Magnetic Nanocrystals Modified Epoxy Photoresist for Microfabrication of AFM probes

C. Ingrosso\textsuperscript{a,b,*}, C. Martin\textsuperscript{c,d}, A. Llobera\textsuperscript{c}, F. Perez Murano\textsuperscript{c}, C. Innocenti\textsuperscript{e}, C. Sangregorio\textsuperscript{e}, A. Voigt\textsuperscript{f}, G. Gruetzner\textsuperscript{f}, J. Brugger\textsuperscript{d}, M. Striccoli\textsuperscript{b}, A. Agostiano\textsuperscript{a,b}, M. L. Curri\textsuperscript{b}

\textsuperscript{a}Dip. di Chimica, Università di Bari, via Orabona 4, Bari 70126, Italy
\textsuperscript{b} CNR-IPCF, Sez. Bari c/o Dip. di Chimica, Università di Bari, via Orabona 4, Bari 70126, Italy
\textsuperscript{c}Institut de Microélectronique Barcelona (IMB-CNM), Campus UAB, Bellaterra 08193, Spain
\textsuperscript{d} Microsystems Laboratory, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne CH-1015, Switzerland
\textsuperscript{e}UdR INSTM and Dip. di Chimica, Università di Firenze, via della Lastruccia 3, Sesto Fiorentino I-50019, Italy
\textsuperscript{f}Micro Resist Technology GmbH, Koepenicker Str. 235, Haus 2111, Berlin 12555, Germany

Abstract

A novel magnetic nanocomposite based on a negative tone epoxy photoresist and magnetic colloidal Fe\textsubscript{2}O\textsubscript{3} nanocrystals (NCs) has been manufactured. The magnetic properties and the UV-photostructurability of the nanocomposite have been investigated. After the incorporation, the Fe\textsubscript{2}O\textsubscript{3} NCs preserve their magnetism which is conveyed to the photoresist and retained after the UV-lithography process. High aspect ratio 3D microstructures have been fabricated by processing the nanocomposite with conditions comparable to those used for the pure photoresist. AFM probes on the Fe\textsubscript{2}O\textsubscript{3} NC modified photoresist have been fabricated to confirm suitability and applicability of the preparation procedure and of the novel nanocomposite.

Keywords: colloidal nanocrystals; epoxy photoresist; magnetic nanocomposite; UV-lithography; fabrication; AFM probes

1. Introduction

Nanocomposites based on polymers and nanoparticles represent a class of high impact functional materials, able to convey the unique size- and shape-dependent properties of the nano-objects to highly processable resins\textsuperscript{1}. The incorporation of nanocrystals (NCs) in epoxy-type photoresists allows conveying properties to such class of outstanding photo-structurable polymers which lack of inherent functionalities, but grant superior lithographic performances when patterned by standard UV-lithography\textsuperscript{2}. The current challenge consists on the incorporation of magnetic colloidal Fe\textsubscript{2}O\textsubscript{3} NCs in a negative tone epoxy-type photoresist to convey magnetism maintaining its patterning resolutions required for manufacturing bio-micronanoelectromechanical systems (Bio-MEMS/NEMS). Iron oxide nanoparticles have been recently attracted interest for their magnetic properties exploited in high-density magnetic information storage devices, magnetic resonance imaging and drug-delivery vehicles and for their photo/catalytic and gas-sensing properties used in environmental purposes\textsuperscript{3}. In this work, the approach recently optimized by the authors\textsuperscript{4} for the incorporation of luminescent colloidal core shell CdSe@ZnS NCs in the same epoxy photoresist has been applied. The nanocomposite preparation has relied on the dispersion of organic capped
Fe₂O₃ NCs in an epoxy photoresist formulation by using a common solvent. Pre-synthesized colloidal Fe₂O₃ NCs have been incorporated in an anisole based epoxy photoresist formulation that has shown a promising chemical compatibility with the organic surface capping of colloidal NCs providing a successful fabrication of 3D high-aspect-ratio microstructures. After the incorporation in the photoresist, the Fe₂O₃ NCs retain their magnetic properties which are conveyed to the photostructurable matrix and are not affected by the UV-lithography fabrication process. Nanocomposite films of the Fe₂O₃ NC modified photoresist have been patterned in conditions comparable to those used for the pure resist and permanent structures have been fabricated with a micrometer scale resolution, confirming the preservation of the overall UV-structuring capability.

Finally, the suitability and applicability of the preparation procedure and of the novel magnetic nanocomposite in fabricating permanent components have been demonstrated. The new material has shown outstanding properties as structural material for AFM probes. The achieved protocol can be extended to the fabrication of permanent functional microstructures to integrate in Bio-/MEMS and miniaturized devices for sensing, environmental, information storage and biomedical purposes.

