), after ethanol exposure and ethanol rinse (B), and after exposure

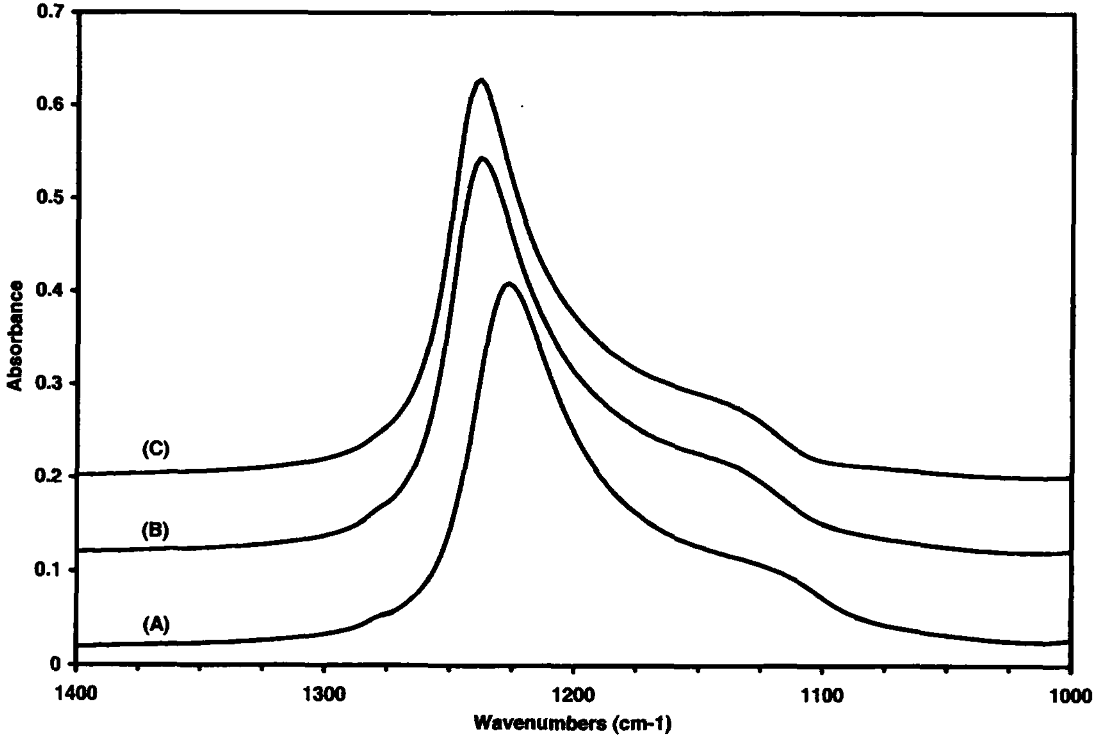

FIGURE 5 Expanded 1000 $cm^{-1}$ to 1400 $cm^{-1}$ region of the RAIR spectra for the silica-like films (A) as deposited, (B) after exposure to ethanol, and (C) after exposure to DEA in ethanol.

