INTERFACIAL ELECTRONIC STRUCTURE AND FULL SPECTRAL HAMAKER CONSTANTS OF Si_3N_4 INTERGRANULAR FILMS FROM VUV AND SR-VEEL SPECTROSCOPY

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Abstract

The interfacial electronic structure, presented as the interband transition strength $J_{\text{CV}}(\omega)$ of the interatomic bonds, can be determined by Kramers Kronig (KK) analysis of vacuum ultraviolet (VUV) reflectance or spatially resolved valence electron energy loss (SR-VEEL) spectra. For the wetted interfaces in Si_3N_4 , equilibrium thin glass films are formed whose thickness is determined by a force balance between attractive and repulsive force terms. KK analysis of $J_{\text{CV}}(\omega)$ to yield $\mathcal{E}_2(\xi)$ for the phases present, permits the direct calculation of the configuration-dependent Hamaker constants for the attractive vdW forces from the interfacial electronic structure.

Interband transition strengths and full spectral Hamaker constants for Si_3N_4 samples containing a SiYAlON glass have been determined using SR-VEELS from grains and grain boundaries and compared with results from bulk VUV spectroscopy on separate samples of glass and nitride. The A_{121} Hamaker constant for Si_3N_4 with glass of the bulk composition is 8 zJ ($\text{zJ} = 10^{-21}$ J) from the more established optical method. The EELS method permits the determination of vdW forces based upon actual local compositions and structure, which may differ noticeably from bulk standards. Current results show that full spectral Hamaker constants determined from VUV and SR-VEEL measurements of uniform bulk samples agree, but care must be taken in the single scattering and zero loss subtraction corrections, and more work is ongoing in this area. Still the results show that for the grain boundary films present in these polycrystalline Si_3N_4 samples the glass composition is of lower index of refraction. This can arise from increased oxygen content in the intergranular glass and leads to an increased value of the Hamaker constant (24 zJ) determined in situ from the SR-VEELS of a particular grain boundary film.

Introduction

The spatial variation of the electronic structure at interfaces is critical to both interatomic bonding at atomically abrupt interfaces such as grain boundaries¹ and also to the development of van der Waals (vdW) attraction forces at wetted interfaces^{2,3,4}. This interfacial electronic structure, as represented by the interband transition strength,⁵ can be determined by Kramers Kronig (KK) analysis of vacuum ultraviolet reflectance or spatially resolved valence electron energy loss (SR-VEEL) spectra. For the case of quantitative analysis of SR-VEELS, a series of corrections and transforms of the data are needed, including single scattering deconvolution, convergence correction, and KK analysis. Our current progress in developing these VEELS analyses is emphasized in this paper.

Si_3N_4 ^{6,7} exhibits equilibrium thin glass films^{8,9} whose thickness is determined by a force balance, where the contribution of the van der Waals (vdW) attractive force is dictated by the interband transition strengths of the electrons in the interatomic bonds. The vdW attraction

forces, as given by the Hamaker constant A , arise from transient induced dipoles associated with interatomic bonds. Hamaker constants¹⁰ can be calculated directly from the interfacial electronic structure using Kramers Kronig analysis of $J_{CV}(\omega)$ to yield $\mathcal{E}_2(\xi)$ for the phases present, producing full spectral values for the configuration-dependent Hamaker constants for the vdW forces.

There have been numerous studies of the electronic structure of Si_3N_4 including the LDA OLCAO (local density approximation, orthogonalized linear combination of atomic orbitals) band structure calculations of Ching¹¹, Robertson's Bond Orbital study¹², and the empirical electronic structure calculations of Sokel¹³. Of interest to the present focus on polycrystalline Si_3N_4 as a structural ceramic exhibiting thin intergranular glass films, is the work of Ching on a silicon oxynitride composition $\text{Si}_2\text{N}_2\text{O}$ ¹⁴. In addition, driven by the use of silicon nitride films in electronics,¹⁵ there have been many studies of the visible and UV optical properties of silicon nitride,¹⁶ silicon-oxynitride¹⁷ and silicon-fluoronitride films¹⁸. Recently there has been an extensive study of silicon nitride thin film optical properties up to 9.5 eV reported by Petalas et al.¹⁹