2. Experimental Section

Oleic acid (OLEA)-capped Fe₂O₃ NCs, 11 nm in diameter, have been prepared and then dispersed in toluene. For the nanocomposite preparation, 200 µl of a 0.75 M toluene solution of Fe₂O₃ NCs have been added to 5 g of an anisole based epoxy photoresist formulation. The overall NC concentration in the photoresist solution is 2 × 10⁻³ M. The mixture has been sonicated with ultrasounds at room temperature until complete dispersion of the NCs in the photoresist solution.

Magnetic measurements have been performed using a Quantum Design SQUID magnetometer. Hysteresis loops have been measured at 2.5 K in the field range ± 5 Tesla. The data have been corrected for the diamagnetic contribution of the substrate which has been separately measured.

The fabrication procedures have been performed in clean room under yellow light. Resolution tests have been carried out in order to obtain the best exposure doses for the modified resist. Layers of photoresist have been spin-coated with a thickness of 5 μm and exposed with an UV-lamp (365 nm). All the processes (soft bake, post-exposure bake, development and hard bake) have been carried out as reported elsewhere. The fabrication process of photoplastic AFM probes has been based on multiple spin-coating, exposure and development steps of the negative tone epoxy photoresist on a silicon wafer, being the latter used as a mould for the tip. Scanning Electron Microscopy (SEM) micrographs have been obtained coating the structures with a thin layer of evaporated gold (~ 20 nm), which can slightly modify the final dimension of the imaged features.

3. Results and discussion

OLEA-capped magnetic NCs have been synthesized by the well-assessed colloidal technique occurring with the thermal decomposition of the precursors in hot coordinating solvents. After a post-synthetic procedure toluene solutions of the NCs have been dispersed in an anisole based formulation of a negative tone epoxy photoresist. Such a formulation provides the best suitability for NC dispersion. The nanocomposites have been deposited onto silicon substrates as thin films by spin-coating and have been thermally treated according to the typical pre-baking process of the photoresist to allow the evaporation of the solvent and enhance the adhesion to the substrate. Fig. 1 compares the magnetic properties of the bare NC solution with those of the nanocomposite before and after the UV-light exposure.
As shown by Figure 1, the hysteresis curves measured at 2.5 K, after the removal of the diamagnetic contribution of the substrate, do not significantly differ upon NC incorporation in the nanocomposite and after the UV-lithography process. At low temperature for all the investigated samples the particles are in the blocked state providing open hysteresis loops with coercivities of 55 mT and reduced remnant magnetizations, $H_{0T}/H_{5T}$ between 0.25 and 0.35.

Both the pure resist and the Fe$_2$O$_3$ NC modified epoxy photoresist have been processed in a clean-room environment under the same UV-lithography conditions. 5 μm thick finger-like structures have been fabricated on both the nanocomposite and on pure resist with different widths and pitches to determine and compare dose and resolution. Then, the fabricated structures have been characterized morphologically.

Fig. 2 shows the scanning electron microscopy (SEM) top-view image of the finger-like structures on the Fe$_2$O$_3$ NC modified epoxy photoresist.

A reduction in the resolution of the nanocomposite with respect to that of the bare photoresist has been observed. As shown by Fig. 2 the width and pitch of the developed finger-like structures on the Fe$_2$O$_3$ NC modified epoxy photoresist are 3.8 μm and 6.1 μm, respectively, while those of the pure resist are 2.2 μm and 4.0 μm (data not...
shown), respectively. At the same time, the need to increase of the exposure dose of the nanocomposite with respect to that of the pure photoresist has been recognized. Namely, the nanocomposite has been patterned with an exposure dose of 108 mJ/cm² and the pure photoresist with a dose of 72 mJ/cm². Such evidence can be reasonably accounted for by a decrease of the optical transparency of the photoresist upon the NC incorporation.

AFM investigations of the finger-like structures show morphology compatible with the formation of NC aggregates as well as the occurrence of holes, whose sizes range from few to tens of nm on the surface of the microstructures (data not shown). The aggregation could be reasonably ascribed to possible phase separation phenomena that occur at the interfaces between the NCs and the photostructurable matrix, probably originated from a low chemical compatibility of the NC surface chemistry with the host resist. In addition, the NC superstructures can also originate from an inhomogeneous assembly induced by interdigitation of the NC capping alkyl chains. Both the confined phase separation phenomena and the NC aggregation can reasonably explain the occurrence of the holes. Finally, the segregation phenomena locally occurring at the nanocomposite surface can also likely provide a local change in surface tension with a concomitant, confined, variation of solvent evaporation during film deposition.