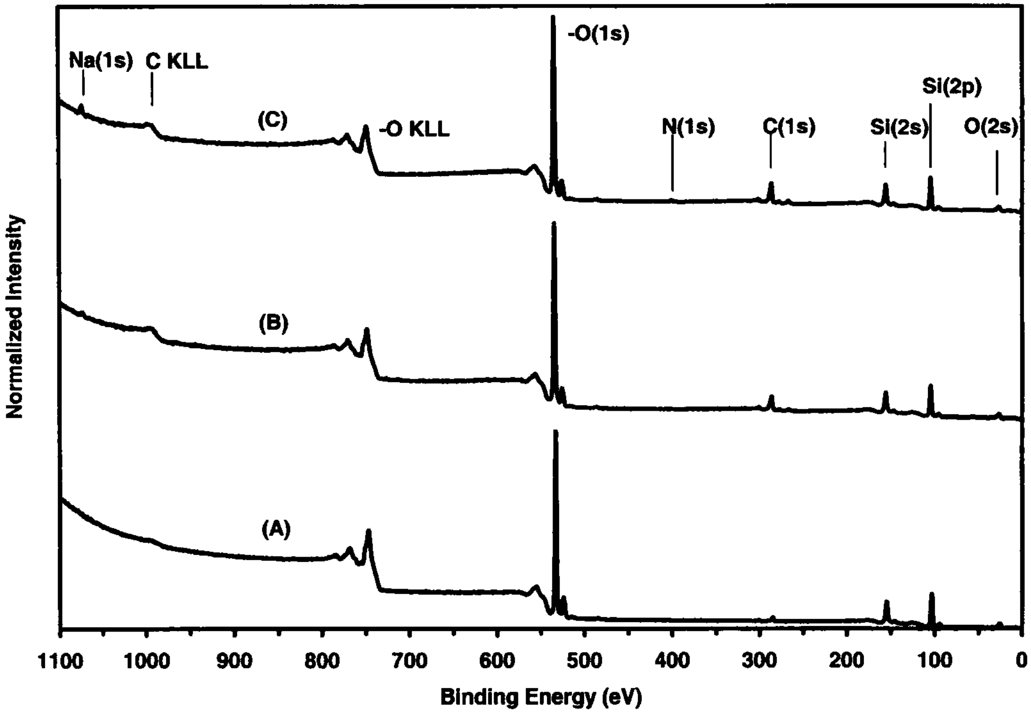

FIGURE 6 XPS survey spectra of plasma polymerized silica-like films (A) as deposited, (B) after exposure to ethanol, and (C) after exposure to DEA in ethanol.

to the DEA solution and ethanol rinse (C). The presence of nitrogen on the silica-like film exposed to the DEA solution showed that a small amount of DEA had adsorbed. The intensity of the nitrogen signal reduced when the take-off angle was changed from 15° to 75°, which indicated that the adsorbate was on the surface of the silica-like film and not within it. The high-resolution C(1s), Si(2p), and O(1s) spectra for the silica-like film as deposited (A), after ethanol exposure and ethanol rinse (B), and after exposure to the DEA solution and ethanol rinse (C) are shown in Figures 7, 8, and 9, respectively. For convenience, the intensity of all the spectra have been normalized. The elemental compositions of all the samples are shown in Table I. The C(1s) spectra showed similar spectra due to airborne contaminants on all three substrates. However, in comparison with the similar carbon concentrations on the solution-treated substrates (*ca.* 17–20 atomic percent), the as-deposited sample had a much lower carbon concentration (*ca.* 6 atomic percent) due to the short exposure time to the atmosphere between deposition and analysis. The Si(2p) spectra showed no significant difference between the as-deposited silica-like film and the films that were exposed to ethanol and DEA. In each case the binding energy of the silicon was approximately 103.5 eV, typical of amorphous $SiO_2$ [17]. Also, the O(1s) spectra showed no significant differences between the as-deposited silica-like film and the films that were exposed to ethanol and DEA. All the O(1s) spectra showed a peak centered near 531.5 eV which was typical for amorphous $SiO_2$ networks [17]. For the substrates exposed to the ethanol and DEA solutions, a peak around 1072 eV indicated that a small amount of sodium had contaminated the substrates. The glassware used for the solutions was a likely source for this contaminant.

Figure 10 shows the high resolution N(1s) spectra for the silica-like film after exposure to ethanol (A), and after exposure to ethanol and heating at 200°C for one hour in UHV (B). The negligible nitrogen signal before and after heating in the UHV chamber attached to the XPS indicated that heating in the UHV chamber did not induce any contamination of the specimens.

Figure 10 also shows the high resolution N(1s) spectra for the silica-like film after exposure to DEA in ethanol (C) and after exposure to DEA in ethanol and heating at 250°C for five hours in UHV (D). Both spectra showed a significant nitrogen peak (*ca.* 1 atomic percent) due

