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Electron beam writing of epoxy based sol–gel materials

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Abstract We report the use of an epoxy based hybrid sol–gel material as negative resist for electron beam lithography (EBL). The matrix has been prepared starting from 3-glycidoxypropyltrimethoxysilane as specific organic–inorganic precursor and the synthesis has been strictly controlled in order to preserve the epoxy ring and to obtain a proper inorganic cross-linking degree. The film has been exposed to an electron beam, inducing the polymerization of the organic part and generating the film hardening. Preliminary results of a resolution test on the synthesized epoxy based sol–gel material, performed with electron beam lithography, are presented. Structures below 300 nm were achieved. The direct nanopatterning of this hybrid sol–gel system simplify the nanofabrication process and can be exploited in the realization of photonic devices. A demonstration has been carried out doping the hybrid films with commercial Rhodamine 6G and reproducing an already tested laser structure.

Keywords Hybrid organic–inorganic materials · Sol–gel · Glycidoxypropyltrimethoxysilane · Epoxy · Electron beam lithography

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1 Introduction

Over the years, patterning of sol–gel hybrid materials became a field that have attracted progressively more attention because of its important role in device realization. The versatility of the sol–gel process can be really exploited to match the device requirements, tailoring the chemical (corrosion resistance, hydrophobicity...) and physical properties (refractive index, mechanical resistance...) of the materials. In literature, many examples of UV patterning can be found on photosensitive sol–gel materials, being the UV light the most used source in the field of microfabrication. Several waveguiding structures have been obtained especially on sol–gel materials containing double bond precursors such as vinyltriethoxysilane, allyltriethoxysilane or trimethoxysilylpropylmethacrylate [1–5]. The more advanced and studied material is based on methacryloxypropyltrimethoxysilane (MAPTMS) often mixed with zirconium propoxide chelated by methacrylic acid. These materials behave as resists thanks to the polymerization process activated by the presence of a radical photocatalyst sensitive to the UV light [6]. However, for the greatest number of cases in these materials the polymerization is uncompleted and the final properties are not optimized because the free radicals, especially in coating processes, are inhibited by oxygen.

Epoxy based systems are considered a good alternative to methacrylic and acrylic materials because of their low shrinkage under UV polymerization and their good adherence on various substrates [7–9]. In addition, the epoxy groups undergo cationic photopolymerization, which is known to be insensitive to oxygen.

Whereas there are many examples of UV sol–gel patterning, works about the direct patterning of sol–gel materials after e-beam exposures are very limited,

especially regarding the organic–inorganic hybrids [13].

In most cases, the sol–gel structures are obtained by the deposition of a sol–gel solution on EB pre-pattern structure realized using commercial resists (resist mold) [10, 11]. After thermal treatment, the resist template is removed by a chemical solution, leaving only the sol–gel features.

M. Saifullah et al. [12] have synthesized a sol–gel system based on titanium *n*-butoxide, $Ti(OBut)_4$ chemically modified with benzoylacetone (BzAc) that behaves as a EB sensitive material. This system acts as a negative resist because of the rapid breakdown, under electron beam, of the chelating rings as well as the phenyl groups.

In this work, we report some examples of nanostructures obtained by patterning an epoxy based sol–gel system, without the addition of a photocatalyst. The use of electrons as writing source allows to reach higher resolution compared to the UV light, commonly used with hybrid sol–gel materials. Finally, the more representative properties of a photoresist have been investigated. In particular, preliminary results on the smaller features obtainable employing the synthesized hybrid sol–gel material have been presented.

2 Experimental

2.1 Materials

3-Glycidoxypropyltrimethoxysilane (GPTMS), germanium tetraethoxide (TEOG) and 2-Methoxyethanol (MeEtOH) were purchased by Aldrich and employed without further purification. 2-Methoxyethanol was used as solvent, bidistilled water for hydrolysis and hydrochloric acid (1N) as catalysts.

2.2 Synthesis of a hybrid patternable sol–gel material

3-Glycidoxypropyltrimethoxysilane (GPTMS) is the main precursor of the sol. This compound bears an epoxy ring acting as silica network modifier before the polymerization process. GPTMS is mixed with TEOG, a tetrafunctional alkoxide contributing to the inorganic network formation.

The solution, labelled G8Ge2, was synthesized in acidic conditions with a final concentration of 65 (SiO_2 + GeO_2) g/L. The detailed procedure was already described [13].

Films were deposited by spin coating technique on silicon substrates. After deposition all the samples were pre-baked 0.5 h at 80 °C. Thickness ranging from about 200 to 500 nm was achieved by varying the spinning rate between 1,500 and 6,000 rpm.

