Nano-scale effects on Young’s modulus of nanoimprint polymers measured by photoacoustic metrology

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Abstract. The ultrashort laser pulse photoacoustic method has been used to characterise the physical properties of spin-coated PMMA layers onto Si wafers with thicknesses from 586 to 13 nm. Acoustic speeds of polymer films were derived from the measured time of flight of acoustic waves in polymers and from their calculated visco-elastic properties. A 12% increase, in comparison to the PMMA bulk value, of the acoustic speeds was measured for polymer films with thicknesses below 80 nm, which corresponds to an increase in Young’s modulus of 26%. In addition, we found that adding a hexamethyldisilazane primer monolayer between the polymer film and the Si substrate lessen the increase in Young’s modulus, suggesting that the nanoscale changes are due to interface effects.

1. Introduction
Nanoimprint lithography (NIL) is an alternative high resolution, low cost, lithography method for fabricating structures with features as small as ten nanometers [1], by using a rigid stamp to pattern thin polymer films [2]. NIL has been proposed as an alternative lithography technique for the 32 and 22 nm nodes of the International Technology Roadmap for Semiconductors (ITRS) [3]. Alternatively, the imprinted layers can be used directly for various devices such as photonic crystal structures [4], fluidic channels [5]. Physical parameters such as Young’s modulus and glass transition temperature of printable polymers, dictate the optimum temperature, pressure and time required for reliable pattern reproduction, as well as determining the stability of the polymer structures that are produced [6].

Most measurement techniques and parameter values used for nanoimprinting are taken from bulk processes. However, physical properties of polymers can change significantly at thicknesses less than 100 nm due to the increased importance of surface and interface effects [7]. For instance the most commonly observed effect due to nanoscale dimensions in polymers is a change in the glass transition temperature, $T_g$, measured using ellipsometry to detect a change in the thermal expansion. For free-standing polystyrene films, and those on a Si substrate, a decrease in $T_g$ of up to 80K has been measured for 20 nm thick films compared to the bulk value [9, 10].

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We have shown that photoacoustic metrology is a suitable method to characterize nanoimprint layers both physically and dimensionally on the nanometer scale [8], complementing established techniques such as scanning electron microscopy and atomic force microscopy. The entire experimental setup is simulated numerically, and the laser acoustic measurements are compared with ellipsometry measurements in order to quantify the mechanical properties of the polymer films.

2. Experimental
The current measurements are performed with a pump probe setup (Figure 1) which is described fully by Vollmann et al [11]. The laser beam (pulses <100 fs, repetition rate 81 MHz, wavelength 800 nm) is split into a pump and a probe beam for excitation and detection, respectively. The acoustic wave is generated by absorption of the laser pulse in a covering layer of aluminium, of between 30 and 60 nm (+/-2 nm), grown by e-beam assisted evaporation. This is sufficiently thick to fully absorb all of the light. The acoustic waves, partially reflected from each interface, are recorded at the surface by a slight change of the reflectivity.

3. Viscoelastic material model
Numerical simulations are performed using the finite difference (FD) method. The temperature distribution in the top metal layer heated by the laser pulse is calculated with a two temperature model [12]. The propagation of the wave packets is calculated using a viscoelastic material model, providing the temporal and lateral distribution of strain and stress. The optical reflectivity change at the surface \( \Delta R(t) \) is calculated from the strain distribution \( \varepsilon(z, t) \). The viscoelastic model describes the material as elastic, with a damping effect characterized by an attenuation coefficient of approximately 21,000 cm\(^{-1}\), which has been calculated previously using samples of thickness between 300 – 600 nm [13].

4. Results and Discussion
Photoacoustic measurements were made on samples of PMMA (mr-I PMMA75k300, provided by Micro Resist Technology GmbH) of thickness from 586 to 13 nm; with thicknesses measured by ellipsometry. Figure 2 shows the measured reflectivity change from a 51 nm thick polymer sample. The measurement is begun at 30 ps before the arrival of the pump laser pulse, to ensure that the full photoacoustic signal is recorded, and due to the fact that for this first 10 ps it is very difficult to estimate the temperature influence on the reflectance change, which has to be subtracted in order to get the pure acoustic contribution to the reflectance change. The absolute position of time zero is not important, as the calculation of acoustic speed is based on the difference between the time of arrival of the first reflection from the bottom of the Al layer and the bottom of the polymer layer. For thin polymer films, due to superposition of the peaks from the PMMA/Al and PMMA/Si interfaces, the acoustic speed is calculated by comparison with a curve generated using the FD model of viscoelastic wave propagation, with the attenuation value calculated previously from thick samples [13]. At less than 80 nm thickness, the acoustic speed increases, by approximately 12% on average, above the bulk
value calculated at thicknesses greater than 100 nm (Figure 3(a)). Corresponding values of Young’s modulus are obtained by fitting the data to curves generated using the FD model, and by assuming that the Poisson’s ratio and density remain constant [14, 15].

Figure 2. Measured Photoacoustic data from 51 nm thick sample, showing signal from the aluminium-polymer interface (blue circles) and from the polymer-silicon interface (red diamonds).

Corresponding values of Young’s modulus are obtained by fitting the data to curves generated using the FD model, and by assuming that the Poisson’s ratio and density remain constant [14, 15]. Previously, changes in Young’s modulus and stiffness have been found to be due to the greater number of molecules at surfaces and interfaces, when dimensions are reduced, rather than to a change of density which is not significant [15].

The values of the modulus as a function of thickness are presented in Figure 3(b), showing an increase of up to 26% on average above the PMMA bulk value.

Figure 3. (a) Acoustic speed and (b) Young’s modulus as a function of thickness (including moving average trendlines)

Samples were then coated with a monolayer of Hexamethyldisilazane (HMDS) primer before spin-coating of the PMMA, with the result that the increase in the measured value of acoustic
speed (Figure 4), was less (5% increase in acoustic speed, 11% increase in Young’s modulus) than for those samples without HMDS. This may be due to the reduction in surface energy by adding HMDS, and suggests that the increase in acoustic speed is due to the greater importance of the interaction of molecules with the interfaces of Si and Al, rather than due to confinement of the PMMA molecules, whose radius of gyration is approximately 7 nm, much less than the dimensions at which nanoscale effects are observed (80 nm).

Figure 4. (a) Acoustic speed and (b) Young’s modulus measured with and without a layer of HMDS.

5. Conclusion
Photoacoustic metrology has been used to measure an increase in Young’s modulus above the bulk value for film thicknesses below 80 nm, of approximately 26% on average. This is probably due to the increased importance of interface effects at nanoscale dimensions, since a smaller increase is measured if the samples are coated with a primer layer. These results have implications in NIL processes development, in which polymers are forced into dimensions of the range of tens of nanometres, and may impact upon the materials and surface treatments used for the substrate and stamp.

Acknowledgements: The authors would like to acknowledge the financial support of the EC-funded project NaPANIL (Contract No. NMP2-LA-2008-214249)

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