

**Photothermal AFM-IR Analysis of High Extinction Coefficient Materials:
A Case Study with Silica and Silicate Glasses**

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Abstract

Photothermal atomic force microscopy coupled with infrared spectroscopy (AFM-IR) brings significant value as a spatially-resolved surface analysis technique for disordered oxide materials such as glasses, but additional development and fundamental understanding of governing principles is needed to interpret AFM-IR spectra since the existing theory described for organic materials does not work for materials with high extinction coefficients for IR absorption. This paper describes theoretical calculation of a transient temperature profile inside the IR-absorbing material considering IR refraction at the interface as well as IR adsorption and heat transfer inside the sample. This calculation explains differences in peak positions and amplitudes of AFM-IR spectra from those of specular reflectance and extinction coefficient spectra. It also addresses the information depth of the AFM-IR characterization of bulk materials. AFM-IR applied to silica and silicate glass surfaces has demonstrated novel capability of characterizing sub-surface structural changes and surface heterogeneity due to mechanical stresses from physical contacts as well as chemical alterations manifested in surface layers through aqueous corrosion.

1. Introduction

The development of atomic force microscopy coupled with infrared spectroscopy (AFM-IR) based on the photothermal detection principle was a breakthrough in IR spectroscopic imaging with nanoscale image resolution, which is far beyond the conventional diffraction limit of the IR wavelength.¹ It is a hybrid technique that correlates the IR absorption by the sample with the local height change (Δh) detected with an AFM probe upon thermal expansion of the sample.²⁻⁴ The photothermal AFM-IR is known as a versatile spectroscopic imaging technique that can be applied to a wide range of materials.⁵⁻¹¹ One common aspect of literature examples in which this technique was demonstrated successfully is that the extinction coefficient of sample, which is the imaginary part (k) of the complex refractive index ($n + ik$), is relatively small and they are often deposited as a thin film on a substrate that does not absorb IR radiation.

In the photothermal AFM-IR theory derived by Dazzi et al.³, the absorbed IR power (P_{abs}) is described as:

$$P_{abs}(\lambda) = \frac{2\pi}{\lambda} c \epsilon_0 \frac{9 k(\lambda) n(\lambda)}{(n(\lambda)^2 + 2)^2} |E_{inc}|^2 V \quad (1)$$

where λ is the wavelength of IR light, c is the speed of light, ϵ_0 is the vacuum permittivity, $n(\lambda)$ and $k(\lambda)$ are the real and imaginary parts of complex refractive index at λ , respectively, E_{inc} is the electric field of the incident IR, and V is the sample volume within which absorption takes place. For most organics which have relatively small $k(\lambda)$ compared to $n(\lambda)$, $n(\lambda)$ does not vary drastically over the absorption band. Then, after normalization with the input IR power, $P_{abs}(\lambda)$ can be approximated to be proportional to $k(\lambda)$:³

$$P_{abs}(\lambda) \propto \frac{n k(\lambda)}{\lambda(n^2 + 2)^2} \quad (2)$$

Through mathematical derivations solving the Fourier heat equation with the thermal diffusivity (α) and thermal conductivity (κ) of the sample and multiplying the temperature change with the coefficient of thermal expansion (CTE), Dazzi et al. have shown that $\Delta h(\lambda)$ is proportional to $k(\lambda)$.³ For such systems, AFM-IR generates a spectrum that closely resembles the transmission absorption spectrum of the sample.¹²

This theory, however, cannot be applied to AFM-IR analysis of strongly IR absorbing modes of high- k materials such as oxide glasses. Due to the Kramers-Kronig relationship, $n(\lambda)$ also varies drastically in the strong absorption band region. As an example, Figure 1 compares the

complex refractive index, $n(\lambda)$ and $k(\lambda)$,¹³ and AFM-IR spectrum of fused quartz as well as $P_{abs}(\lambda)$ calculated from eq. (2). For comparison, the specular reflectance infrared (SR-IR) spectrum is also plotted. Although all spectra embody the vibrational responses of the same material upon absorption of the same IR, there are stark differences among the spectra. Neither the AFM-IR spectrum nor the $P_{abs}(\lambda)$ plot resembles the $k(\lambda)$ spectrum. Since the existing model fails to predict the AFM-IR spectra of highly absorbing materials, interpretations of AFM-IR spectral feature require more rigorous theoretical processing.

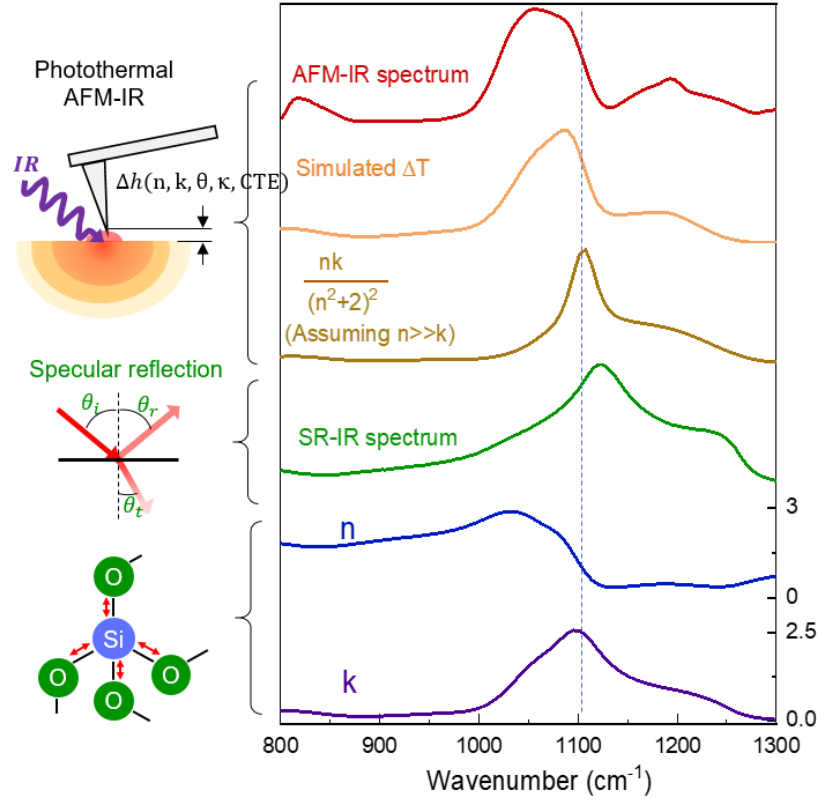


Figure 1. Comparison of complex refractive index (n, k),¹³ SR-IR and AFM-IR spectra of fused quartz. The spectrum predicted using eq.(2) derived by Dazzi et al.³ and the temperature change (ΔT) calculated in this work are also shown for comparison. Details of the SR-IR and AFM-IR data collection and the ΔT calculation are described in Sections 2.2 and 2.3, respectively.