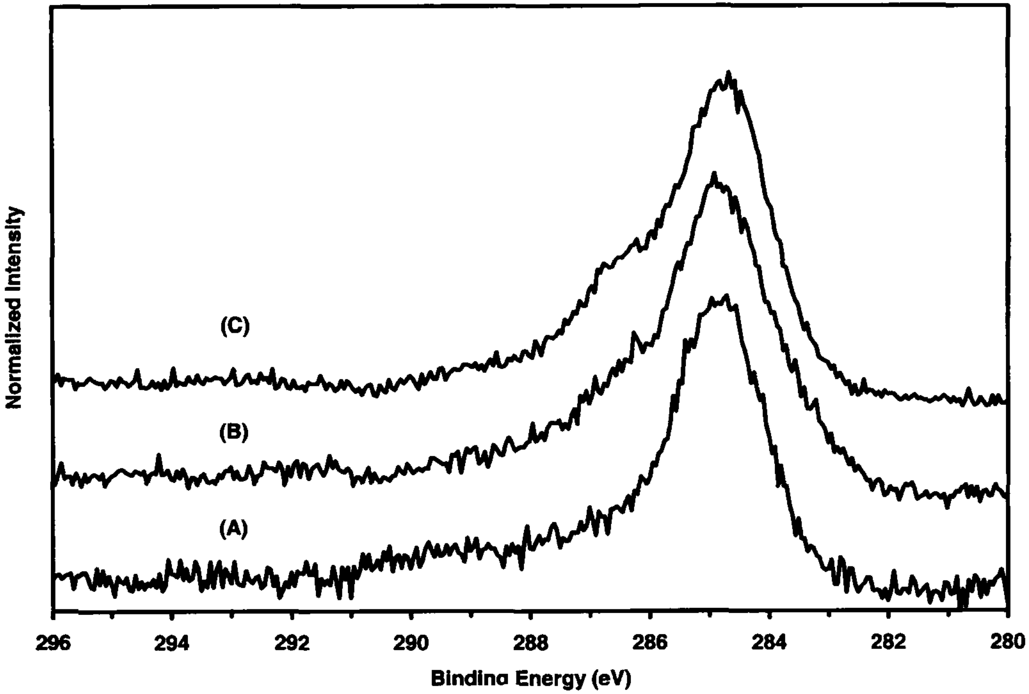

FIGURE 7 High resolution C(1s) photoelectron spectra for plasma-polymerized silica-like films (A) as deposited, (B) after exposure to ethanol, and (C) after exposure to DEA in ethanol.

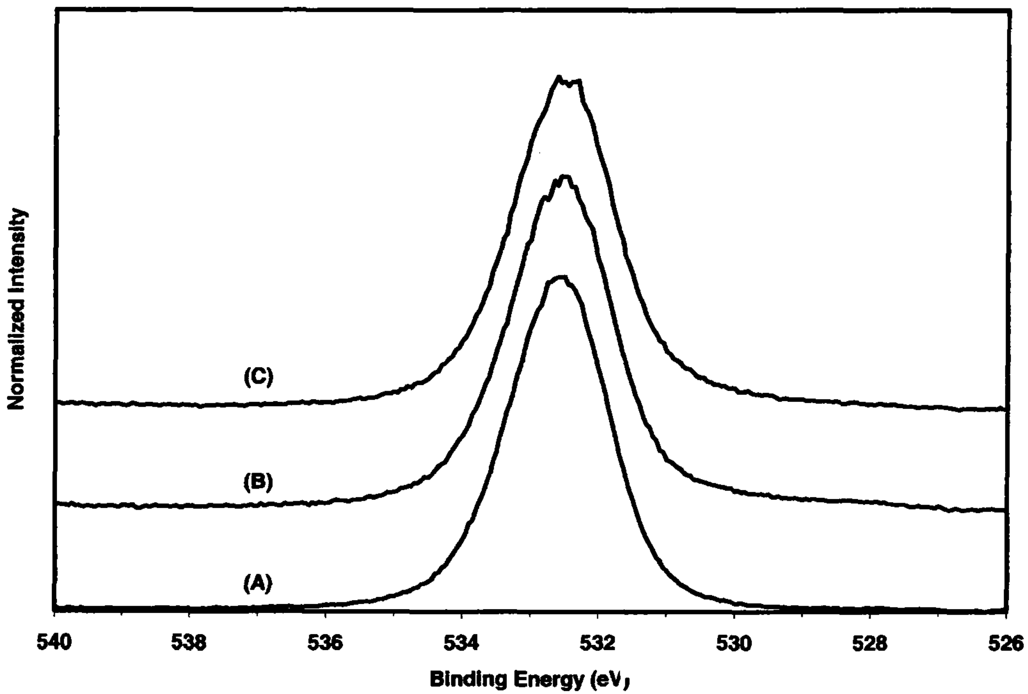

FIGURE 8 High resolution O(1s) photoelectron spectra for plasma-polymerized silica-like films (A) as deposited, (B) after exposure to ethanol, and (C) after exposure to DEA in ethanol.

