Fabrication and Characterization of Glassy Carbon MEMS

Olivier J. A. Schueller, Scott T. Brittain, Christian Marzolin, and G. M. Whitesides*

Harvard University, Department of Chemistry and Chemical Biology, 12 Oxford Street, Cambridge, Massachusetts 02138

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This paper describes the fabrication of free-standing high-carbon microstructures by soft-lithographic techniques; these structures ranged in complexity from simple beams to complex, suspended deflectors. Microstructures of polymeric precursors (copolymers of furfuryl alcohol-phenol) to high-carbon solids were fabricated using poly(dimethylsiloxane) (PDMS) molds. Carbonization of these microstructures under argon resulted in mass loss (up to 45%) and shrinkage (up to 20% linearly); the density increased to reach a plateau value of ~1.5 g/cm³ at ~900 °C. Microstructures pyrolyzed at 900 °C were electrically conductive, with a conductivity of ~10⁻² Ω cm. Elementary microelectromechanical functions were demonstrated in these microstructures: electrostatic actuation induced deflection or vibrations of suspended structures. The measurement of the frequency of resonance of high-carbon cantilevered beams allowed the determination of Young’s modulus for the solid: typical values were ~15–20 GPa. The microelectromechanical properties of more complex structures (microresonators, light deflectors) were also determined. This paper demonstrates that high-carbon microstructures can be easily fabricated that have potential use as the active components of MEMS.

Introduction

This paper describes the preparation and characterization of carbon microelectromechanical systems (MEMS) fabricated by procedures based on micromolding of a polymeric precursor to form the carbon structure, followed by thermal treatment to give it the desired electrical and mechanical properties. This procedure is very different from that used in silicon structure, in which a polymeric precursor is used to form the carbon structure, followed by micromolding in capillaries (MIMIC), or in which micromolding in capillaries (MIMIC) is followed by thermal treatment to give it the desired electrical and mechanical properties.

We have previously developed a wide array of techniques for the fabrication of microscopic and nanoscopic structures in organic polymers: these techniques include microcontact printing (μCP) on planar and curved substrates, micromolding in capillaries (MIMIC), and microtransfer molding (μTM). We have also demonstrated methods for rapid prototyping of these structures. Here we describe the application of this set of techniques to the preparation of microstructures of polymers that are precursors to high-carbon solids, and the successful conversion of these polymers to functional high-carbon solids at high temperatures (400–1800 °C) under an inert atmosphere. The resulting microstructures can be either free-standing or supported. The overall shape of the microstructures is retained during carbonization, but the physical, mechanical, and chemical properties of these solids are strongly and controllably influenced by the heat treatment.

We are especially interested in the fabrication of microstructures of glassy carbon. Glassy (or vitreous) carbon is typically a hard solid prepared by heat-treatment at elevated temperatures (1000–3000 °C) of polymer precursors such as copolymer resins of phenol–formaldehyde or furfuryl alcohol–phenol. These polymers are used because of their high carbon yield on pyrolysis (the ratio of carbon present after/before carbonization is ~50%). The physical properties of glassy carbon make it a potential candidate for the preparation of MEMS. It is isotropic, electrically conducting, and impermeable to gases and has a low coefficient of thermal expansion. Glassy carbon has a lower density (1.3–1.5 g/cm³) than graphite (2.27 g/cm³) or diamond (3.52 g/cm³); this density reflects its porous microstructure. The voids constituting the pores are, however, not connected; this fact accounts for the low density of glassy carbon.

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gas permeability observed for that material. Carbon is thermally stable in a non-oxidizing environment at temperatures higher than 3000 °C. Because of its high corrosion resistance and inertness under a wide variety of conditions, glassy carbon is used in extremely corrosive environments (for example, in crucibles for the decomposition of ores in analytical chemistry). Glassy carbon is also widely used as an electrode material for electrochemical applications.\(^{(15-18)}\) It resists strong acids and bases and is inert over a wide range of electrical potentials.\(^{(19)}\) The surface chemistry of glassy carbon allows tailoring of its interfacial properties (surface energy, electron-transfer kinetics) by physisorption or chemisorption of molecules, polymers, or metals, or by procedures involving electrochemical pretreatments, polishing, or laser activation.\(^{(16-19)}\) Sensors and biosensors have been prepared by immobilization of recognition elements and enzymes on the surface of glassy carbon electrodes.\(^{(20)}\)

