

# Novel Hybrid Organic–Inorganic Spin-on Resist for Electron- or Photon-Based Nanolithography with Outstanding Resistance to Dry Etching

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It is uncommon that materials that need to be incorporated into micro- or nano-device architectures can be structured directly by lithography. More often the functional material is structured indirectly, first by patterning a sacrificial material – the resist – and then by a pattern transfer step by which the functional material inherits the pattern of the sacrificial layer on top. In order to be able to employ in devices the extremely wide “palette” of technologically relevant functional materials, the majority of which are not suited to a direct application of lithographic methods, it is essential to decouple the properties of the functional material from those of the resist.

The resist's properties are in particular extremely relevant to the outcome of the nanofabrication. They need to be optimized both for the specific lithographic technology adopted and for the subsequent process of pattern transfer, typically performed by dry etching.

With a few exceptions, for which it is desirable that the resist is etched simultaneously with the functional material (e.g., for the transfer of three-dimensional structures by proportional etching<sup>[1,2]</sup>), the resist should ideally remain unaffected during the entire plasma etching process so that the dimensional control of the structures is not compromised. High selectivity of the resist towards the functional material during etching process is desirable also in applications in which high-aspect-ratio structures need to be achieved.

Insufficient selectivity leads to significant degradation of the mask pattern during the etching, resulting in sloping sidewalls, line edge roughness, and limitations on the achievable depth of the structures. Increasing the resist's thickness may partially compensate the effects of erosion, potentially introducing different types of side-effects, such as a limitation of the lateral resolution or, in the case of high-aspect-ratio structures, pattern collapse during development and drying. Although commercial resists offer the simplicity of a single process step, they generally

exhibit poor dry-etching selectivity, as they are usually carbon-based materials. Inductively coupled plasma (ICP) cryogenic reactive ion etching (RIE), a process assisted by cryo-cooling, or the Bosch process (alternating passivation and etching steps) are known for being able to enhance the process selectivity using photoresists compared to standard RIE, but are complicated by the need for low temperatures or a discontinuous process, and hence advanced and sophisticated processing equipment.<sup>[3–6]</sup>

In order to overcome this problem, inorganic masks, mainly metals such as chrome (Cr) and nickel (Ni), are often introduced as a patterned intermediate layer, via the process of lift-off. The enhanced etch selectivity towards the functional material has, even in this case, the drawback of increasing the number of patterning steps and is not fully reliable and thus avoided in industrial applications.<sup>[7–9]</sup>

A slightly simplified method has been obtained by means of a two-step developing process: after a partial development, a ~4 nm thin metal film is deposited on the nanopatterned resist, which is then fully developed.<sup>[10]</sup> This method allows an enhancement of the aspect ratio of the resist features but is still too complex.

Recent studies have focused on aluminum oxide-based resists, since alumina in fluorine-containing plasmas leads to the formation of non-volatile compounds (AlF<sub>3</sub>, for instance sublimates at ca. 1250 °C) and therefore etches extremely slowly and is easily removable by wet etching. This was confirmed in a first study that demonstrated a selectivity of 68:1 for the etching of silicon vs. an alumina mask deposited by reactive magnetron sputtering of aluminum in a mixed argon and oxygen process gas, enabling the fabrication of dense arrays of nanopillars with smooth and steep sidewalls. However, also in this case the process included the additional step of alumina lift-off.<sup>[11]</sup>

An example of a fabrication process using alumina as an intermediate hard mask to improve organic resist performance is presented by Kravchenko et al.:<sup>[12]</sup> a soft azopolymer mask is directly patterned by interference lithography without the need of a development step and used as a mask for transferring the structures to the 5 nm alumina layer and silicon. However, even if the use of azobenzene-functionalized polymers as a resist reduces the number of patterning process steps, it needs alumina to improve the selectivity.

A different approach is proposed by Frommhold et al.:<sup>[13]</sup> the use of a fullerene-based spin-on carbon intermediate hard mask to transfer the pattern enabled the group to achieve aspect ratios in excess of 11:1, though with imperfect control of the slope of the sidewalls.