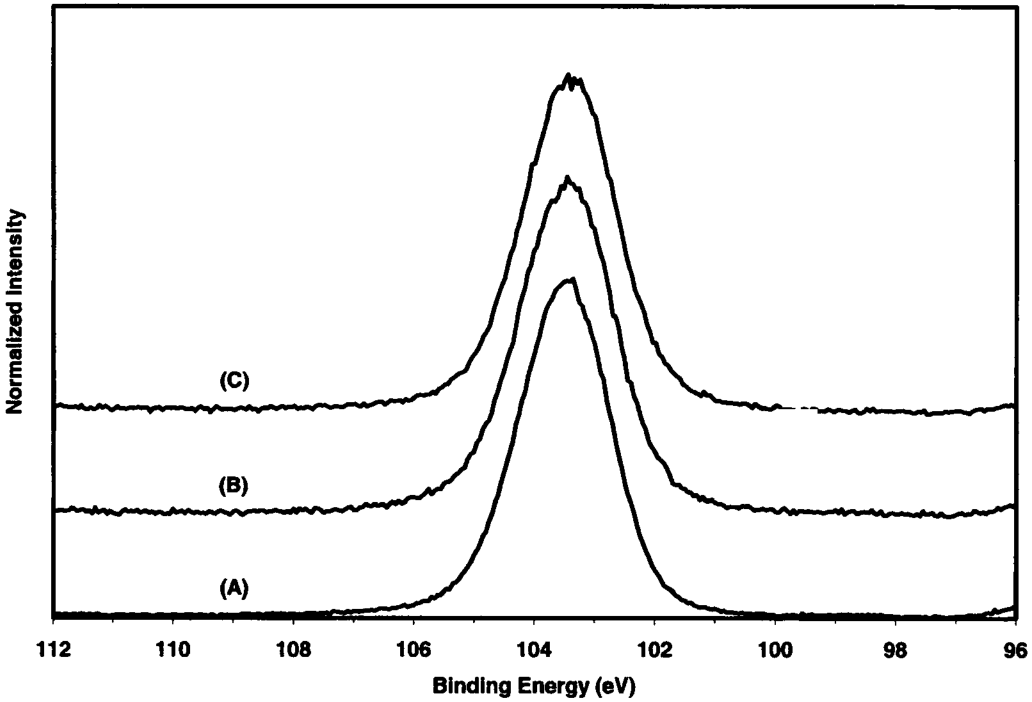

FIGURE 9 High resolution Si(2p) photoelectron spectra for plasma-polymerized silica-like films (A) as deposited, (B) after exposure to ethanol, and (C) after exposure to DEA in ethanol.

TABLE I XPS atomic concentrations of elements detected on silica-like films as-deposited, exposed to ethanol, and exposed to ethanol solutions of diethanolamine.

| | *Atomic percent* (%) | | |
|---|---|---|---|
| *Element* | *As-deposited* | *Exposed to ethanol* | *Exposed to ethanol solutions of DEA* |
| C | 5.7 | 17.4 | 20.9 |
| O | 66.7 | 58.5 | 55.1 |
| Si | 27.6 | 23.8 | 22.3 |
| N | — | — | 1.0 |
| Na | — | 0.3 | 0.7 |

to DEA adsorbed on the surface of the silica-like film. The persistence of the adsorbate after heating for 5 hours at 250°C indicated that the adsorption of the DEA to the silica-like film occurred through a strong chemical interaction. Molecules that have chemically interacted with a substrate to form ionic or covalent bonds will typically desorb in UHV at temperatures above 225°C, whereas molecules that bond through hydrogen bonding or van der Waals forces would completely desorb from the substrate in UHV at much lower temperatures (*ca.* 100°C).

Curve fitting the N(1s) spectrum of the sample exposed to DEA revealed two binding energy components, one at 399.5 eV and the other at 401.5 eV, as shown in Figure 11. The low binding energy component at 399.5 eV was representative of an amine with a very slight positive charge, in other words, weakly interacted. The high binding energy component at 401.5 eV indicated that some of the DEA had interacted strongly with the substrate to form ammonium ions [18]. Other amine-based model adhesives adsorbed onto metal/metal-oxide substrates have shown high binding energy N(1s) components [4–6]. Similar results were observed by Fowkes *et al.*, who characterized amines bound to glass surfaces as quaternary ammonium ions with binding energies of about 401.5 eV on the glass surface and 399 eV in the bulk [19]. It seems here that the DEA molecules have bonded to the surface of the silica-like primer film in a similar fashion.