In this paper we present our current results on the interband transition strengths and full spectral Hamaker constants for Si_3N_4 samples containing a SiYAlON glass which have been determined using SR-VEELS from grains and second phase pockets and compared with results from bulk VUV spectroscopy on separate samples of glass and nitride. Much of the work discussed involves developing the analytical tools which permit the quantitative analysis of the SR-VEEL spectra, with quantitative comparisons to VUV results. In the case of Si_3N_4 it is impossible to obtain large single crystals for optical experiments. In the present paper we have used material with 95% Si_3N_4 and only 5% glass component and approximated this to represent pure Si_3N_4 . The SR-VEELS experiments, on the other hand, offer the advantage that extremely small volumes (diameters of approximately 1 nm, specimen thickness of approximately 50 nm) can be irradiated, therefore yielding localized information.

Experimental Methods and Results

Sample Preparation

Two silicon nitride samples were prepared²⁰ with approximately 95% and 80 % Si_3N_4 phase (5% and 20% glass phase respectively) from UBE Si_3N_4 powder with additions of Y_2O_3 and Al_2O_3 and SiO_2 and sintered for 60 minutes at 1840 °C with a maximum gas pressure of 10 MPa N_2 and a cooling rate of 28 °C/minute to 1000 °C. The starting composition for these two Si_3N_4 samples were 81.85 wt.% Si_3N_4 , 12.28 wt.% Y_2O_3 , 5.54 wt.% Al_2O_3 and 0.33 wt.% SiO_2 for the 80 % Si_3N_4 sample and 95.4 wt.% Si_3N_4 , 3.17 wt.% Y_2O_3 , and 1.43 wt.% Al_2O_3 for the 95 % Si_3N_4 sample. The bulk glass sample's composition was chosen because it is known to be essentially saturated with Si_3N_4 at 1700 °C. The bulk glass composition is 52.12 wt.% Y_2O_3 , 12.48 wt.% SiO_2 , 11.87 wt.% Si_3N_4 and 23.53 wt.% Al_2O_3 or in atom% it is 13.1 atom% Y, 13.1 atom% Al, 13.1 atom% Si, 51.1 atom% O and 9.6 atom% N, and is referred to in this paper as a SiYAlON glass. The bulk glass sample was sintered for 30 minutes at 1700 °C with a maximum gas pressure of 1.0 MPa N_2 and a cooling rate of 100 °C to 1000 °C.

All three samples (95% Si_3N_4 , 80% Si_3N_4 and Bulk Glass) were cut and either optically polished for VUV spectroscopy or thinned for STEM SR-VEEL spectroscopy using standard ion beam thinning techniques²¹.

Vacuum Ultraviolet Spectroscopy

Normal incidence optical reflectivity spectra (Figure 1.) were measured for the three samples using both vacuum ultraviolet and optical spectroscopy from 2700 to 28 nm (0.46 to 44 eV) with a resolution of 0.2 and 0.6 nm. The spectrophotometers were a VUV instrument²² using a Laser Plasma Light Source²³, and a Perkin Elmer Lambda 9 NIR/Vis/UV instrument. Once the reflectivity is measured, its value in the visible is compared to that calculated from the index of refraction determined using spectroscopic ellipsometry²⁴ on these same samples (shown in Fig. 2). The long wavelength index of refraction, determined by this more direct ellipsometric measurement, is 1.97, 1.96 and 1.78 for the 95% Si₃N₄, 80% Si₃N₄ and the bulk SiAlYON glass samples, respectively. Inconsistencies between the measured value of the optical reflectivity may arise from a light collection error in the spectrophotometer and can be corrected by a simple multiplicative constant to bring the measured reflectance into agreement that expected from the index of refraction in the visible.

Figure 1. Optical reflectivity of the two Si₃N₄ samples, 95% Si₃N₄ and 80% Si₃N₄, and the bulk SiAlYON glass sample.

