Ionic liquids—a novel material for planar photonics

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Abstract
Electron beam patterning is an important technology in the fabrication of miniaturized photonic devices. The fabrication process conventionally involves the use of radiation sensitive polymer-based solutions (called resists). We propose to replace typical polymer resists with eco-friendly solvent-free room temperature ionic liquids (RTILs), which are polymerized in situ and solidified by an electron beam. It is demonstrated that the shapes of polymerized structures are different for high-viscous Cl-based RTILs and low-viscous NTf₂-based RTILs. Due to the satisfactory quality of the polymerized spatial microstructures and their light transmission properties, the RTIL-derived microstructures are potentially attractive as photonic elements for near-infrared.

Keywords: ionic liquids, electron beam patterning, polymer photonics

(Some figures may appear in colour only in the online journal)

1. Introduction

Photonic integrated circuits play a significant role in many application areas including telecommunications, medicine, military and consumer equipment. Passive components of these planar systems such as waveguides or microresonators can be made of polymers, which have become a popular material for micro-optical elements because of their low cost of manufacturing, broad bandwidth and tailorability [1–4]. The microfabrication of integrated optical elements typically incorporates patterning techniques (for instance, photolithography or electron beam lithography), in which solvents (e.g. gamma-butyrolactone or ethyl lactate) are normally used either to dissolve a polymer prior to its application on a substrate or to develop microstructures after exposure to radiation. However, the usage of solvents has its drawbacks. After deposition and spin-coating of a polymer solution (i.e. resist) on a substrate, a solvent must be evaporated from the film. Besides the apparent solvent loss associated with this, the evaporation of solvents is a serious health, as well as environmental, issue. Furthermore, solvent-based resists are not suitable for many polymer substrates and structures, and require extensive optimization of other patterning methods.

Therefore, the concept of excluding harmful solvents from lithography process has drawn researchers’ attention in recent years. Chuang et al proposed a multicomponent resist, containing polyvinyl alcohol and water as a solvent [5]. In a series of papers [6–9] Takei et al suggested the application of resists based on natural polysaccharides [6] as well as biomass-derived sugar [7], cellulose [8] or dextrin [9]. In the present study, we discuss another approach to this problem which utilizes simpler substances, i.e. polymerizable room temperature ionic liquids.

Room temperature ionic liquids (RTILs) are organic salts that are in liquid state at room temperature. Potential applications,
as well as properties of these substances, often called green solvents for the future [10–12], have been extensively examined in recent years [13–31]. RTILs are known to be nonvolatile and nonflammable, which makes them particularly attractive in terms of safety and environmental concerns. Moreover, ionic liquids have high ionic conductivity. These features of RTILs enable one to insert them into a vacuum chamber and expose them to an electron or ion beam without the charging effect, which has been demonstrated by Kuwabata et al. [32–34].

In one of the cited papers, Minamimoto et al. described (for the first time in the literature) fabrication of spatial polymer microstructures on Si substrate by polymerization of an imidazolium-based RTIL using an electron beam [34]. However, in the experimental procedure the silicon surface was functionalized with 3-aminopropyltriethoxysilane (APTES) in order to improve ionic liquid adhesion. Furthermore, the resist was not solvent-free since the ionic liquid was diluted with ethanol prior to dropping onto the substrate. What is more, the authors did not consider the light transmission properties of polymerized RTIL, which is crucial with regard to photonic elements manufacturing.

In this work, we show that polymerizable ionic liquids can be shaped by means of the electron beam patterning method (which is briefly illustrated in figure 1) in order to obtain infrared photonic components. The suggested procedure is less complicated and more eco-friendly because, before application of an ionic liquid, the silicon substrate is subjected to oxygen plasma cleaning and no further surface functionalization is needed. Moreover, ethanol is used only as a developer, not as a constituent of the resist. In other words, an RTIL is deposited onto the substrate in pure form, without using any solvent.