Figure 12 shows the curve-fitted N(1s) spectrum of the adsorbed amine after heating in UHV. An additional band at 402.4 eV was curve-fit to the spectrum and was likely due to oxidation of the adsorbed amine during heating in UHV. In addition, the high temperature desorption test may have resulted in additional protonation

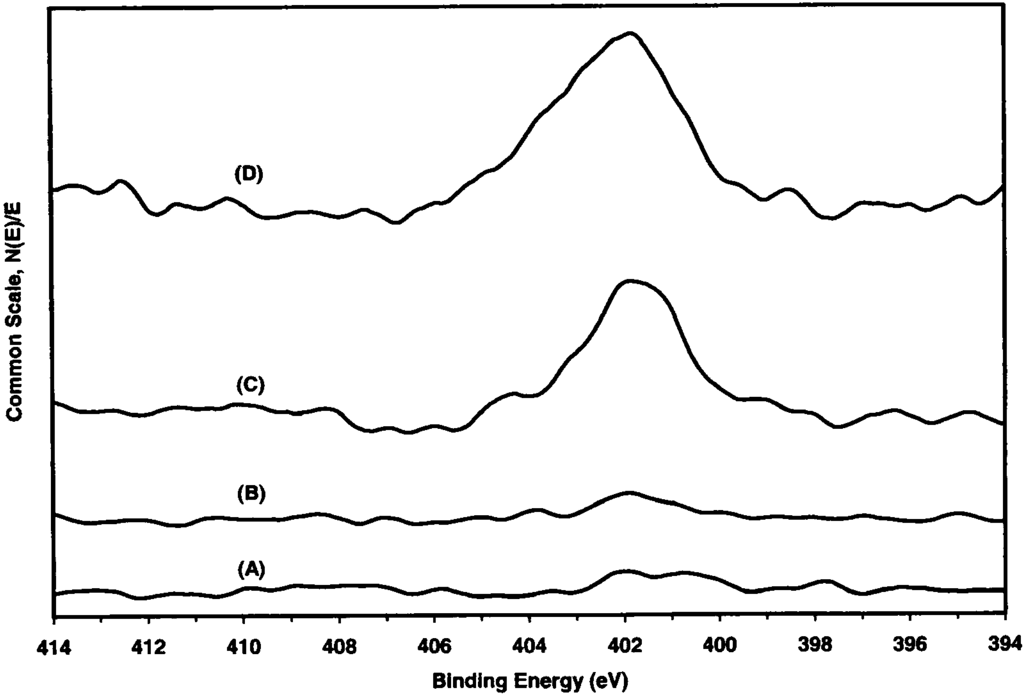

FIGURE 10 High resolution N(1s) spectra from XPS for the silica-like films (A) after exposure to ethanol, (B) after exposure to ethanol and 200°C for one hour in UHV, (C) after exposure to DEA in ethanol, and (D) after exposure to DEA in ethanol and 250°C for five hours in UHV.