Glassy carbon structures could be used in lieu of silicon in applications where lightweight, high chemical resistance to strong bases, or thermal stability are required properties. The lower Young's modulus of glassy carbon (10-40 GPa)\(^{(24)}\) compared to that of silicon (190 GPa for monocrystalline silicon, 40-170 GPa for polysilicon)\(^{(25)}\) can be an advantage in applications where the brittleness of silicon is a limiting factor, or where the extreme stiffness of silicon is a disadvantage (for example, in electrostatically driven actuators). Furthermore, silicon surfaces have a high surface energy since they are covered with a 10-20 Å thick native oxide layer. Surfaces with high free energies will be subjected to capillary forces when in close proximity. Stiction—what is, the adhesion between two surfaces—depends on van der Waals, electrostatic, and capillary forces.\(^{(21)}\) The contribution of capillarity accounts for most of the forces responsible for stiction. Stiction often limits the performance of MEMS: once two surfaces are in contact, only a restoring force can separate them. The density of oxygen-containing, polar surface functional groups is lower on carbon (typically 2-10%) than on Si/SiO\(_2\). The ability to functionalize the surface of oxidized carbon further to introduce hydrocarbon or fluorocarbon groups offers a route to materials with very low surface free energies and low potential for stiction.\(^{(16,21,22)}\) The relatively rough surface of carbon solids (relative to silicon etched along a crystal face) may also prevent stiction since the true area of contact between rough surfaces is smaller than between smoother surfaces.\(^{(23)}\)

This paper is organized in two parts. In the first part, we describe the fabrication of structures and microstructures of various degrees of complexity. In the second part, we report initial testing of the microelectromechanical properties of these structures.

### Results and Discussion

**Fabrication of Microstructures.** MEMS are typically prepared from silicon or occasionally from other materials (gallium arsenide, metals, glasses, ceramics, or plastics) by microfabrication techniques that have been exhaustively developed in the integrated circuit industry.\(^{(7)}\) These techniques rely heavily on photolithography and selective etching procedures and therefore require the design of chrome masks, access to a clean room, and use of other facilities used in microfabrication. We have relied on the less expensive soft-lithographic techniques that we have developed: a key element in these techniques is the availability of convenient, inexpensive methods for the preparation of polydimethylsiloxane (PDMS) molds that are used throughout these techniques, and the use of these PDMS molds to generate microstructures in polymeric materials that are precursors to carbon solids.

The PDMS molds were prepared as described previously, by casting PDMS on a photographically generated master.\(^{(3,24,25)}\) The masks used in photolithography were generated by rapid prototyping.\(^{(14,26)}\) In this technique, a computer file of the design of interest was generated using Freehand 5.5. The file was printed on a transparent film with a high-resolution (>3300 dpi) printer, and that transparent film was used as a mask to generate surface relief patterns in films of photoresists coated on Si wafers. This technique has a very short turnaround time and therefore allows many structures to be prepared and tested.\(^{(14)}\) Changes in the design of microstructures can be readily implemented in order to compensate for unexpected flaws in a structure. Numerous low-cost iterations can be performed using rapid prototyping.

The carbon precursor used in the present study was a furfuryl alcohol-modified phenolic resin. This type of polymer is widely used as a precursor to carbon solids because of its low cost and relatively high carbon yield (~50%).\(^{(4,27)}\) Patterns of that polymer were generated by either MIMIC or µTM. In MIMIC, the liquid polymer spontaneously fills the capillary channels defined by a surface relief of the PDMS mold in conformal contact with a substrate.\(^{(1,12,13)}\) This technique is ideal for the preparation of continuous structures such as wires and grids (Figure 1). On the other hand, µTM allows the formation of discrete, unconnected structures (Figure 2).\(^{(3)}\) In µTM, the liquid polymer is applied to the recessed patterns of the PDMS mold. The excess polymer is removed by gently scraping with the edge of a second piece of PDMS. The PDMS mold is placed in contact with the substrate; this contact constrains the remaining polymer in the recessed channels of the mold. We observed that an excessive quantity of polymer prevents conformal contact of the PDMS mold with the
A substrate. In this case, a thick film of polymer formed between the PDMS mold and the substrate that induced dewetting of the recessed structures. It was therefore important to minimize the quantity of polymer applied to the stamp. The liquid polymer was cured within the mold by placing the substrate on a hot plate. The surface temperature was increased slowly from ∼80 to 150 °C over ∼45–60 min in order to induce further cross-linking of the liquid polymers. A fast cure distorted or destroyed the structure. Prolonged contact between the PDMS mold and the polymer was also detrimental, as the cured polymer tended to remain trapped in the mold rather than being transferred to the substrate. We obtained reproducible results when the procedure (application of the polymer followed by curing) was performed in less than 1.5 h.

