Mechanical and thermal properties of nanomaterials at sub-50nm dimensions characterized using coherent EUV beams

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ABSTRACT

Coherent extreme ultraviolet beams from tabletop high harmonic generation offer several revolutionary capabilities for observing nanoscale systems on their intrinsic length and time scales. By launching and monitoring hypersonic acoustic waves in such systems, we characterize the mechanical properties of sub-10nm layers and find that the material densities remain close to their bulk values while their elastic properties are significantly modified. Moreover, within the same measurement, by following the heat dissipation dynamics from 30-750nm-wide nanowires, we uncover a new thermal transport regime in which closely-spaced nanoscale heat sources can surprisingly cool more efficiently than widely-spaced heat sources of the same size.

Keywords: Ultrafast X-Rays, nanometrology, nano-mechanical properties, ultrathin films, nondiffusive thermal transport, mean free path spectroscopy, photoacoustic, photothermal

1. INTRODUCTION

Advanced materials development and device design require reliable characterization tools to discover, optimize and monitor new nanomanufacturing techniques. Moore's Law has pushed the frontiers of nanofabrication so far that the thinnest films and smallest nanostructures being made today cannot easily be measured using current metrology techniques[1]. Yet precise characterization of materials in nanostructured devices is necessary for understanding the unique physics which applies to such small-scale systems: how elastic properties change from monolayers to bulk material[2,3] for example, or how phonon spectra in materials govern thermal dissipation in the deep nanoscale regime << 100nm[4,5].

Many techniques for nondestructive metrology of microscopic systems utilize visible-wavelength laser light to study materials in a sensitive, non-contact manner. The interaction of light with acoustic waves enables the characterization of mechanical properties. For example, the optical properties or physical profile change as an acoustic wave propagates, as in picosecond ultrasonics[6-11], and this can be detected using visible light. However, the sensitivity of these techniques to nanostructured materials << 100nm is inherently limited by visible wavelengths of hundreds of nanometers. Direct scattering mechanisms between photons and acoustic phonon modes can be exploited by Brillouin light scattering. This technique can characterize ultrathin films down to ~20nm in thickness[12]. However, the interpretation is more complex due to the weak intensity of scattered light and the difficulty of properly identifying the phonon modes, so that film characterization is strongly dependent on the experimental accuracy attained[13].

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Visible-light techniques have also been applied to the study of thermal transport. In many of these techniques, the absorption of laser light creates the heat source, either in a single pump spot[14,15] or in a transient grating induced by the interference of two pump laser beams[16]. A visible probe beam then interacts with the modified properties of the heated material, displaying a change in reflectance as a function of temperature as the heat dissipates. Visible wavelengths limit these techniques in three ways. First, visible probes will limit sensitivity to nanoscale structures in the same ways as in photoacoustic experiments. Second, the relatively large diffraction limit precludes shrinking the pump absorption area below ~500 nm. Heat source size can only be reduced further by utilizing systems in which only nanostructures absorb pump light[17]. Third, visible wavelengths are sensitive to changes in reflectivity due to electron temperature, material density and changes in surface deformation, leading to an entangled signal requiring a more complex interpretation to account for all the significant dynamics.

To overcome these limitations for precisely characterizing the elastic and thermal properties of ultrathin films and nanostructured systems with << 100nm characteristic dimensions, we implement a non-destructive photoacoustic/photothermal technique that uses coherent extreme ultraviolet (EUV) light from tabletop high harmonic generation (HHG) in place of more conventional visible-wavelength laser sources. The shorter wavelength of EUV beams is sensitive to picometer-scale displacements of the surface regardless of material, while diffraction changes arise only from a deformation of the surface with no contribution from hot electrons. Moreover, the femtosecond duration of HHG pulses is fast enough to capture the sub-picosecond thermal and acoustic dynamics in few-nm structures[18]. As a result, EUV nanometrology using HHG sources offers a novel and unique capability for characterizing the elastic and thermal properties of nanostructured materials.