The results obtained from the morphological investigations of the Fe₂O₃ NC modified epoxy photoresist demonstrate that the lithography properties of the nanocomposite match the requirements for MEMS and microdevices fabrication, because a micromachining process can be effectively carried out achieving a micrometer scale patterning resolution. Namely, light reflection, scattering and diffraction phenomena may assist the cross-linking of the photoresist matrix upon exposure with UV-light. In addition, multiple diffraction and scattering of light allow for the exposure of the photoresist volume behind the NCs being the used exposure wavelength larger than the dimension of the NCs dispersed in the photoresist. At the same time, multiple scattering and reflection phenomena of light from the NC aggregates aid further light penetration in the photosensitive moiety.

AFM probes on the novel magnetic Fe₂O₃ NC modified epoxy resist have been designed and fabricated in order to confirm the suitability and applicability of both the preparation protocol and novel material for MEMS and integrated microdevice purposes. Fig. 3 shows a SEM image of a manufactured AFM probe.

![SEM image of an AFM probe made of the Fe₂O₃ NC modified epoxy based photoresist. (b) Zoom of the tip apex.](image)

The AFM probe presents a tip apex radius below 30 nm (Fig.3 b) attesting for the outstanding feasibility of the novel nanocomposite material for fabricating permanent components which possess highly resolved features.

**4. Conclusions**

Novel nanocomposite material based on a negative epoxy photoresist and magnetic colloidal Fe₂O₃ NCs have been successfully manufactured by setting up suited processing protocol. The incorporation of the magnetic NCs adds magnetic characteristics to the photoresist without modifying its outstanding UV-structurability. The Fe₂O₃ NC modified epoxy photoresist has been successfully patterned by applying UV-lithography parameters typically used for commercially available epoxy formulations and the micromachining process does not negatively affect the
magnetism. Multiple diffraction and scattering phenomena arising from the NCs and diffraction and reflection from related aggregates allow the proper photopolymerization of the photoresist. 3D high aspect ratio microstructures have been fabricated with a micrometer scale resolution that complies well with the resolution required for MEMS and integrated microdevices. The efficiency of the method and the suitability of the novel material for permanent application have been demonstrated by fabricating microcomponents as AFM probes. The promising properties of such a novel nanocomposite can be exploited for manufacturing functional microcomponents to integrate in Bio-/MEMS and miniaturized devices for sensing, environmental, information storage and biomedical purposes. In addition, the achieved modification protocol can be extended to other classes of colloidal NCs with specific (semi)conductive, mechanical and optical functionalities.

Acknowledgements

This work was partially supported by the EC-funded Project NOVOPOLY (Contract no. STRP 013619) and Italian MIUR SINERGY program (FIRB RBNE03S7XZ).

References

1. Balazs AC, Emrick T, Russell TP. Nanoparticle Polymer Composites: Where Two Small Worlds Meet. Science 2006; 314: 1107-1110.
2. Lorenz H, Despont M, Fahrni N, Brugger J, Renaud P, Vettiger P. High aspect ratio ultrathick, negative-tone near-UV photoresist and its applications for MEMS. Sens. & Act. A 1998; 64: 33-39.
3. a) Jain TK, Torres MM, Sahoo SK, Leslie-Pelecky D, Labhasetwar V. Iron Oxide Nanoparticles for Sustained Delivery of Anticancer Agents. Molecular Pharmaceutics 2005; 2: 194-205. b) Artemov D, Mori N, Okolie B, Bhujwalla ZM. MR molecular imaging of the Her-2/neu receptor in breast cancer cells using targeted iron oxide nanoparticles. Magn. Res. Med.. 2003; 49: 403 – 408.
4. Ingrosso C, Fakhfouri V, Striccoli M, Agostiano A, Voigt A, Gruetzner G, Curri ML, Brugger J. An Epoxy Photoresist Modified by Luminescent Nanocrystals for the Fabrication of 3D High-Aspect-Ratio Microstructures. Adv. Funct. Mat. 2007; 17:1999-2006.
5. a) Casula MF, Jun Yw, Zaziski DJ, Chan EM, Corrias A, Alivisatos AP. The concept of delayed nucleation in nanocrystal. Demonstration for the case of iron oxide nanodisks. J. Am. Chem. Soc. 2006; 128: 1675–1682. b) Park JG, Noh HJ, Kim JY. Controlled synthesis of monodisperse magnetic iron oxide nanoparticles. Angew. Chem. Int. Ed. 2005; 44: 2872-2877.
6. Martin C, Llobera A, Villanueva G, Voigt A, Gruetzner G, Brugger J, Perez-Murano F. Stress and aging minimization in photoplastic AFM probes. Microelectron. Eng. 2009; 86: 1226-1229.
7. Shenhar R, Norsten TB, Rotello VM. Polymer-Mediated Nanoparticle Assembly: Structural Control and Applications. Adv. Mater. 2005; 17: 657-669.
8. Huang QR, Volksen W, Huang E, Toney M, Frank CW, Miller RD. MSSQ/P(MMA-co-DMAEMA) Nanocomposites. Chem. Mater. 2002; 14: 3676-3685.