Modification of Conductivity and of Mechanical Properties of Electroactive Polymer (EAP) Thin Films by Titanium Ion Implantation

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Modification of conductivity and stiffness of electroactive polymer (EAP) thin films by metal ion implantation

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Dielectric electroactive polymer (DEAP) actuators have a very large percentage displacement, often exceeding 100%, and therefore require compliant electrodes. Macro-scale (cm and larger) devices, often referred to as artificial muscles, have electrodes made of carbon or metal powder or of conductive grease. This electrode fabrication method is not applicable to micro-scale devices for which electrodes patterned with micron resolution are required. Simple evaporation or sputtering of metal electrodes is not suitable due to the 4 orders of magnitude larger Young modulus of the metals compared to the elastomers, and due the fracture of metal films at very small strains.

We have shown [1] that it is possible to create compliant electrodes by implantation of metal ions into poly-dimethylsiloxane (PDMS) elastomers. Low energy (2 to 35 keV) implantation creates a thin conductive layer a few nm below the surface of the polymer without forming a continuous metallic layer, and thus without the stiffening expected from a metal layer. Electrical conductivity of a few kΩ/ square can be reached with less than 1 MPa increase in Young's modulus for doses of order 10^{16} ions/cm^2. The implanted polymer electrodes can repeatedly tolerate strain greater than 0.3 without change in conductivity.

In this work we present the influence of the implantation technique, metal ion species, ion energy, and dose on the mechanical and electrical properties of PDMS membranes and films. The field of ion implantation in polymers is largely unexplored.

Two techniques to fabricate electrodes on PDMS were used: Filtered Cathodic Vacuum Arc (FCVA) and Low Energy broad beam Implanter (LEI). Ti was implanted at 5 keV with the FCVA, at 10keV and 35 keV with LEI. Au was implanted at 5 keV with FCVA.

The higher the energy and the atomic number of the ions, the longer their stopping distance in the polymer and the larger their distribution or straggle. This is illustrated in Fig.1, which is a numerical simulations of ion distribution in PDMS [2], ignoring the effect of metal ions in the

membrane. Lower implant energies are therefore preferred to obtain the required concentration and hence conductivity with the lowest possible dose.

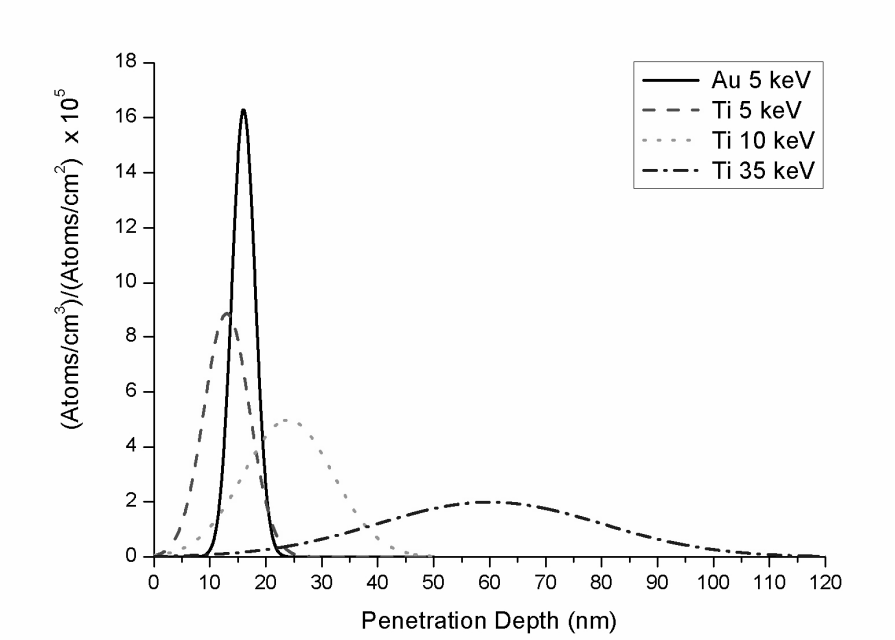

Fig.1. Density vs. penetration depth of Gold and Titanium for different Energies, simulated with TRIM.

