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Directly patternable high refractive index ferroelectric sol–gel resist

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HIGHLIGHTS

- A new formula directly patternable PZT high refractive index resist is presented.
- The gel is sensitive to both UV and electron beam exposure.
- The refractive index can vary from 1.68 up to 2.33 (@400 nm).
- Direct nanopatterning by means of Focused Ion Beam (FIB) lithography was verified.
- High aspect ratio hollow nanostructures will be presented.

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ABSTRACT

The development of a ferroelectric negative tone sol–gel resist for Ultraviolet (UV) and Electron Beam (EB) lithography is presented. A new system based on Lead Zirconate Titanate (PZT, with formula $PbZr_{0.52}Ti_{0.48}O_3$) was synthesized by sol–gel method. The lithographic performances were investigated and several structures spanning from the micron range down to less than 50 nm have been achieved by UV and EB lithography. The system interaction with UV light and Electron beam was thoroughly characterized by FT-IT spectroscopy. The exposed PZT was annealed at high temperatures in order to study the crystalline phase evolution, the optical constants values and stability of patterned structures. After exposure and annealing, the refractive index of the material can vary from 1.68 up to 2.33 (@400 nm), while the ferroelectric behaviour seems to be maintained after high temperature annealing. These results suggest a possible application of PZT resist not only as ferroelectric but also as nanopatternable high refractive index material. Moreover, direct nanopatterning by means of Focused Ion Beam (FIB) lithography was verified and the potentiality for the preparation of high aspect ratio hollow nanostructures will be presented.

1. Introduction

During the recent years there was a growing interest in the application of nanostructured ceramic coatings. Materials such as transition metals oxides: Hafnia Oxide (Hf_2O_3), Titania (TiO_2), Zirconia (ZrO_2), Alumina (Al_2O_3), Silica (SiO_2), Indium Tin Oxide (ITO) and Lead Zirconate Titanate (PZT) can be applied in a wide variety of fields thanks to their chemical and thermal stability, mechanical resistance and advanced optical, structural and electrical properties. In order to extensively apply these materials in nanofabrication processes, it's of great interest to engineer the material in order to make it directly patternable. In fact, the traditional lithography and nanopatterning of inorganic films consists in complicated and time consuming processes. These comprises physical deposition onto a pre-patterned organic resist which is then removed by the lift-off process leaving the patterned structures on the substrate [1].

Among other ceramic films, PZT had found enormous interest in several fields of applications. Thanks to its perovskite structure PZT is currently the most frequently used intelligent ceramics material. Through the use of its properties such as piezoelectrics, ferroelectrics and pyroelectrics it can be used as many important components such as transducers [2], actuators [3], non-volatile memory [4], infrared sensors [5], etc. Moreover, during the very last years, perovskite materials have started to emerge as the next generation photovoltaic technological solution [6], hence, as one of the most important perovskite nanostructured material, PZT can find interesting application also in this field [7].

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In this context, to use PZT films in all these fields of application it could be of great impact to develop the material in a form that can be easily patternable both at micro and at nanometric scale level. Several approaches were reported for easy patterning techniques of PZT: for instance Banerjee et at [8]. reported a single step epitaxial lift-off technique for submicron patterning without using any etching. Another interesting approach for nanometric PZT patterning was reported by Lee et al. [9] that used an ultrathin anodic alumina membrane as a lift-off mask to deposit PZT nanostructures at high temperatures. In order to avoid multiple processing steps of fabrication a direct lithography approach can be used. Two main methods exist for such a porpoise, soft lithography (see for example [10–12]) and sol–gel process. In particular, the sol–gel process provides a method to fabricate directly patternable PZT films, by using a suitable sensitive sol. Different papers reported examples of direct patterning of PZT gel films (see for example [13–18]), but they are mainly focused on low resolution direct photolithography performed by means of UV radiation. To the best of our knowledge, only one example of direct high resolution electron beam lithography was reported by Park et al. [18]. They were the first to investigate a method for the direct-patterning of PZT films with resolution down to 50 nm via electron beam with a very high exposure dose (4.5 mC/cm^2).

In the current paper we will present a material synthesis that allows direct patterning of PZT ($PbZr_{0.52}Ti_{0.48}O_3$) by means of both electron beam and UV light. PZT thin films were obtained by sol–gel route, starting from an organically modified system. Chemical modifications through Polyvinylpyrrolidone (PVP) or acetylacetonate as stabilizing agents were commonly proposed [19]. In this case, an organic chelating molecule bearing a polymerizable functionality will be exploited. We will focus our attention on the study of the PZT resist interaction with UV light and electron beam, especially on the evolution of organic components and the refractive index change. We will investigate how the exposure impacts the crystallization at high temperature and how the ferroelectric properties are altered. To the best of our knowledge, direct nano-patterning by means of Focused Ion Beam will be tested on PZT films for the first time and the preparation of high aspect ratio hollow nanostructures will be presented.