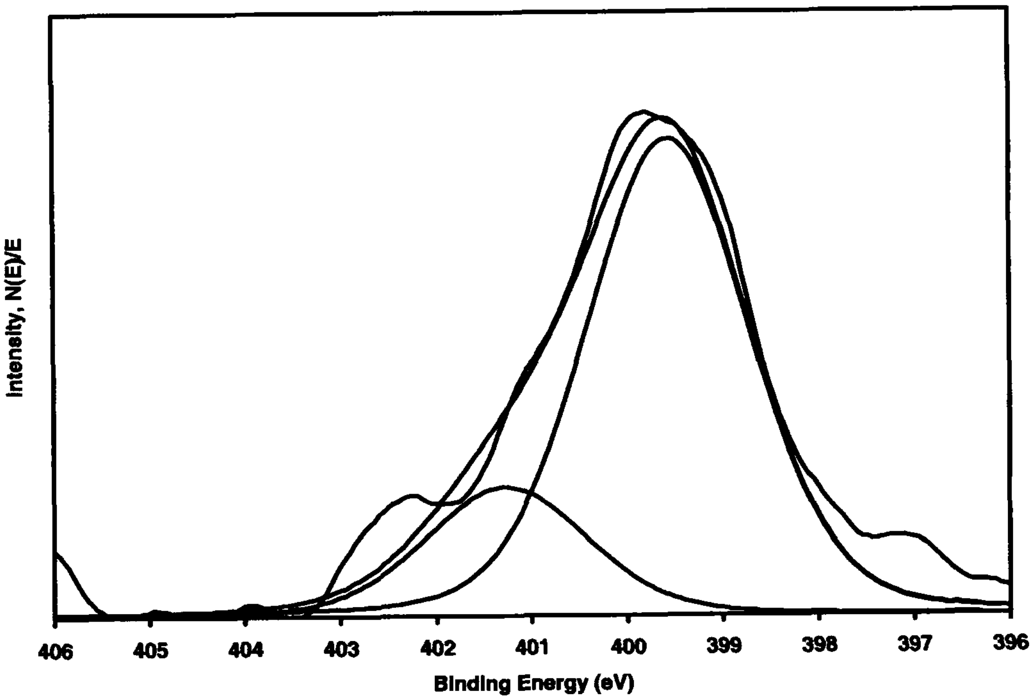

FIGURE 11 Curve-fitted high-resolution N(1s) spectra for the silica-like film exposed to DEA in ethanol.

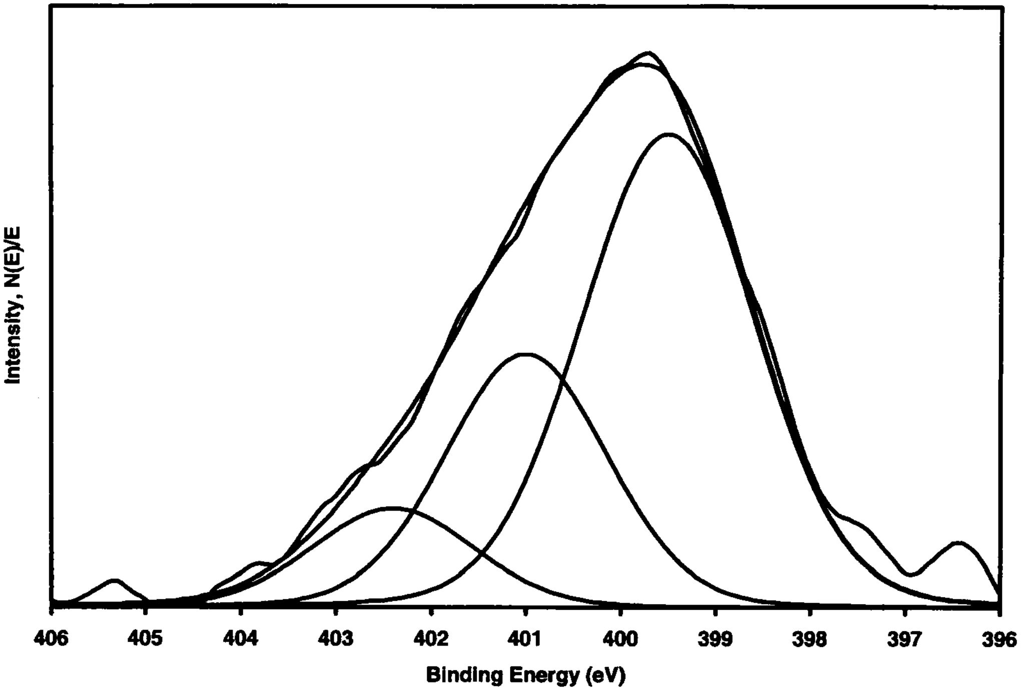

FIGURE 12 Curve-fitted high-resolution N(1s) spectra for the silica-like film exposed to DEA in ethanol and 250°C for 5 hours in UHV.

of amine groups, since the band at 401.5 eV appeared to have intensified after heating the substrate/adsorbate.

In addition to reacting with the amine group, adsorption to the silica-like primer film could have occurred through hydrogen bonding of the polar alcohol groups (-ROH) on the DEA molecule to siloxane groups (Si-O-Si) on the surface of the primer film. Bonding through the alcohol groups of the DEA molecule could also have occurred by the formation of an alkoxy species by a condensation reaction similar to the one shown above. In this case, a silanol group (SiOH) would react with the alcohol functionality (-ROH) to form a covalent bond (-ROSi-) and water. SIMS data for similar model compounds on oxidized aluminum have supported both hydrogen bonding [4] and alkoxy group formation [6]. Although the analytical techniques used here could not directly detect either of these interactions, the high adsorption strength was compelling evidence for an interaction between the alcohol functionality of the DEA and the primer film in addition to the adsorption of the amine group.