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Tseng et al.<sup>[14]</sup> demonstrated a method to enhance the etch resistance of poly(methyl methacrylate) (PMMA) by alternately infiltrating it with vapors of trimethyl aluminum and water and in situ synthesis of alumina, according to atomic layer deposition (ALD) technology. Fine (sub-20 nm) and dense PMMA lines, reinforced by the incorporation of alumina, were successfully transferred into silicon with amplification of their aspect ratio. Again, the process still appears too complex and costly to be considered a practical solution in micro- or nanofabrication.

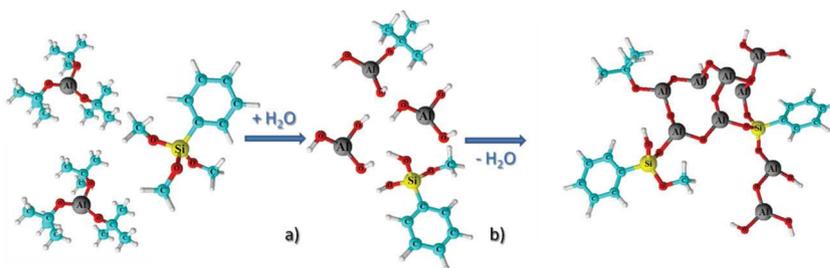
The need for directly patternable spin-on hard masks that already possess the proper dry etching resistance with respect to silicon is thus increasing. Suitable modifications to improve the properties of high resolution electron-beam (EB) resists have also been reported: chemical amplification (molecular structure or chemical composition modification) and doping with 1–3 nm metal nanoparticles of positive and negative tone resists (PMMA, ma-N, ZEP) have been proposed: the former still presents the problems typical of organic resists, whereas the latter have a better dry etching resistance (generally in between the commercial resist and the metal used) but still lower than silicon.<sup>[15,16]</sup>

In a previous contribution we reported a first attempt to obtain a resist based on a hybrid organic–inorganic (HOI) system loaded to 80% with boehmite nanoparticles ( $\text{Al}_2\text{O}_3/\text{AlO}(\text{OH})$ ).<sup>[17–21]</sup> Dry etching selectivity for silicon in excess of 60:1 (comparable to metallic masks under the same etching conditions) was obtained with this system in a set of tests involving deep X-ray lithography (XRL) and a fluorine-based RIE-ICP etcher. However, the surface and line edge roughness of the pattern were far from optimal owing to the size of the nanoparticles filled in. A similar strategy was followed by Brewer Science Inc., which studied the effect of incorporating metal oxide ( $\text{HfO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$ , and  $\text{TiZrO}_2$ ) nanocrystals into polymer-based spin-on hard mask coatings.<sup>[22]</sup>

These last encouraging results justify the use of mostly inorganic resists directly patternable with high resolution, as in the case of titania-based resists or hydrogen silsesquioxane (HSQ), which both show selectivity up to 10 with respect to InP or Si; however, a high temperature treatment is needed to decrease the etch rate.<sup>[23,24]</sup>

The urgent demand for spin-on materials ready for direct patterning and that behave as an etching mask is confirmed by the recent patent by EKC Technology Inc., in which a metal-organic precursor is transformed by radiation into an imaged etching mask; however, no commercial product with similar characteristics is available yet.<sup>[25]</sup>

We present here the development of a spin-on alumina-based resist with outstanding etching properties. The new resist combines the exceptional properties of alumina as an etching mask with the ease of deposition and patterning processes typical of organic resists, with the further advantage of being patternable by several lithographic techniques. The versatile HOI system, exempt from the above-mentioned drawbacks, can be used as a resist for UV, X-ray, EB, and nanoimprint lithography (NIL), and exhibits excellent performances in terms of both lateral



**Scheme 1.** Hydrolysis (a) and condensation (b) reactions of metal-organic precursors with formation of an organically modified partially condensed aluminum oxide network. The structure represents that of the spin-coated film before exposure.

resolution achievable and etch resistance in fluorine-based dry etching processes. The new resist system was synthesized by the sol-gel method starting from aluminum-tri-*sec*-butoxide and a phenyl-modified silane precursor. Details of the resist preparation are given in the Experimental Section.

This spin-on resist is unique, as it is spin coated from a sol whose main part consists of an alumina precursor, which after deposition reaches an adequate condensation degree to transform into an alumina-like organically modified film (**Scheme 1**), without the need to be loaded with a solid fraction (nanoparticles, nanocrystals).