2. NANOMETROLOGY USING COHERENT EUV LIGHT

In order to study the elastic and thermal transport properties unique to nanostructured systems, we use a pump-probe setup to directly observe their dynamics. We employ periodic gratings of metallic nanowires deposited on dielectric or semiconductor substrates. A femtosecond 800nm laser pump pulse is focused onto the samples to impulsively heat the nanostructures and launch acoustic waves: surface acoustic waves (SAWs) in the substrate with a wavelength set by the grating period, and longitudinal waves (LAWs) within the nanostructures and the substrate. All these dynamics can be monitored simultaneously by diffracting a 30nm-wavelength EUV probe beam from the surface[18,19]. Expansion and cooling of the nano-gratings, as well as acoustic wave propagation, dynamically change the EUV diffraction efficiency. This signal is recorded by a CCD camera as a function of delay time between pump and probe pulses (see Fig. 1).

The nanowire gratings serve several important functions. First, the preferential pump laser absorption in the metallic nanowires creates the impulsive stress needed to excite the acoustic resonances that will probe the mechanical properties of the material layers or components in which they are confined. In particular, they have been used to launch the shortest-wavelength SAWs observed to date (< 45nm)[19], which are fully confined within only the first ~10nm below the surface. Second, the nanowires serve as nanoscale heat sources as small as 30nm in linewidth, and their cooling rates reveal important transitions in the nature of thermal transport over short length scales[4,17,20]. Finally, the nanowire periodicity allows for efficient diffraction of the EUV probe light, enabling the phase sensitivity which yields picometer-scale resolution in the deformation of the surface[21].

3. ELASTIC PROPERTIES OF FEW-NANOMETER FILMS

The acoustic wave velocity in a material is determined by its density and its elastic properties. Thus, by exciting waves of known wavelength – such as SAWs with wavelength matching the nanowire grating periodicity in our samples, or the LAW resonances extending across the thickness of the nanowires themselves – and observing the oscillation frequencies that result, we gain information about the elasticity of the materials in which the different acoustic modes are confined. In the past we have used this technique for complete nondestructive elastic evaluation of isotropic ultrathin films[18,22].

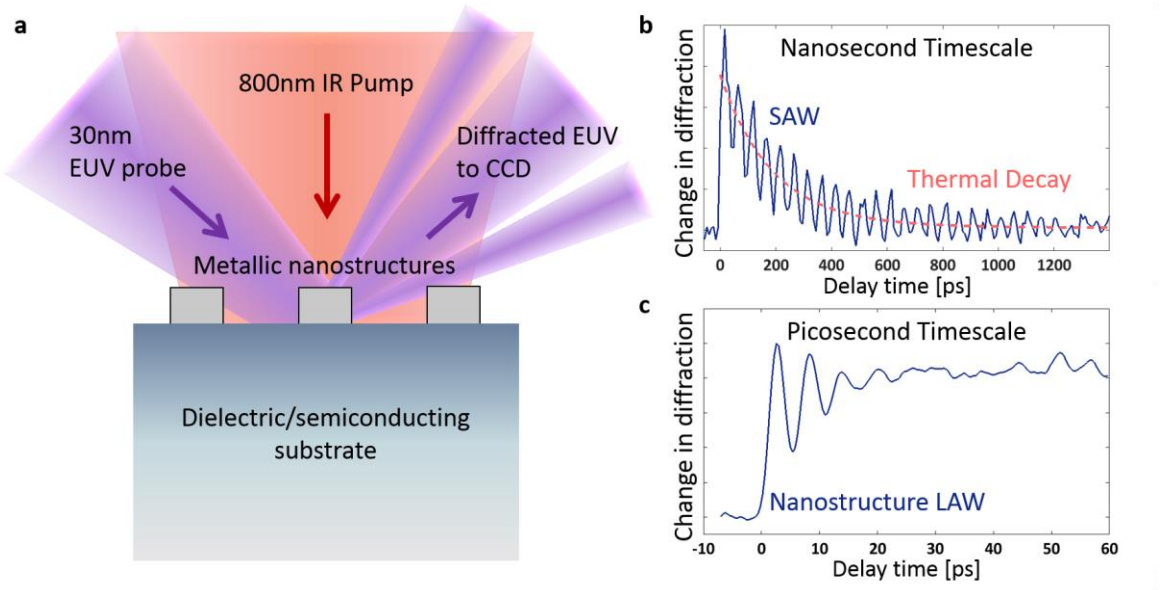

Figure 1. a) Samples consist of metallic nanostructures patterned on a dielectric or semiconducting substrate. The nanostructures absorb a femtosecond infrared pump pulse centered at 800nm, causing an impulsive thermal expansion. After a variable time delay, a 30nm EUV probe pulse diffracts from the excited nanostructures to an X-ray-sensitive CCD camera to track the dynamics of the surface profile. b) On the nanosecond timescale, changes in the diffraction efficiency reveal the thermal relaxation of the system (red dashed line) superimposed with the oscillations of the SAWs launched in the substrate with wavelength set by the nanostructure periodicity (blue solid line). c) In the first tens of picoseconds, the resonant LAW oscillation of the nanostructures is visible.