Moreover, Eq.(1) is based on the electric dipole approximation in which the sample size is assumed to be much smaller than the IR wavelength.³ Thus, the previous theory cannot address the probe depth question of AFM-IR. Since $k(\lambda)$ of the vibrational modes of oxide glasses are large, the penetration or attenuation depth of IR inside the sample also varies substantially. This

affects the probe depth at a given λ . Moreover, the AFM-IR signal intensity, $\Delta h(\lambda)$, arises as a convoluted outcome of multiple parameters including complex refractive index of the sample, the IR incident angle, IR attenuation in the sample,¹⁴ as well as the thermal properties of the sample (α , κ , and CTE). The convoluted spectral features make the vibrational bands in AFM-IR spectra distinctly different from those of reflective and transmission IR spectra, as highlighted in Figure 1. This paper addresses the convoluted effects of these parameters in AFM-IR analysis of the network vibrations of various types of silicate glasses. Applications of AFM-IR characterization to spectroscopic analysis of glass surfaces subjected to mechanical indentation,¹⁵ frictional wear,¹⁶ and aqueous corrosion¹⁷⁻¹⁸ are also discussed.

2. Experimental Details and Theoretical Calculation

2.1 2.1 AFM-IR and SR-IR experiments

Commercially available silica (fused quartz), silicate (soda lime silicate, SLS), borosilicate (Schott Zerodur[®]), boroaluminosilicate (Corning[®] Eagle XG[®] and international simple glass, ISG¹⁹) glasses were used. Nano-indentation and scratch marks on fused quartz and aqueous corrosion layer on ISG²⁰ were analyzed with AFM-IR. Polystyrene films deposited on fused quartz and silicon wafer were also analyzed for comparison. AFM-IR analysis was performed with a NanoIR3 system (Bruker) using a gold-coated silicon nitride probe (0.07-0.4 N m⁻¹ spring constant, 13 $\pm$ 4 kHz resonant frequency, Bruker) in a contact scan mode. SR-IR spectra of glasses were measured by using a Bruker Vertex 80 FTIR spectrometer combined with a Hyperion 3000 FTIR microscope. Details of sample preparations as well as measurements conditions are in the Supporting Information (SI).

2.2 Theoretical calculation of local temperature rise under AFM-IR condition

There are several modes of operating AFM-IR to detect the small $\Delta h(\lambda)$ responses of the sample.⁴ All modes are based on the local height change caused by oscillatory temperature fluctuation (ΔT), which can be modeled as a series of the ΔT profile by each IR laser pulse arriving at a set repetition rate. Once the ΔT profile of a single pulse is obtained, $\Delta h(\lambda)$ can be approximated by multiplying CTE to the average temperature change per pulse.¹² Figure 2 describes the experimental geometry of AFM-IR and the axisymmetric model used for theoretical ΔT calculation.

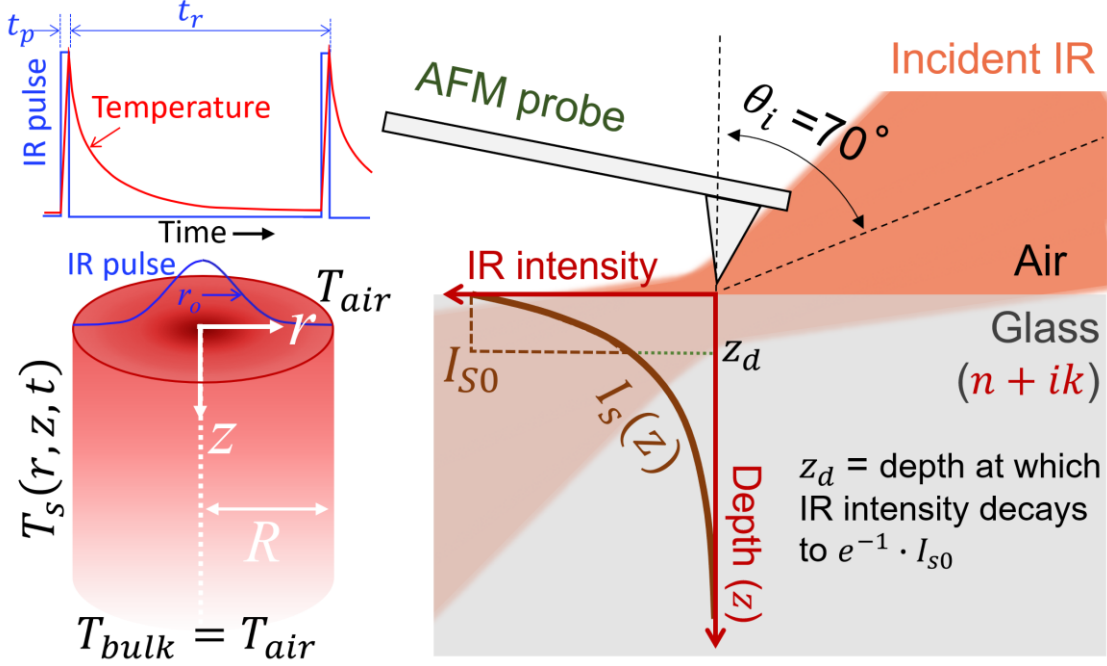


Figure 2. Schematic of AFM-IR experiment. The narrow-band IR pulse with a temporal pulse width t_p and a repetition time t_r is focused from the side of the AFM probe with an elliptical reflection mirror. The incidence angle (θ_i) defined by the center axis of the focused beam and the surface normal direction is 70° . Since most IR power delivered to the sample is confined within the area that is defined by three times the Gaussian beam radius (r_o), we consider a cylinder with a radius $R = 3r_o$. In our experimental setup, $r_o \approx 50 \mu\text{m}$. The model assumes that the temperature profile decays to the bulk temperature at the boundary of the cylinder.

