Modification of vibrational damping times in thin gold films by self-assembled molecular layers

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The mechanical contact between a thin gold film and a silicon substrate is investigated by ultrafast pump-probe spectroscopy providing quantitative values on the damping time of coherent longitudinal vibrations of the gold film. A distinct increase in damping times is observed when a self-assembled molecular layer is introduced between the gold film and the substrate. We deduce the frequency dependence of the damping times by varying the thickness of the gold films. Experimental results are compared to numerical simulations based on a visco-elastic model and the acoustic mismatch model. © *2011 American Institute of Physics*. [doi:10.1063/1.3604790]

Heat transfer at the nanoscale is a topic which attracted a lot of attention during the last decade due to the continuous downscaling of electronic devices.[1] Self-assembled monolayers of molecules are also of growing importance in nanotechnology where they can be used as versatile tools in engineering of thermal and electrical contacts on the nanoscale, e.g., to immobilize DNA,[2] nanoparticles,[3] and for the assembly of devices based on molecular electronics.[4,5] Especially, for the latter, a fundamental understanding of the thermal transport properties is required.

We apply an ultrafast pump-probe method to investigate the influence of self-assembled molecular layers (SAMs) at the interface between gold films and silicon substrates on the mechanical energy transfer. In the case of thin gold films, the vibrational mode damping in these films has been shown to be highly sensitive to interfacial layers and ion implantation of the substrate.[6,7] We extend these studies to the influence of SAMs at a metal-semiconductor interface.

Ultrafast pump-probe experiments are performed using high-speed asynchronous optical sampling. Details are published elsewhere.[8,9] All experiments are carried out in reflection geometry with pump and probe powers of 400 mW and 6 mW, respectively. The diameters of the laser spots on the sample are about 50 μm and the wavelength of pump and probe beam is set to 790 nm and 815 nm, respectively.

In order to study the effect of self-assembled molecular layers at interfaces, four different types of layered systems are investigated in this paper: For sample type (a), the films are evaporated directly onto the bare silicon substrate, while for sample type (b), the native silicon oxide layer is present. In samples of types (c) and (d), two different SAMs are introduced at the Au/Si interface. Two types of molecules are used: octadecyltrichlorosilane (OTS, sample (c)) and 3-aminopropyltriethoxysilane (APTES, sample (d)). Both molecule types are known to form self-assembled molecular

layers on silicon substrates.[10,11] All samples are prepared on Si(100)-wafers, which are cleaned by the standard Radio Corporation of America procedure.[12] The gold films are deposited by thermal evaporation.

The samples without SAMs are prepared in two different ways: For layer system (a), silicon wafers are dipped in 1% hydrofluoric acid for 2 min in order to remove the native oxide. Consequently, the corresponding layer system consists of a gold film and the silicon substrate (denoted as Au/Si sample). For layer system (b), silicon wafers are cleaned additionally with an oxygen plasma for 5 min, leaving the thin native SiO$_2$ layer and resulting in Au/SiO$_2$/Si samples.

For layer systems (c) and (d) with SAMs, the silicon wafers are prepared as for sample (b). Subsequently, the SAMs are prepared in a nitrogen atmosphere by submerging the wafers into a molecule solution for approximately 48 h. The molecule solution consists of 60 ml toluene with 15 μl of the molecule (OTS or APTES). Afterwards, the samples are processed for 5 min in chloroform in an ultrasonic bath. In order to remove residual molecule conglomerates a carbon dioxide snow jet method[13] is applied. After these preparation steps, the gold films are evaporated on the SAMs. In the following, the two layer systems are indicated as Au/OTS/Si and Au/APTES/Si.

In Fig. 1, the transient reflectivity change of an Au/APTES/Si sample with 23 nm gold film thickness is displayed. The peak at zero time delay originates from the electronic contribution to the change in reflectivity and is caused by the ultrafast heating of the electron gas in the gold film by the pump pulse.[14,15] Clearly visible are superimposed decaying oscillations, which show the acoustic contribution to the change in reflectivity. The energy deposited in the film by the pump pulse establishes an impulsive thermal stress, which causes the film to vibrate in its fundamental thickness mode. Although the film thickness exceeds the optical penetration depth of around 13 nm for most of the samples, hot electron diffusion during the generation process[21] causes the films to be excited homogeneously. The stress distribution present in the gold film changes the reflectivity of the film.[6,7] Because the acoustic impedance mismatch between the gold