After completion of the curing step, the PDMS mold was removed, and the supported polymeric structures were converted into free-standing high-carbon structures by carbonization (400–1000 °C) under an inert atmosphere (argon). In some cases, we observed (after completion of the curing step) the presence of a very thin film (∼100 nm) connecting the discrete structures dispersed on the surface. The thickness of the film was small compared to that of the microstructures; in general, it did not survive the thermal processing and the mechanical stress introduced during carbonization. If it did survive, it was easily removed after the carbonization step by gently blowing on the microstructures.

The substrates used in the present study consisted of silicon wafers coated with thin chromium films (400 Å) prepared by electron beam evaporation. We found that, unlike other substrates, the chromium on silicon substrates prevented fracture of the structures during carbonization. The structures spontaneously released from the chromium surface as they shrunk. Substrates that were unsuccessfully tested include silica, silicon wafers, commercially available glassy carbon pellets, and titanium, nickel, silver, or gold films on silicon/SiO₂ wafers. It is unclear why chromium performed better than other metals, but we hypothesize that its high melting point (1857 °C) and lower chemical reactivity may be important factors.

In the work reported here, the lateral dimensions of the microstructures are determined by the resolution of the rapid prototyping technique; we have found that this technique is quite practical for the preparation of structures with features >20 µm; for smaller features, we believe that other techniques will be successful, but we have not yet explored these smaller structures. The PDMS molds prepared on these patterns reproduce with fidelity the edge roughness (∼1 µm) of the original photolithographic master, and this low edge resolution is transferred to the polymers used in µTM. The thickness of the microstructures is determined by the depth of the surface relief in the PDMS mold, i.e., the thickness of the film of photoresist used to produce the master. Thicker patterns of photoresist were prepared by spin-coating successive films of photoresist and soft-baking each film after application to the wafer. We were able to obtain thick patterns of photoresist (up to 40 µm) by spin-coating four films of photoresist prior to exposure.

Characterization of the Carbon Solids. The evolution of the density, the weight loss, and the lateral shrinkage experienced by the solids as a function of heat-treatment temperature were investigated and are plotted in Figure 3. The density of the cured polymer before carbonization was 1.29 g/cm³. The density (measured at room temperature) reached a minimum of 1.22 g/cm³ at 400 °C before increasing to 1.51 g/cm³ at 1000 °C. The trend and values are in good agreement with literature reports. The weight loss is attributed to the elimination of solvent and unreacted monomers and to the elimination of heteroatoms. A total weight loss of ∼45% occurs by ∼800 °C. Shrinkage of the solid appears to be isotropic and steady over the range of temperatures investigated. At 800 °C, the solid has shrunk by ∼20%. Above that temperature, additional
shrinkage is minimal (<3%). By anticipating a linear shrinkage of 20%, the lateral dimensions as well as the thickness of the carbon microstructures can be predicted well from the dimensions of the initial photoresist pattern.

**Evolution of the Microstructures during Carbonization: Differentiation between Surfaces.** Figure 4A shows scanning electron micrographs of the surface of the carbon solid in contact with the chromium substrate (bottom) and on the surface away from the chromium substrate (top) during curing and carbonization. The bottom surface remained featureless during carbonization and appeared smooth by electron microscopy, whereas the top surface was slightly curved and dimpled. The dimples (0.5–1 µm wide, 0.1–0.2 µm deep) are probably due to the outgassing of the solvent during polymerization. The presence of these dimples will affect the reflective properties of the carbon surface as light will be scattered by the irregularities of the surface. The surface composition of the carbon solids prepared by heat treatment at 1000 °C was investigated by X-ray photoelectron spectroscopy (XPS). Figure 4B shows XPS survey spectra performed on the top and the bottom surfaces. The atomic compositions of both surfaces are similar, consisting mainly of carbon (>90%) and oxygen (up to 8%). Chromium and zinc (<1% each)
are detected on the bottom surface but not on the top surface. The presence of zinc stems from the fact that a solution of ZnCl₂ was introduced into the resin in order to catalyze its polymerization to a cross-linked solid. The oxygen concentration is twice as high on the bottom surface (8%), suggesting that the residual metals may be present as metal oxides.