First, the fraction of the irradiated IR going into the sample is estimated to be $(1 - R_i)$, where R_i is the reflectance of IR at the air / sample interface at the experimental incidence angle ($\theta_i = 70^\circ$) which can be calculated with the Fresnel coefficient equations and the complex refractive index of the sample ($n + ik$).²¹ The IR beam propagating inside the sample is attenuated due to absorption. The characteristic attenuation length (z_d), at which the electric field of IR decreases to 36.7% (e^{-1}) of its original magnitude, is calculated using the extinction coefficient (Figure S1a). Assuming the absorbed IR energy to be the heat source, the rate of thermal energy generation per unit volume of the sample can be written as:

$$s(r, z, t) = s_{\max} e^{\left[-\frac{z}{z_d} - \left(\frac{r}{r_o}\right)^2\right]} \delta(t) ; s_{\max} = \frac{E_{\text{input}}(1 - R_i)}{\pi r_o^2 z_d} \quad (3)$$

where E_{input} is the energy of each IR pulse, which is the input power (W) times the pulse repetition time (t_r), and the irradiated volume of the sample is approximated as $\pi r_o^2 z_d$. Note that R_i and z_d

are functions of λ (Figure S1a). Using the characteristic scale R for length, R^2/α for time, and $R^2 s_{max}/\kappa$ for temperature difference (where α and κ are the thermal diffusivity and conductivity of the sample, respectively), the dimensionless equations governing the temperature distribution in the semi-infinite cylinder of radius R (bounded by a plane at $z = 0$) are given by:

$$\frac{\partial \theta}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \theta}{\partial r} + \frac{\partial^2 \theta}{\partial z^2} + S(r, z, t) \quad (4)$$

$$\theta(1, z, t) = 0 ; \quad \left. \frac{\partial \theta}{\partial z} \right|_{z=0} = Bi \theta(r, 0, t) ; \quad \left. \frac{\partial \theta}{\partial z} \right|_{z \rightarrow \infty} = 0 ; \quad \theta(r, z, 0) = 0 \quad (5)$$

where $\theta = \kappa(T_S - T_{air})/R^2 s_{max}$ is the dimensionless temperature, all independent variables are dimensionless, $S = s(r^*, z^*, t^*)/s_{max}$, and $Bi = h_c R/\kappa$ is the Biot number (with h_c denoting the convective heat transfer coefficient).

In this calculation, α and κ of silica will be used, which are $8.3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and $1.4 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. The incident IR beam is assumed p -polarized for calculation of R_i in Eq. (3). Since the length scale of the system under consideration ($R=150 \text{ }\mu\text{m}$) is small, Bi is on the order of 10^{-3} for a typical value of $h_c = 10 \text{ W m}^{-2} \text{ K}^{-1}$ in air. In addition, the laser pulse duration ($t_p = 100 \text{ ns}$) is much shorter than the thermal diffusion time in the system ($R^2/\alpha \approx 100 \text{ ms}$). Thus, the location of the maximum temperature at the end of each pulse must be at the sample surface. This surface temperature (T_{S0}) can be estimated by neglecting thermal diffusion in Eq. (2) and integrating over a laser pulse duration to yield:

$$T_{S0} = T_{air} + \left[\frac{E_{input}(1-R_i)\alpha}{\pi r_0^2 z_d \kappa} \right] e^{-9r^2} \quad (6)$$

These equations are solved to calculate the spatial and temporal temperature profiles inside the sample after heating by the IR pulse (see SI). For extremely small Biot numbers (i.e., convective heat loss to air is negligible compared to heat conduction to the bulk), the temperature distribution within the sample (eq. S8-S10 in SI) can be expressed as:

$$\theta(r, z, t) = e^{t/z_d^2} \left[e^{\frac{z}{z_d}} \text{erfc} \left(\frac{\sqrt{t}}{z_d} + \frac{z}{2\sqrt{t}} \right) + e^{\frac{-z}{z_d}} \text{erfc} \left(\frac{\sqrt{t}}{z_d} - \frac{z}{2\sqrt{t}} \right) \right] \sum_{n=0}^{\infty} \frac{f(\beta_n)}{J_1^2(\beta_n)} J_0(\beta_n r) e^{-\beta_n^2 t} \quad (7)$$

3. Results and Discussion

3.1 Temperature profile calculated for irradiation with a single IR pulse

Figures 3a and 3b displays the temperature profiles inside the fused quartz sample irradiated with a 1100 cm^{-1} IR beam with a 2 mW power and a 100 ns pulse width. For comparison,

we also calculated the temperature profiles inside a polystyrene sample irradiated with a 1452 cm^{-1} IR beam with the same power and pulse width, which are shown in Figures S2. At the end of the IR pulse, the surface temperature at the center of the Gaussian beam, $T_S(r = 0, z = 0, t = t_p)$, increases by $\sim 6 \text{ K}$ for the fused quartz surface (Figure 3a). In the polystyrene case, the temperature rise is calculated to $\sim 0.4 \text{ K}$ (Figure S2a). The system temperature exponentially decays and becomes close to the ambient temperature at a depth of $\sim 3 \times z_d$.

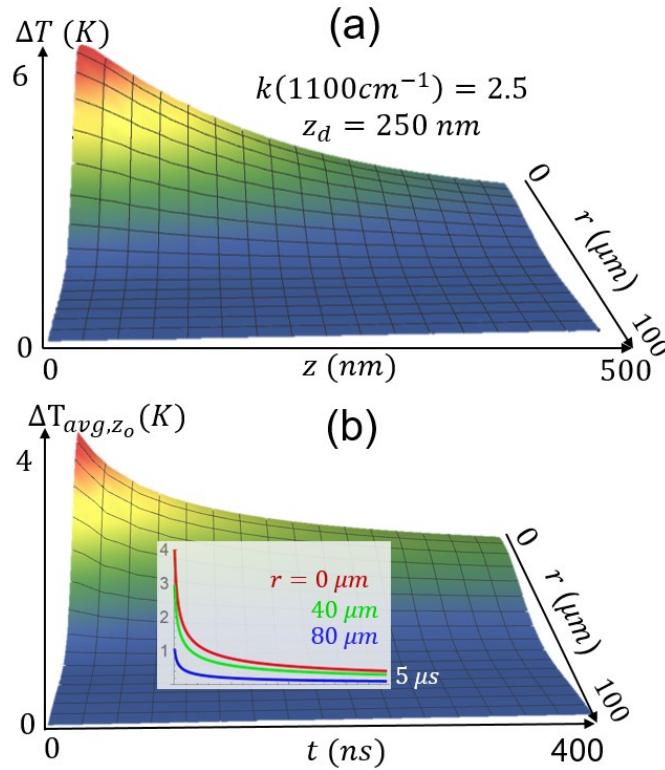


Figure 3. (a) Radial and depth distribution of temperature inside the fused quartz irradiated with a 1100 cm^{-1} pulse (2 mW) for $t_p = 100 \text{ ns}$ and (b) temporal decay of temperature inside the fused quartz (averaged over z_d). The inset plots the temperature decay over the repetition time at three locations from the center of the beam. The calculation results of a polystyrene sample are also shown in Figure S2 for comparison.

