Transient grating measurements of film thickness in multilayer metal films

Rebecca M. Slayton and Keith A. Nelson
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

A. A. Maznev
Philips Analytical, 12 Michigan Drive, Natick, Massachusetts 01760

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A transient grating technique has been used to measure film thicknesses in five multilayer film structures. Through-plane acoustic responses are observed through time-resolved diffraction that reveals their return to the free surface after partial reflections within the structure. Optical heterodyne detection with a controlled reference field amplitude permits optimization of the signal/noise ratio relative to detection of the signal against the far stronger incident probe field or against a dark background (homodyne detection). In-plane acoustic waves are also generated and observed.


I. INTRODUCTION

The ability to generate and detect acoustic waves in thin films has proved useful for probing a wide range of physical phenomena. Acoustic properties are sensitive to film thickness, film–substrate adhesion, and elastic properties. Acoustic probing of elastic properties has in turn been used to study phase transitions,1–3 surface quality, defects, and interactions with chemical species at a surface.4–11 Nondestructive probing through the use of acoustic waves is of particular interest in the microelectronics and coatings industries, and a variety of techniques have evolved including Brillouin scattering,12 acoustic microscopy,2,13–21 and techniques which use lasers to generate acoustic waves.22–32

Lasers generate acoustic responses in optically absorbing samples through sudden electronic excitation and subsequent lattice thermalization and expansion. Such techniques are receiving increased attention because they not only afford a noncontact probe, but are also capable of generating higher frequencies than conventional acoustic techniques.33 The high-frequency content of laser generated acoustic waves is limited by either the duration τ of the optical pulse, through the condition ωτ<1, or the length scale d over which the thermal driving force is exerted, through the condition kd<1, where ω or k are the acoustic frequency or wave vector, respectively, and ω/k=ν, the speed of sound. With femtosecond pulse durations, i.e., τ≈10−13 s, the first condition is satisfied even for the highest acoustic frequency that a sample can support. In this case the high-frequency limit in the acoustic response to the pulse is dictated by the second condition, i.e., kmaxd≈1, where d is the size of the heated region. For acoustic responses propagating in the plane of a thin film, the frequency content may be varied continuously by controlling the size of the excitation beam. For example, a beam focused to a line of several microns width at the sample may generate a broadband acoustic wave packet containing frequencies as high as 350 MHz. The frequency content of through-plane acoustic waves is determined by the depth of the heated region, typically 10–100 nm in metals. This depth may be varied to some extent by varying the excitation wavelength or the thickness of the absorbing material. The through-plane acoustic wave packet generated in aluminum by 800 nm femtosecond pulses includes substantial frequency components over 100 GHz.

Following pulsed excitation, in-plane acoustic wave packets propagate across the surface of a sample and may be monitored using a probe beam that is displaced spatially from the excitation region. Analysis of the frequency content and dispersion of these waves may be used to determine density, Young’s modulus, Poisson’s ratio, and film thickness.27,34 Through-plane wave packets propagate into a sample, partially reflect off of interfaces between different layers, and are detected upon their return to the surface. Film thickness may be determined by the round-trip time required for the acoustic echoes to return to the free surface, and elastic constants may be determined by the intensities of the partial reflections. Acoustic responses are sensitive to film thickness even when the film is much thinner than the incoming acoustic wave packet; for example, nanometer and subnanometer films buried in thicker metal films produce distinctive acoustic signatures.35

The high frequency content of the through-plane acoustic pulse has also proven particularly useful for studies of thin amorphous films, which may be too highly damped at high frequencies to be studied by conventional ultrasonic techniques.33,36–42

Both the in-plane and through-plane responses may be detected at the surface by optically measuring either the strain or the displacement associated with the waves. The strain causes a modulation in the complex index of refraction, leading to a modulation in the phase and intensity of a reflected beam.28,41–44 Displacement, or buckling of the surface, may be detected by measuring the angular deflection of a reflected beam55,45,46 or by using interferometric techniques.47–54

An alternate approach involves the use of two crossed excitation pulses in a four-wave mixing or transient grating measurement which has been labeled “impulsive stimulated thermal scattering” (ISTS).22–27,31,55–57 In the transient grating technique, the two excitation laser beams of wavelength λE crossed at angle θE generate an optical interference pat-
tern with spatial period $\Lambda = \lambda_f / (2 \sin(\theta_f/2))$. Electronic excitation followed by rapid thermalization results in spatially periodic heating, launching acoustic waves with in-plane wave vector magnitude $q = 2 \pi / \Lambda$. The resulting spatially periodic modulation ("ripple") of the sample surface can be detected through time-resolved diffraction of probe light, permitting characterization of the acoustic response. The transient grating method permits facile generation of tunable, narrowband in-plane acoustic waves with frequencies up to a few GHz, higher than those conveniently accessed through excitation with a line source. This can be advantageous for characterization of relatively thin films.\textsuperscript{27,34} The method has been used for assessment of film elastic moduli, thickness, delamination, residual stress, cure kinetics, and other properties.

Transient grating excitation with ultrashort pulses also launches broadband through-plane acoustic wave packets, one at each interference maximum. These propagate into the film, and at buried interfaces they undergo partial reflection back toward the heated surface. When they reach the surface, the reflected wave packets increase or decrease the intensity of diffracted probe light, revealing the acoustic round trip time.