Shrinking during carbonization reduces the dimensions of the microstructures. It is also responsible for the slight buckling consistently observed on carbonaceous microstructures. Once the PDMS mold filled with the liquid resin, whether by MIMIC or µTM, the temperature was increased in order to induce curing. The viscosity of the polymer decreased as the temperature increased; this decrease in viscosity, coupled with the increase in density as the polymerization proceeded, resulted in sagging of the polymeric liquid within the capillary channels. The large coefficient of thermal expansion of PDMS (≈10⁻⁵ m/(K m)) may also have contributed to the deformation of the mold during curing. When the temperature of curing was reached, the sagged polymeric structure solidified. While the bottom of the microstructure (the part in direct contact with the planar substrate) remained flat, the top of the microstructure became slightly curved during curing. Further carbonization and densification accentuated the buckling of the microstructure.

Microelectromechanical Functions. We investigated the microelectromechanical functions of these high-carbon structures. As the microstructures are free-standing, they were mounted by hand (Figure 5). The structures were typically glued with conductive silver paint to an insulating substrate (glass slides, polyimide films). The resistivity of the carbon solids prepared at 1000 °C is ≈0.03 Ω cm. Application of a voltage between the carbonaceous microstructure and a counter electrode...
in close proximity generated an electrostatic force between both electrodes and induced a deflection. A photodiode recorded the modulation of the laser beam by the moving part.

(a) Cantilevered Beams. We tested simple structures such as suspended beams fixed at one end (Figure 5A). Individual carbon beams obtained by clipping comb structures prepared by MIMIC were used for the sake of simplicity, but arrays of suspended beams could have been tested as easily; these arrays would give access to a large range of vibrations determined by the length of each beam.²⁸ We were able to measure the frequency of vibrations of beams in both reflection and transmission modes. In both cases, the laser beam was focused on the end of the beam. In reflection mode, we recorded the displacement of a reflected light spot projected on a screen. The reflection mode was used for the determination of the deflection of the end of the beam. In transmission mode, we recorded the modulation of the light reflected by the surface of the silver counterelectrode. The transmission mode was more useful for the determination of the natural frequencies of vibrations.

The deflection of the tip of a cantilever beam (1.17 mm long) as a function of applied dc voltage is plotted in Figure 6A. The deflection of the tip of the cantilever was calculated with eqs 1 and 2 based on simple geometric considerations:

\[ \delta = l \sin \theta \]  
\[ d_s = D \tan 2\theta \]  

where \( \delta \) represents the deflection of the tip of the cantilever, \( l \) the length of the cantilever, \( \theta \) the angular displacement of the cantilever, and \( d_s \) the displacement of the projected spot on a screen located at a distance \( D \) from the cantilever.

The voltage required to induce deflection of the beam is large but would be much smaller if the distance between the MEMS and the counterelectrode were smaller. The deflection of the tip can be fitted to a second-order polynomial, indicating that the electrostatic force can be approximated to a localized force applied vertically at the extremity of the beam.

Young’s modulus of the carbon solid can be deduced from the resonance frequencies \( f_r \) of vibrations of a cantilever beam using eq 3.²⁹

\[ f_r = \frac{1}{2\pi} \left( \frac{EI}{A \rho} \right)^{1/2} \]  

where \( f_r \) is the frequency of resonance, \( E \) is Young’s modulus, \( l \) is the moment of inertia of the cantilever beam, \( l \) is the length of the beam, \( A \) is the cross section of the cantilever perpendicular to the length, \( \rho \) is the density of the material, and \( \lambda_r \) is the root of the frequency equation (4). For a beam of rectangular cross-section (width \( w \), thickness \( t \)), \( l = wt^3/12 \).