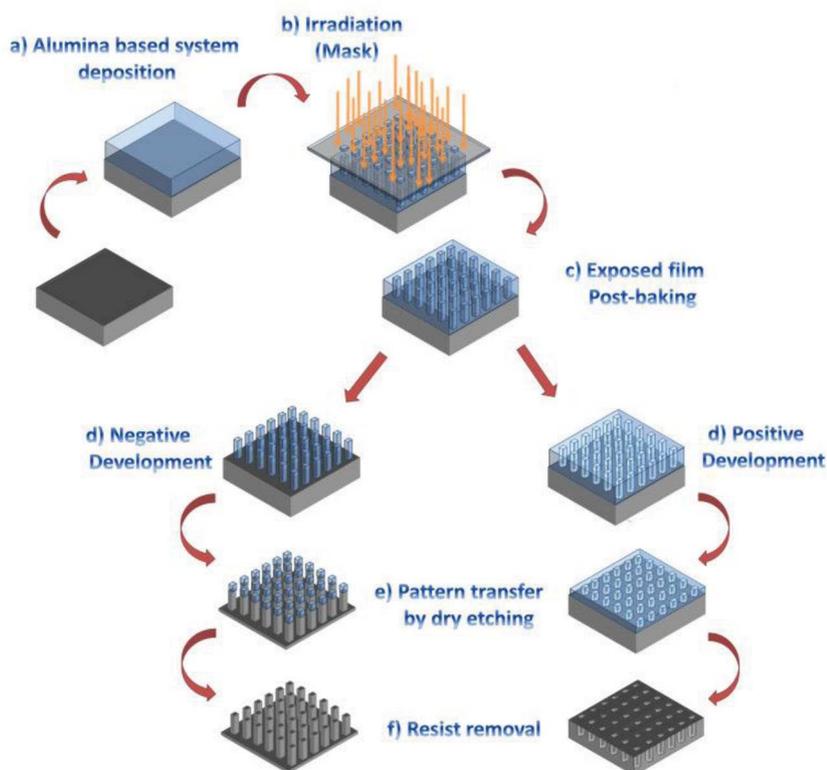
Hence, the desired directly patternable etching mask is produced in one step, eliminating the need for complex synthesis or post-processing.

In our tests this system was shown to act as a resist with outstanding and distinctive properties. In particular, silicon nanostructures could be etched in an ICP reactor with a plasma of  $\text{SF}_6$ ,  $\text{C}_4\text{F}_8$ , Ar gas mixture with selectivity exceeding 100:1 with respect to the resist and deliberately avoiding the use of techniques such as the Bosch process or cryogenic plasma etching. Under the same etching conditions HSQ hard masks present a selectivity up to 6:1.<sup>[26]</sup> The measured outstanding selectivity of 100:1 reported here is comparable with the selectivities achievable with metallic masks yet avoids the steps, cost, and risk of vacuum deposition of metal and subsequent lift-off in organic solvents. Furthermore, for the present sol formulation no high-temperature annealing step was required, as generally used in other protocols, to obtain completely inorganic etch-resistant patterns. A distinctive feature not shared by any of the known resists and that may prove interesting for special applications is that our formulation behaves as either a positive-tone or a negative-tone resist, depending on the solvent used for the development (**Figure 1**).

Examples of the structures obtained by UV, X-ray, and EB lithography with positive and negative development are presented in **Figure 2**.