Here we study a series of tantalum/nickel bilayer nanowire gratings on SiO_2/Si with a constant linewidth of 1 μm (large enough that behavior will essentially be like that of ultrathin films) and 50% duty cycle. The Ni thickness is kept constant at 10nm while the Ta capping layer thickness varies from 1 to 6nm. The changing Ta thickness implies both a change in material volume and a change in mass, which can be detected by a frequency shift in the SAW launched by the periodic grating as mass loading on the surface slows the SAW velocity in the substrate[23]. From this information we can experimentally determine that the nanoscale density ratio between Ni and Ta remains unchanged from that of their bulk counterparts.

The resonant LAW frequency of the nanowires, visible in Fig. 1c, also shifts with changing Ta thickness, analogous to a lengthening organ pipe. From the thicknesses, densities and longitudinal velocities of the Ni and Ta layers, the resonance frequencies can be calculated[24]. However, predictions derived from bulk values for the mechanical properties are significantly different from the actual values observed, as shown in Fig. 2. By instead using the two longitudinal velocities as fit parameters in a least-squares optimization algorithm, we extract the LAW velocities exhibited by the ultrathin layers. Interestingly, we observe that the nanoscale Ni appears significantly slower (or softer) than bulk Ni, while nanoscale Ta appears faster/stiffer than the bulk material, suggesting that the two ultrathin layers may well affect each other such that their elastic moduli become more similar.

While thus far this work has focused on essentially thin film resonant modes, the sensitivity of EUV measurements to both nanowires and nanodots as small as 20nm in linewidth[19] implies this method could be readily extended to the study of materials with two or three nanoscale dimensions. In this way we can study how lateral confinement may further influence the elastic properties exhibited by materials in lithographically patterned nanoscale structures and whether such structures will be influenced by the same mechanisms that dictate the elastic properties of materials grown as nanoscale objects like nanoparticles and nanotubes[25,26].

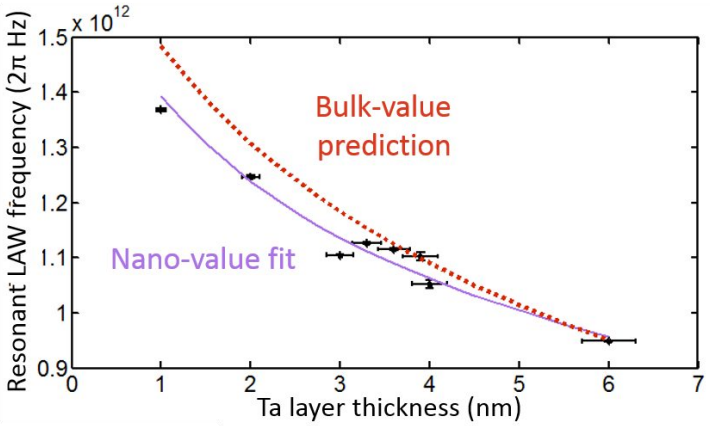

Figure 2. In ultrathin bilayers with 10nm of nickel and 1-6nm of tantalum on a SiO_2/Si substrate, the resonant LAW frequency scales with the overall thickness as open-pipe-type modes (black points). However, prediction based on the bulk properties of the two materials (red dotted line) fails to match the observed frequencies. Fitting the data in a least-squares optimization algorithm allows extraction of the nanoscale longitudinal material velocities in these sub-10nm layers (purple solid line).

4. NANOSCALE THERMAL TRANSPORT

Nanoscale thermal management poses an increasingly important challenge with persistent scaling to smaller components in nanoelectronics, development of thermoelectric devices and nano-enhanced photovoltaics, and the exploration of nanoparticle-mediated thermal therapies in medicine. Yet basic understanding of thermal transport from nanoscale heat sources is still limited. A complete fundamental description of energy flow in materials is still elusive and current theory is hindered by a lack of experimental validation.