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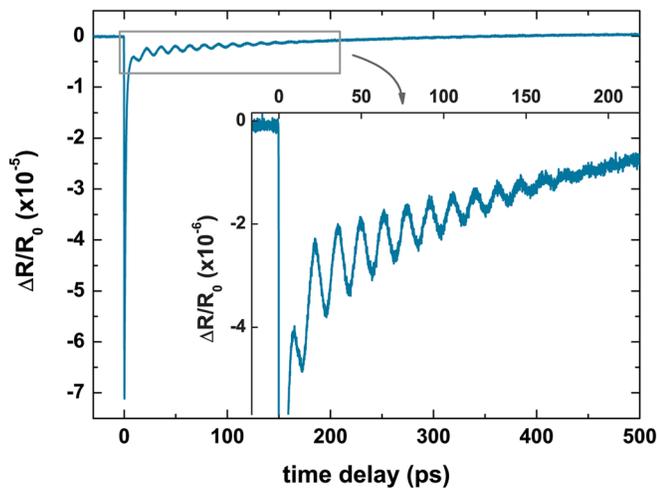
FIG. 1. (Color online) Typical transient obtained from a Au/APTES/Si sample showing the temporal modulation of the reflected probe beam. The oscillations are plotted at a larger scale in the inset.

and the substrate is large, the oscillation can be described as that of a free-standing membrane, i.e., the film thickness d and oscillation frequency f are related by $f \approx v_l/2d$ with v_l the longitudinal sound velocity. We obtain the oscillations for all four layer systems by subtracting the electronic background. These are displayed (blue, thick lines in the background) in Fig. 2(a)–2(d). The gold film thickness is around 25 nm in all cases. In order to determine the damping time of the thickness oscillation, the transients are fitted (red, thin lines in the foreground) by using the sum of two exponentially damped sine waves, accounting for the effect of the beating between the Au film vibration and a weaker additional oscillation due to Brillouin scattering in the silicon substrate.[16,17] The Brillouin scattering is most pronounced in

the Au/SiO$_2$/Si system, where the low adhesion between the gold film and the SiO$_2$ causes the gold film to be not fully closed.[18]

From Fig. 2, it is evident that a change in damping times occurs when the interface between the gold film and the silicon substrate is modified. The smallest damping time is observed for the Au/Si system displayed in panel (a). A slight increase occurs when the native silicon oxide layer is present at the interface. Adding a molecular layer at the interface causes a distinct increase in damping times as is evident from the data displayed in panels (c) and (d). Furthermore, a difference between the two types of molecular layers can be observed.

Another intriguing question is how the damping times depend on the resonance frequency of the Au films. We investigated the frequency dependence of the damping times for all four layer systems by measuring samples with film thicknesses ranging from 10 nm to about 30 nm. The results are depicted in Fig. 3. The data points with black borders correspond to the values extracted from the transients displayed in Fig. 2.

For sample type (a), Au/Si (pentagons), we observe the smallest damping times over the whole measured frequency range. A slight increase of damping times occurs for the Au/SiO$_2$ system (triangles) for all frequencies. While measurements at different positions on each sample show a relatively broad scattering of about ± 8 ps, for the damping times of the Au/SiO$_2$/Si layer system, the Au/Si system exhibits excellent reproducibility. This is due to the enhanced adhesion of the gold films to the substrate when the native silicon oxide is removed.[18] Therefore, the Au/Si system is set as reference system for comparison of the obtained damping times. In the low GHz regime, a strong increase in damping times by a factor of
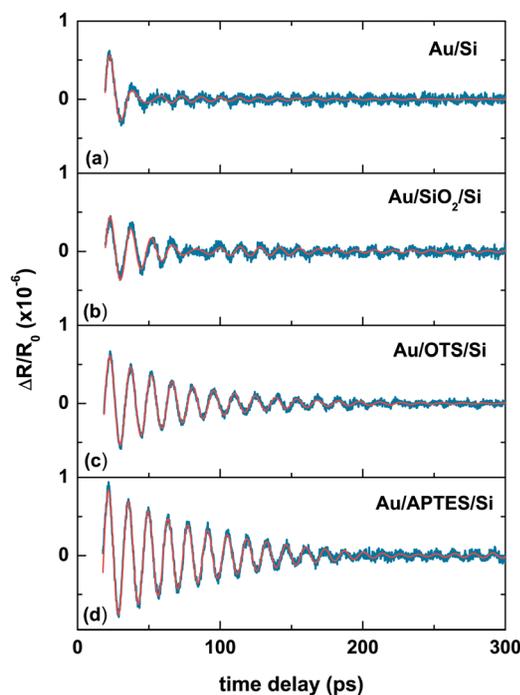