## 4. CONCLUSIONS

Plasma-polymerized silica-like primer films prepared from HMDSO monomer and oxygen underwent significant chemical changes during exposure to ethanol and ethanol/DEA solutions. Infrared results indicated that siloxane (Si-O-Si) bonds were formed and the Si-O-Si network relaxed upon exposure to the solutions. Signals from the DEA adsorbate were too weak for detection by infrared spectroscopy.

XPS results clearly indicated a strong chemical interaction between diethanolamine and silica-like plasma-polymerized HMDSO primer films. The N(1s) spectrum of the DEA adsorbate consisted of two components, one typical of amine groups at 399 eV, and the other indicative of protonation at 401.5 eV. Protonation most likely occurred through the well-known acidic nature of silica-like surfaces. As further evidence for strong chemisorption, the DEA resisted desorption by heating in UHV at 250°C for an extended period. Although the interaction between the DEA model compound and the silica-like primer film was strong, the low surface coverage of the adsorbate was evidence of the fact that acidic sites on the silica-like primer film were sparse. Certainly, more chemisorption sites would benefit the adhesive/primer interface in terms of strength and stability. The fabrication of plasma-polymerized silica-like films with higher silanol surface coverage is of obvious future interest.

## Acknowledgement

This work was funded in part by the National Science Foundation.

## References

[1] Turner, R. H., Segal, I., Boerio, F. J. and Davis, G. D., *J. Adhesion* **47**, 1 (1997).
[2] Taylor, C. E., Boerio, F. J., Ward, S. M., Ondrus, D. J., Dickie, R. A. and Brutto, M. M., *J. Adhesion* **69**, 237 (1999).
[3] Turner, R. H., Segal, I., Boerio, F. J. and Davis, G. D., In: *Proceedings of the 20th Annual Meeting of the Adhesion Society*, Drzal, L. T. and Schreiber, H. P. Eds. (The Adhesion Society, Blacksburg, VA, 1997), p. 695.
[4] Affrossman, S. and MacDonald, S. M., *Langmuir* **12**, 2090 (1996).
[5] Kelber, J. A. and Brow, R. K., *Appl. Surf. Sci.* **59**, 273 (1992).
[6] Abel, M. L., Rattana, A. and Watts, J. F., *Langmuir* **16**, 6510 (2000).
[7] Marsh, J., Minel, L., Barthés-Labrousse, M. G. and Gorse, D., *Appl. Surf. Sci.* **113**, 270 (1998).
[8] Boerio, F. J. and Hong, P. P., *Mater. Sci. Eng.* **A126**, 245 (1990).
[9] Sellitti, C., Koenig, J. L. and Ishida, H., *Mater. Sci. Eng.* **A126**, 235 (1990).
[10] Dillingham, R. G. and Boerio, F. J., *J. Adhesion* **24**, 315 (1987).
[11] *Handbook of Optical Constants of Solids*, Palik, E. D. Ed. (Academic Press, San Diego, CA, 1998), Vol 1, p. 759.
[12] Iler, R. K., *The Chemistry of Silica*, (Wiley, New York, NY, 1979).
[13] Cerofolini, G. F. and Meda, L., *J. Non-Cryst. Solids* **216**, 140 (1997).
[14] Morrow, B. A. and McFarlan, A. J., *J. Non-Cryst. Solids* **120**, 61 (1990).
[15] Parada, E. G., Gonzalez, P., Pou, J., Serra, J., Fernandez, D., Leon, B. and Perez Amor, M., *J. Vac. Sci. Technol. A* **14**, 436 (1996).
[16] Fitch, J. T., Lucovsky, G., Kobeda, E. and Irene, E. A., *J. Vac. Sci. Technol. B* **7**, 153 (1989).
[17] Wagner, C. P., Riggs, W. M., Davis, L. E., Moulder, J. F. and Muilenberg, G. E., *Handbook of X-ray Photoelectron Spectroscopy*, (Perkin-Elmer, Eden Prarie, MN, 1979).
[18] *Practical Surface Analysis*, Briggs, D. and Seah, M. P. Eds. (John Wiley, 1990), 2nd edn.
[19] Fowkes, F. M., Dwight, D. W., Cole, D. A. and Huang, T. C., *J. Non-Cryst. Solids* **120**, 47 (1990).