Samples for resistivity measurements consist of 25 μm thick PDMS films on Si chips. Resistivity is measured on a 5x1 mm² zone between gold electrodes. For the stress (σ) and Young modulus (E) measurements a "bulge test" setup was used that measures the deflection of a membrane due to an applied gas pressure. Samples consisted of 25 μm thick square and circular PDMS membranes of lateral dimensions 2 to 3 mm.

The doses and energies used were chosen around the region where electrodes are sufficiently conductive (resistivity less than 100 kΩ/square) yet sufficiently compliant (Young's modulus less than 3 MPa) that efficient micro-actuators can be fabricated based on them.

The results obtained by FCVA 5 keV Gold implantation are shown in Fig.2. Due to the formation of nano-composites, an increase in membrane stiffness and a decrease of resistivity are observed with increasing dose. Because stable electrodes are required, resistivity as a function of time was measured and shows two regimes (Fig.3): for high conductivity samples the resistivity decreases slightly then stabilizes, and for lower conductivity samples the resistance rapidly increases. Au is well known to form islands when deposited in thin films [3]. The annealing of thin gold films has been extensively studied [4] and occurs for films that exceed a critical thickness. This annealing

explains the decrease in resistivity observed at higher doses. For thinner discontinuous films, conduction occurs by a number of conduction mechanisms between islands. If the islands coalesce or their spacing increases due to annealing and grain growth, the conductivity of the film will decreases rapidly once the islands are below the percolation threshold. We believe this explains the increases in resistance with time of the low dose samples. For comparison, a dose of $2x10^{16}$ ions/cm^2 corresponds to a film thickness of 3 nm if all ions were deposited at the surface.

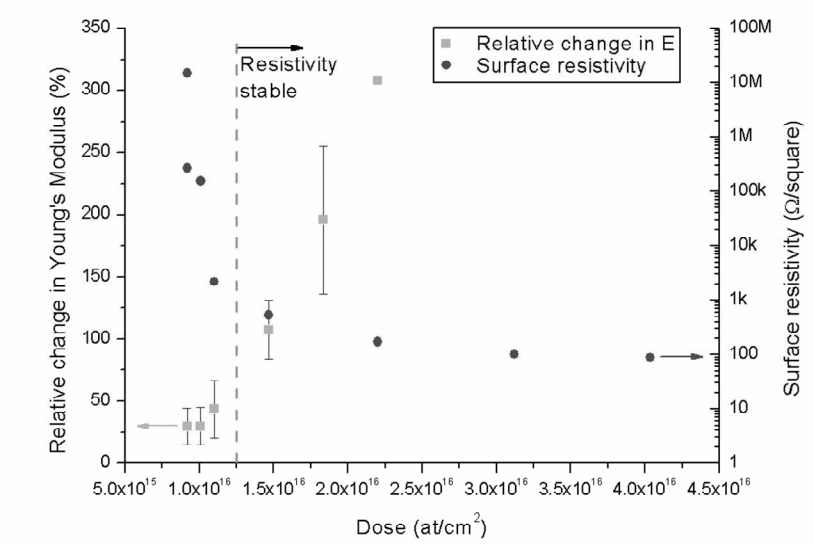

Fig.2.: Surface resistivity and relative Young's modulus vs. ion dose for PDMS films implanted with Au at 5 keV by FCVA. The initial value of the Young's modulus is 0.85 MPa.

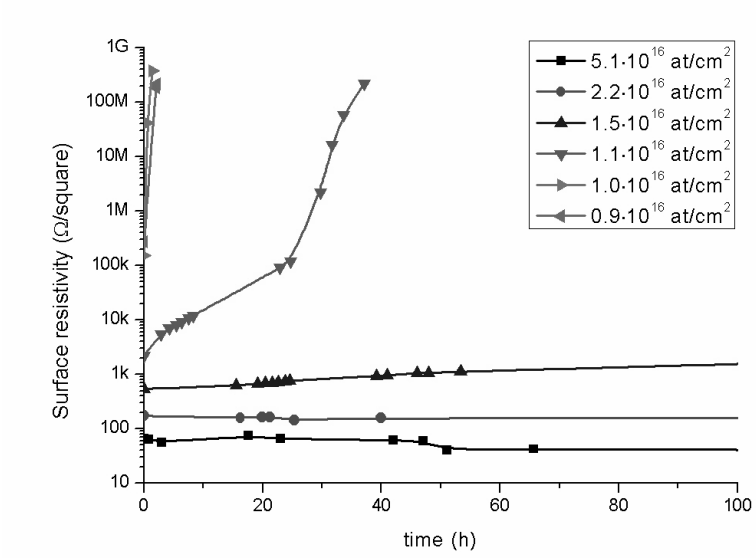

Fig.3: Surface resistivity vs. time for PDMS films implanted with Au 5 keV (in LEI) stored at 100°C. High doses lead to metallic films that can be annealed. Low doses lead to island formation and degradation of conductivity with time.