Electron beam lithography (EBL) was performed by means of a Carl Zeiss X-beam 1540, located at Elettra Synchrotron (Trieste) [14], using 30 keV beam acceleration and 30 pA current. A test pattern made up of lines and small gratings was used (Fig. 1). In addition to the resolution study, the pattern was exploited to make even a dose matrix. Therefore, the structures become progressively smaller from left to right in a range of 2 μm–50 nm and the dose increases of a factor 30 from bottom to up.

3 Results and discussion

The final structure of G8Ge2 system is an essential key point for the patterning process. Exploiting the flexibility of the sol–gel method and through a precise synthetic strategy is possible to control the materials properties. In spite of the presence of a Lewis acid alkoxide, the choice of a right molar ratio between the precursors allows to preserve the epoxy ring, which is critical for this class of systems. It is well known that a TEOG molar content of about 20% does not open the epoxide, even in acidic condition [15].

The films were exposed to an electron beam, inducing the polymerization of the organic part and generating the film hardening [13]. Figure 1 shows the test pattern made up of lines and gratings of different sizes. The same horizontal line has different dimensions with similar dose, while the same column has identical size with increasing doses. By this way, the resolution increases in abscissa and the electron dose become higher in ordinate. This simple design contains several information and allows to estimate the critical resolution of this particular epoxy based system and the right dose for each size.

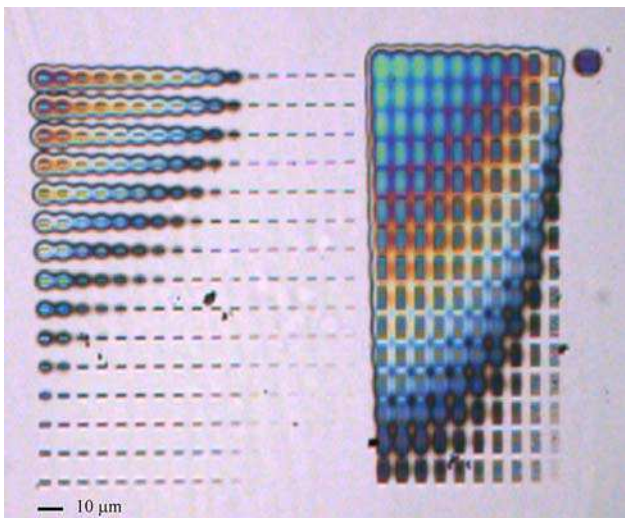

Fig. 1 Optical microscopy of the whole pattern (line and gratings) used for the resolution test of G8Ge2 matrix by electron beam lithography (EBL)

To explore a wider range of doses, the test pattern was replicated four times with a different initial electron dose D_0. Figure 2 compares the lines structures obtained with starting doses of 5, 10, 20 and 40 μC/cm^2. As can be noted, increasing the value of D_0 the number of over-exposed structures raises, especially for the lines with larger width. On the contrary, the features with high resolution require larger doses.

The small grating reported in Fig. 3 confirms this statement. The structure with nominal line width of 100 nm shows instability and shape deformation. The too low exposure probably causes an incomplete polymerization of the organic part and an insufficient hardening of the system.

By using the formula $D_f = x^{(n-1)} D_0$, where n is the matrix dimension and x is the dose scaling factor between to close structures, it is possible to calculate the minimum dose necessary for this feature size. To avoid these problems, the gratings of 100 nm nominal dimension have to be exposed at least at 30 μC/cm^2.

Figure 4 reports a grating of the same resolution exposed with a dose of about 40 μC/cm^2. The pattern does not show instability and appear to have a quite good definition. Therefore, this test demonstrates the possibility to simply realize different sets of gratings with a precise dimension.

The performance of any photoresist can be characterized by its contrast curve. The contrast curve is a logarithmic sensitivity plot showing resist thickness versus exposure dose. The contrast γ is defined as the linear slope of the transition region and describes the ability of the resist to distinguish between exposed and unexposed areas. In a previous work [16], a contrast value γ of about 2.2 was estimated for the G8Ge2 system developed in MF-319 for 20 s.