Once the reflectivity of the sample is determined over a wide energy range, encompassing the interband transitions of the valence electrons, the Kramers Kronig (KK) transform²⁵ can be used to calculate the reflected phase ϕ of the light from the reflectance amplitude r , since they are conjugate variables.

$$\phi(\omega) = -\frac{2\omega}{\pi} P \int_0^{\infty} \frac{\ln r(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (1)$$

where $\hat{R} = R + i\phi$ is the definition of the complex reflectance, and $r = \sqrt{R}$, and ω is the frequency. The KK transform arises from the KK dispersion relations which are direct results of the physical principle of causality. Since the KK dispersion relation is formally correct only when the values of one variable of a conjugate pair are known at all frequencies from $\omega = 0$ to ∞ , we approximate the infinite frequency range by adding analytical extensions, or wings, to the reflectance data to extrapolate these down to 0 eV on the low energy (low frequency) side and typically up to 1000 eV on the high energy (high frequency) side. We use a Fast Fourier

transform (FFT) based program²⁶ running under GRAMS/386²⁷..to perform the KK transform integrals to speed the analysis and increase its accuracy.

FIGURE 2 The dispersion of the index of refraction from spectroscopic ellipsometry. of the two Si₃N₄ samples, 95% Si₃N₄ and 80% Si₃N₄, and the bulk SiYAION glass sample.

Once the real and imaginary parts of one of the optical properties are determined, then calculation of any other optical properties such as the dielectric constant and the interband transition strength²⁸ [$J_{cv} = \frac{\hbar^2 \omega^2}{8\pi^2} i(\epsilon_1(\omega) + i\epsilon_2(\omega))^*$] (Figure 3.) is straight forward using simple algebraic expressions.²⁹

Figure 3. Interband transition Strengths (Re[J_{cv}]) for the two Si₃N₄ samples and the SiYAION Bulk Glass Sample.

Figure 4. SR-VEELS line scan taken in the bulk SiYAION glass sample. The composition of the glass is expected to be spatially uniform. The length of the scan is 2000 angstroms.

Figure 5. SR-VEELS line scan taken in the 95% Si_3N_4 sample across a grain boundary with a thin glass film. The length of the scan is 200 angstroms.

Spatially Resolved - Valence Electron Energy Loss Spectroscopy

SR-VEEL spectra were acquired on the three samples with a Gatan 666 parallel EEL spectroscopy system fitted to a Vacuum Generators HB501 dedicated scanning transmission electron microscope (STEM) operating at 100 keV. The incident beam convergence semi-angle was 10 mrad for all measurements while the collection semi-angle was either 6.5 or 13 mrad. The energy resolution was better than 0.7 eV determined as the full width half maximum of the zero-loss peak. Single spectra were acquired by the GATAN software.³⁰ To detect subtle changes at the interface, we stepped the beam along a line across the interface recording a VEEL spectrum at each pixel. This was made possible by hardware additions to the GATAN Digiscan, a digital beam control, and a newly developed extensive package³¹ implemented within the GATAN software. This method improves the spatial resolution considerably and reduces the effects of instrument instability. Typical data sets contain 200 spectra acquired along a line of 20 nm length. A SR-VEELS line scan acquired on a bulk SiYAION glass sample, which should show no dramatic spatial variation is shown in Figure 4., while a SR-VEELS line scan taken in the 95% Si₃N₄ sample across a grain boundary film is shown in Figure 5.

The analysis of the SR-VEELS line scans, including dark current, gain, single scattering correction and convergence correction were performed using Veels.ab³² The multiple scattering (MS) was removed using a Fourier-log deconvolution³³ technique to arrive at the single scattering energy loss function. This single scattering correction is one of the most critical steps in the quantitative analysis of SR-VEELS spectra and depends crucially on an accurate knowledge of the zero-loss peak. Slight inaccuracies can strongly change the shape of the single scattering corrected spectra near the band gap and thereby cause large changes in the final interband transition strength. Even after correction there always remained a finite band-gap absorption intensity which may be caused in part by errors in the data analysis and corrections, and in part due to energy losses resulting from relativistic retardation effects (Čerenkov and transition radiation). Therefore after the single scattering correction, the spectra were de-tilted by a linear baseline subtraction to remove the intensity arising from these effects. Additional work is ongoing to improve the accuracy of each of these analytical steps. The resulting spectrum was corrected for the incident beam convergence and the finite collection angle at each energy loss with a program based on Egerton's Concor routine³⁴. The spectra resulting from this analysis are the single scattering bulk energy loss functions shown in Figure 6 for the bulk glass and Figure 7 for a line scan across an intergranular film.

