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Zirconia based functional sol–gel resist for UV and high resolution lithography

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ABSTRACT

The development of a functional negative tone sol–gel resist for Ultraviolet (UV) and Electron Beam (EB) lithography is presented. A new highly inorganic system based on ZrO_2 is synthesized by sol–gel method.

The lithographic performances have been optimized and several structures spanning from the micron range down to less than 50 nm have been achieved by UV and EB lithography. Moreover, in order to test the bio-affinity of the developed system, a genomic DNA probe has been attached onto the ZrO_2 film surface. Different thermal treatments have been applied to the samples and preliminary results show different degrees of anchoring, depending on the final ZrO_2 film structure (hybrid → inorganic or amorphous → crystalline). FT-IR characterization confirms the successful DNA functionalization of the patternable ZrO_2 system, especially in the crystalline phase, opening the way to the design of new biosensor architectures.

1. Introduction

The study of novel photoresists is of paramount importance in several application-oriented fields, ranging from microelectronics to photonics, nanofabrications and sensors development. In whatever domain the realization of micro/nanostructures on photoresist is required, a high spatial resolution together with the possibility of adding innovative and advanced materials features are strongly pursued [1,2]. Recently, the research on novel photosensitive systems which could replace the existing commercial photoresists is greatly focused on the later aspect, in order to directly exploit these structurable materials also as final constituents of the device. In particular, increasing attention has been devoted to sol–gel materials as potential candidates for innovative resists. In the last years, few works have been published on the use of these systems as high resolution resists for electron beam lithography (EBL) [3] and organic inorganic sol–gel hybrids have demonstrated the potentiality to integrate functional and advanced capabilities (e.g. etching resistance, high refractive index, porosity, etc.) conferring outstanding advantages beyond the simple patterning ability to these class of materials [4,5].

The development of a highly inorganic functional ZrO_2 sol–gel resist for UV and EB lithography is herein presented.

Inorganic resists have increasingly attracted the attention for their advanced characteristics both in the fabrication of micro structures by UV lithography [6–8] as well as high resolution resists for EBL [3,9].

Hydrogen silsesquioxane (HSQ), is a commercially available inorganic material for writing high-resolution features with small line-width roughness, but with huge limitations in terms of sensitivity [10]. Metal oxide sulfate compounds have been proposed as alternative resist materials [11] and chemical modification of several metal oxides such as TiO_2, Al_2O_3, ZrO_2 and HfO_2, by using chelating agents (e.g. β-diketones), has been reported as frequent strategy to obtain inorganic systems sensitive to UV light and electron beam [9]. In the latter case, sub-10 nm structures have been achieved with a 100 keV EBL apparatus, nevertheless the resist sensitivity remains still low (around 10–15 mC/cm^2) [3,9].

A different approach has been here investigated and a new negative tone system based on ZrO_2 is synthesized through the sol–gel method, starting from a phenyl modified silica precursor and the respective transition metal alkoxide.

Furthermore, nowadays there is a great interest in methods for preparing nanostructured biointerfaces. Nanoscale inorganic matrices have good mechanical properties and thermal stability, and are also resistant to microbial attack and organic solvents, so nano-sized zirconia particles and films have been exploited as a suitable substrate for the immobilization of bioactive molecules [12,13].

Hence, the hybrid patternable sol–gel material presented here has been also considered as potential solid supports for the immobilization of biomolecules, allowing to realize innovative

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architectures for new generations of biosensors. In order to test the bio-affinity of the developed hybrid sol–gel systems, the ZrO_2 film surface has been functionalized with a genomic DNA probe and a fluorescent single strand DNA (ssDNA).

2. Experimental

2.1. Synthesis of ZrO_2 based system and DNA functionalization

A Hybrid Organic Inorganic (HOI) system based on organically modified silica and a Zr alkoxide has been prepared by sol–gel process, through hydrolysis and condensation of the precursors. All the reagents were purchased from Aldrich® and used without further purification. Zirconium butoxide (ZrBut) has been mixed with ethanol and stirred for 15 min at room temperature (RT). After this reaction time, the phenyl modified silane (PhSi) had been added to the sol (molar ratio ZrBut:PhSi = 9:1) and the solution has been left to react for 1 h at 80 °C. The final synthesized system consists in a three dimensional inorganic network of mixed Zr–O–Zr, Si–O–Si and Zr–O–Si bonds with pendant organic phenyl groups acting as network modifier and sensitive elements [14,15]. The final sol concentration has been set between 25 ÷ 100 g/l ($SiO_2 + ZrO_2$) according to the desirable thickness. The solution has been filtered by a microporous membrane (0.2 μm Millipore®) to remove large particles and improve the resist spin-coating quality. Moreover, the sol remains stable for up six months even in the more concentrated condition.