We propose 1-allyl-3-methylimidazolium chloride (acronym [Allmim][Cl]) (see figure 1), which has already been used for cellulose processing [35–38], but not as an electron beam-sensitive material. This compound is similar to the one reported in [34], though its cation has a methyl instead of an ethyl group and a large NTf_2^– ion is replaced by a small Cl– anion. It should be noted that ionic liquids with shorter alkyl substituents on the imidazolium cation are generally considered less harmful whereas the influence of an anion on toxicity is perceived to be definitely lower [39–41]. Additionally, we compare [Allmim][Cl] with [Allmim][NTf_2^–] (that is 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide) in terms of the impact of the anion on the electron beam shaping process.

The proposed polymerizable RTIL can work as an electron beam resist as well as the final material for passive optical components. Such a material can combine benefits of the polymer host matrix with special adds like dyes and nanoparticles.

2. Experimental

The [Allmim][Cl] ionic liquid was synthesized as follows. A solution of 1-methylimidazole (12.94 g, 0.158 mol) in MeCN (150 ml) was placed in a two-neck round-bottomed flask equipped with a reflux condenser in one neck and a septum in the other, and heated to 60 °C with simultaneous stirring with a magnetic stirrer. Then allyl chloride (12.66 g, 0.166 mol) was added dropwise (with an addition rate of 5 ml h^-1). The resulting mixture was stirred at 60 °C for 96 h. Next, the solvent was evaporated using a rotary evaporator, and the obtained product was dried under vacuum to produce a pure product which was a yellow liquid (24.50 g, 98%).

In order to obtain [Allmim][NTf_2^–] ionic liquid, the synthesized [Allmim][Cl] (3.00 g, 18.93 mmol) was dissolved in distilled H_2O (40 ml) and transferred into a separating funnel. Next, DCM (30 ml) was added, followed by an aqueous solution of lithium bis(trifluoromethanesulfonyl)amide (LiNTf_2^–) (80%, 6.93 g, 19.31 mmol). The resulting mixture was shaken vigorously for a few minutes. The obtained layers were then separated, and the organic layer was washed with distilled H_2O twice (2 × 15 ml) and H_2O (15 ml) with a small addition of aqueous solution of LiNTf_2^– (80%, 136 mg, 0.38 mmol). The washing procedure was repeated three times. After that the organic layers were combined and evaporated under reduced pressure and dried under vacuum to give a pure product, which was a yellow liquid (6.79 g, 89%).

The commercially available Si (100) substrates were cleaned in oxygen plasma (600 W, GIGAbatch microwave system by PVA TePla) for 5 min. The thin films of the RTILs on Si substrates were formed by spin coating at 60 rps for 60 s, at room temperature. After the formation of the thin film, a substrate with an RTIL was placed in the SEM microscope (FEI Helios 660), which was pumped to acquire a high vacuum, and then a sample was patterned by irradiation with an electron beam, controlled by a Raith ELPHY MultiBeam.

One of the most important parameters describing the process of electron beam patterning is the exposure dose D [mC cm^-2], which is defined as:

\[
D = \frac{I_B \times \text{dwell}}{x_{\text{pitch}} \times y_{\text{pitch}}}
\]

where \(I_B\) is the beam current, \(\text{dwell}\) is the dwell time, \(x_{\text{pitch}}\) and \(y_{\text{pitch}}\) are the distances between exposure points in the vertical and horizontal directions, respectively.

The dwell time is the exposure time of a single location (i.e. one pixel). In the present study: \(I_B = 26\, \text{nA}\), \(x_{\text{pitch}} = 50\, \text{nm}\),...
The dwell time was varied to obtain a proper dose. The acceleration voltage of electrons was set at 30 kV.

Samples were imaged using the FEI SEM Helios microscope and characterized by the Bruker Dektak contact profilometer with a 12.5 μm radius stylus. The thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed by means of a simultaneous thermal analyzer (STA 6000) by Perkin Elmer. The viscosities of the liquids were determined using a rotary rheometer equipped with a 40 mm Peltier steel plate, with a shear rate of 200 s⁻¹, a gap of 1000 μm and a compression velocity of 100 μm s⁻¹ in a temperature range of 25°C–100°C (ramp duration 15 min). The light transmission properties of samples were measured using an Evolution 300 UV–vis spectrophotometer and a Nicolet iS50 FT-IR spectrometer by Thermo Scientific.