Recent work has shown the rate of heat dissipation from a heat source is reduced significantly below that predicted by Fourier's law for diffusive heat transport when the characteristic dimension of the source is smaller than the mean free path (MFP) of the dominant heat carriers (phonons in dielectric/semiconductor materials)[14-17,27]. This is due to a breakdown of the fundamental assumption of heat diffusion: that there are enough collisions between heat carriers to establish local thermal equilibria and a continuous temperature gradient along which energy dissipates. At length scales that are small compared to the phonon MFP, these collisions are no longer likely to occur, and the concept of a continuous temperature gradient no longer applies. Furthermore, a gradient approximated by a large temperature difference over a small distance clearly results in the prediction of unphysically fast heat diffusion. Thus the true rate of heat dissipation as thermal transport transitions into a ballistic regime will be significantly lower than the diffusive prediction. To complicate matters more, heat-carrying phonons in materials have a wide distribution of MFPs, from several nanometers to hundreds of microns. For a given heat source size, phonons with MFPs shorter than the hot spot dimension remain fully diffusive and contribute to efficient heat dissipation and a high thermal conductivity (or equivalently, a low thermal resistivity). In contrast, phonons with long MFPs travel far from the heat source before scattering, with an effective thermal resistivity far larger than the diffusive prediction. Phonons with intermediate MFPs fall in between: heat transport is quasi-ballistic with varying degrees of reduced contributions to the conduction of heat away from the nanoscale source.

The thermal decay component of the signals from our samples shown in Fig. 1b serves as a direct measurement of the rate of heat dissipation from heat sources ranging in size from 750 to 30nm with periodicity set to 4 times the linewidth. Here, the use of nano-patterned metal structures rather than visible laser absorption on a uniform surface allows us to explore heat sources much smaller than the diffraction limit of visible light.

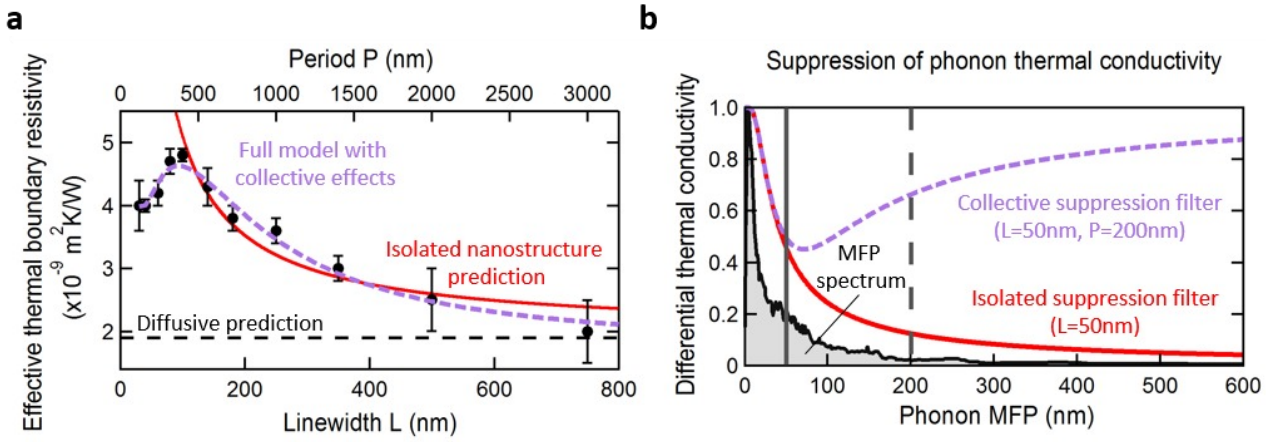

Figure 3: a) By fitting the thermal decay visible in the dynamic EUV diffraction signal to a model of diffusive heat transport with a varying effective thermal boundary resistivity, r_{eff}, we quantify the deviation from diffusive predictions (black dashed line) for a series of nickel heat source linewidths on a sapphire substrate. Initially the deviation increases with decreasing linewidth. However, once the heat source period becomes comparable to the average phonon MFP in sapphire, we observe a recovery toward the diffusive prediction. Only the initial rise in r_{eff} can be explained by a model of isolated nanoscale heat sources (red solid line). By accounting for the collective effects allowed by nearby heat sources, we can fit the whole range of observations (purple dashed line) b) The trends in r_{eff} can be explained by the interplay of the differential thermal conductivity spectrum of phonon MFPs in sapphire (grey spectrum) and the effective suppression filter introduced by various heat source geometries. A small, isolated heat source will suppress the contributions to thermal conductivity of phonons with MFPs larger than its linewidth L (red solid line). But if the period P is also small, it will modify the suppression filter and reintroduce the contributions of phonons with MFPs larger than P (purple dashed line).