The resistivity of samples implanted with Ti at 10 keV by LEI remained unchanged to a few percent after some initial oxidation.

After the successful implantation by FCVA at 5 keV, implantation with more traditional implanters was tried. The dose dependence of Young's modulus (E) and resistivity (R) for PDMS membranes implanted with Ti by LEI at 10 keV is shown in Fig.4. The overall trend of E and R vs. dose is the same as for Au at 5 keV. To reach similar resistivity an approximately 50% larger dose is required, consistent with Figure 1. However the Young's modulus is 2 orders of magnitude larger than for 5keV Au, a much larger increase than can be explained by the slightly larger dose if a simple linear superposition model is used.

This difference is not primarily due to the nature of the ion, but to the nature of the implantation process. The FCVA process is pulsed (600 μs pulses every second, 3.7 x 10^{13} ions/cm^2/pulse), probably generates large local heating at every pulse, and requires a total time of order 500 s, whereas the LEI process rasters a continuous 3 μA beam over the surface, requiring several hours to complete the implantation. Charging is known to play a large role in the detailed microstructure of the films (see AFM roughness studies below) and the two implantation techniques provide order of magnitude difference in average beam current. Increasing the Ti ion energy to 35 keV (LEI) gives samples with Young's modulus even higher than at 10 keV. FCVA implantaion with Ti at 5 keV gives results very similar to 5 keV Au by FCVA.

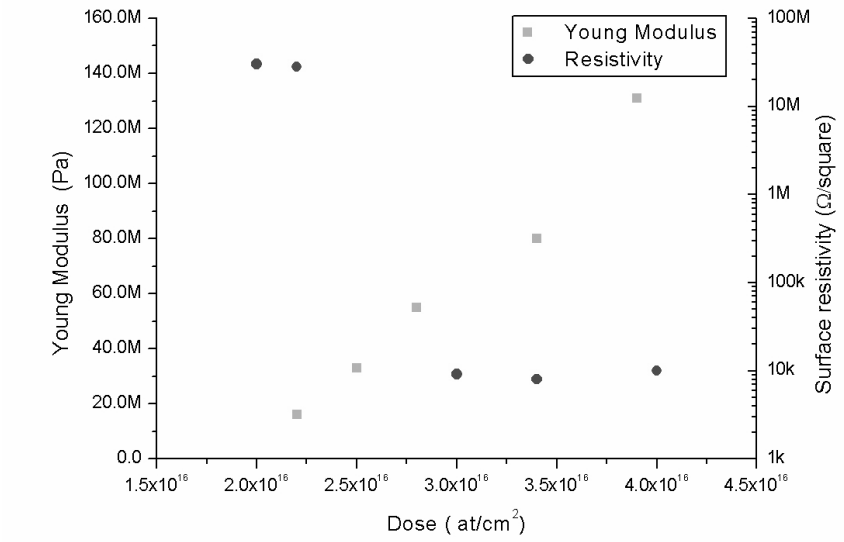

Fig.4. Surface Resistivity and Young's modulus of PDMS films after implantation with Ti at 10 keV by LEI. The initial value of the Young's modulus is 0.85 MPa

Implantation has a strong influence on surface roughness of polymers due to sputtering, local stress modification, charging and heating. The PDMS films had initial roughness of 3 nm rms. Figures 5 and 6 show the roughness increase as a function of implant dose and implant technique. The FCVA increase roughness up to 100 nm, while the LEI tool yields films with roughness of over 1 μm. This is an indication of the dramatic difference in microstructure obtained at comparable doses but with different implanters, which is reflected in the nearly 100 fold difference in Young's modulus of LEI compared to FCVA.

