Attenuated Total Reflection of Dielectric/Metal Interfaces

L. L. Clemen, M. R. Strunk and T. M. Niemczyk

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131, U.S.A.

D. M. Haaland

Sandia National Laboratories, Albuquerque, New Mexico 87185, U.S.A.

An experimental system for the characterization of metal/dielectric interfaces has been developed. Attenuated Total Reflection (ATR) spectroscopy of a dielectric on a thin metal film, deposited on a multiple reflection ATR element, yields information about the bonding, or lack thereof, at the metal/dielectric interface. At a certain metal thickness, the absorbance due to molecules at the interface, relative to the signal from the bulk dielectric, is at a maximum. A model which uses the Fresnel equations in matrix form, has been used to predict the best metal thickness for each dielectric/metal/ATR element system. The ATR element may be placed in an environmental chamber in which the temperature, humidity etc. can be varied, in order to test the integrity of the interface to hostile environments. Chemometric analysis of the IR spectral data maximizes our ability to measure small changes in the interface properties. Preliminary results from polyimide/metal samples are presented.

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INTRODUCTION

In the semiconductor industry, it is necessary to have the strongest possible interface between dielectric films and metal films. Lately new, low dielectric constant (low k) polymers are being developed for use. There is a need to non-invasively monitor and characterize metal/dielectric interfaces made in a realistic manner. With this goal in mind, we have developed a procedure for the characterization of the metal/dielectric interface, using Attenuated Total Reflectance (ATR) infrared (IR) spectroscopy. In this paper, we use computational methods to derive the optimal metal film thickness for maximizing the spectral sensitivity of the ATR technique to the metal/dielectric interface. The interfaces to be studied are made by depositing a metal layer on the ATR element with a polymer film spun-cast on top. The IR/ATR technique is very sensitive to the interface region, is non-destructive and will enable us to monitor the interface bonding while changing the temperature, humidity, etc.

ATTENUATED TOTAL REFLECTION

Attenuated total reflection spectroscopy relies on the fact that when light passes from a material with a high index of refraction to a material with a lower index of refraction, at angles of incidence greater than a critical angle, the light will be totally reflected at the interface. An evanescent wave is then formed at the interface which penetrates into the second layer as shown in Figure 1. The second material is absorbing, the evanescent wave is attenuated, producing a change in the intensity of the reflected light. Because the evanescent wave decays exponentially into the second layer, only a small thickness of the second material is sampled. Under normal

FIGURE 1. Schematic diagram of a typical ATR experiment.

The ATR crystal provides multiple sampling of a thin layer on top of the ATR crystal via absorption of the evanescent wave.
conditions the penetration depth in an IR/ATR experiment is 200-400 nm, or too great to be interface specific.

The ATR technique has been used with some success (1,2) to monitor a metal/electrolytic interface by depositing a thin metal layer on an ATR element and then placing an electrolyte on top. As long as the metal film is thin enough that the evanescent wave can penetrate to the electrolyte (10-40 nm), the interface may be easily studied. The experiment proposed here is analogous to the study of the metal/electrolyte interface.

MODEL OF ABSORBANCE

A modeling study has been carried out prior to experimentally testing the concept. The model was designed to investigate the behavior of the reflectance of the multilayered ATR crystal/metal film/polymer system, using a computer program written to run in MATLAB. To make the program versatile and simple to use, the matrix form of the Fresnel equations was employed (3). The Fresnel equations predict the amplitude, phase and direction of parallel light falling on flat, parallel boundaries. There are no adjustable parameters in the equations, they are exact as long as the complex index of refraction is known for all the materials involved. The complex index of refraction is well known for the waveguide materials and for metals, but less well known for polymeric materials. However, the real part of the index of refraction is well known for polymers and the imaginary part is known to be small enough that the details of the calculation are not sensitive to that parameter. The software may be used to calculate the penetration depth of the electro-magnetic wave when layers are absorbing, to calculate the best thickness for intermediate layers, to optimize the angle of incidence, and to find the best material for the ATR element.

Using boundary conditions of the electric and magnetic fields at each surface, the reflected and transmitted fields may be calculated.

\[
\begin{bmatrix} U_1 \\ V_1 \end{bmatrix} = M_2 M_3 \cdots M_{N-1} \begin{bmatrix} U_{N-1} \\ V_{N-1} \end{bmatrix} = M \begin{bmatrix} U_{N-1} \\ V_{N-1} \end{bmatrix},
\]

where the \( M_j \) are 2x2 matrices defined below and \( U_k \) and \( V_k \) are the tangential components of the field amplitudes at the boundary \( k \). For TE polarization, \( U_1 = E_y^0 \) and \( V_1 = H_y^0 \) and for TM polarization, \( U_1 = H_y^0 \) and \( V_1 = E_y^0 \).