Most work to date explored the reduction in heat transport from functionally isolated micro- and nanoscale heat sources[14-17,27]. However, by extending our measurements to heat sources of unprecedented small size and spacing, our experiments reveal that heat source size is not the only relevant length scale to consider.

4.1 Non-diffusive transport from closely-spaced nanoscale heat sources

We uncovered a new regime of nanoscale thermal transport, occurring when the separation between nickel nanostructures on a sapphire substrate is smaller than the phonon MFP (see Fig. 3)[4,20]. Decreasing the size of an isolated heat source would imply a steadily rising effective thermal boundary resistivity, r_{eff}, as diffusive theory progressively over-predicts the rate of heat transfer away from the source (red curve). However, the peak and subsequent return toward lower r_{eff} that we observe marks the transition to this new regime where the spacing of heat sources begins to dominate the thermal transport. In this case, close proximity between neighboring heat sources counteracts the quasi-ballistic reduction in heat dissipation from individual sources, to such an extent that the collective behavior restores heat transfer efficiency to near the diffusive limit.

This surprising result can be understood through the schematic illustrated in Fig. 3b. The linewidth L and period P of the heat sources define the location and width of an effective filter that suppresses the contributions to the total thermal conductivity of those phonon modes with MFP falling between L and P. Thus, when only L decreases, an increasing number of phonon modes are suppressed relative to the diffusive prediction due to the lack of collisions close to the heat source, resulting in the rise in effective boundary resistivity[17]. But when P is also decreased, phonons originating from neighboring heat sources can interact as though they had originated from one large heat source. Thus long-MFP modes can be reintroduced, resulting in the recovery in heat dissipation efficiency at small L that we observe in samples of constant duty cycle $P = 4L$[4,20].

Whenever the MFP-dependent thermal conductivity is known for a given substrate material (either from theoretical calculation or experimental measurement), one could exploit the phonon filtering effect by selecting *L* and *P* to filter in or out specific portions of the spectrum, thus tuning the heat dissipation efficiency. In particular, this implies that this new 'collectively-diffusive' regime could be used to mitigate scaling problems for thermal management in nano-systems by placing small heat sources close enough together for their interactions to favor heat dissipation into the substrate.

4.2 Measuring phonon mean free path spectra

While methods have recently been developed for calculating the MFP-dependent phonon thermal conductivity in simple materials[5,28], the importance of these spectra for determining heat transfer in nanostructured systems demands experimental validation of theoretical calculations and a measurement technique that can also be used for more complex materials. The direct relationship between the new 'collectively-diffusive' thermal transport regime we discovered and the particular phonon spectrum of the substrate materials suggests that it can be applied as a new approach to MFP spectroscopy.

As illustrated in Fig. 3b, the heat source linewidth and period define a particular suppression filter in the phonon MFP spectrum. By observing the effective conductivity suppression for a series of linewidth-period pairs, we can thus map out the contributions to total thermal conductivity of all the different regions in the spectrum. Furthermore, because of the sensitivity of EUV nanometrology to a wide range of heat source sizes and periods down to dimensions well below 100nm, this technique enables for the first time characterization of these differential phonon MFP spectra, to date extending down to MFPs of 14nm[4].

5. CONCLUSIONS

We have demonstrated several unique capabilities of EUV nanometrology for the characterization of materials in nanostructured systems. With its sensitivity to the acoustic dynamics imprinted in picometer-scale displacements of a surface coated with ultrathin bilayers of nickel and tantalum, it allows us to measure the density and elastic properties of these materials confined to sub-10nm thickness. Furthermore, by exploiting its sensitivity to the dynamics of structures with unprecedented small size and spacing, we discovered the new collectively-diffusive regime of nanoscale thermal transport. Through systematic observations of this new regime, we demonstrated how EUV nanometrology enables new access to information about the phonon MFP spectra of materials with the detail necessary to make predictions about heat dissipation in nanostructured systems. While technological development continues to push the boundaries of device size ever more deeply into the nano-regime, new metrology tools like this one will become increasingly important for discovering the new physics which dominates at small size scales, for exploring how materials behave in ever smaller layers and structures, and for monitoring the consistency of those processes used to fabricate nanostructured devices.

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