Figures 3b plots the average temperature rise over z_d , $\Delta T_{avg}(r, t) = \frac{1}{z_d} \int_0^{z_d} T_S(r, z, t) dz$, for the first 400 ns; the insets show the ΔT_{avg} change over the entire duration of the repetition time between laser pulses ($t_r = 5 \mu\text{s}$ at a 200 kHz repetition). The temperature of fused quartz decreases fast after the pulse because the temperature gradient is large; but it does not decrease completely

to the initial temperature before the next pulse comes. This means that the temperature of the irradiated region will gradually increase to a steady state value that will be determined by heat loss to the surrounding area beyond the boundary of the cylinder considered in this calculation (Figure 2). In AFM-IR experiment, the oscillatory height change matching with the repetition rate is detected with a lock-in-amplifier.

3.2 Comparison of AFM-IR spectra and calculated temperature profile of fused quartz

Figure 4 compares the experimental AFM-IR spectra of fused quartz collected at various locations within the irradiated area and the average temperature change over z_d by a single IR pulse, $\Delta T_{avg}(r, t_p)$, at the center, r_o , and $2r_o$ of the Gaussian beam profile. The agreement between the shape and relative intensity of the AFM-IR spectra and the $\Delta T_{avg}(r, t_p)$ profiles are quite reasonable. This supports the main thesis of AFM-IR that the height change detected by AFM is due to thermal expansion caused by local temperature change inside the sample upon IR absorption.

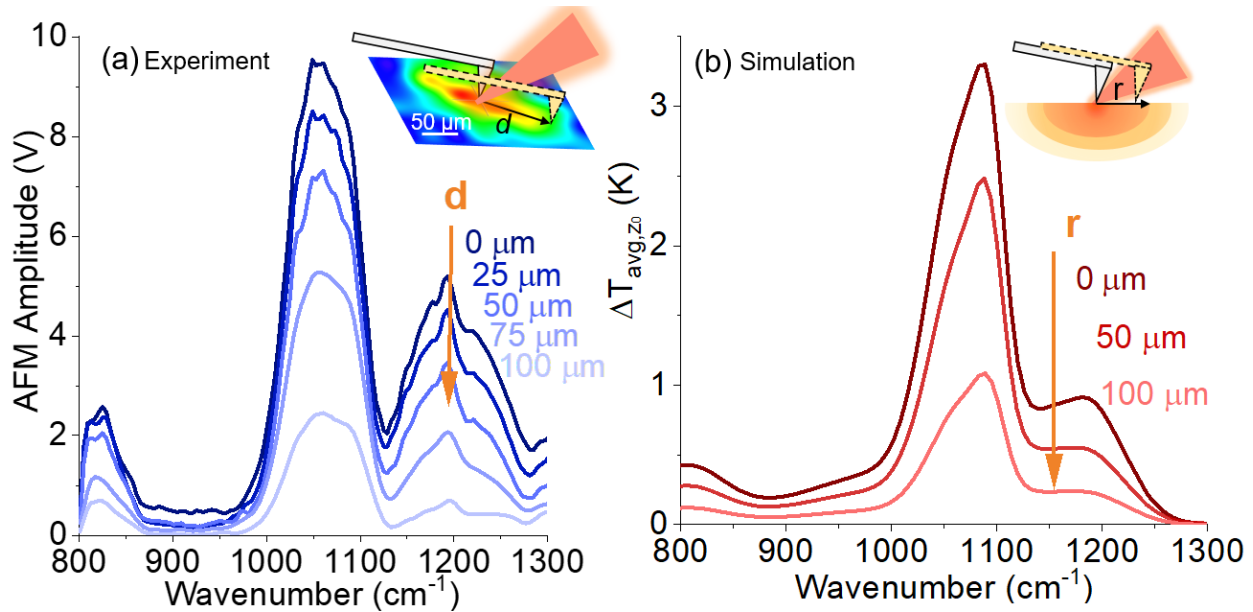


Figure 4. (a) AFM-IR spectra of fused quartz collected at locations with varying distances from the laser focal point. The inset image with a color scale shows the AFM-IR amplitude change over a 200 $\mu\text{m} \times 200 \mu\text{m}$ area. The AFM probe is displaced by the distance shown in the figure (d) along the IR irradiation direction. (b) Local average temperature, $\Delta T_{avg}(r, t_p)$, inside fused quartz as a function of IR wavenumber at $r = 0$ nm, 50 μm , and 100 μm at a 70° incidence angle. The IR pulse power in the calculation is 2 mW, which is the average power of IR laser pulses also used in the experiment. The calculation results for 50° and 60° incidence angles are shown in Figure S1b.

There are some discrepancies between the experimental AFM-IR spectra and the theoretical ΔT_{avg} spectra. In Section 2.3, the absorbed IR energy is assumed to heat the sample with a constant efficiency, regardless of vibrational modes. This might be an oversimplification. The different vibrational modes of amorphous silica network may have different contributions to thermal conductivity of the sample.²²⁻²³ So, the temperature increase per absorbed IR energy may vary depending on how the excited vibrational mode dissipates the absorbed photon energy to the surrounding. Also, the calculation is done for a constant θ_i which is set to 70° (based on the specification of the instrument provided by Bruker). But in experiment, the IR incidence angle varies over a broad range because the beam is focused from a large elliptical reflection mirror (Figure 2). As the incidence angle decreases, the transmittance ($1 - R_i$) near the 1200 cm^{-1} region increases significantly, while that near the 1100 cm^{-1} main band remains relatively constant (Figure S1a). Thus, the smaller incidence angle portion of the beam will greatly enhance the AFM-IR signal intensity around 1200 cm^{-1} (see the example for $\theta_i = 50^\circ, 60^\circ$, and 70° in Figure S1b). Also, any reflection of the IR beam by the gold-coated cantilever will be near surface normal direction and thus amplify this incidence angle effect. The features near 820 and 1200 cm^{-1} in Figure 4 (a) look larger as compared to the same bands in Figure 4 (b). It might be possible that the 1060 cm^{-1} main band in AFM-IR is nearly saturated because the optical attenuation depth is smaller than the thermal diffusion length.

3.3 AFM-IR spectra of multicomponent silicate glasses

Figure 5a compares the AFM-IR spectra, SR-IR spectra, and extinction coefficient $k(\lambda)$ of various multicomponent silicate glasses as well as fused quartz (type-I silica).²⁴ The vibrational bands around $1050 - 1100\text{ cm}^{-1}$ in the $k(\lambda)$ spectra of silica and silicate glasses are attributed to the asymmetric stretch of Si-O bonds in the network.²⁵⁻²⁶ In the SR-IR spectra, the Si-O stretch band appears slightly blue-shifted compared to the $k(\lambda)$ spectra. This is because $n(\lambda)$ is smaller in the higher wavenumber side of the absorption band (Figure 1), so that the reflectance (R_i) is enhanced in that region.^{25, 27} In the AFM-IR amplitude spectra, however, the main Si-O stretch band is slightly red-shifted as compared to the $k(\lambda)$ spectra. This could be attributed to the fact that the transmittance ($1 - R_i$) is enhanced in the lower wavenumber side of the absorption band (Figure S1a).