Once the single scattering energy loss functions have been determined then another Kramers Kronig integral³⁵, Eqn. 2, can be used to calculate the real part of the energy loss function

$$\text{Re.} \left[\frac{1}{\hat{\epsilon}(E)} \right] = 1 - \frac{2}{\pi} P \int_0^{\infty} \text{Im} \left[\frac{-1}{\hat{\epsilon}(E')} \right] \frac{E' dE'}{E'^2 - E^2} \quad (2)$$

from its imaginary part. The interband transition strengths and their variation with position in the sample can then be calculated, as shown in Figure 8 for the bulk glass and Figure 9 for the 95% Si₃N₄ sample.

Figure 6. Single scattering energy loss function of the SR-VEELS line scan in the bulk SiYAION glass sample. The length of the scan is 2000 angstroms.

Figure 7. Single scattering energy loss function of the SR-VEELS line scan in the 95% Si_3N_4 sample. The length of the scan is 200 angstroms.

Figure 8. Interband transition strength from SR-VEELS line scan in bulk Si_3AlON glass sample. The length of the scan is 2000 angstroms.

Si_3N_4 95% 5M 20nm 0.05 GB D,G,SS,CC,Rescale G1K

Figure 9. Interband transition strength from the SR-VEELS line scan in the 95% Si_3N_4 sample. The length of the scan is 200 angstroms.

Full Spectral Hamaker Constant Calculations

Experimentally acquired VUV and SR-VEEL spectra have been transformed in to the complex optical properties such as the interband transition strength J_{cv} . The next step is to calculate the magnitude of the Hamaker constant³⁶ A , (as defined in Eqn. 3)

$$A = -12\pi L^2 E \quad (3)$$

which is the configuration-dependent scaling coefficient for the van der Waals interaction energy for two materials #1 and #3 separated by an intervening material #2 as shown in Figure 10. Here L is the thickness of the intervening film while E is the van der Waals interaction energy. As reported here Hamaker constants are in units of zepto-joules ($\text{zJ} = 10^{-21}$ Joules).

Figure 10. Configuration of Materials for a A_{123} Hamaker constant where the intervening film is of material #2 and the two adjacent grains are of material #1 and #3. For the simpler case of a A_{121} or A_{1v1} , the two grains are considered to be of the same material #1 and the intervening film is of material #2 or of vacuum (v).

To calculate the Hamaker constant using the full spectral method³⁷ it is necessary to perform another Kramers Kronig-based integral transform so as to produce the London dispersion spectrum of the interband transitions for the two grains and the intervening film. Following Lifshitz³⁸, 1961 Dzyaloshinskii, Lifshitz and Pitaevskii³⁹, Ninham and Parsegian⁴⁰, and Hough and White,⁴¹ we proceed to use the London dispersion transform

$$\varepsilon_2(\xi) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \varepsilon_2(\omega)}{\omega^2 + \xi^2} d\omega \quad (4)$$

to calculate the London dispersion spectrum⁴² $\varepsilon_2(\xi)$, an intrinsic physical property of the material. Once the London dispersion spectra are calculated, then particular values of the Hamaker constants for any configuration can be determined using Eqn. 5 by evaluating the integrals of the functions G (Eqn. 6) which are simple differences of the London dispersion spectra (Eqn. 7).

$$A = \frac{-3\hbar L^2}{\pi} \int_0^\infty \rho d\rho \int_0^\infty \ln G(\xi) d\xi \quad (5)$$

$$G_{121}^{NR}(\xi) = 1 - \Delta_{12}^2 e^{-2a\rho} \quad (6)$$

$$\Delta_{ij} = \frac{\varepsilon_{2,k}(\xi) - \varepsilon_{2,j}(\xi)}{\varepsilon_{2,k}(\xi) + \varepsilon_{2,j}(\xi)} \quad (7)$$

Therefore after the London dispersion spectra $\varepsilon_2(\xi)$ are calculated, they are accumulated in a spectral database⁴³ from which any combinations of them can be used to calculate the Hamaker constants of interest. Hamaker constants for the current case of Si_3N_4 with SiYALON glass are tabulated in Table 1.