Transient grating measurements of through-plane acoustic responses offer several potential advantages over conventional methods involving a single excitation pulse and time-resolved measurement of reflected probe light. The transient grating experimental geometry (shown schematically in Fig. 1) allows convenient optical heterodyne detection to both increase signal modulation and optimize signal to noise ratios. A phase mask automatically generates a reference field, serving as a nonadjustable reference. \textsuperscript{5} The resulting spatially periodic modulation of the sample surface induces changes in the optical reflectivity that are detected through time-resolved diffraction of probe light, revealing the acoustic round trip time.

![Diagram of transient grating experiment](image)

**FIG. 1.** Transient grating experiment. A phase mask diffracts both the pump and probe beams, and the $\pm 1$ diffraction orders are horizontally focused, recollimated, and projected onto the sample plane by cylindrical lenses L1 and L3. The beam pairs are focused vertically and crossed at the sample plane by cylindrical lens L2. A filter attenuates one of the diffracted probe orders, providing a variable intensity reference beam. A glass slide of similar thickness (not shown) is inserted into the other diffracted probe order to preserve temporal overlap. The inset shows the transient displacement grating induced in the sample.

where we assume that $E_D \ll E_R$. The reference beam amplifies the diffracted field over other sources of noise, but also adds noise due to laser fluctuations. Since the optimal intensity of the reference beam depends on the relative magnitude of shot noise and noise due to laser fluctuations, it should be continuously variable. In practice, we typically find optimal signal to noise ratios with the reference field far weaker than the probe, roughly $E_R / E_{probe} \approx 10^{-3}$. Typical diffraction efficiencies of $E_D / E_{probe} \approx 10^{-3}$ then yield a signal modulation of $\Delta I_{refl} / I_{refl} \approx 10^{-2}$. On the other hand, changes in reflectivity (by far the most commonly measured quantity) are typically observed as very small signal modulations $\Delta I_{refl}$ of the reflected probe intensity $I_{refl}$, i.e., typically $\Delta I_{refl} / I_{refl} \approx 10^{-5}$. Here the entire reflected probe beam reaches the detector, essentially serving as a nonadjustable reference field.

Optical penetration introduces a second difficulty in the use of reflectivity changes to measure film properties. Because the strain induces reflectivity changes beneath the surface, modeling of the total change in reflected intensity requires a convolution of the strain profile and the optical penetration profile, which may not be well known. Although in principle the diffraction efficiency is sensitive to changes in both optical reflectivity and surface displacement, it has been shown to be dominated by the latter (i.e., by surface modulation or “ripple”),\textsuperscript{59} permitting straightforward modeling of signal intensity and time dependence. Finally, in transient grating measurements, the in-plane acoustic waves may also be observed, yielding complementary information about film mechanical or thickness properties.

In this article we present transient grating measurements of thickness and density in five multilayer films. Grazing-incidence x-ray (GIXR)\textsuperscript{60,61} measurements of the same samples were also conducted for comparison. A theoretical model of the signal is presented and used to determine best-fit film parameters including thickness and density. The present results build on preliminary measurements\textsuperscript{59} of bilayer film structures in which the results were simulated semiquantitatively to determine film thickness values.

II. EXPERIMENT

Pulses from an amplified Ti:sapphire laser system (duration 250 fs, wavelength 800 nm, energy $\sim 6 \mu J$, repetition rate 250 KHz) are split into pump ($\sim 4 \mu J$) and probe ($\sim 2 \mu J$) pulses. The probe is delayed using a variable delay line, and the pump and probe beams are aligned parallel to each other with a slight vertical displacement. The transient grating setup is shown in Fig. 1. A binary phase mask pattern diffracts both the pump and probe beams, and all but the $\pm 1$ diffraction orders are blocked. A pair of imaging lenses horizontally focuses and recollimates these to a width of $\sim 1$ mm, spatially overlapping them in the plane of the sample. A third cylindrical lens is used to cross the pump and probe beams at the sample and to focus them in the vertical dimension to $\sim 40 \mu m$. The grating spacing at the sample for all data shown here was 21 $\mu m$.

An optically heterodyned signal was collected by filtering one of the diffracted probe orders by a factor of $\sim 10^5$ to provide the reference beam which was directed into the pho-
III. THEORY

A complete description of the displacement generated by impulsive heating requires solving the equation of motion

$$\rho \frac{\partial^2 u}{\partial t^2} = \sum_{j=1}^{3} \frac{\partial \sigma_{ij}}{\partial x_j},$$  \hspace{1cm} (2)

with the stress tensor

$$\sigma_{ij} = \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) + \delta_{ij} \left( K - \frac{2}{3} \mu \right) \sum_{k=1}^{3} \frac{\partial u_k}{\partial x_k} - 3 \beta K \Delta T \delta_{ij}. \hspace{1cm} (3)$$