Strictly related to the contrast value is the resist final resolution. Figure 5 reports one of the patterned lines. The structure shows a relevant broadening respect the theoretical value and measures about 300 nm. A possible explanation could be that the scattering broadens the beam inside the sol–gel hybrid resist and the resist is exposed on a larger area than the initial spot, even if the beam spot on resist top surface is very small. Interactions in solid limit the minimum size and the increase in the effective beam diameter, due to forward scattering, is given by d_{eff} (nm) = 0.9 $(t/\text{V})^{1.5}$, where t is the resist thickness in nm and V is the voltage in kV [17]. This effect is minimized by

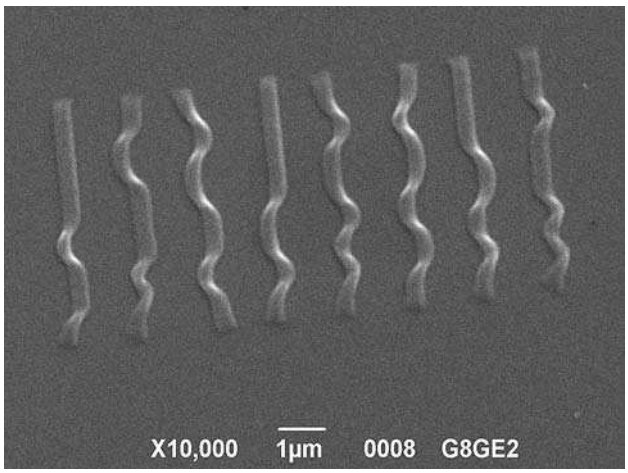

Fig. 3 Examples of initial direct patterning problems due to a too low exposure dose and poor adhesion

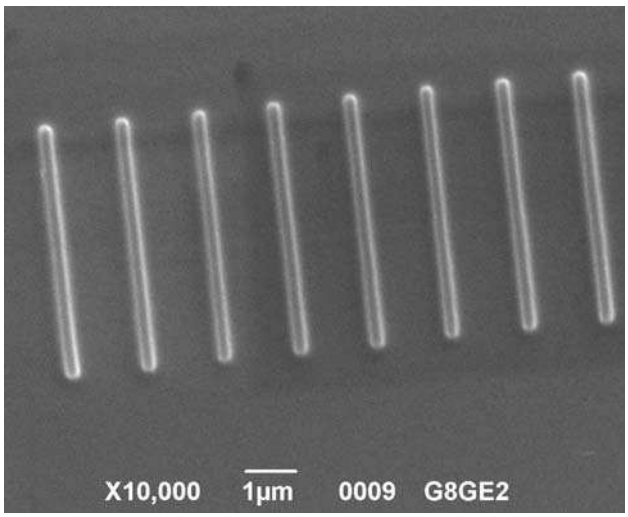

Fig. 4 Example of a good grating structure achieved by EBL

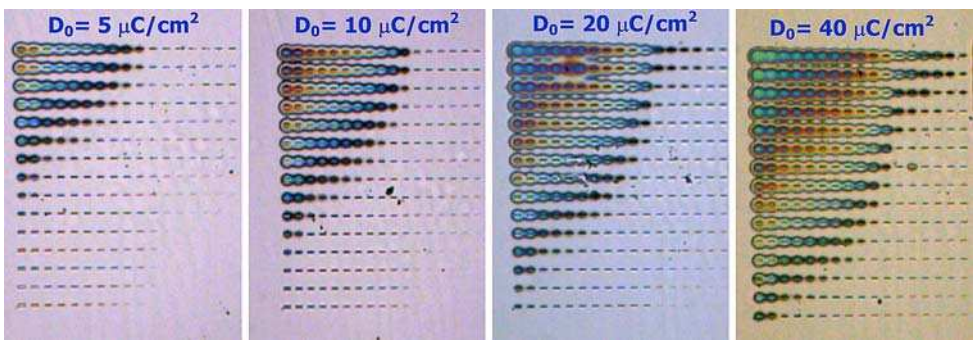

Fig. 2 Details of the test pattern (lines). The dose matrix starts at different initial exposure dose D_0