Discussion

Recent work has developed the ability to calculate full spectral Hamaker constants from experimental interband transition strengths, while at the same time quantitative analysis of SR-VEELS data can supply the required interband transition strength results. The approach is to use direct SR-VEELS line scans to determine the full spectral Hamaker constants for the locally measured intergranular glass films present in a Si_3N_4 with a SiYAION glass, an effort which requires both experimental and analytical developments.

The results determined for Si_3N_4 and the SiYAION glass from vacuum ultraviolet spectroscopy (Fig. 3) can be used as reference standards for and guidance in our analysis of the SR-VEELS data. The VUV results demonstrate that as the glass content of the Si_3N_4 sample increases, both the reflectivity and the transition strengths decrease, while the volume-averaged index of refraction decreases from 2.0 to 1.78, the value for bulk SiYAION glass. The interband transitions show a sharp peak in the Si_3N_4 samples at about 9 eV which can be associated with the 2-dimensional interband transitions observed in AlN^3 at the same energy.

The analysis of SR-VEELS data is more complex than the analysis of VUV reflectance data since it involves multiple steps, including single scattering deconvolution to remove the zero loss peak and the multiple scattering and the KK analysis to determine the real part of the energy loss function from the measured imaginary energy loss function. Currently, our major focus has been to develop an accurate single scattering correction to supply a quantitative energy loss function as input to the KK analysis.

Egerton⁴⁴ provides a computer program to perform single scattering correction by Fourier log deconvolution based on an assumption of small zero loss peak width using his approximate equation 4.13. If only the broad plasmon peak seen in the valence region were of interest, then the assumption that the width of the zero-loss peak is small compared to the width of single-scattering spectral features may be acceptable, as Egerton shows in his Fig. 4.1. Since our focus here is on features in the interband transitions which appear in the measured energy loss function as the small fluctuations on the low energy side of the plasmon peak, which can be sharper than our 0.7 eV VEELS energy resolution, we have chosen to avoid this small width approximation. The instrument response function is removed using an experimentally measured zero loss peak from the data before doing the multiple-scattering correction, and then the single-scattered result is reconvolved with the instrumental response after Fourier-log deconvolution. This is equivalent to Egerton's "exact" Fourier-log method given by his Eqn. 4.11. This approach does not rely upon assumptions about the shape, symmetry, or asymmetry of the zero loss peak, and the experimental single-to-noise properties of the zero loss peak are considered in the analysis. Still, using an separate zero loss peak to estimate the scattering power can introduce errors since the complex zero loss line shape varies with both microscope and sample parameters. Additional

work is ongoing to develop methods to extract the zero loss peak from the experimental line scan. Apart from these modifications, our Fourier-log deconvolution is similar to that given by Egerton.

The line scans analyzed here represent an over-sampled measurement where the SR-VEELS spectra are acquired at spacings smaller than the probe size. Therefore any dramatic changes between adjacent spectra provide information about the statistical nature, inaccuracy, or instability of the measurement. By transforming 100 spectra in a uniform sample, as done for the bulk glass sample, it is easier to observe the variations in the experimental data and analysis and to separate these from significant changes in the properties of the sample. It is through this kind of analysis, observing the results of the corrections and the KK analysis on the calculated interband transitions while comparing them to the VUV results, which illuminates the necessary data analysis steps. To date the most dramatic errors have arisen from vertical offsets of the spectra, such as tilted baselines or unusual asymptotic behavior of the spectra approaching low or high energies. These vertical offsets can produce strong artifacts because KK analysis is a sensitive spectral shape analysis which can emphasize very small features in a linear response function as it is integral-transformed into its conjugate variable.