3. Results and discussion

The results of the electron beam activated polymerization of chloride- and NTf₂-based ionic liquids are shown in figure 2. The presented structures were patterned in an inward direction, which means that their outer parts were irradiated first. Despite the same circular pattern, the shapes of solidified structures are very different. Irradiation of RTIL with a Cl⁻ anion results in regular shape and uniform thickness. Interestingly, the structure formed from the ionic liquid with a larger anion is considerably deformed. The outer part of the structure is very thick as compared to its center which almost does not contain any solidified material. Such a ring-shaped structure has a rounded, relatively smooth surface. This feature could be used for the fabrication of waveguides, ring resonators and microlenses.

In this context, it should be noted that areas exposed to the high-energy electron beam are heated. As demonstrated in figure 3, viscosities of ionic liquids decrease with temperature. Liquids with decreased viscosity can be more easily deformed before and during polymerization, which may influence the final shape of solidified structures. Moreover, the viscosity of RTIL with a larger anion is definitely lower, which is expected because of the weaker electrostatic attraction between large ions. The above relation between the two liquids is preserved even at high temperatures when the viscosity of the Cl-based liquid is significantly reduced. This explains why [Allmim][Cl] is more deformed than [Allmim][NTf₂].

In order to further understand the temperature-dependent behavior of the RTILs, TGA and DSC were performed and the results are presented in figure 4. The mass loss in the range of 72 °C–153 °C and the enthalpy change between
53 °C and 176 °C for [Allmim][Cl] can both be attributed to evaporation of water from the ionic liquid [42]. The specific temperature of thermal decomposition is about 273 °C, which is similar to values for imidazolium-based chloride ionic liquids presented in the literature [42, 43]. It is also generally in line with the long-term thermal stability of [Allmim][Cl] examined by Hao et al who additionally used the TGA technique coupled with mass spectrometry to indicate two possible decomposition routes of this RTIL at 200 °C–350 °C [44].

As compared to NTF2-based ionic liquid, the decomposition temperature of [Allmim][Cl] is quite low (see also reference [43]). Nevertheless, the influence of this fact on electron beam activated polymerization is unknown, since the temperature increase within an area exposed to the electron beam is difficult to evaluate. The energy delivered to the RTIL area is not only spent on heating but also on, inter alia, the emission of x-ray radiation and secondary electrons.

The results of detailed examination of [Allmim][Cl] patterning by means of electron beam are shown in figure 5. In order to achieve microstructures of polymerized RTIL, the dose had to be at least 10 mC cm\(^{-2}\), which is two times lower than a value reported by Minamimoto et al [34]. The good quality lines of 1 and 2 μm width (in the right and left corner of the image, respectively) are readily achievable if a dose is at least 20–25 mC cm\(^{-2}\). Nevertheless, application of a higher dose (40–50 mC cm\(^{-2}\)) results in a lateral widening of microstructures, most visible for square patterns.

As seen from the above, an appropriate dose must be chosen taking into consideration the minimal value for polymerization and the lateral widening. A dose as low as 20 mC cm\(^{-2}\) can be used to obtain optical microelements of a good resolution and a low roughness based on 2 μm wide waveguides (figure 6). The distance between a waveguide and a resonator ring of below 1 μm is possible (figures 6(a), (b)). It is also feasible to fabricate a grating coupler whose profile is almost binary (figure 6(c)). Moreover, due to the above-mentioned change of shape related to the viscosity of the RTIL, grating couplers of different shapes (e.g. sinusoidal) are potentially achievable using the discussed technique.

