Temperature dependent elastic properties and glass transition of nanometric PMMA films by picosecond ultrasonics

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Background – Temperature dependent properties of polymer materials are crucial informations for many applications. A prime example is the glass transition observed between the glassy and rubbery state in polymeric materials. Despite the many developments to measure these quantities in a wide variety of systems from bulk to nanometric films complementary techniques are still of interest in the advent of newly emerging hybrid materials. The idea to use picosecond ultrasonics as a tool for monitoring temperature dependent properties and in particular the glass transition was proposed [1] already early in the beginning of the field. However, only just recently first demonstrations [2-3] emerged. Here, we want to add another approach to the toolset of picosecond ultrasonics that allows to determine the glass transition temperature in soft materials and yields information about temperature dependent film properties.

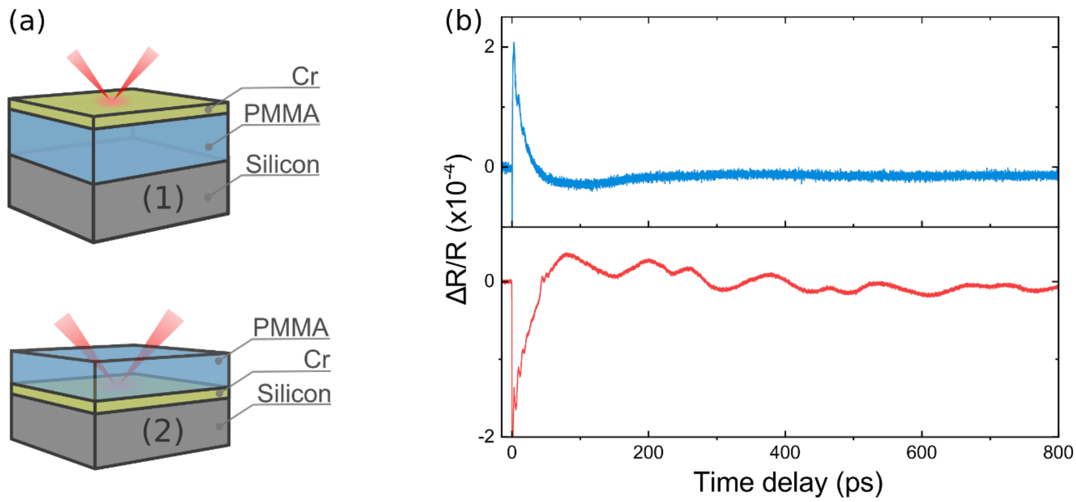

Fig. 1. a) Sketch of sample geometries b) Corresponding time domain signals

Methods – We employ picosecond ultrasonics, based on a femtosecond-resolved pump-probe method, to the investigation of thin PMMA films with thicknesses ranging from 458-32nm. The pump-probe scheme is realized by asynchronous optical sampling. We tested two different sample configurations aiming at different working regimes: pulse-echo and acoustic eigenmode characterization. The thickness of the spin-coated PMMA films was additionally measured by ellipsometry. Chromium thin films were added to the sample structure by thermal evaporation as opto-acoustic transducers.

Results – As an initial step we compared the signal of the two sample configurations in Fig. 1(a) and (b). We found no clear indication of measurable pulse echoes in configuration I but strong oscillatory components for configuration II. These correspond to the longitudinal acoustic eigenmodes of the PMMA films. In a next step we tracked the individual modes during temperature dependent measurements, i.e. heating of the sample above the expected glass transition temperature. We found a distinct shift of the modes towards lower frequencies and a kink in the temperature-frequency slopes as a direct indicator for the glass transition temperature for all PMMA thicknesses. WE supported these findings by a further analysis based on the assumption of a negligible influence of thickness changes below the glass transition temperature. Additionally the observation of higher order modes provides a convenient way to cross check obtained fitting result of the data.

Conclusions – We observed closed organ pipe modes in thin PMMA layers and tracked their temperature dependent behaviour across the glass transition temperature. The glass transition is observable by a kink in temperature-frequency slopes. We also discuss the current issues in this configuration arising from spurious heating and difficulties arising in the data evaluation due to mode shifts and possible improvements to the presented methodology

References

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