Once the single scattering energy loss functions shown in Figures 6 or 7 are calculated then the KK analysis is performed, which requires that the energy loss function (measured in arbitrary counts) must be scaled to the right amplitude. Use of the refractive index (RI) sum rule (Egerton Eqn. 4.29) is a reasonable way to scale the VEELS spectra for known bulk materials, but uncertainty arises for materials such as the grain boundary glass, since its index is unknown. This is another case where SR-VEELS line scans provide an advantage. If we assume that the VEELS scaling is a geometrical correction which is independent of the material's properties, then we can calculate the scaling coefficient for the line scan averaging over the RI sum rule applied to all spectra measured in the Si_3N_4 grains, and then use the same scaling for the spectra going through the grain boundary region. After the analysis, the RI sum rule can be used to calculate the refractive index for the grains and grain boundary phases. If the resulting index of the grain boundary phase is reasonable, we have additional confidence in the analysis. For the grain boundary glass of the 95% Si_3N_4 sample analyzed here the refractive index of the intergranular film determined using the RI sum rule is 1.61, while the refractive index determined in the full spectral Hamaker constant analysis of this material is 1.56, demonstrating consistency in the analysis of this data.

If the interband transitions of the 95% Si_3N_4 determined from VUV and SR-VEELS data are compared as shown in Figure 11, it is apparent that the amplitude of the transition strengths quantitatively agree, with peak values of about 12. There are variations among the values measured inside the Si_3N_4 grains which arise due to experimental and analytical uncertainties in the data, as shown by the two different VEELS results shown in the figure. These lead to changes in the band gap and the energy of the major observed peak. Figure 12 shows that there

are larger discrepancies observed for the VUV and SR-VEELS results for the bulk SiYAION glass, where both the amplitudes of the transition strengths and the features differ to some degree. This again can be attributed to the presence of vertical offsets and baselines present in the experimental data, and more development of the analytical techniques to remove them is needed. These artifacts lead to variability in the calculated values of the interband transitions and are also seen in the full spectral Hamaker constants shown in Table I.

Figure 11. Interband transition strengths for the 95% Si₃N₄ sample from VUV and SR-VEEL spectroscopy. The two SR-VEELS results show the variations arising due to analytical uncertainties.

Figure 12. Interband transition strengths for the SiYAION glass from VUV and SR-VEEL spectroscopy. The bulk glass measurements are from the same sample while the grain boundary glass result is from the 95% Si₃N₄ sample.

With the interband transition strengths determined, the London dispersion spectra and full spectral Hamaker constants are calculated. In Table I the relevant Hamaker constants calculated from VUV and SR-VEELS results are tabulated. The A_{IV1} Hamaker constant for Si₃N₄ increases from 163.8 to 174.3 zJ as the glass content of the sample used for the VUV measurement decreases. This is consistent with the A_{IV1} value determined from direct localized SR-VEELS measurement in a Si₃N₄ grain of 190 zJ. With an intervening film present, the Hamaker constant decreases. For SiYAION glass of the bulk composition, the Hamaker constant decreases to 8.35 zJ. Hamaker constants for arbitrary configurations of grains and films can be calculated once the London dispersion spectra have been entered into a spectral database. For intervening film of PbAlSiO glass,⁴⁵ for example, the Hamaker constant increases to 20.7 zJ. It is interesting to note that for Si₃N₄ the Hamaker constant remains nearly unchanged with intervening films of either undoped SiO₂ or silicon, with values 33.3 and 29.4 zJ respectively, even though the indices of these two materials are considerably different. This demonstrates that Hamaker constants estimated from simple refractive index relations, such as the Tabor-Winterton Approximation, can be misleading.

Full spectral Hamaker constants calculated from SR-VEELS results are comparable to the VUV values for the 95% Si₃N₄ with vacuum or the bulk composition SiYAION glass as the intervening film. The close agreement of these results demonstrates the feasibility of effort

presented here. Variability in the interband transition strengths determined for the Si_3N_4 and the SiYAION samples, arising from the analytical issues discussed above, lead to variations in the calculated full spectral Hamaker constants. An effort to quantify this variability arising from spectroscopic issues is included in Table II where two different spectra from the two Si_3N_4 grains shown in Figures 5, 7 and 9 are used in the Hamaker constant calculations. The value of A_{1v1} varies from 190 to 209 zJ. If two different spectra are chosen from the uniform bulk SiYAION glass spectra shown in Figures 4,6 and 8, the value of A_{121} can vary from 4.3 to 15.5 zJ. For the spectrum centered in the intergranular film from the 95% Si_3N_4 sample, full spectral Hamaker constants of 22.5 and 31.4 zJ are calculated. If we choose the analyzed SR-VEELS spectra which are most consistent with the VUV results, we arrive at Result 1 for Si_3N_4 and Result A for SiYAION as most representative and use these calculated Hamaker constants as the most reasonable values for inclusion in Table I. Improved analytical methods currently being developed should decrease these uncertainties.