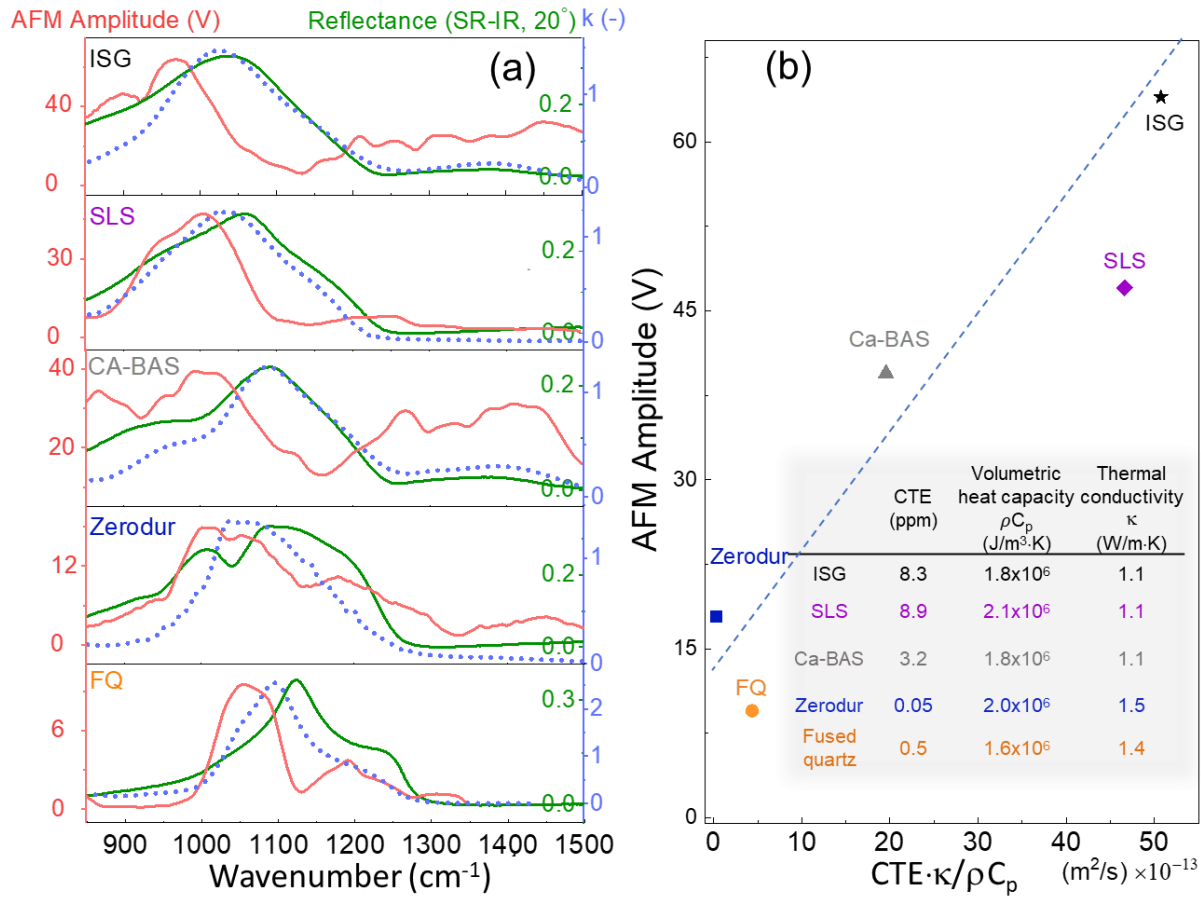


Figure 5. (a) AFM-IR amplitude spectra (red; left scale), SR-IR spectra (green; right inside scale), and extinction coefficient (blue dots; right outside scale) of ISG, SLS, Ca-BAS, Zerodur[®], and fused quartz. (b) Comparison of the $\text{CTE}/(\rho C_p \cdot \kappa)$ magnitude and the AFM-IR amplitude of the glass studied.

In the case of borosilicate and boroaluminosilicate glasses, the weak bands around 1400 cm^{-1} in the $k(\lambda)$ spectra are ascribed to the B-O stretch of the three-coordinated BO_3 unit in the glass.²⁸⁻²⁹ The four-coordinated boron species are expected to appear as a weak band around $\sim 900 \text{ cm}^{-1}$,³⁰⁻³² which often overlaps with the Si-O stretch mode involving nonbridging oxygen groups.²⁵ The intensities of these bands in the SR-IR spectra of ISG and Ca-BAS, which do not have nonbridging Si-O bonds, are significantly larger than those in the $k(\lambda)$ spectra. At this moment, there is no good theoretical explanation for this observation; the only speculative explanation for this discrepancy could be the possibility that the conversion of the absorbed photon energy to heat might be more efficient for the B-O stretch mode than the Si-O stretch mode.²²⁻²³

In the spectral scanning mode of AFM-IR, the wavenumber of the irradiated IR pulse is changed stepwise while monitoring the height change at the AFM contact resonance frequency to which the IR pulse repetition rate is tuned. If the IR-induced thermal expansion of the sample is instantaneous and fully reversible (i.e., the response is fully elastic), then there would be no loss component in detection of the thermal expansion of the sample, and the phase difference between the thermal excitation (IR pulse) and the detected signal (AFM-IR amplitude) would be constant. However, the AFM-IR phase signal (Figure S3) varies as the IR wavenumber is scanned. There are many processes involved in detection of $\Delta h(\lambda)$. To name a few, they include the thermal dissipation of the absorbed IR photon energy, heat loss to the surrounding volume, propagation and accumulation of thermal expansion from the subsurface region to the surface, dynamic coupling of the surface height change to the lock-in detection of AFM, and so on.^{12, 33-35} Unless all these parameters are known, it would be difficult to quantitatively interpret the phase signal of AFM-IR. In the case of Zerodur, the phase change is quite large over a very broad spectral range (Figure S3). Note that Zerodur is not a pure glass with a homogenous structure; it is a glass ceramic containing crystalline ceramic particles (~50 nm in diameter) with negative CTE dispersed in glass with positive CTE.³⁶ Maybe, this heterogeneity introduces additional loss processes in heat dissipation and thermal expansion, creating a large phase shift.