\[ 1 + \cos \lambda \cosh \lambda = 0 \]

This equation has an infinite number of real positive roots. The first three roots are \( \lambda_1 \sim 1.875 \), \( \lambda_2 \sim 4.694 \), and \( \lambda_3 \sim 7.854 \). Each of these roots corresponds to a resonance frequency \( f_r \) that satisfies eq 3.²⁹

The resonance frequencies can be determined by two different methods. In the forced oscillations mode, an ac voltage is applied between the microstructure and the counterelectrode. The frequencies \( (f_1, f_2, ...) \) at which the cantilever beam is in resonance with the applied voltage are recorded. In the free oscillations mode, the cantilever is excited with a short pulse and relaxes at its resonance frequency of vibration \( f_r \). Both approaches allow the determination of the quality factor \( Q \), which characterizes dissipation. The quality factor is defined by eq 5,

\[ Q = \frac{f_r}{|v_1 - v_2|} \]  

where \( v_1 \) and \( v_2 \) are the frequencies of vibration off-resonance at which the amplitude of the signal is equal to the maximum signal amplitude (i.e., at resonance) divided by \( \sqrt{2} \).²⁹
We measured the resonant frequencies of vibration of cantilevered beams of different lengths and thicknesses and deduced Young’s modulus for carbon solids prepared by heat treatment at 1000 °C (Table 1). The value of Young’s modulus (∼15–20 GPa) is consistent with values reported for carbon solids prepared under similar conditions.4 Low-quality factors (10–20) were measured for thin (6 µm) vibrating beams operated at ambient pressure in air. Higher quality factors (∼90) were obtained for thicker beams (17 µm). Air damping is the dominant mechanism for the dissipation of energy. Much higher quality factors would be measured if the experiment were performed under reduced pressure.8,30–33

Figure 6B plots the variation of the amplitude of vibration for a thicker (∼17 µm) beam as a function of the frequency of the applied ac voltage. The small difference (∼50 Hz, less than 1%) in the frequency of resonance (∼7.4 kHz) after continuous operation for >500 million cycles is within the margin of error for our measurements.

(b) Complex Microstructures. We tested the microelectromechanical properties of microstructures such as those displayed in Figure 2. These structures were mounted as depicted in Figure 5B,C, respectively. The determination of Young’s modulus from the frequencies of vibration of these microstructures is complicated by their more complex geometries and is beyond the scope of this paper.

Capacitive sensors generate an electrical signal as a result of the displacement of a suspended electrode relative to a fixed electrode.34 As the distance between the electrodes constituting the capacitor changes, so does the capacitance of the capacitor defined by the geometry of the system. Numerous pressure-sensing devices and accelerometers have been prepared that rely on changes in capacitance.34

The carbon microstructure displayed in Figure 2B could potentially be used as an uniaxial accelerometer: the vertical displacement of the suspended inner frame induced by acceleration or deceleration would induce a change in the capacitance between the carbon microstructures and a counter-electrode. We prepared microstructures with one or two supporting arms extending from the outer frame to the inner frame. The zigzag design of the supporting arms greatly reduces the probability of fracture of the microstructures during carbonization, relative to microstructures with straight supporting beams. This difference is probably due to the fact that shrinkage is distributed over the entire zigzag rather than concentrated unidirectionally in a simple beam. Vibrations of the inner frame were electrostatically induced as indicated in Figure 5B. The modulation of a laser beam by the vibrating structure was recorded with a photodiode. Figure 7 plots the variation of the amplitude of vibration for carbon microstructures of different thickness as a function of the frequency of the applied ac voltage. Higher-order resonances were also recorded at higher frequencies (up to 85 kHz) for some of these structures.