The \( M_j \) matrices for each layer are:

\[
\begin{bmatrix} \cos \beta_j & -i \frac{p_j}{\cos \beta_j} \\ -i p_j \sin \beta_j & \cos \beta_j \end{bmatrix} \quad \text{for TE polarization},
\]

\[
\begin{bmatrix} \cos \beta_j & -i \frac{q_j}{\cos \beta_j} \\ -i q_j \sin \beta_j & \cos \beta_j \end{bmatrix} \quad \text{for TM polarization}
\]

where

\[
\beta_j = \frac{2\pi}{\lambda} \xi_j h_j, \quad \xi_j = (n + ik) \cos \theta_j
\]

\( h_j \) = thickness of \( j \)th layer

\( p_j = \left( \frac{\varepsilon_j}{\mu_j} \right)^{1/2} \cos \beta_j \)

\( q_j = \left( \frac{\varepsilon_j}{\mu_j} \right)^{1/2} \cos \beta_j \)

The reflection and transmission coefficients are then:

\[
r_\pm = \frac{E_{y1}^0}{E_{y1}^0}, \quad t_{\pm} = \frac{E_{yN}^0}{E_{y1}^0}, \quad t_{\pm} = \frac{E_{yN}^0}{E_{y1}^0} \frac{(m_{11} + m_{12} p_N) p_1 - (m_{21} + m_{22} p_N)}{(m_{11} + m_{12} p_N) p_1 + (m_{21} + m_{22} p_N)}
\]

\[
r_{\parallel} = \frac{H_{y1}^0}{H_{y1}^0}, \quad t_{\parallel} = \frac{H_{yN}^0}{H_{y1}^0}, \quad t_{\parallel} = \frac{H_{yN}^0}{H_{y1}^0} \frac{(m_{11} + m_{12} q_N) q_1 - (m_{21} + m_{22} q_N)}{(m_{11} + m_{12} q_N) q_1 + (m_{21} + m_{22} q_N)}
\]

\[
\begin{bmatrix} \mu_y \hat{n}_1 \cos \theta_1 & \mu_y \hat{n}_1 \cos \theta_1 \hat{n}_N^0 \end{bmatrix} \hat{t}_{\parallel}, \quad \hat{t}_{\parallel} = \frac{\mu_y \hat{n}_1 \cos \theta_1}{\mu_y \hat{n}_1 \cos \theta_1} |t_{\parallel}|^2, \quad \delta_{\parallel} = \arg(t_{\parallel})
\]

and the reflectance \( R \) and transmittance \( T \) are:

\[
R_\pm = |r_\pm|^2, \quad \delta_\pm = \arg(r_\pm)
\]

\[
T_\pm = \frac{\mu_y \Re\left(\hat{n}_y^0 \cos \theta_1\right)}{\mu_y \hat{n}_1 \cos \theta_1} |t_{\pm}|^2, \quad \delta_\pm = \arg(t_{\pm})
\]

\[
R_{\parallel} = |r_{\parallel}|^2, \quad \delta_{\parallel} = \arg(r_{\parallel})
\]

\[
T_{\parallel} = \frac{\mu_y \Re\left(\hat{n}_y^0 \cos \theta_1 / \hat{n}_N^0 \right)}{\mu_y \hat{n}_1 \cos \theta_1} |t_{\parallel}|^2, \quad \delta_{\parallel} = \arg(t_{\parallel})
\]
Simulations were run for ATR crystals made from Zinc Selenide (ZnSe) and Silicon (Si). First, the best thickness for the metal layer was found by calculating the absorbance of a thin (10 nm) polymer layer on the metal layer at 1000 cm\(^{-1}\) for varying metal thicknesses. The resulting absorbance enhancement factors for p-polarized light are shown in Figure 2 as a function of metal thickness. Light polarized perpendicular to the plane of the films (not shown) exhibits a much smaller increase in absorbance enhancement at slightly lower thicknesses.

The dependence of the maximum absorbance metal thickness on wavelength was also investigated. In the spectral region of interest (3-10 µm), the metal thickness at which the absorption from a 10-nm polymer film is maximized does not change appreciably.

The electric field which is normal to the interface will decrease in each layer as \( \exp \left( -\frac{2\pi}{\lambda} \frac{d_j}{\lambda} \text{Im}(\varepsilon_j) \right) \) where \( \varepsilon_j \) is defined above and \( d_j \) is the thickness of the layer. The penetration depth into the sample, defined as the point at which the fields have dropped to 1/e, or 37%, of their original value, may be found for any sample of films with known film thickness and composition. The absorbance of a material is proportional to the square of the electric field so that at the point where the field is one penetration depth into the material, the absorbance has dropped to 1/2e or 18% of their original value. Thus one penetration depth is a good measure for how much of the film is being sampled. To find a maximum thickness for the metal films, it is interesting to look at the penetration depth of the metal films. For Al, Au and Cu, the penetration depths are found to be 1.8, 2.9, and 3.4 nm, respectively, for a ZnSe/ metal interface with 45-degree angle of incidence.