Here $\rho$ is the density of the elastic medium, $\mu$ is the shear modulus, $K$ is the bulk modulus, $\beta$ is the coefficient of thermal expansion, and $\Delta T$ is the temperature change from equilibrium. The first two terms describe mechanical stresses, while the third is a source term describing the thermal stress due to sudden heating. For the case of transient grating excitation by a short pulse of light (~200 fs), the source term is determined by

$$\Delta T = \frac{(1-R)I_E}{\rho C_\varepsilon} \theta(t)(1+e^{iqs})e^{-z/\zeta}, \hspace{1cm} (4)$$

where $R$ is the reflectivity of the metal surface, $I_E$ is the excitation energy per unit area, $C$ is the heat capacity per unit mass, $\theta(t)$ is the Heaviside step function, $\zeta$ is the penetration depth of the light, and $q$ is the wave vector of the transient grating. Assuming zero initial displacement, Eq. (3) shows that the gradient of the applied thermal stress governs displacement at early times. Since the transient grating spacing is generally much larger than the light penetration depth ($2\pi/q \gg \zeta$), this stress gradient is much larger through the plane of the sample than in the plane of the sample, and we are able to neglect the effects of $u_i$ and $u_k$ at early times. We denote $T=\left(1-(1-R)I_E/\rho C_\varepsilon \zeta \right)(1+e^{iqs})$; then combining Eqs. (2)–(4) we find that $u_z$, the displacement to which the experimental observable is proportional, is given by

$$\rho \frac{\partial^2 u_z}{\partial t^2} = \rho \nu^2 \frac{\partial^2 u_z}{\partial z^2} + \frac{3 \beta K T}{\zeta} \theta(t) e^{-z/\zeta}. \hspace{1cm} (5)$$

This is the equation of motion for longitudinal plane waves propagating through the plane of the sample, with a step-function driving term that decays exponentially from the front of the sample inward and varies sinusoidally across the plane of the sample. The amplitude of the longitudinal waves varies across the plane of the sample with the amplitude of the source term.

Equation (5) describes the generation and propagation of waves into the film. Each interface in the multilayer film will reflect some portion of the waves, returning them to the surface. We want to know the surface displacement as a function of time. A straightforward approach to the problem is to solve the equation of motion in the frequency domain for each layer, and then apply the boundary conditions at the interfaces and the free surface. Fourier transformation of Eq. (5) reads

$$-\rho \omega^2 \tilde{u} = \rho \nu^2 \frac{\partial^2 \tilde{u}}{\partial z^2} - \frac{3 \beta K T}{\zeta} \frac{e^{-z/\zeta}}{i \omega} \tilde{u}. \hspace{1cm} (6)$$

For layer 1, the general solution is

$$\tilde{u}_1 = \frac{3 \beta K T \zeta}{\rho \nu} \frac{e^{-z/\zeta}}{i \omega(\omega^2 \zeta^2 + \nu_1^2)} + \tilde{A}_1 e^{ik_1 z} + \tilde{B}_1 e^{-ik_1 z}, \hspace{1cm} (7)$$

where $k_1 = \omega/\nu_1$. The first term contains a nonpropagating term corresponding to thermal expansion, as well as propagating and counterpropagating waves produced at the free surface. The second and third terms correspond to waves traveling away from and toward the surface, respectively, as a result of reflections from interfaces in the multilayer film.

In each underlying layer $n$, the source term in Eq. (6) is zero, and the solution is

$$\tilde{u}_n = \tilde{A}_n e^{ik_n z} + \tilde{B}_n e^{-ik_n z}, \hspace{1cm} (8)$$

where $k_n = \omega/\nu_n$. The wave amplitudes $\tilde{A}_n$, $\tilde{B}_n$ are determined by requiring continuity of displacement and stress at each interface and zero stress at the free surface. Solving for these coefficients (see the Appendix) gives the mechanical response of the entire multilayer film to sudden heating in the top layer. Inserting $\tilde{A}_1$, $\tilde{B}_1$ into Eq. (7) and taking the inverse Fourier transform at the surface gives the surface displacement as a function of time

$$u(t,z=0) = \frac{1}{2 \pi} \int_{-\infty}^{\infty} \frac{3 \beta K T}{\rho \zeta} \frac{1}{i \omega(\omega^2 + \nu_1^2)} \left[ e^{-z/\zeta} \right] d\omega + \tilde{A}_1 + \tilde{B}_1 e^{i \omega t} d\omega. \hspace{1cm} (9)$$

IV. RESULTS AND ANALYSIS

Figure 2 shows the diffracted probe pulse intensity as a function of pump–probe delay for a Ta/SiO$_2$/Si multilayer film–substrate system. The sharp peak at zero time delay is an artifact of nonlinear electronic interactions between the pump and probe beams in the sample. The subsequent rise in diffracted intensity is due to a combination of thermally induced reflectance changes and thermal expansion. The portion of the thermal signal arising from reflectance changes decays as energy diffuses into the tantalum film past the penetration depth of light. This decay is commonly seen in reflectance measurements. It is fit well in Ta by a single exponential decay with a time constant of 100 ps. Also accounted for in the data analysis is the steady-state diffracted
signal due to thermal expansion at the grating peaks. This signal persists until it is washed away by thermal diffusion from grating peaks to nulls, with a time constant of 4.8 ms for Ta with the grating fringe spacing selected.