2. Experimental

2.1. The synthesis of PZT based system, film deposition and thermal treatment

An organically modified Lead Zirconate Titanate system with formula $PbZr_{0.52}Ti_{0.48}O_3$ was prepared by low temperature sol–gel route, through hydrolysis and condensation of alkoxide precursors. All the reagents were purchased from Aldrich® and used without further purification.

Titanium(IV) Isopropoxide was mixed with 2-methoxyethanol (ratio v/v 1:5) and stirred for 15 min at room temperature (RT). The titanium precursor is very reactive and sensitive to water, so this solvent allows to control and hinder the rate of sol–gel network formation in order to avoid precipitation of a TiO_2 particulate. After this reaction time, Zirconium butoxide and methacrylic acid (MAA) [molar ratio MAA: (Ti + Zr) = 0.5:1] were added to the sol in order to promote the formation of a three dimensional inorganic network and an homogeneous distribution of the oxides (ZrO_2 and TiO_2) within the material, without phase separation. This solution was stirred for 30 min at RT, before the addition of Lead acetate, $Pb(CH_3CO_2)_2 \cdot 3H_2O$. MAA molecules, thanks to the carboxyl group, act as chelating agent, binding the metal ions through coordinate bonds and stabilizing the solution. Therefore, the final synthesized system consists in inorganic oxides network surrounded by MAA chelating agent playing the role of network modifier and sensitive element through the presence of polymerizable C=C functionality.

After the complete dissolution of Lead acetate, the PZT system was heated at 80 °C and refluxed for 2 h. An excess of 10 wt% PbO with respect to the nominal composition (Pb:Ti:Zr = 100:48:52) was adopted in order to compensate for PbO loss during annealing at high temperatures. The final sol concentration was set to 100 g/l ($PbO + TiO_2 + ZrO_2$) according to the desired thickness. The solution was filtered by a microporous membrane (0.2 μm Millipore®) to remove dust or large particles and improve the resist spin-coating quality. Moreover, the sol remains stable for up to 1 year even in the more concentrated condition [150 g/l ($PbO + TiO_2 + ZrO_2$)].

PZT films with suitable thickness were deposited by spin coating technique on $Pt/SiO_2/Si$ surfaces, showing no adhesion problems. In particular, Pt layer deposited on silicon acts as a buffer layer, which prevents the Pb ions from diffusion into silicon substrates during the annealing treatments at high temperatures and helps the crystallization of PZT films. The Pt layer has also the function of bottom electrode during the ferroelectric characterization.

All the film samples were thermal treated on a hot plate at 80 °C for 15 min in order to remove the residual solvent (post application-bake, PAB) before the lithographic processes.

Finally, spin coated films were also annealed at high temperatures in order to promote the crystalline phase formation and study the optical constant evolution: annealing temperature of 750 °C was applied for 30 min to some samples.

2.2. Fabrication tools and characterization methods

Microstructures were made using a Hamamatsu LC5 HgXe UV spot light source, enhanced in the deep UV (250 nm band) and having a power density of around 150 mW/cm^2 on the sample surface. The PZT MAA films were illuminated in air for 2, 5 and 10 min (corresponding doses 18, 45 and 90 J/cm^2, according to the features resolution), through a quartz chromium mask with different patterns.

Nano-patterning was achieved by means of electron beam lithography (EBL) by using a FEI HeliosNanolab650 dual beam system having an electron acceleration voltage of 30 kV. EBL tests was performed on films with thickness in the 100–400 nm range. Different beam currents were used for the exposure. High resolution structures were created by using a current of 40 pA and the used electron beam dose was 1.5 mC/cm^2. After the exposure, the samples were post-baked for 90 s at 150 °C (post exposure bake, PEB), and finally the films were developed in 200:1H_2O:HCl for 30 s to obtain the pattern.

Very large uniform areas (500 × 500 μm^2) were also EB exposed by using a current of 9.3 nA in order to investigate the material interaction by means of micro-infrared measurements. A dose range between 1÷50 mC/cm^2 was explored.

The FEI dual beam system was also used for direct focused ion beam (FIB) lithography. Only few examples of such particular lithographic technique were reported so far [20,21]. FIB, in fact, is a well-known method for direct milling of any material and can be obviously also used with PZT [22]. However, during the ion milling process secondary electrons are emitted and can be exploited for a direct impression of a sensible material. By means of this particular approach, very high aspect ratio hollow nanostructures can be achieved [21]. In our experiment we used a 30 kV Ga+ ion flux with a current of 80 pA and we exposed our films with a corresponding (ion) dose of 0.5 mC/cm^2.

The same apparatus used for EB and FIB lithography combines ultra-high resolution field emission Scanning Electron Microscopy