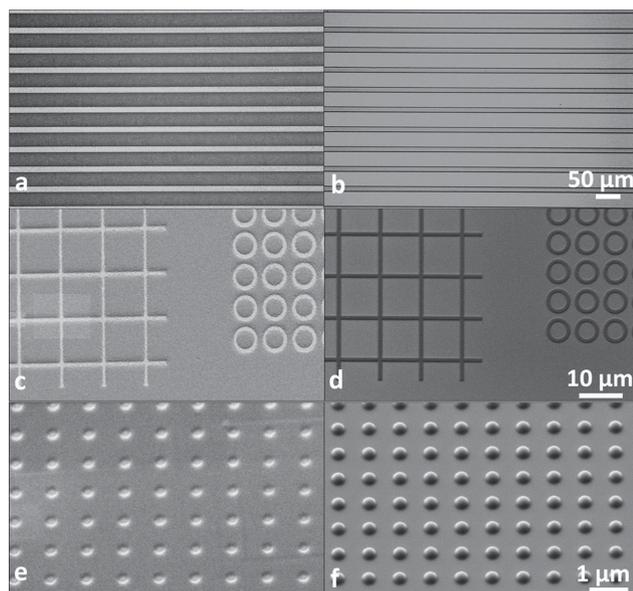
The chemical-physical processes responsible for the sensitivity to radiation of this HOI resist can be easily investigated by analyzing large areas of non-irradiated and UV- or X-ray-irradiated films by IR spectroscopy.

The exposure of the spin-coated films to UV light and X-rays modifies the film, degrading the organic component of the system and condensing the inorganic network, as can be seen in the Fourier transform infrared (FTIR) spectra reproduced in **Figure 3**.



**Figure 1.** Scheme of the lithographic and pattern transfer processes using the alumina-based organic-inorganic hybrid system. After post-exposure annealing (c) the film can be developed either as a positive (right) or as a negative (left) tone resist (d) depending on the solvent used.

The peaks related to the aromatic rings in the phenyl-silica precursor (peaks at  $3070\text{--}3040\text{ cm}^{-1}$ , arising from the aromatic C–H stretching vibration, and at  $1120\text{ cm}^{-1}$ , ascribed to the stretching



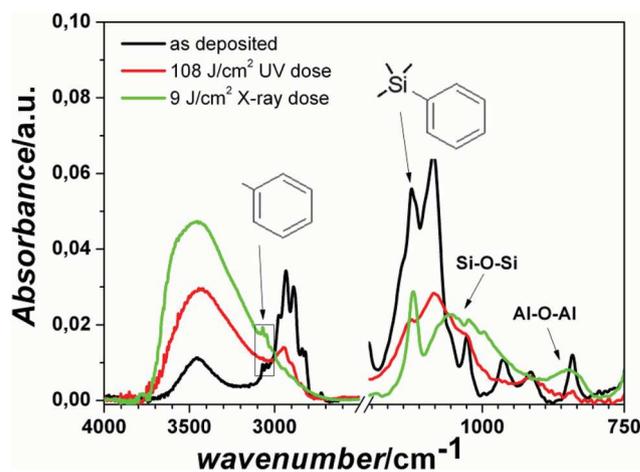
**Figure 2.** Optical and SEM images of the positive (a,c,e) and negative (b,d,f) developments obtained by UV (a,b), X-rays (c,d) and EB (e,f) lithography.

of the phenyl–silicon bond) were clearly diminished in the exposed films, confirming the degradation of the organic network modifiers. The decrease of the peaks related to the aliphatic C–H symmetric and asymmetric stretching ( $2830\text{--}2970\text{ cm}^{-1}$ ) accompanied by the increment of the OH absorption band, centered at  $3400\text{ cm}^{-1}$ , confirms the promotion of the hydrolysis reactions of the alkoxide associated with an increase in the crosslinking of the inorganic network.<sup>[27]</sup> This is confirmed by the Si–O–Si ( $1100\text{--}1030\text{ cm}^{-1}$ ) and Al–O–Al (broad bands between  $1000$  and  $500\text{ cm}^{-1}$ ) absorptions visible in the spectrum of the alumina-based resist films after exposure.<sup>[28,29]</sup>