The dip at 48 ps corresponds to the first reflection of the acoustic wave packet from the Ta/SiO₂ interface. This feature repeats and slowly damps away due to transmission into the SiO₂. The decay rate is determined as described in the Appendix by the impedance mismatch between Ta and SiO₂. The multiple reflections in the top layer send a pulse train into the SiO₂ layer, which reflects at the SiO₂–substrate interface. This reflected pulse train becomes just visible at 180 ps as a series of positive-going pulses.

Figure 2 also shows the surface displacement $u(t)$, which was simulated using the model described in the Appendix. For all simulations, rough initial parameters for film thickness were determined by visual comparison between the data and simulation. These parameters were then optimized by minimizing the $\chi^2$-squared difference between the data and simulation with a Nelder Mead simplex algorithm. All film thicknesses were varied simultaneously while all densities were held fixed at literature values and acoustic velocities were held at calibrated values (see discussion below). For tantalum, the acoustic pulse width was determined by fitting the observed pulse width "by eye."' The best fit was produced by an optical penetration depth of 28 nm, in rough agreement with the value of 37 nm that is calculated from the literature value of the absorption coefficient at 800 nm.62 An exponentially decaying signal component (time constant 100 ps) and a steady-state signal level were included in the simulations as discussed above.

Figure 3 shows typical data and simulation for a Cu/SiO₂/Si multilayer assembly. A comparison of Figs. 2 and 3 shows that the acoustic pulse generated in tantalum is much narrower than the pulse generated in copper, even though the optical penetration depth expected in tantalum (~37 nm) is larger than that in copper (~25 nm). The low electron–phonon coupling rate in copper allows electron diffusion to significantly broaden the initial temperature profile, and thus the acoustic pulse launched by thermal expansion. Models accounting for nonequilibrium electron diffusion have suggested that the pulse shape in copper is well approximated by simply broadening the exponentially decaying optical penetration profile by a factor of 5 (to ~125 nm).45 The data shown in Fig. 3 were best fit by a pulse width of 150 nm, and this value was used for the acoustic pulse width in simulations for samples 2–5. In general, the best fit simulations are very insensitive to changes in the acoustic pulse width.

Typical data and simulations for samples 3–5 are shown in Figs. 4–6. For each sample, we collected multiple data sets and determined film thicknesses by minimizing $\chi^2$ squared between each data set and the simulations. Averages and standard deviations for transient grating film thickness measurements are presented in Table I. GIXR measurements were also used to independently measure the thickness of Ta and Cu films in samples 1 and 3–5. GIXR could not be used to determine the thickness of the SiO₂ or Cu layers in sample 2 because these layers were too thick, so SEM was used to gain an independent measure of thickness in these samples. All results are summarized in Table I.

V. SOURCES OF UNCERTAINTY

Here we discuss uncertainties in the film parameters determined due to uncertainties in our knowledge of film properties (acoustic velocity and density) used as fitting param-
eters, due to limitations in the model used, and due to sample complexity including heterogeneity and acoustic dispersion. We note that the considerations discussed here apply as well to other measurement methods (including time-dependent reflectivity measurements) involving through-plane acoustic waves for film characterization. To some extent, the transient grating method offers advantages in that the signal from each returning acoustic wave packet, arising as it does from surface modulation, is of shorter duration than signals arising from changes in surface reflectivity. This reduces the extent of temporal overlap between signals from different wave packets that return to the surface at similar times, thereby facilitating separation of distinct signal contributions.

The largest standard deviation in any measurement of film thickness is less than 4%, indicating that the data themselves are highly reproducible. In general, the degree of uncertainty depends on details of the multilayer film structure. In the case that acoustic waves from different interfaces return to the surface at well separated times, film thickness measurements may show high precision and, if other material parameters are known well, high accuracy. However, when reflections from different interfaces return to the surface at similar times, their signal contributions are temporally overlapped and we note an increased level of uncertainty.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Average/standard deviation of thickness measured from transient grating data (Å)</th>
<th>Independent measure of film thickness (Å)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ta 994±6</td>
<td>992±10 (GIXR)</td>
<td>0.20%</td>
</tr>
<tr>
<td></td>
<td>SiO₂ 4035±7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cu 9555±66</td>
<td>8800 (SEM)</td>
<td>8.6%</td>
</tr>
<tr>
<td></td>
<td>SiO₂ 4103±50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Cu 1695±47</td>
<td>1640±16 (GIXR)</td>
<td>3.35%</td>
</tr>
<tr>
<td></td>
<td>SiO₂ 4067±115</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Cu 1097±5</td>
<td>1079±11 (GIXR)</td>
<td>1.67%</td>
</tr>
<tr>
<td></td>
<td>Ta 259±8</td>
<td>262±3 (GIXR)</td>
<td>1.15%</td>
</tr>
<tr>
<td></td>
<td>SiO₂ 3858±72</td>
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<td></td>
</tr>
<tr>
<td>5</td>
<td>Cu 468±7</td>
<td>452±5 (GIXR)</td>
<td>3.54%</td>
</tr>
<tr>
<td></td>
<td>Ta 217±5</td>
<td>264±3 (GIXR)</td>
<td>17.8%</td>
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<tr>
<td></td>
<td>SiO₂ 3998±29</td>
<td></td>
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</tr>
</tbody>
</table>