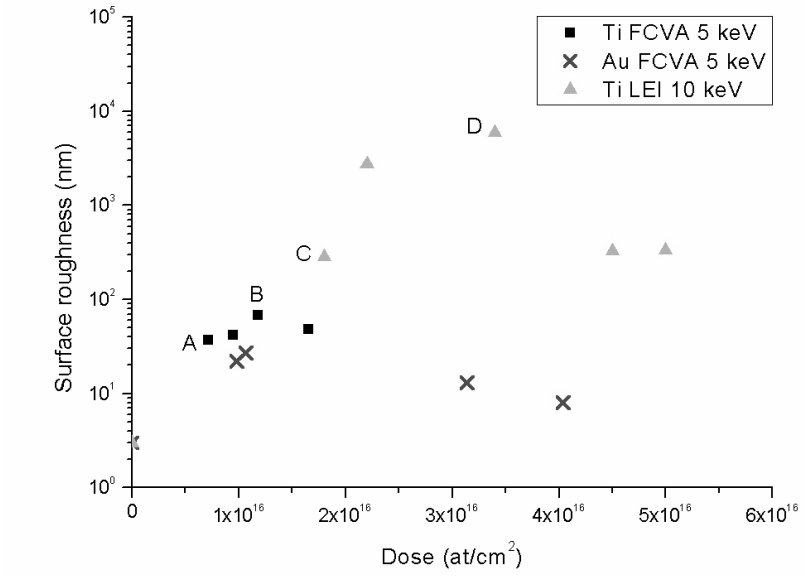

Fig.5. Surface Roughness of PDMS films as a function of ion dose for different implantation methods and ion species. Letters A through D refer to sample shown in more detail in Figure 6.

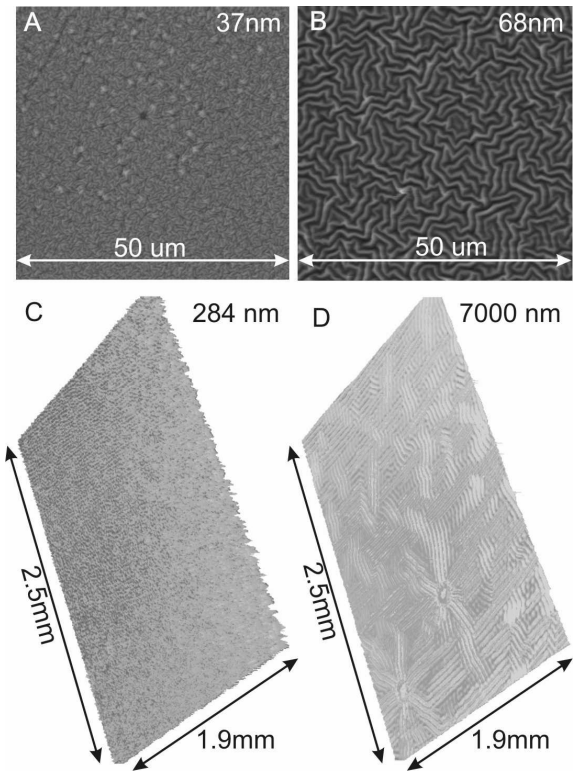

Fig.6. Surface roughness of implanted PDMS: A – Ti 5 keV FCVA, $7x10^{15}$ at/cm^2; B – Ti 5 keV FCVA, $1.2x10^{16}$ at/cm^2; C – Ti 10 keV LEI, $1.8x10^{16}$ at/cm^2; D – Ti 10 keV LEI, $3.4x10^{16}$ at/cm^2.

To better understand the modification of physical properties due to the metal ion implantation a special cryogenic preparation technique was developed, tested and used to prepare TEM lamella of implanted PDMS membranes. In TEM transmission mode the arrangement of clusters can be observed, where else in diffraction mode, important information about the crystalline film structure of high dose Ti implanted elastomer is revealed.

This study enabled the definition of the ion dose and energy domain where a stable low resistivity can be obtained simultaneously with limited stiffening of the polymer membrane. To create compliant electrodes, the FCVA type of implanter is much better suited than conventional implanting equipment. We are currently performing more systematic measurements to provide a comparison between different ion species implanted in similar conditions. Our research focuses on the TEM and AFM observation, and modeling of the nano-structure created in the PDMS.

Acknowledgments:

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