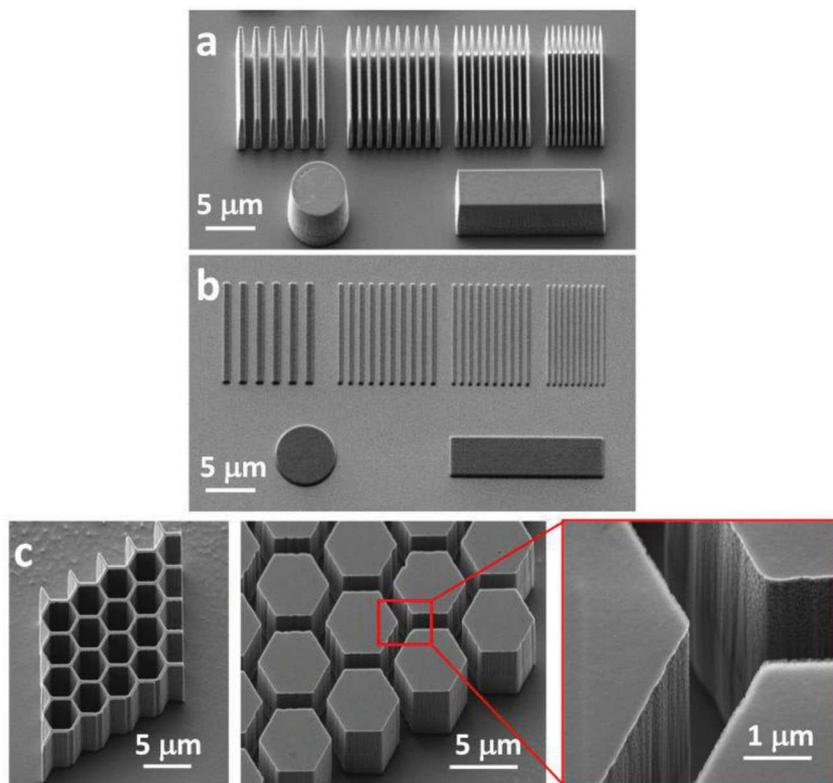
The modification of the organic component of the exposed areas of the films (i.e., the content of the phenyl modifiers of the inorganic network and residual alkoxide groups) leads to the possibility of developing it as either a positive or a negative resist. This depends on the chemistry of the developers, which are simply buffered oxide etch (BOE) and hydrochloric acid (1N in water) diluted in isopropyl alcohol for the positive- and negative-tone behavior, respectively. In fact the former is a good etchant for inorganic networks and affects directly the exposed areas of the resist whereas the latter is active when the phenyl groups are present, as is the case in the unexposed zones. A more detailed

explanation of the peculiar behavior of the resist exhibiting both positive- and negative-tone development is given in the Supporting Information.

Structures with sub-micrometer resolution features were etched down to a depth of  $3\text{ }\mu\text{m}$ , with only  $30\text{ nm}$  thick resist masks, resulting in a selectivity of 100:1. The continuous etching process was obtained with  $400\text{ W}$  radio frequency (RF) power applied to the coil and  $20\text{ W}$  applied to the platen, and a plasma generated with a mixture of  $\text{SF}_6$ ,  $\text{C}_4\text{F}_8$ , and Ar gases



**Figure 3.** FTIR spectra of the alumina-based HOI system films before and after exposure to a UV dose of  $108\text{ J cm}^{-2}$  and an X-ray dose of  $9\text{ J cm}^{-2}$ .



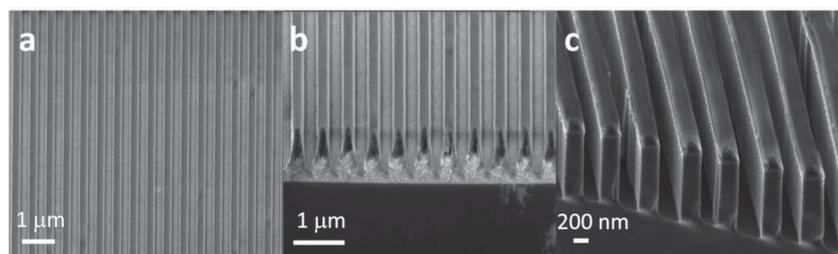
**Figure 4.** SEM images of the developed resist (a) and of the etched silicon structures obtained using the EB (b) and X-ray (c) alumina patterns as etching masks. The magnified view of the etched pattern shows the achievable sidewall verticality and smoothness.

with fluxes of 60, 30, and 10 sccm, respectively, at a pressure of 8.0 mT, with a resulting bias of 90 V. Under these operating conditions, the silicon etching rate was  $170 \text{ nm min}^{-1}$ .

Examples of the structures obtained using the X-ray and EB patterns as etching masks for silicon are shown in **Figure 4**.