Even though all dynamic details cannot be fully captured, comparing the AFM-IR amplitude with thermal properties could provide a rule-of-thumb that might be useful for comparison of signal intensities of different materials. For the same amount of energy taken up by the material through IR absorption, the instantaneous or adiabatic temperature rise (during t_p) will be determined by the volumetric heat capacity, which is the product of density and specific heat capacity (ρC_p). During the repetition period (t_r), heat loss to the surrounding will occur. The faster heat loss is (i.e., larger κ), the larger the change will be in the temperature profile during the heat dissipation between pulses. Under the elastic response assumption, the height change for a given temperature change will be proportional to CTE. Thus, the amplitude of the cantilever deflection signal will be large when the material CTE is large, heat dissipation is rapid (large κ), and the heat capacity is small. In Figure 5b, the AFM-IR amplitudes of the glasses analyzed in this study are compared with the magnitude of $\text{CTE} \cdot \kappa / \rho C_p$ as a figure of merit combining these thermal attributes.^{24, 37-41} This plot shows that the maximum AFM-IR signal intensity scales roughly with

thermal properties of the sample. Note that this comparison does not include the optical term, $(1 - R_i)$, which is a function of $n(\lambda)$, $k(\lambda)$, and θ_i .

3.4 Effective probe depth of AFM-IR analysis

Unlike other AFM-based vibrational spectroscopic imaging techniques such as tip-enhanced Raman spectroscopy (TERS) and nano-IR with scattering scanning near-field optical microscopy (s-SNOM) that detect only tens of nm deep from the surface,⁴²⁻⁴³ the information depth of AFM-IR is much deeper.⁴⁴⁻⁴⁷ Based on our temperature profile calculation, the heated zone is in the range of tens of microns for organics (Figure S2a); so, any discrimination of the signal from the deeper region must originate from convolution of the thermal expansion of the entire heated zone and its subsequent detection by the AFM cantilever.^{4, 33, 48} In the case of network vibrations of glassy materials, the extinction coefficient in the absorbing region is quite high so that the heated zone is confined very close to the surface—especially at the IR wavelength close to the maximum absorption peak (Figure 3a). For a homogeneous solid (like glass) with high elastic modulus, the entire heated region will contribute to the topographic height change at the surface $\Delta h(\lambda)$. Based on this argument, the effective probe depth (or information depth) is expected to extend to two or three times of z_d . In the case of fused quartz, z_d varies from ~ 250 nm at 1100 cm^{-1} to $5\text{ }\mu\text{m}$ at 890 cm^{-1} (see Figure S1a).

For a layered system, the AFM-IR signal would be the convolution of all contributions from individual layers within the effective probe depth. Figure 6a displays AFM-IR spectra of polystyrene-coated fused quartz surfaces, as well as those of pristine fused quartz and a thick polystyrene film ($\sim 60\text{ }\mu\text{m}$ on a gold surface). Since polystyrene is a weak IR absorber, its AFM-IR spectrum is similar to the $k(\lambda)$ spectrum (Figure S4). The polystyrene-coated fused quartz spectra could be fitted by least squares regression using a linear combination of fused quartz and polystyrene spectra. As shown in Figure 6b, the contribution of the polystyrene film to the overall spectrum increases in proportion to the film thickness. Notably, however, the fitted contribution from the fused quartz (substrate) is relatively constant. Another experiment was conducted with the polystyrene thin films on a silicon wafer and the same trend was observed (Figure S5). These results confirm that the AFM-IR signal is the sum of thermal expansion of all subsurface components within the IR attenuation depth.

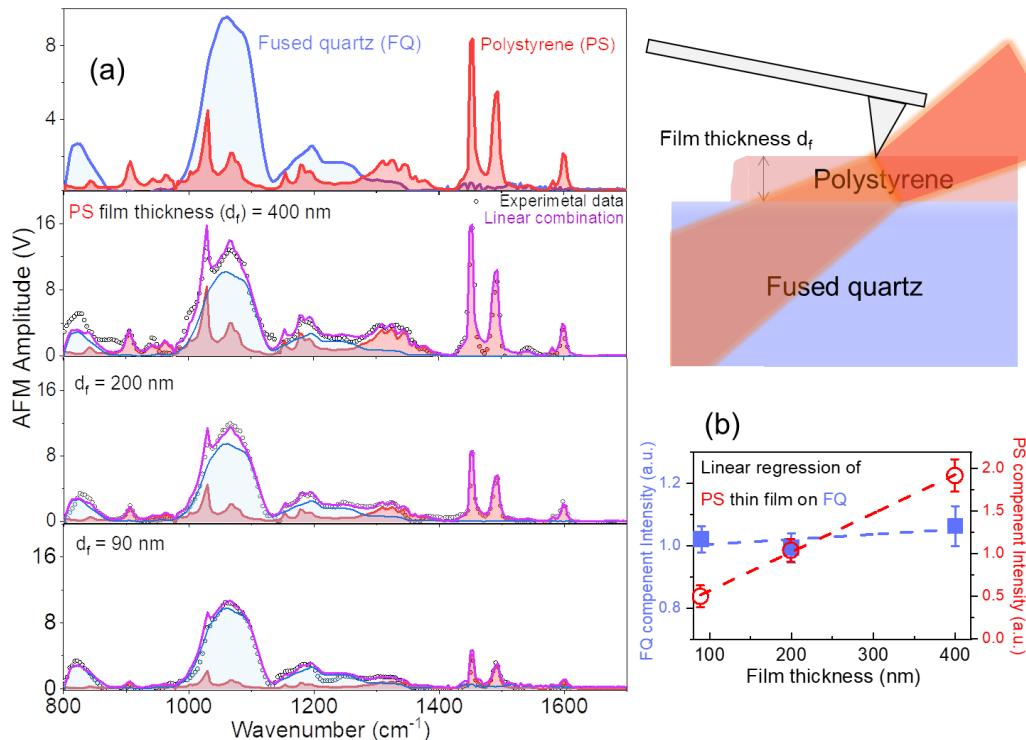


Figure 6. (a) AFM-IR spectra of pristine fused quartz (blue) and thick polystyrene film (red) and those of fused quartz surfaces coated with thin films of polystyrene with a thickness (d_f) of 90 nm, 200 nm, and 400 nm (open circles). In the panels of the 90 nm, 200 nm, and 400 nm thick polystyrene-coated fused quartz, the fit result from multi-component linear regression (pink) as well as the fused quartz (blue) and polystyrene film (red) components are also shown. (b) Least-squared linear regression result of the AFM-IR spectra of polystyrene-coated fused quartz. The thickness dependence of the polystyrene contribution is statistically significant ($p < 0.009$), while the changes in the fused quartz contribution is statistically insignificant ($p > 0.18$).

