Contact Resonance Force Microscopy (CR-FM) is a leading AFM technique for measuring viscoelastic nanomechanical properties. Conventional piezo-excited CR-FM measurements have been limited to imaging in air, since the "forest of peaks" frequency response associated with acoustic excitation methods effectively masks the true cantilever resonance. Using photothermal actuation results in clean contact resonance spectra, that closely match the ideal frequency response of the cantilever, allowing unambiguous and simple resonance frequency and quality factor measurements in air and liquids alike. This extends the capabilities of CR-FM to biologically relevant and other soft samples in liquid environments. We demonstrate CR-FM in air and water on both stiff silicon/titanium samples and softer polystyrene-polyethylene-polypropylene polymer samples with the quantitative moduli having very good agreement between expected and measured in both environments.
In contrast to the clean single contact resonance peak obtained by photothermal actuation, the shape of the contact resonance peak obtained with piezoacoustic actuation is plagued by the “forest of peaks.”

Figure 2 shows a 5 µm × 10 µm area of a titanium film evaporated on silicon sample that was first imaged in air and subsequently in water; both images were acquired using photothermal excitation.

Topography images (figures 2a and 2a’) reveal ~200 nm high, rough titanium stripes on a smooth silicon surface. The contact resonance frequency (figure 2b) is higher (~290 kHz) on silicon surface in comparison to titanium (~280 kHz), which correlates well with the expected higher silicon stiffness. The frequency contrast remains the same (higher on silicon, lower on titanium) regardless of the imaging conditions (air or water). Images of Q factor values, associated with energy dissipation, are shown in figures 2c and 2c’. Q values observed on titanium were higher than those measured on silicon. The expectation for the energy dissipation to be lower on silicon was not observed in our experiments. Squeeze-film damping due to the ~200 nm height difference between the silicon and titanium and other considerations beyond the scope of this work may effectively lower the Q values observed on silicon.

Calculated storage moduli (E’) of silicon and titanium, in air and water, are shown in figure 2d and 2d’. The results presented here were obtained using internal calibration approach where silicon was chosen as the reference material and its median E’ value was assumed to correspond to 165 GPa. The expected and calculated E’ values for all the materials studied are summarized later in the text, in table 1.

Next, we measured a soft “ternary” blended polymer composed of polypropylene (PP), polyethylene (PE), and polystyrene (PS) with expected moduli ranging between 2 and 3 GPa (see Table 1) using photothermal CR-FM in air and water. Figure 3a shows the air topography of the sample. The topography image acquired in water (figure 3a’) shows improved imaging resolution presumably due to reduced tip-sample adhesion.
The contact resonance frequency values shown in Figures 3b and b’ were highest on PS and lowest values on PE, as expected. Figure 3c and c’ show the Q factor images. PS inclusions are well distinguished from PE and PP domains, however, the two latter components show very little contrast between each other, indicating their relatively similar dissipation. Figure 3e, compares histograms of $E'$ values calculated from the images performed in air and in water, clearly differentiating the three components.

As with the stiffer sample, an internal standard was used for the polymer, where the matrix material (PP) was set to be the reference standard with $E'$ of 2.5 GPa. Images showing the calculated storage moduli and the associated histograms for each component are shown in Figures 3d, 3d’ and 3e. Table 1 summarizes all of the calculated storage moduli for the materials investigated in this study, in air and water. The three components of the sample were clearly distinguished between each other and their storage moduli exhibited the same elasticity trend as reported previously where PE < PP < PS.

The agreement between the previously reported values and the results shown here demonstrate the efficacy of photothermal actuation for CR imaging. Both stiff (silicon/titanium) and softer materials (polymer blend) were successfully imaged and analyzed providing storage moduli values using CR-FM with photothermal excitation. Strong contrast was observed in the frequency data when imaged in water, even for very similar materials. In the future, quantitative CR-FM maps of biological tissues may prove valuable for cells, proteins and biomaterial engineering of materials, such as implants, that are primarily used in liquid settings.

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