A. Uncertainties in film parameters

The data were fit with simulations using literature values for the bulk densities of all materials and for the longitudinal acoustic velocities of SiO₂ and the substrate. However, bulk values may not be accurate for the thin films deposited here. For example, assuming that the GIXR thickness measurements are accurate to within 1%, the timing of the first peaks in Figs. 2 and 4 gives velocities of 4208±43 and 4686±234 m/s for thin tantalum and copper films, in comparison with literature values of 4100 and 4700 m/s, respectively. Fitting of data from samples 1 and 2 with the literature values for acoustic velocity results in systematic errors, as demonstrated by the fact that the GIXR measurements of film thickness lie well outside the standard deviation of the transient grating measurements. For example, using literature velocity values to fit data from sample 1 results in an average transient grating measurement of 966±6 Å for Ta thickness, in contrast to the GIXR measurement of 992±10 Å. Similarly, using literature velocities to simulate data from sample 3 results in an average transient grating measurement of 1701±8 Å, in contrast with a GIXR measurement of 1640±16 Å. To avoid this systematic error, we used the velocity values calibrated such that the GIXR and ISTS results from samples 1 and 3 were in agreement to simulate data for all of the samples. Our results indicate that velocities in the thin films under study differ by less than 3% from the literature values for the corresponding bulk materials. Thus, in the general case that the velocities cannot be calibrated by an independent measure of film thickness, the use of literature values can be expected to introduce a modest uncertainty in the accuracy of film thickness measurements.

Another parameter contributing to uncertainty in the accuracies is density. The densities of films deposited in vacuum have been shown to depend on a variety of conditions, and are likely to vary from the densities of bulk metals. If we assume that the acoustic velocities are well known, then the densities alone will determine the reflected amplitude at each interface between different layers through their acoustic impedances, \( Z = \rho v \). We might hope to calibrate the film density by holding film thickness and acoustic velocity constant, however, due to limitations in the model used, and due to sample complexity including heterogeneity and acoustic dispersion.
values fixed and optimizing the simulations by varying the densities. However, calibration of densities in this manner for sample 1 resulted in densities of Ta and SiO₂ that are, respectively, 25% higher and 6.0% lower than the literature values. Since we have no independent measure of film density, we were unable to assess the accuracy of these density measurements, but it is unlikely that the densities vary to this degree. Nonetheless, the uncertainty in density is substantial, and deviations from the literature values used to simulate all data here may account for some discrepancy between the data and simulations.

In the case that reflections from different interfaces are distinctly resolved, uncertainties in density values are unlikely to affect either the accuracy or the precision of thickness measurements, because film densities will affect the intensities of the acoustic echoes, but not their timing. However, when reflections from different interfaces return to the surface at similar times, uncertainties in density values frustrate deconvolution of the overlapping signals since their relative amplitudes are not known accurately. This increases the uncertainties of the thickness measurements, even when the acoustic velocities are well known. The need to deconvolute overlapping acoustic reflections also limits attempts to simultaneously determine both film thickness and density values. Although in principle, given accurate velocity values, the arrival times, and intensities of the signals from acoustic reflections reveal the film thickness and density values, respectively, in practice the uncertainties of simultaneous thickness and density measurements increase when reflections from different interfaces are strongly overlapping.

B. Limitations in the model for idealized and complex samples

Another source of uncertainty in transient grating measurements arises from limitations in the model used to simulate the data. First, although Eq. (5) is valid at short propagation distances the acoustic pulse is diffracted at long distances and can no longer be considered a longitudinal plane wave. In the present case, we do not expect diffraction to be significant for distances smaller than \( \Lambda^2/\xi \) (~10,000 \( \mu \)m for the data taken here). Second, in the derivation of Eq. (5) it was assumed that stresses giving rise to shear waves were negligible at early times; at long times (sufficient for significant in-plane acoustic responses, nanoseconds for our present measurements), shear waves will contribute to surface displacement. Given the long distance and time scales required for manifestations of these limitations, we conclude that for idealized samples the model is adequate.

A third limitation of Eq. (5) is the assumption that the material responds linearly to the acoustic waves. Displacement amplitude in the acoustic wave is approximately equal to \( 2(1 − R)βE/ρC \), which, for our experimental conditions, yields \( \sim 0.2 \) Å if the top layer is Cu. Acoustic Mach number \( M \), i.e., the ratio of the material velocity to the speed of sound (which is approximately the same as the amplitude of the strain, \( σu(x,z)/σz = β\Delta T \) is \( \sim 0.0002 \), i.e., the nonlinearity is weak but not necessarily negligible. Acoustic pulse broadening due to nonlinearity would become significant at the acoustic propagation length \( L_{NL} \sim \xi/\epsilon M \), where \( \epsilon \) is the nonlinear parameter of the medium (typically on the order of unity) and \( \xi \) is the initial spatial width of the acoustic pulse.\(^6\)

We expect \( L_{NL} \sim 200 \mu \)m, and thus we expect that any nonlinearities in the material are negligible. This expectation was confirmed by our observation that the shape of the data did not change as we varied the excitation energy.

