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Formation and characterization of microcantilevers produced from ionic liquid by electron beam irradiation

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ABSTRACT

Recently, ionic liquids (ILs) have been recognized to have significant potential as precursors or reaction media in nanolithography and MEMS component technologies. In this work, we demonstrate straightforward fabrication of positioned and well-defined microscale structures by electron beam (e-beam) irradiation of two different ILs: 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM TFSI) and 1-(6-hydroxyhexyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM-OH TFSI). The study includes comparison between the compositions and mechanical properties of corresponding e-beam-irradiated ILs. The average Young's moduli of prepared IL microcantilevers measured in beam bending tests were found to be 7.2 ± 0.9 GPa and 3.5 ± 1.3 GPa for HMIM-OH TFSI and HMIM TFSI, respectively. Infrared spectroscopy indicated the formation of polymer in e-beam-irradiated HMIM-OH TFSI, while structures from HMIM TFSI melted in ambient conditions. The presented results showcase the potential IL precursors in microscopic 3-D printing approaches for mechanical elements in MEMS technologies as well as for developing reversibly solidified precursors for lithography.

1. Introduction

Room temperature ionic liquids (RTIL) have been extensively studied [1,2] and have been demonstrated to have great potential in various applications [3,4] because of their unique combination of electrical [5], thermal [6], chemical [7], tribological [8] and other properties. Due to their characteristic low vapor pressure, RTIL can be used in high-vacuum conditions and studied by scanning electron microscopy (SEM) [9]. As recognized and demonstrated in earlier works, such combination of features can suggest vacuum technologies with new and exciting possibilities. In addition to functions in material characterization methods [10], ILs can serve as a medium for localized synthesis of various structures by electron beam (e-beam) irradiation. Schmuki et al. demonstrated the formation of Ag nanodendrites on anatase TiO_2 surface in 1-butyl-3-methylimidazlium tetrafluoroborate [BMIM][BF4] under exposure to e-beam in a high-vacuum SEM chamber [11]. Imanishi et al. have reported e-beam-promoted synthesis of Au nanoparticles in an IL via a reductive reaction [12] and pointed to the method's potential application in nanolithography, if those particles could be attached to the surface.

In addition to serving as a functional reaction medium, ILs themselves can undergo polymerization. Polymerized ILs have been found to have many interesting properties suitable for a range of applications including polymeric electrolytes [13], microwave-absorbers [14], ionic conductors [15], and porous materials [16]. Pre-polymerized forms of ILs have been used as a nonvolatile conductive component in producing composites [17]. Among other strategies, polymerization of ILs can be driven by exposure to radiation. Ionizing radiation (e.g. e-beam) interacts with matter and yields reactive species such as radical ions and solvated electrons [18]. These reactive species may initiate several fragmentations, modifications and chemical reactions, including IL polymerization.

Recently, polymerizable RTILs precursors have also been applied to micro- and nanoscale lithography to produce positioned patterns on substrates. Bocharova et al. [19] reported direct writing in IL by strong electric fields localized by the tip of an atomic force microscope (AFM). E-beam-induced polymerization of up to 1 μm thick 1-allyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide [AllylEtIm][TFSI] layers was demonstrated by Minamimoto et al. [20]. By the latter method, various three-dimensional structures were produced on Si substrate with sub-100 nm resolution. However, the applicability of 3D printing in RTIL should not be limited to on-substrate lithography. The availability of different ionizing radiations at different energies and the wide

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range of ions that can be combined in RTILs with suitable susceptibility suggest that direct writing of suspended and cantilevered domains of polymerized IL is also possible.

In this paper, e-beam-induced polymerization was applied to RTILs 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM TFSI) and 1-(6-hydroxyhexyl)-3-methylimidazolium bis (trifluoromethylsulfonyl)imide (HMIM-OH TFSI) to produce free-standing microcantilevers (MC) attached to a silicon AFM tip. Observations were made on the geometry of formed structures, and IR spectroscopy was used to monitor differences in the changes that occur in similar ILs. A real-time nanomanipulation technique inside an SEM [21–24] was applied to determine the mechanical properties of the obtained ionic liquid microcantilevers (ILMC) in situ in order to demonstrate the potential of the applied approach in direct bottom-up 3D writing of mechanical elements for MEMS and to explore the influence of hydroxyl group IL on the behavior and properties of the ILMCs.

2. Experimental

2.1. Materials

N-methylimidazole (Aldrich), lithium bis(trifluoromethanesulfonyl) imide (Merck), dichloromethane (Lachner), HMIM TFSI (Merck) and all solvents were used as received. α,ω-Bromoalcohols were synthesized from the corresponding α,ω-diols (Aldrich) using a standard procedure [25]. HMIM-OH TFSI was prepared by treating *N*-methylimidazole (0.1 mol) with 6-bromoalcohol (0.1 mol) at room temperature under inert atmosphere for 24–48 h as reported previously [26]. 1-(6-Hydroxyhexyl)-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (HMIM-OH TFSI) was prepared through an anion exchange with 1-(6-hydroxyhexyl)-3-metylimidazolium bromide using a standard protocol [27].