To verify whether the polymerized RTIL-based structures can be useful as photonic elements the optical properties were measured. The square polymerized structures (of 1 mm\(^2\) area and of about 1 μm thickness) prepared on glass substrates were used for the studies. As can be seen from the absorption/transmittance spectra (figure 7) the polymerized RTILs are partially transparent in the visible range and completely transparent in the near-IR. Besides, the refractive indices, evaluated based on ellipsometry measurements, are about 1.6–1.7 in the wavelength range of 600–2000 nm for both polymerized RTILs. This value is a little higher than the refractive index (about 1.5) of a typical soda lime glass, and allows for photonic waveguide fabrication, which is often done using glass substrates. The propagation of light in a polymerized RTIL waveguide, fabricated on SiO\(_2\)/Si substrate, was experimentally confirmed, as shown in figure 8. The light from the supercontinuum laser source (NKT Photonics SuperK Versa) was introduced to the waveguide by optical objective and the image was collected by another objective and captured by visible light CCD camera.

Therefore, the electron-beam-activated polymerization of RTILs seems to be a good method for the fabrication of photonic elements, especially for infrared. The applicability of the method for visible light components can be also considered, but with respect to the limited light transmission. Besides, it should be mentioned that, due to low throughput of electron beam patterning, the proposed fabrication technique is mainly applicable in low-volume manufacturing.

As a final point, it was presumed in this work that solidification of RTIL is caused by electron beam activated polymerization. This assumption results from the fact that [Allmim]-based RTILs have a polymerizable allyl group (−CH\(_2\)=CH=CH\(_2\)). It is known that imidazolium-based ionic liquids with vinyl group (−CH=CH\(_2\)) can be polymerized via
a free radical mechanism using polymerization initiators such as compounds having an azo group \([45-49]\). In our experiments, we do not use any added initiators and the polymerization is triggered by high-energy electron irradiation. Electron beam induced polymerization has already been studied by other researchers \([50, 51]\) but they have not considered polymerizable ionic liquids except for the pioneering work by Minamimoto et al who suggested allyl group oligomerization of RTIL based on FT-IR and Raman spectra measurements \([34]\). The energy of electron beam radiation (30 keV in this study) is sufficient to cause cleavage of chemical bonds to form radicals from RTIL species. Wishart, Shkrob and their co-workers have shown that various radicals can be created from ionic liquids by ionizing radiation \([52-54]\). Therefore, it is reasonable to think that in our experiments RTIL-derived radicals produced by high-energy electrons initiate free radical polymerization by means of allyl groups. On the other hand, it is also possible that polymerization is not only initiated but also propagated by the electron beam \([55]\) which would imply a more complicated route of reactions.

With regard to the above discussion, it is noteworthy that polymerized RTIL is also present in unexposed areas, especially in spaces between close-packed structures (see figure 6(c)). Although this phenomenon could be caused by the proximity effect, typical for electron beam lithography, polymerization initiated by radicals that were formed by the electron beam and flowed to unexposed areas cannot be excluded.

4. Conclusions

In summary, it was demonstrated in this study that polymerizable RTILs can be used as base materials for the fabrication of micro-optical elements operating in the IR range. Electron beam activated polymerization of \([\text{Allmim}]\text{[Cl]}\) enables one to obtain polymer microstructures of satisfactory quality, low roughness and with good adhesion to silicon and glass substrates. In comparison to \(\text{NTf}_2\)-based ionic liquid, the chloride-based RTIL is more viscous and consequently less deformed under a high-energy electron beam. This effect allows one to fabricate microstructures of almost binary shape for \([\text{Allmim}]\text{[Cl]}\) liquid, whereas low-viscous \([\text{Allmim}]\text{[NTf}_2]\) seems to be a prospective material for the fabrication of smooth, rounded or sinusoidally-shaped structures.

The proposed method of fabrication of optical components yields repeatable results. The RTIL film preparation is relatively simple and a popular ethanol is used for development after electron exposure. Most importantly, solvent-free ionic liquid is used for thin film formation, which makes the whole procedure novel and green.

Finally, the obtained results open up new prospects for the structuring of spatial structures, including the fabrication of 3D components and gray scale e-beam lithography. The use of ionic liquids with different viscosities and their mixtures allows us to control the shape and thickness of fabricated components.
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