The microstructure displayed in Figure 2D is the basic unit for a rudimentary display system when mounted as shown in Figure 5C. The microstructure is glued over the edges of two cover slips separated by ∼1 mm. The central plate is electrostatically actuated simulta-

<table>
<thead>
<tr>
<th>Length (µm)</th>
<th>Thickness (µm)</th>
<th>Density (g/cm³)</th>
<th>Frequency (kHz)</th>
<th>Young's modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1130</td>
<td>6</td>
<td>1.51</td>
<td>2.55</td>
<td>18</td>
</tr>
<tr>
<td>1140</td>
<td>6</td>
<td>1.51</td>
<td>2.20</td>
<td>15</td>
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<tr>
<td>1400</td>
<td>6</td>
<td>1.51</td>
<td>1.58</td>
<td>16</td>
</tr>
<tr>
<td>1140</td>
<td>17</td>
<td>1.51</td>
<td>7.35</td>
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<tr>
<td>1400</td>
<td>17</td>
<td>1.51</td>
<td>10.0</td>
<td>16</td>
</tr>
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a Young’s modulus can be determined from either the 1st or 2nd resonant frequencies of the carbon cantilevers.
componentes in MEMS in conditions under which silicon would fail.

Experimental Section

Fabrication of the Microstructures. Fabrication of the PDMS molds was performed according to procedures previously reported.\textsuperscript{24,25} The PDMS molds were prepared by casting PDMS (Sylgard 184, Dow Corning) on photolithographically generated masters consisting of patterned films of photore sist (Microposit STR 1075, Shipley, MA). The masks used in the photolithographic step were prepared by rapid prototyping.\textsuperscript{34} The substrates used for the preparation of the polymeric microstructures and subsequent carbonization were obtained by e-beam evaporation of chromium thin films (40 Å) onto silicon wafers. The furfuryl alcohol-modified phenolic resin was obtained from Q.O. Chemicals (Furcarb LP-520). Curing of the latter resin required the addition of a latent, heat-activated catalyst such as a 50% aqueous solution of ZnCl\textsubscript{2}. The amount of catalyst never exceeded 10% (w/w) of the resin in order to prevent a too rapid cure and potential deformation of the microstructures. Caution: Mixing an acid catalyst with furfuryl alcohol-modified resins induces an exothermic reaction. Curing of the polymer was done in a hot air box at 100 °C. Carbonization was performed in a Blue M/Lindberg MiniMite tube furnace fitted with a quartz tube. The samples were placed in an alumina boat and introduced in the quartz tube. The chamber was deoxygenated by a rapid flow of argon for ~20 min prior to carbonization. Carbonization was performed under a positive pressure of argon. The temperature increased at a rate of 5 °C/min up to the final temperature. The samples were kept at the final temperature for 10 min and then let cool to room temperature.

Characterization of the Carbon Solids. Resistance measurements were performed with a hand-held voltmeter. The density of the solids was estimated by floating the solids in liquids of known densities. One limitation of this technique is that it underestimates densities of solids containing hydrophobic voids, which trap gas. Liquids used (density in g/cm\textsuperscript{3}): nitrobenzene (1.197), 1,2-dichloroethane (1.256), 1-bromobutane (1.276), 1,1,1-trichloroethane (1.338), 1-bromopropane (1.354), trichloroacetonitrile (1.440), bromoethane (1.460), bromobenzene (1.491), 1,7-dibromoheptane (1.510). SEM was performed on a JEOL JSM-6400 scanning electron microscope operated at 15 keV. The samples were either glued to conductive carbon tape or glued to a silicon substrate with silver paint. X-ray photoelectron spectra were obtained on a SSX-100 spectrometer (Surface Science Laboratories) using a monochromatic Al K\textalpha\ X-ray source. The spot size was ~1 mm\textsuperscript{2} with an analyzer pass energy of 150 eV.

Testing of the Microelectromechanical Properties. The carbon microstructures were glued with silver paint onto glass slides (Figure 5). The counter electrode in Figure 5A consisted of a silver thin film (500 Å) on glass prepared by e-beam evaporation. The counter electrode in Figure 5B consisted of a metallicized piece of a silicon wafer glued on the edge of a glass slide. The silver counter electrodes used for the testing of the deflector (Figure 5C) were prepared by etching a silver thin film deposited on a self-assembly monolayer.\textsuperscript{35,36} An ac or dc voltage was applied between the microstructure and the counter electrode using a function generator (WaveTek Model 187 (San Diego, CA)) and an amplifier (Burleigh high-voltage DC OP AMP PZ-73). Frequencies of vibrations were measured by recording the modulation of a He–Ne laser (633 nm) by the moving structure using a photodiode and an oscilloscope (Tektronix 2445A).

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