HOI films, with suitable thickness, have been deposited by spin coating technique on silicon wafer (100), fused silica slides and gold coated surfaces, showing no adhesion problems. Substrates with a maximum area of 5 × 5 cm^2 have been used with no need of any treatment to prevent de-wetting phenomena. In Fig. 1, the spin curves of just two concentrations are reported showing as a wide range of thicknesses can be obtained; even more diluted solutions can be used to realize films of less than 60 nm with good optical quality and no pin-hole formation. This gives the possibility to fit the requirements of a great number of applications. All the samples have been 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.

In order to test the bio-affinity of the developed hybrid sol–gel systems, a genomic DNA probe (Clostridium perfringens from S. Aldrich®), (phosphate group in 5′), has been attached onto the ZrO_2 film surface (which should guarantee an high affinity towards phosphate groups) by immersing ZrO_2 samples deposited on Si into 5 μM aqueous solution for 12 h and rinsing them with doubly distilled water for the removal of unadsorbed DNA. The same procedure has been followed for the immobilization of a fluorescent ssDNA (15 base pairs) on an UV patterned ZrO_2 surface obtained on fused silica.

2.2. Fabrication tools and characterization methods

Microstructures have been made by using a Hamamatsu LC5 HgXe UV spot light source, enhanced in the deep UV region (250 nm band) and having a power density around 180 mW/cm^2 on the sample surface. The ZrO_2 films spin coated on silicon and fused silica have been illuminated in air for 60–120 s (dose between 10 and 20 J/cm^2), through a quartz chromium mask with different patterns.

Nano-patterning has been achieved by means of electron beam lithography (EBL) by using a FEI Nova600i dual beam system with an electron acceleration voltage of 30 kV. Preliminary dose matrix tests have been performed on films deposited on Si in order to find the optimal exposure conditions by varying the doses between 1 and 35 pC/μm^2. A set of process parameters, such as post-exposure bake (PEB) and the development time have been systematically varied to explore the sol–gel system behavior. The same apparatus which combines an ultra-high resolution field emission Scanning Electron Microscopy (SEM) has been exploited to characterize the ZrO_2 based patterned structures.

The thicknesses of the films have been measured by means of a mechanical profilometer (Alpha-step IQ, KLA Tencor). Fourier transform infrared spectroscopy (FT-IR) has been carried out by using a Jasco FT-IR 620 spectrometer in order to follow the structural evolution of hybrid ZrO_2 system after thermal treatments (150 °C for 30 min, 500 °C and 800 °C for 15 min) and for the detection of the functional groups present on the surface of the sol–gel films before and after DNA functionalization. The analyses have been performed in transmission mode, within the 400–4000 cm^{-1} range, with a 4 cm^{-1} resolution for a total of 32 scans.

3. Results and discussion

The resist formulation has been driven by the final goal to obtain an almost inorganic resist based on ZrO_2, potentially sensitive to UV light and electron beam. The capability to engineer innovative materials by sol–gel chemistry has been exploited and a phenyl organically modified precursor has been selected to reach the target. The presence of phenyl functionalities covalently linked to

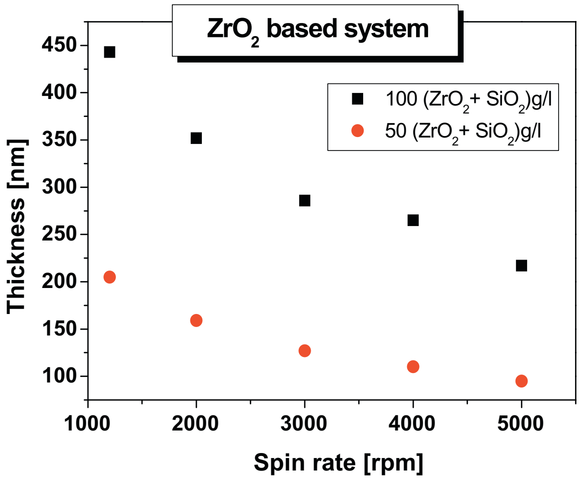

Fig. 1. Spin curve of ZrO_2 based system for 50 and 100 gl sol concentration.

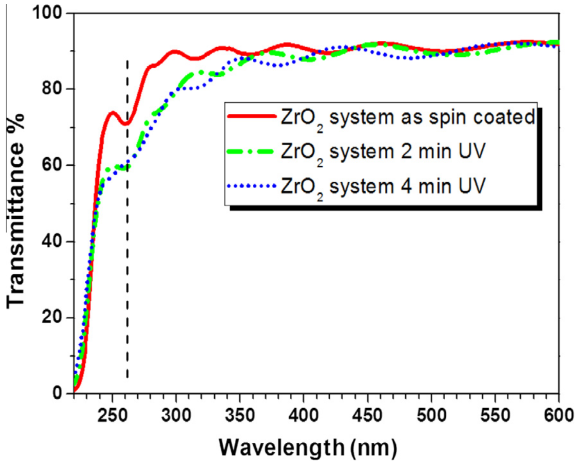

Fig. 2. UV–Visible spectra of the ZrO_2 based film spin coated on fused silica and UV irradiated for increasing exposure time.