Neglect of various types of sample complexity should also be considered. One limitation in the model is the assumption that the films do not show frequency-dependent dispersion in the acoustic velocity or attenuation rate. Figure 3 shows that the acoustic pulse has a “tail” that is not reproduced in the simulation, and acoustic pulses in aluminum samples show a similar asymmetry. Acoustic waves propagate through a crystalline solid with a frequency dependent velocity, often approximately following the relationship \( \bar{v} = v_0(1 − A\omega^2) \), where \( A \) is a small positive constant, so we might expect slower, high-frequency components to produce a tail in the signal as they arrive behind the low-frequency components. For example, reflectance measurements of acoustic pulse broadening have been used to determine the parameter \( A \) in Si.\(^6\) However, modification of the equation of motion to include velocity dispersion and use of the new results for simulations produced oscillatory responses in the trailing end of the acoustic pulse, rather than the smooth broadening seen in the data. It is possible (but unlikely in our view) that inclusion of dispersion in the attenuation rate would yield improved agreement. Higher damping rates are expected for higher-frequency phonons, due to spontaneous decay into lower energy phonons or to scattering off of thermal phonons in the crystal.\(^6\)\(^5\)\(^6\)\(^6\) Since the highest frequencies contained in the acoustic wave packet are still substantially lower than the average thermal phonon frequency at room temperature, we expect scattering off of thermal phonons to be the dominant mechanism.\(^6\)\(^7\) Significant attenuation has been observed in 56 GHz phonons propagating through GaAs. Physically, this attenuation was accounted for by considering the propagating strain to shift the frequencies of the thermal phonons out of equilibrium.\(^6\)

Another possible source of the apparent broadening in the acoustic echoes is sample inhomogeneity over the region probed. In general, deposited metal films are not single crystals. They consist of a layer of randomly oriented crystalline grains, and often include stacking faults (i.e., discontinuities in the plane of the film). Single crystals have been grown on H-terminated Si(001) surfaces; however, even these films contain inhomogeneities due to CuO formation up to 20 nm thick, along with dislocations and stacking faults, all of which increase in density for films over 50 nm thick.\(^6\)\(^8\) The grain size typically increases linearly as film thickness increases; for example, measurements of Cu that were deposited on pyrex by magnetron sputtering show that the average grain size in a 400 Å thick Cu film is 200 Å, while the average grain size in a 11 060 Å thick Cu film is 1400 Å.\(^6\)\(^9\) In multilayer films, the situation is complicated by effects of underlying film texture on overlayer textures.\(^7\) In general, we expect that the copper films probed here consist of a layer of randomly oriented crystalline grains between 200 and 1400 Å wide, introducing a significant variation across the
longitudinal plane waves (i.e., across each 10.5 μm half period of the transient grating).

Increased roughness has been observed in Cu films of thickness greater than 400 Å. Thus, we might expect that crystalline grains cause an apparent acoustic pulse broadening by causing different parts of a longitudinal plane wave or different waves (i.e., different interference fringes in the transient grating) to travel different distances through the film. However, scattering measurements on copper films deposited on polished metal substrates suggests an rms roughness of about 14 nm for features 700 nm in length, and 40 Å for features 50 μm in length. Since this amount of roughness would result in less than 3 ps of broadening, we conclude that surface roughness is not a significant source of broadening in the data shown here.

The grains might also broaden the pulse through phonon–grain boundary scattering. Phonon scattering has been correlated with grain size in diamond films and bulk copper. A comparison of acoustic pulse propagation through polycrystalline and epitaxial films might potentially clarify the sources of acoustic pulse broadening seen in these data. The transient grating method could potentially provide a good indicator of the quality of epitaxial films.

Finally, randomly oriented crystalline grains might cause apparent pulse broadening by causing different parts of the plane wave or different plane waves to travel at different speeds. For example, in Cu, the longitudinal waves travel at 4340 m/s in the 100 direction, 4960 m/s in the 110 direction, and 5160 m/s in the 111 direction. Plane waves traveling through a 1 μm Cu film, composed of grains oriented in each of these directions, would return to the surface up to 71 ps apart. Although the random orientation of the grains makes a realistic picture much more complex, this time delay matches well with the broadening seen in data on the 1 μm Cu film (see Fig. 3). We consider orientation-dependent variation in acoustic velocity the likely source of the broadening observed experimentally.

In the current model, we assume wave propagation through a single crystal with a single acoustic velocity. We determined the acoustic velocity in Cu by comparison of the acoustic echo time in transient grating data and the GIXR thickness measurement on sample 3 (see discussion above). Because this model does not account for broadening, some systematic error is introduced in the thickness measurements. For example, the optimized film thickness for sample 2 is 8.6% too large, although the relative standard deviation is only 0.52%. This is a result of the fitting routine shifting the simulated acoustic pulse to later times in order to match the broadened tail in the data. However, the thickness of Cu as determined from the dip position in the data is 9370±120 Å, in better agreement with the SEM measurement. (Note that the SEM and transient grating measurements may have been taken from different points in the sample plane, contributing to the discrepancy between measurements.)