3.5 AFM-IR characterization of glass surface heterogeneity

Inhomogeneity of the glass surface and subsurface structure may have a huge impact on the chemical and mechanical durability of glass.⁴⁹⁻⁵² Therefore, it is important to characterize such defects with a high spatial resolution in both lateral and depth dimensions. AFM-IR provides a unique opportunity to perform vibrational spectroscopic analysis with excellent lateral resolution; the depth resolution would be determined by the optical and thermal properties of the material as well as the detection mode.^{35, 44, 53} Here, we present two examples from which the surface sensitivity and lateral resolution of AFM-IR can be gauged qualitatively.

Figure 7a shows the topographic image and line profile of a nanoindentation mark on a fused quartz surface made with a Berkovich tip, along with the AFM-IR amplitude spectra

acquired both inside and outside of the indentation mark. It is well known that fused quartz undergoes densification upon indentation.⁵⁴⁻⁵⁶ Previous studies have shown that subsurface densification induces elongation of the bridging Si-O bond length distribution, which manifests as a red-shift of the Si-O stretching band in IR spectra.^{26, 57} In Figure 7a, the AFM-IR band between 1000 cm^{-1} and 1100 cm^{-1} is slightly red-shifted in the spectrum taken at the bottom of the indent (position-2) compared to that taken outside the indent (position-1). Upon annealing of the sample at a temperature 0.9 times glass transition temperature (T_g), the densification is fully reverted, and the surface topography is partially recovered.⁵⁸⁻⁵⁹ The spectrum taken at the bottom of the annealed indent mark is almost identical to the reference spectrum taken from the un-indented outside region.

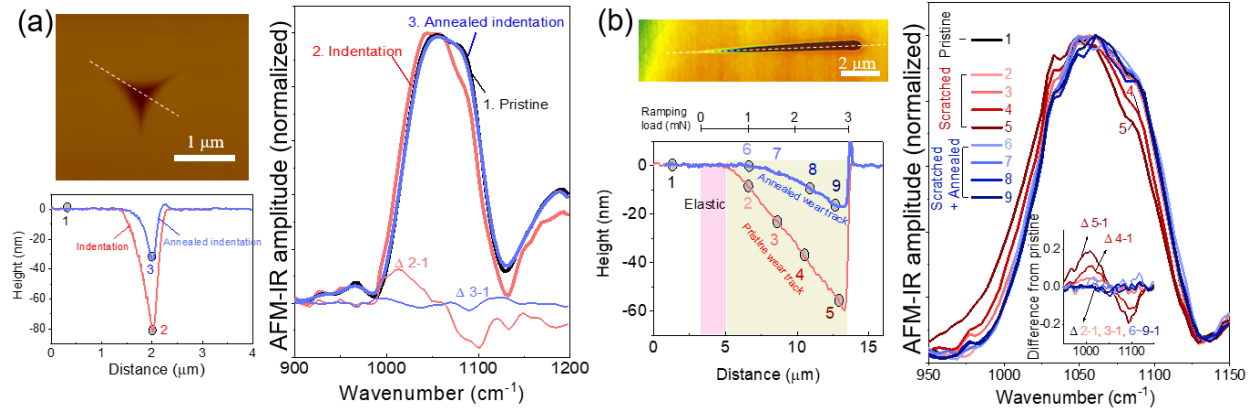


Figure 7. (a) Topography, line profile, and AFM-IR spectra of a nanoindent on fused quartz made with a Berkovich indenter at a 5 mN load. (b) Topography, line profile, and AFM-IR spectra of a nanoscratch on fused quartz made with a conospherical tip (radius = 150 nm) at a ramp load from 0 mN to 3 mN while sliding over a 10 μm distance. The same samples were analyzed before and after sub- T_g annealing. The differences (Δ) between local spectra are also shown.

Figure 7b shows the AFM-IR analysis of a nanoscratch mark on fused quartz made with a conospherical tip translating at 1 $\mu\text{m/s}$ while the load was ramped from 0 to 3 mN. Along the nanoscratch direction, the degree of red-shift in the AFM-IR amplitude peak gradually increases as the load increases (e.g., comparing positions 3 $\rightarrow$ 4 $\rightarrow$ 5). This is because the degree of subsurface densification increases with the applied load.^{13,47} At position-2 where plastic deformation is relatively small (thus, subsurface densification is minute), the red-shift of the Si-O stretch band is not readily discernable. This is in contrast to the s-SNOM-based nano-IR analysis result showing a noticeable red-shift in this same region.¹⁵ Even in the elastic contact regime (pink region in Figure 7b), s-SNOM-based nano-IR was able to detect a very small red-shift.¹⁵ The

discrepancy between these photothermal-IR and s-SNOM-IR data can be explained by inherent differences in the probe depths of the two techniques. The s-SNOM method relies on the scattering of the evanescent field in the near field, so its probe depth is on the order of tens of nm.^{15, 42} In contrast, the AFM-IR system relies on photothermal expansion. Since the IR attenuation by absorption takes place in the far field (which can be characterized by z_d , Figure 4a), the AFM-IR spectrum will have much larger contributions from the deeper region, implying much less surface sensitivity of the photothermal AFM-IR process compared to the s-SNOM process.