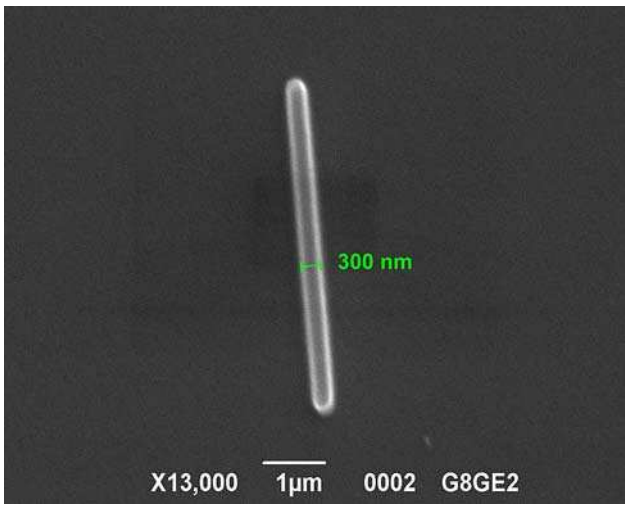

Fig. 5 Example of a structure achieved by EBL, with a resolution of about 300 nm

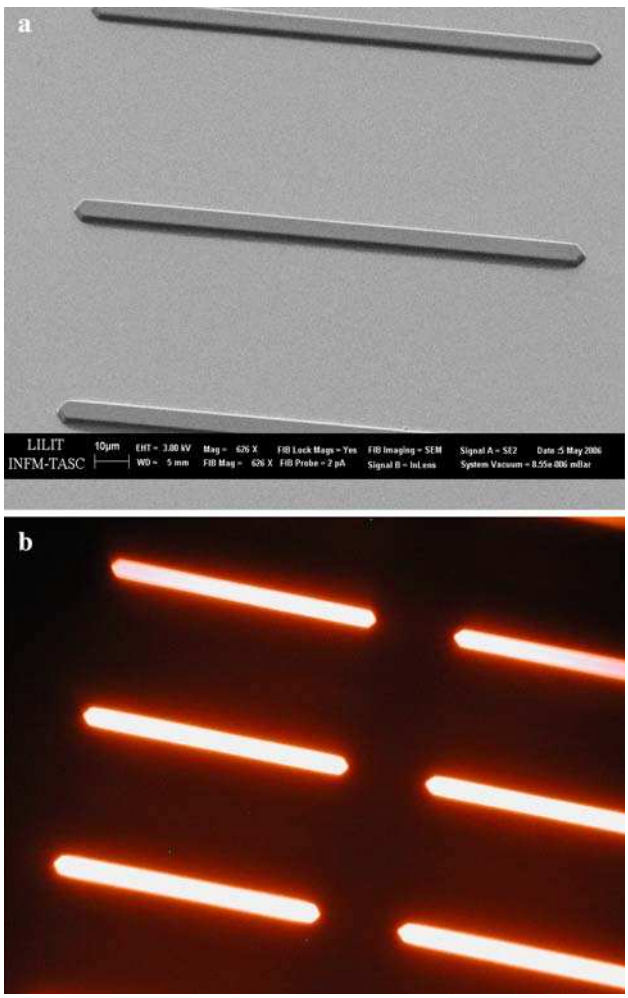

Fig. 6 Examples of patterned structures achieved by EBL on Rh6G doped G8Ge2 films. The figure shows (**a**) the SEM image and (**b**) the fluorescence of the structures

using the thinnest possible resist and the highest accelerating voltage.

In this case, the film thickness was about 350 nm, probably too thick and the beam energy was 30 KeV with a spot size of 30 nm. To achieve higher resolution, an optimization of these experimental parameters is necessary. Anyway, the results can also reveal that this is the critical feature in term of sensitivity for this class of hybrid sol–gel resists.

To demonstrate the worth of this approach, a microfabricated light source containing the laser dye Rhodamine 6G was realized via EB lithography. In particular, the structure can work as a laser [18]. The device is based on the waveguiding action from a strip of doped hybrid film on top of a silicon dioxide surface surrounded by air.

Since the refractive index of G8Ge2 hybrid ($n = 1.51$) is higher than air and silicon dioxide ($n = 1.46$), the strip will function as a light waveguide. The triangular ends of the structure waveguide reflect light via total internal reflection, and the patterning of this tip shape requires a high resolution. The light is subject to total internal reflection on each of the 45° surfaces before it returns into the waveguide. The reflection happens in both ends of the waveguide, yielding the optical feedback that could form an optical resonator [18].

Figure 6 shows the desired structures obtained on a rhodamine 6G doped G8Ge2 film by direct patterning.

4 Conclusion

The possibility of using sol–gel materials as resists can offer many advantages in the device fabrication. The versatility of sol–gel process can be exploited to synthesize active sol–gel systems with tailored properties that at the same time behave as resist, allowing the realization of selected patterns. This could strongly simplify the realization of active devices.

An e-beam patternable GPTMS based hybrid sol–gel material was prepared. The main properties typical of a resist were investigated such as the contrast curve. Particular attention was paid to the relation between the dose and features' size, showing that smaller dimension required higher electron dose. Different micro and nanostructures were succesfully patterned, reaching a final resolution of about 300 nm. Exploiting these results, a laser structure was patterned using a Rhodamine 6G doped G8Ge2 matrix.

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