C. Uncertainties due to overlapping signal contributions

In general, since pulse broadening does not significantly change the positions of acoustic echoes, film thicknesses can be accurately determined from the positions of individual peaks or dips, provided acoustic velocities are well known. However, not knowing the pulse shape accurately limits both the accuracy and precision of thickness measurements when the timing cannot be determined from distinguishable reflections. For example, Fig. 5 shows a dip at 60 ps corresponding to a reflection from the Ta/SiO₂ interface, but because the Ta layer is very thin, reflections from the Cu/Ta interface are not easily distinguishable from the larger reflections from the Ta/SiO₂ interface. On average, simulations were optimized by a Cu film thickness of 1097±5 Å; the GIXR measurement of 1079±11 Å lies just outside of the standard deviation of the measurement. The same problem of temporally overlapping signal contributions limits the accuracy of the best fit for sample 5.

To quantify the increase in uncertainty of simultaneous thickness measurements when films are not well demarcated by individually resolved reflections, we analyzed the χ-squared difference between simulation and fit as a function of film thicknesses. We calculated the Hessian at the minimized thickness values, and then plotted the percent change in the width of the simulated peaks or dips, provided acoustic velocities are well known. However, not knowing the pulse shape accurately limits both the accuracy and precision of thickness measurements when the timing cannot be determined from distinguishable reflections. For example, Fig. 5 shows a dip at 60 ps corresponding to a reflection from the Ta/SiO₂ interface, but because the Ta layer is very thin, reflections from the Cu/Ta interface are not easily distinguishable from the larger reflections from the Ta/SiO₂ interface. On average, simulations were optimized by a Cu film thickness of 1097±5 Å; the GIXR measurement of 1079±11 Å lies just outside of the standard deviation of the measurement. The same problem of temporally overlapping signal contributions limits the accuracy of the best fit for sample 5.

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either the parameters or particularly the model result in measurements which are both less accurate and less precise.

The methods used here could be applied to the characterization of complex materials whose ultrahigh-frequency acoustic responses are of interest in their own right. Experiments on supercooled liquids with complex structural relaxation components at many GHz frequencies are currently underway.

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APPENDIX

We assume a structure of \( N \) layers, layer 1 being the top layer. The thicknesses of layers 1 through \( N \) will be denoted \( d_1, d_2, \ldots, d_N \). To simplify notation later, we give each layer \( n \) a separate coordinate \( z_n \), which we set to zero at the top of each layer. (We have this freedom since coefficients \( \tilde{A}_n \) and \( \tilde{B}_n \) have not yet been determined.) The displacement induced in the top layer of a thin film and in all other layers is given by Eqs. (7) and (8), respectively,

\[
\tilde{u}_1 = \frac{3 \beta KT_0}{\rho_1} e^{-z_1/\xi} + \tilde{A}_1 e^{ik_1 z_1} + \tilde{B}_1 e^{-ik_1 z_1},
\]

and

\[
\tilde{u}_n = \tilde{A}_n e^{ik_n z_n} + \tilde{B}_n e^{-ik_n z_n}.
\]

The corresponding stress in the top layer is

\[
\tilde{\sigma}_1 = M_1 \frac{\partial \tilde{u}_1}{\partial z} = M_1 \left[ -\frac{3 \beta KT_0}{\rho} \frac{e^{-z_1/\xi}}{i \omega (\xi^2 + \nu_1^2)} + \tilde{A}_1 i k_1 e^{ik_1 z_1} - \tilde{B}_1 i k_1 e^{-ik_1 z_1} \right],
\]

and in every other layer the stress is

\[
\tilde{\sigma}_n = i M_n k_n \left[ \tilde{A}_n e^{ik_n z_n} - \tilde{B}_n e^{-ik_n z_n} \right].
\]

Here \( M_n = \rho_n \nu_n^2 \) is the acoustic modulus of layer \( n \). In the following discussion, we will use the acoustic impedance \( Z_n = \rho_n \nu_n \), making the replacements \( M_n \rightarrow Z_n \nu_n \) and \( M_n k_n \rightarrow Z_n \omega \).

To determine the amplitudes of the waves in each layer, we impose the boundary conditions of continuous stress and displacement. These conditions give the following set of equations.

At the free surface, \( z_1 = 0 \), the total stress from displacement and the applied force \( \tilde{G} = 3 \beta K \delta \tilde{t} \) add to zero. Since

\[
\tilde{G} \big|_{z=0} = \frac{3 \beta KT}{i \omega},
\]

we have
\[
\begin{align*}
\frac{3\beta KT}{i\omega} + Z_1\nu_1 - \frac{3\beta KT}{\rho_1} &\frac{1}{i\omega(\xi^2 \omega^2 + \nu_1^2)} + A_1ik_1 \\
- B_1ik_1 &= 0, \\
Z_1(A_1 - B_1) &= 3\beta KT \left( \frac{1}{\omega^2} - \frac{Z_1\nu_1}{\rho_1\omega^2(\xi^2\omega^2 + \nu_1^2)} \right).
\end{align*}
\]