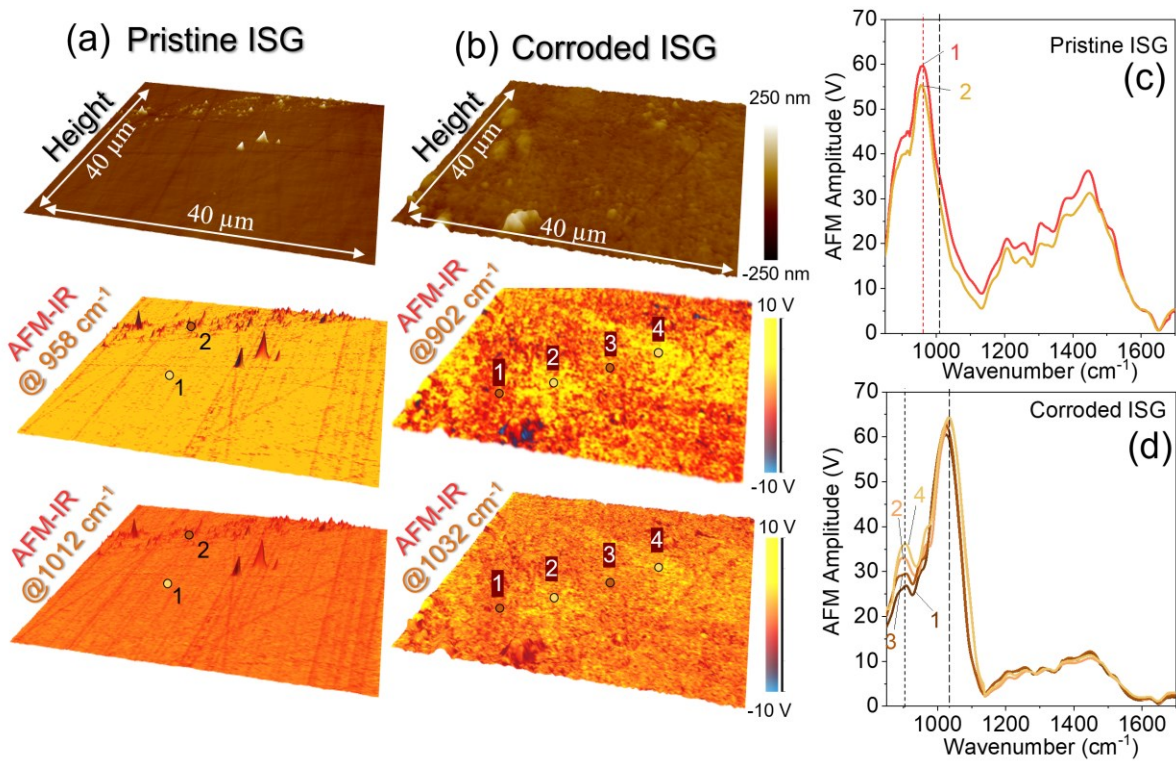


Figure 8. Topography and AFM-IR intensity map of (a) pristine and (b) corroded ISG surfaces. The wavenumber of the IR beam used in the mapping is shown in the left of each image. (c,d) AFM-IR spectra collected at various locations marked in the AFM-IR intensity map on (c) pristine and (b) corroded ISG surfaces. The corrosion was conducted in a pH 7 solution pre-saturated with soluble silica at 90 °C for 14 days.

Aqueous corrosion of glass can lead to alteration of the glass matrix and changes in glass network structure within a surface layer.^{18, 20} In the case of ISG, a borosilicate glass studied as a model nuclear waste vitrification,¹⁹ about 2 μm thick corrosion layer is formed within several days of immersion in silica-saturated aqueous solutions at pH 7, and this ultrathin layer

can protect the glass from further corrosion for more than 20 years (which is the longest time tested so far).^{20, 60} Figure 8 displays the topography and AFM-IR intensity images of pristine and 14-days corroded ISG glass surfaces, as well as their AFM-IR spectra. In the AFM-IR spectrum of pristine ISG (Figure 8c), the main peak at 958 cm^{-1} corresponds to the 1030 cm^{-1} peak in the $k(\lambda)$ and SR-IR spectra (see Section 3.3). The broad band in the $1300 - 1500\text{ cm}^{-1}$ region originates from the B-O stretch in the glass.⁶¹ In the topography and AFM-IR intensity maps, some scratch marks and debris can be identified. The AFM-IR spectral features collected at such locations (for example, position-2 in Figure 8a) are almost identical to the spectra collected in flat regions, except for small differences in the overall intensities due to topographic artifacts (Figure 8c).⁶² The convolution from topographic artifacts is further explained in the Supporting Information (Figure S6).

The corroded ISG surfaces (Figure 8d) show spectral features that are drastically different from the pristine samples. The decrease of the signal intensity in the $1300 - 1500\text{ cm}^{-1}$ region is due to the loss of boron species from the glass network.^{29-30, 63} Although time-of-flight secondary ion mass spectrometry depth profiling showed that the boron is almost completely depleted in the corroded layer,^{60, 64} AFM-IR still shows clearly discernable bands in the B-O stretch region. This comes from the boron species in the bulk below the $\sim 2\text{ }\mu\text{m}$ thick boron-depleted layer, and again exemplifies the relative deep probe depth of AFM-IR in the weakly-absorbing spectral region. In the corroded ISG spectra, the $\sim 958\text{ cm}^{-1}$ band is diminished, while the main band is blue-shifted to $\sim 1032\text{ cm}^{-1}$. This blueshift is interpreted as an indication of the transition to a “silica-like” network structure (Figure 5).^{26, 65} The probe depth at this maximum intensity position of the Si-O stretch mode (Figure S1a) is smaller than the corrosion layer thickness.

Local inhomogeneity can be seen in the AFM-IR intensity maps of corroded ISG; this inhomogeneity does not correlate with the topographic height change (Figure 8b). Positions-1,3 show the major band at $\sim 1022\text{ cm}^{-1}$ and a smaller band at $\sim 900\text{ cm}^{-1}$, while positions-2,4 have the main bands at 1032 cm^{-1} and a larger intensity at $\sim 900\text{ cm}^{-1}$. Considering that the AFM-IR peak position is red-shifted from the $k(\lambda)$ spectrum (Section 3.3), the $\sim 900\text{ cm}^{-1}$ band can be putatively ascribed to the vibrational modes involving non-bridging Si-O species, which normally appears as a shoulder band at $\sim 950\text{ cm}^{-1}$ in SR-IR spectra. Alternatively, it could be due to differences in the population of four-coordinated boron species (Figure 5a) near the interface between the alteration layer and the bulk glass.⁶⁰ The finding of such local inhomogeneity in glass network structure of the aqueous-corroded surface layer is unprecedented. Its implication on the overall chemical

durability and stability of the surface layer formed by aqueous corrosion has not been investigated and would be the subject of a future study.

4. Conclusion

This work examines the theory and application of the resonance-enhanced photothermal AFM-IR technique to materials that exhibit relatively strong absorption peaks in the mid-IR wavelength region, with a focus on silica and silicate glasses. These materials show very large extinction coefficients for the primary network vibration ($k(\lambda) > 1$) in comparison to organic materials, which invalidates some of the underlying assumptions that are commonly made when connecting the measured AFM-IR spectral response to the IR absorption behavior. These effects notably manifest in distortion of the AFM-IR spectra in comparison to the true absorption spectra. Modeling of the IR absorption and subsequent heating and cooling behavior of silica shows a large local temperature change and corresponding thermal gradients as a function of both time and distance from the focal spot during laser pulse. The subsequent impact to the measured signal could be verified across a variety of silicate glasses, and exemplifies the need to more holistically consider thermal properties (e.g., CTE, heat conductivity, heat capacity, etc.) of highly absorptive materials. Finally, we highlight in this work, through both experiment and modeling, the relatively deep information depth of AFM-IR (implying relatively low surface-sensitivity). Although this inherent limitation poses a challenge to reliably detect changes in glass structure in some instances of shallow surface modification, AFM-IR can still reasonably detect structural changes that occur under high-load diamond indentation or in relatively thick, corrosion-induced surface alteration layers.

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Supporting information: Experimental details, theoretical derivations and supplementary calculation and AFM-IR spectra.

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