TABLE I. A_{121} Full Spectral Hamaker Constants for Si_3N_4 Intergranular Glass Films				
Glass Film Composition	A_{121} (zJ) [VUV]	A_{121} (zJ) [SR-VEEL]	Index of Grain	Index of Film
Bulk SiYAION		4.3***	2.	1.83
Bulk SiYAION	8.35*		2.02	1.78
PbAlSiO	20.7*		2.02	1.62
Grain Boundary SiYAION		22.5***		1.56
Silicon	29.4*		2.02	3.44
SiO_2	33.3*		2.02	1.5
Vacuum	163.8**		2.0	1
Vacuum	174.3*		2.02	1
Vacuum		190.2***	2.	1

*For a 95% Si_3N_4 bulk sample as the grain. **For an 80% Si_3N_4 bulk sample as the grain. ***Using a spatially resolved measurement of a single grain in 95% Si_3N_4 sample.

Table II. Variation of A_{121} Full Spectral Hamaker Constants From SR-VEELS Due to Spectral Differences (zJ)				
Material 2	Vacuum (n=1)	SiYAION Bulk Glass Result A (n=1.83)	SiYAION Bulk Glass Result B (n=1.72)	SiYAION Grain Boundary Glass (n=1.56)
Material 1				
95% Si_3N_4 Result 1 (n= 2.0)	190.2	4.28	9.43	22.5
95% Si_3N_4 Result 2 (n=2.11)	209.0	8.56	15.5	31.4

Having discussed full spectral Hamaker constants determined from bulk uniform samples measured using both the volume-averaging VUV method and the spatially resolved VEELS

method, it is interesting to consider Hamaker constants determined for the spectra measured in situ from a thin intergranular glass film. Using the VEELS spectrum from the 95% Si_3N_4 sample line scan from the center of the film (and therefore exhibiting the greatest differences from the adjacent grains), we arrive at a full spectral Hamaker constant of 22.5 zJ for the in-situ SiYAION film in this grain boundary. Note in Table II that the spread in the values of A_{121} for the bulk SiYAION glass and the grain boundary glass film do not overlap, with the highest bulk value being 15 and the lowest value for a glass of the grain boundary composition being 22.5. There is a statistically significant difference between the Hamaker constant determined for the in situ film, and the bulk equilibrium glass composition. If we consider that the Hamaker constant of Si_3N_4 with an intervening film of undoped SiO_2 is 33.3, then the increased value of the Hamaker constant of the glass in this intergranular glass film is consistent with the glass being more oxidic (or less nitridic) than the composition of the bulk SiYAION glass studied here. Variability in the values of the Hamaker constants are due to experimental and analytical uncertainties, and represent results from one grain boundary film. Nevertheless the techniques developed in this paper are very promising and represent a powerful new tool to apply to intergranular glass film problems.

Conclusions

Interband transition strengths and full spectral Hamaker constants for Si_3N_4 samples containing a SiYAION glass have been determined using SR-VEELS from grains and grain boundaries and compared with results from bulk VUV spectroscopy on separate samples of glass and nitride. The EELS method permits the determination of vdW forces based upon actual local compositions and structure, which may differ noticeably from bulk standards. The A_{121} Hamaker constant for Si_3N_4 with glass of the bulk composition is 8 zJ from the more established optical method, and lies in the range of 4 to 9 zJ from current SR-VEELS results. These results show that full spectral Hamaker constants determined from VUV and SR-VEEL measurements of uniform bulk samples agree, but care must be taken in the single scattering deconvolution and zero loss subtraction, and more work is ongoing in this area. For these polycrystalline Si_3N_4 samples, the grain boundary glass composition is found to be of lower index of refraction, which is consistent with an increased oxygen content in the intergranular glass, and this leads to an increased value of the full spectral Hamaker constant (24 zJ) determined in situ from the SR-VEELS of the grain boundary film.

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