2.2. Formation of the ionic liquid microcantilevers

Neat ILs were drop-casted onto untreated silicon wafer (oxidized, Semiconductor Wafer Inc.) and placed inside the vacuum chamber of the SEM (TESCAN Vega-II SBU) equipped with 3D-nanomanipulator (Smaract) with attached silicon AFM cantilever (ATEC-CONT cantilevers, Nanosensors, $C = 0.2\ N\ m^{-1}$, tip radius approx. 20 nm). The geometry of the AFM cantilever enabled tip visibility from the top.

Prior formation of the microstructure from the IL, the AFM tip was immersed and held in the IL droplet (Fig. 1(a)). SEM imaging at this stage was performed under low current density ($\ll 1\ A\ m^{-2}$) to avoid unintentional structural changes in the IL. Then, the rectangular area adjacent to the AFM tip was chosen and locally irradiated with e-beam of the much higher current density (on the order of $1\ A\ m^{-2}$) to cause a local solidification of the IL. Rapid change in contrast in the irradiated area served as an indication of the solidification onset: irradiated areas appeared darker in the SEM image. The polymerization/solidification process was saturated as soon as no further changes in contrast were observed. This process resulted in the formation of a solid rectangular structure on top of the IL droplet surface, attached to the AFM tip from one end. After the solidification, the probing current was decreased to avoid further solidification of the surrounding IL. The tip was then retracted from the IL, exposing the free-standing beam as seen in Fig. 1(b).

2.3. Geometrical and mechanical characterization

Thickness and uniformity of the geometry of ILMCs were measured in SEM in a series of manipulations in which polymerized/solidified ILMC was rotated and tilted at different angles in order to observe it from different points of view.

Young's moduli of the ILMCs were measured in a bending test performed by pushing the free end of the ILMC against the end of the fixed reference AFM cantilever with known stiffness (Fig. 2). The deformation of the reference AFM cantilever enabled the calculation of the force acting on the bent ILMC. The elastic beam theory was applied to fit the experimentally obtained SEM image of the bent ILMC. A flexible beam of length L with Young's modulus E and area moment of inertia I with point load f at its end over axis l of the beam has an equilibrium bending profile governed by the differential equation:

$$EI\theta''(l) + f\cos[\theta(l)] = 0, \qquad (1)$$

and is subject to the following boundary conditions: $\theta(0) = 0$ and $\theta'(L) = 0$, where $\theta(l)$ is the tangential bending angle with respect to the initial straight profile [28]. The area moment of inertia for a beam with rectangular cross-section is expressed as $I = bh^3/12$, where b is the width and h is the thickness of the beam. As a result of the fitting, the Young's modulus for each ILMC was determined.

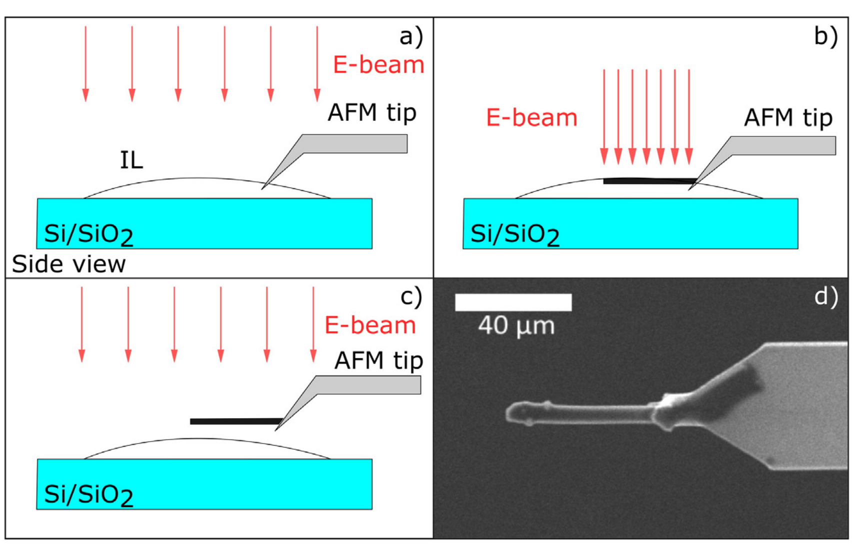

Fig. 1. Schematics of the ILMC formation inside SEM: a) AFM tip submerged in IL under the low current density, b) rectangular area adjacent to AFM tip is irradiated with high current density e-beam causing local polymerization/solidification of the IL, c) free-standing ILMC is exposed by lifting AFM tip, d) experimental image of the ILMC attached to the AFM cantilever.