MULTIVARIATE ANALYSIS

In order to bring out small changes in the spectral data, a multivariate calibration technique, specifically partial least squares (PLS), is used. This technique is described in detail elsewhere [4]. Basically, PLS is a factor analysis method with full spectrum capabilities. If \( m \) different spectra have been taken, each with \( n \) absorbances then PLS finds a new coordinate system of full spectrum basis vectors such that:

\[
A = TB + E_A
\]

where \( A \) is the \( m \times n \) matrix of calibration spectra, \( B \) is a \( h \times n \) matrix with the rows of \( B \) being the basis set of \( h \) full spectrum vectors, called the loading vectors in this paper, and \( T \) is the \( m \times h \) matrix of intensities (scores) in the new coordinate system. The \( E_A \) matrix is the spectral errors or residuals not fit by the model.

PRELIMINARY EXPERIMENTS

The first samples tested were of the Aluminum/BPDA-PDA interface. BPDA-PDA is a aromatic polyimide with a chemical structure as shown in Figure 3. Aluminum films were evaporated on ZnSe ATR elements in a cryopumped system with mass thickness measured via a quartz crystal oscillator thickness monitor. The BPDA-PDA precursor was then placed on the aluminum film and spun at 1000 rpm for one minute to ensure an even coating. The samples were then cured in nitrogen at 180° C for 8 hours (ramping from room temperature at a rate of about 2° C/min) followed by a high temperature cure at 350° C for 3 hours.

![Chemical structure of BPDA-PDA](image)

Absorbance spectra of samples made with aluminum film mass thicknesses between zero and 4.5 nm show strong features in the polyimide region. The most interesting data set at this time is a series of spectra taken of a sample with an aluminum film of 1.3 nm mass thickness, with the aluminum/polyimide film in contact with distilled water. Spectra were recorded every thirty minutes using a Nicolet 800 at 4 cm\(^{-1}\) resolution, 256 scans averaged, with a liquid nitrogen cooled MCT detector. These 28 absorbance spectra are shown in Figure 4. The four most variable peaks, at 1704, 1354, 1078(with 11 19) and 829 cm\(^{-1}\) are likely due to a symmetric C=O stretch, C-N stretch, symmetric (OC)\(_2\)NC breathing mode, and aromatic ring deformation, respectively. The major peaks at higher frequencies show flattened tops. This is likely due to light scattering from
islands in the metal film that acts like stray light limiting the absorbance features.

![Graph](image1.png)

**FIGURE 4.** IR/ATR spectra of BPDA-PDA on 1.3 nm of aluminum. The 28 spectra were taken every 30 minutes while the sample was in contact with distilled water.

The PLS analysis tells us that the first time correlated loading vector accounts for 72% of the variance in the spectra. The second loading vector which correlates with time accounts for another 5% of the variance and is primarily a spectrum of water and water vapor. The first of these loading vectors and the scores vs. time in water are shown in Figures 5 and 6. While all of the four major peaks increased in intensity with time, possibly due to changes in the spectrometer over a period of hours, the intensity ratios of the four peaks have changed markedly. The spectral features at 829, and 1078 cm⁻¹ and to a lesser extent the peak at 1354 cm⁻¹ have grown with respect the other two main peaks. In a trial data set with only cured polyimide on the ATR element (no metal film), the peak at 829 cm⁻¹ increased after several hours of exposure to distilled water. Spectra taken after the sample has dried for several days indicate the water had no permanent effect on the sample, therefore we believe no bond changes at the interface have occurred.

![Graph](image2.png)

**FIGURE 5.** First loading vector for time in water found using the PLS program.

![Graph](image3.png)

**FIGURE 6.** Scores showing correlation of the first loading vector with time.

**CONCLUSIONS**

The method of using ATR spectroscopy under different environmental conditions can be used to characterize a wide variety of interfaces. We have developed a model to calculate the best intermediate metal thickness to yield the greatest signal enhancement for ATR sampling. The ATR method is very interface sensitive so that the signal due to IR vibrations of molecules at the interface will be increased relative to those in the bulk. Multivariate spectral analysis has the potential to further aid in separating the signal due to the interface from that of the bulk materials. Preliminary data from the BPDA-PDA /Aluminum interface indicate that the bonding is resistant to water. Future plans including further testing of the interface in water, tests of the interface at high temperatures and tests of other dielectric/metal interfaces. By spin-coating the polymer on top of a metal film, we are able to effectively create and characterize an interface that is representative of metal-polymer interfaces expected in microelectronic devices (assuming that the metal islands of these thin metals is representative of thicker metal films. This experimental system of ATR spectroscopy, optimal film thicknesses, and multivariate analysis can be used to effectively characterize many different interfaces.

**REFERENCES**

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