At the first interface, \(z = d_1\), \(z = 0\), the stress must be continuous, so
\[
\frac{3\beta KT}{i\omega} e^{-d_1i\xi} + Z_1\nu_1 - \frac{3\beta KT}{\rho_1} \frac{e^{-d_1i\xi}}{i\omega(\xi^2\omega^2 + \nu_1^2)} + A_1e^{ik_1d_1} - B_1e^{-ik_1d_1} = Z_2i\omega[A_2 - B_2] = 0,
\]
\[
Z_1[A_1e^{ik_1d_1} - B_1e^{-ik_1d_1}] - Z_2[A_2 - B_2] = 3\beta KT e^{-d_1i\xi} \left[ \frac{1}{\omega^2} - \frac{Z_1\nu_1}{\rho_1\omega^2(\xi^2\omega^2 + \nu_1^2)} \right].
\]

At the first interface, the displacement must also be continuous,
\[
[A_1e^{ik_1d_1} + B_1e^{-ik_1d_1}] - [A_2 + B_2] = -3\beta KT \xi e^{-d_1i\xi} \left[ \frac{1}{\rho_1} \frac{1}{i\omega(\xi^2\omega^2 + \nu_1^2)} \right].
\]

We can continue this for \(n\) interfaces, writing equations \(2n\) and \(2n + 1\), respectively,
\[
Z_n[A_ne^{ik_n d_n} - B_ne^{-ik_n d_n}] - Z_{n+1}[\tilde{A}_{n+1} - \tilde{B}_{n+1}] = 0,
\]
and
\[
\begin{bmatrix}
A_1 & B_1 & A_2 & B_2 & \cdots & A_N & B_N & \tilde{A}_{N+1} & \tilde{B}_{N+1}
\end{bmatrix} = 3\beta KT \begin{bmatrix}
Z_1
Z_1
\vdots
Z_1
\vdots
Z_1
\vdots
Z_1
\vdots
Z_1
\vdots
\end{bmatrix}.
\]

By inverting \(M\) at every frequency of interest and multiplying by the vector, we can solve for the coefficients \(\tilde{A}_{n+1}\) and \(\tilde{B}_1\). The total amplitude of the displacement at the surface is then given by the Fourier transform of Eq. (9).

Note that when all interfaces in the multilayer film structure are essentially unheated [i.e., \(\xi < d_1\) in Eqs. (2)–(3)], each pair of equations \(2n\), \(2n + 1\) govern reflection and transmission of acoustic waves at interface \(n\). They can be represented in the form
\[
B_n e^{-ik_n d_n} = \tilde{r}_n A_n e^{ik_n d_n} + \tilde{t}_n B_{n+1},
\]
\[
\tilde{r}_n = \frac{Z_n - Z_{n+1}}{Z_n + Z_{n+1}}.
\]
and
\[ \mathbf{\tilde{T}}_n = \frac{2Z_n}{Z_n^2 + Z_n + 1}. \]

Note that the coefficients corresponding to reflected and transmitted stress are different from these, which correspond to reflected and transmitted displacement.

Additionally, we can relate the amplitudes \( \tilde{A}_n, \tilde{B}_n \) in each layer to the amplitudes in the layer beneath it using a transfer matrix equation
\[ \begin{bmatrix} \tilde{A}_n \\ \tilde{B}_n \end{bmatrix} = T_n \begin{bmatrix} \tilde{A}_{n+1} \\ \tilde{B}_{n+1} \end{bmatrix}, \]
with the transfer matrix
\[ T_n = \begin{pmatrix} Z_n^2 + Z_n + 1 & (Z_n - Z_n^2) e^{ikd_n} \\ (Z_n - Z_n^2) e^{-ikd_n} & (Z_n + Z_n^2) e^{-ikd_n} \end{pmatrix}. \]

By multiplying the transfer matrices for each interface \( n \), we can write a single equation for the amplitudes in the top layer in terms of the acoustic impedances of each film layer
\[ \begin{bmatrix} \tilde{A}_1 \\ \tilde{B}_1 \end{bmatrix} = T_1 T_2 \ldots T_N \begin{bmatrix} \tilde{A}_N \\ \tilde{B}_N \end{bmatrix} = \mathbf{T} \begin{bmatrix} \tilde{A}_N \\ \tilde{B}_N \end{bmatrix}, \]
or
\[ \frac{\tilde{A}_1}{T_{11}} = \frac{\tilde{B}_1}{T_{21}}. \]

Here \( \mathbf{T} \) is the transfer matrix for the entire multilayer film structure, and \( \mathbf{T}_{mn} \) refers to the element in row \( m \) and column \( n \). Since the condition of zero stress at the free surface also relates these two amplitudes through Eq. (A1), we can solve for these amplitudes
\[ \tilde{A}_1 = 3 \beta KT \left( \frac{1}{Z_1 \omega^2} - \frac{\nu_1}{\rho_1 \omega^2 (\zeta + \omega^2 + \nu_1^2) \left( T_{11} - T_{21} \right)} \right) \]
\[ \tilde{B}_1 = 3 \beta KT \left( \frac{1}{Z_1 \omega^2} - \frac{\nu_1}{\rho_1 \omega^2 (\zeta + \omega^2 + \nu_1^2) \left( T_{11} - T_{21} \right)} \right) \]

Again, inserting these amplitudes into Eq. (9) gives the surface displacement as a function of time. This transfer matrix approach should be particularly useful in the case where there are a large number of layers in a multilayer film structure.