FIG. 2. (Color online) Extracted oscillations (blue, thick lines in the background) from time domain data for all four layer systems and their respective fits (red, thin lines in the foreground).
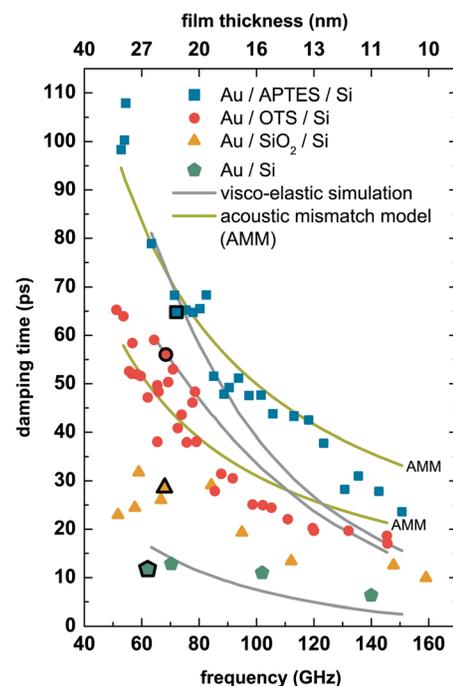

FIG. 3. (Color online) Frequency dependence of damping times of vibrational modes in thin gold films for four different layer systems. The grey lines indicate the results from visco-elastic simulations and green lines (labelled with AMM) are the results obtained from the acoustic mismatch model.

about 6 of the Au/OTS/Si system compared to the Au/Si system is evident. The Au/APTES/Si system shows an even higher increase by a factor of about 10 at these frequencies. In the higher GHz range, the increase with respect to the reference system for both molecules becomes smaller but is still a factor of 2 and 3, respectively. The increase of damping times for all frequencies clearly demonstrates the reduced mechanical coupling of the Au film to the substrate.

A visco-elastic model[19] is applied to simulate the frequency dependence of the observed damping times. The material properties of the gold film and the silicon substrate are kept constant for all frequencies. The best fit to the experimental data is obtained with an interface layer thickness of 2 nm and Young's moduli of the APTES layer of $E_0 = 2.2$ GPa and $E_\infty = 40.2$ GPa with a Poisson ratio $\mu = 0.4$. Here E_0 and E_∞ denote the Young's moduli for high and low frequencies, respectively. This is in agreement with ellipsometry measurements which indicate a layer thickness from 1 up to 4 nm for different samples, corresponding to 1-4 molecule monolayers. The best fit for the OTS layer is achieved with a thickness of 2 nm, Young's moduli of $E_0 = 2.22$ GPa, $E_\infty = 44.4$ GPa, and $\mu = 0.44$. For this analysis, we used the densities 0.946 g/cm^3 and 0.984 g/cm^3 for the APTES and OTS layer, respectively. As can be seen from Fig. 3, the qualitative behavior is well described by adapting the respective elastic moduli and density of the molecular layers. The results are also compared to calculations based on the acoustic mismatch model,[7] denoted as green lines (labeled with AMM) in Fig. 3. Here an interesting fact arises: although the molecular layers consist of a few monolayers only a massless spring model[7] fails to describe the results. However, treating the molecular layer as a continuous film with an acoustic impedance Z_{mol} as free parameter in a least squares fitting routine yields a good qualitative agreement to the observed frequency dependence.

The obtained results demonstrate that the SAMs drastically change the mechanical energy transmission of the interface in the layer systems. The studied SAMs differ in chain length and in their chemical end group, so they form molecular layers with a differing internal structure.[11] This could affect the elastic properties of the molecular layer.

In conclusion, we have presented time-resolved investigations of the influence of self-assembled molecular layers embedded between silicon substrates and gold films on the mechanical energy transfer. A systematic characterization of the vibrational damping times for various frequencies reveals distinct changes between the studied molecules. The experimental data are modeled in good qualitative agreement by a visco-elastic simulation as well as an acoustic mismatch model. These results demonstrate the sensitivity of picosecond ultrasonic measurements to sub-nanometer interface layers and open up new possibilities for the characterization of embedded molecular layers, the study of their elastic properties, and heat conductance as a function of temperature and pressure.[20]

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