The ultimate achievable resolution is still being tested: experimental evidence has shown that 20 nm isolated lines can be obtained by EB lithography. Even if the resolution achievable with commercial resists (i.e., HSQ) is below 10 nm, the combination of outstanding selectivity and resolution remains a distinctive feature of the presented material.

We also demonstrated the possibility of exploiting the alumina system as a NIL resist: it was possible to imprint the material with a thin residual layer (up to 30 nm) at room temperature for 5 min by applying a pressure of 500 bar and to use the obtained pattern as an etching mask for silicon (**Figure 5**). This process



**Figure 5.** SEM images of the patterns obtained using the alumina system as a NIL resist (a,b) and the resulting silicon etched structure (c).

has not been optimized yet but would make it possible to further decrease the number of process steps and costs by using NIL.

In summary, this new spin-on metal-organic resist is unique since it presents a combination of worthwhile properties: a simple processability typical of polymeric resists, direct patternability with various forms of radiation (UV, X-ray, or EB) and NIL, mild post-exposure treatment requirement, positive or negative tone development, and a selectivity greater than 100:1 with respect to the underlying silicon in a fluorine-based non-cryo-cooled continuous plasma etching process; notably, this last property is generally achievable only with more complex lithographic processes using ceramic or metallic intermediate layers (i.e., SiO, SiN, SiGe, Cr, Al). The use of such material for high resolution deep silicon etching would then be time and cost effective compared to the pattern transfer materials generally used.

## Experimental Section

The 80% alumina-based resist was synthesized by the sol-gel method starting with aluminum-tri-*sec*-butoxide (97%, Aldrich) and trimethoxyphenylsilane ( $\geq 95.0\%$ , Aldrich). The aluminum-tri-*sec*-butoxide was stirred continuously with acetic acid in the volume ratio of 1:0.05. After 1 h the phenylsilane was added, 20%, and the solution was stirred at  $80^\circ\text{C}$ .

Silicon substrates were spin-coated at different speeds with the sol diluted in ethanol with variable dilution to give easily adjusted film thicknesses in the 30 nm–1  $\mu\text{m}$  range. As-coated films were baked for 5 min at  $100^\circ\text{C}$  in order to remove the residual solvent and promote sol-gel reactions.

The effects of baking, X-ray, and UV irradiation on the films deposited on silicon wafers were evaluated from the FTIR spectra (spectrometer Jasco FT-IR-620) in the range of 400–4500  $\text{cm}^{-1}$  with a resolution of  $\pm 4 \text{ cm}^{-1}$ . The UV exposure and X-ray lithography were performed with a UV lamp (Hamamatsu Lightningcure LC5) and a soft X-ray source at the LILIT beam line of the Elettra Synchrotron (Trieste, Italy),<sup>[30,31]</sup> respectively.

Dose matrix experiments were conducted for all the lithographic techniques except NIL. The optimal exposure conditions were selected as  $108 \text{ J cm}^{-2}$  UV dose (measured for wavelengths between 260 and 400 nm),  $10 \text{ J cm}^{-2}$  X-ray dose (energy peak at 1.8 keV with an energy window of 1–3 keV), and  $800 \mu\text{C cm}^{-2}$  EB dose at 30 keV acceleration energy. A post-exposure bake (PEB) at  $120^\circ\text{C}$  was applied for 120 s, followed by 3 min development in diluted HCl (10 mN in isopropyl alcohol) for the negative tone or BOE for the positive tone. Imprinting tests were performed with a hot press (P/O/Weber, Remshalden, Germany) for 5 min and 500 bar at room temperature ( $21^\circ\text{C}$ ).

Pattern transfer to the Si substrate was then performed in an ICP dry etcher reactor (SPTS Technologies, Newport, UK) with fluorine-based chemistry. A non-switched process with a gas mixture of  $\text{C}_4\text{F}_8/\text{SF}_6/\text{Ar}$  in the ratio of 60 sccm / 30 sccm / 10 sccm, with a power of 400 W applied to the coil and 20 W applied to the platen (90 V induced bias) resulted in  $170 \text{ nm min}^{-1}$  etching rate for Si.

The resulting samples were inspected by optical microscopy and SEM (Zeiss Supra 40 SEM, Carl Zeiss SMT, Cambridge, UK).

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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