On the ultimate resolution of As_2S_3-based inorganic resists

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The possibility of making lithographic masks based on As_2S_3 chalcogenide glass with ultimately small size of resist elements has been investigated. Interference lithography using synchrotron radiation with a wavelength of 13.4 nm, corresponding to extreme ultraviolet light was used. High-quality masks with elements of 30 nm in size were obtained. In a dynamic light scattering study, resist particles of about 3 nm in size were found in the developer after the development process, which corresponds to the intermediate-range order parameter in the structure of the chalcogenide glass. It is assumed that this grain size determines the ultimate resolution, roughness and unevenness of the edge of the inorganic resist mask.

Key words: chalcogenide glass, lone-pair electrons, inorganic resist, interference lithography, EUV lithography

1. Introduction

Chalcogenide glassy semiconductors (ChGS), discovered in the mid-1950s by Kolomiets and Goryunova [1], possess a number of unique properties, which are due to the presence of lone-pair electron that form the top of the valence band [2,3]. One of such properties is the ability of CGSs to photostructural transformations, which manifests itself in the fact that after exposure of CGSs with light, electron beam or X-ray radiation, their structure changes in a reversible manner [4]. In most chalcogenide glasses, chalcogen atoms are two-coordinated, while the remaining two p-electrons form a lone-pair electron pair (LP). LPs do not participate in the formation of covalent bonds, but occupy an energy position near the top of the valence band, and it

is these that are excited upon absorption of light and are responsible for photostructural transformations [5].
A photostimulated change in the structure leads to a change not only of the optical and electrical properties, but also of a large number of other physicochemical parameters, in particular, the rate of dissolution of the material in various etchants, which opens up possibilities for the practical use of ChGS films as inorganic resists [6-9]. In this case, as advantages, their potentially high resolution is often mentioned.
The question of the ultimate resolution limit of the photoresist is of fundamental importance but for a long time it remained unanswered, which is due to the fact that in order to correctly estimate the resolution limit and obtain extremely small elements, it is necessary, firstly, to use an exposure method that ensures the formation of extremely small elements and, secondly, a technique that allows one to determine the sizes of the resulting elements. At earlier stages of research, the possibilities of such techniques were limited. Recently, the progress of microelectronics and the development of nanotechnology and, in particular, advances in the development of exposure techniques and the progress of high-resolution microscopy, led to an increased interest in nanometer-scale photoresists and in photoresists based on chalcogenide glasses, in particular.

2. **Experimental details**

In this work, we chose As_2S_3 chalcogenide glass as a resist material, whose pronounced change in the dissolution rate after exposure, makes it one of the most promising inorganic resists based on chalcogenide glasses [10,11]. We studied 50 nm thick layers obtained by thermal sputtering in vacuum onto gallium arsenide substrates. The bulk glass used to fabricate this films was obtained by direct synthesis from the starting components.

In order to determine the minimum achievable element size, interference lithography was used. Using this method, a resist sample is exposed by an interference pattern in the form of alternating light and dark stripes formed by the interference of two beams converging at an angle. Since the goal was to obtain elements of the minimum size, the shortest wavelength of exposure radiation available to the authors was used, namely synchrotron radiation with a wavelength of 13.4 nm, corresponding to the extreme ultra violet, EUV .
Figure 1 shows a schematic diagram of an interference lithography experiment. The radiation hits the screen in the form of a mask, the middle part of which is opaque, and the upper and lower rectangular sections are transmission diffraction gratings with horizontal strokes in the form of parallel

slits. The interference pattern is formed behind the central part of the screen where the first order diffraction beam from the lower grating and the minus first order beam from the upper grating interfere. A more detailed description of the setup for interference lithography using synchrotron radiation can be found in [12].

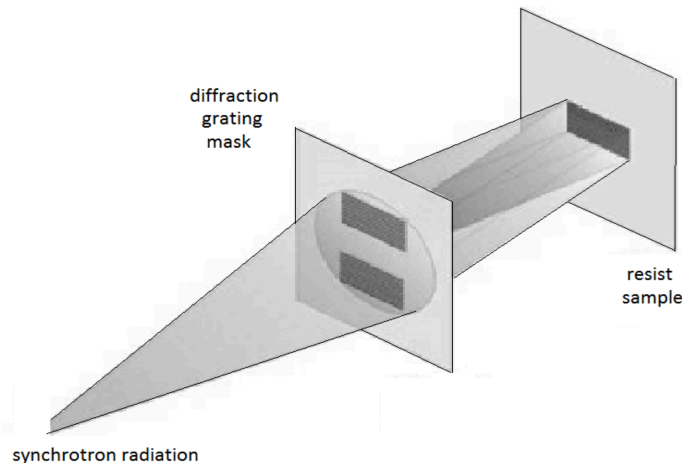


Fig. 1:

Interference lithography experiments were preceded by studies of the optimal exposure dose based on exposure of the samples to a continuous uniform field of synchrotron radiation, followed by measuring the rate of dissolution of the resist in the developer. For this, an interferometric technique of continuous measurement of the film thickness during development was used [13]. The dissolution rate of the unexposed film was about 11 nm/s, while that for the exposed film was 0.9 nm/s; their ratio (chemical contrast) being ca. 11. The exposed samples were developed in an organic alkali solution (amine) in an aprotonic solvent. Namely, a solution of diethylamine in benzonitrile was used. The choice of the developer and development protocol were optimized in order to improve the resolution and contrast [14].

3. Results and Discussion

The rate of dissolution of areas that received a large dose (light fringes of the interference pattern) was significantly reduced in comparison with non-exposed (dark fringes) regions, as is typical for negative-type resists. As a result, after development, a mask in the form of parallel stripes 30 nm wide was obtained in the resist. Figure 2(a) shows a cross-sectional photograph of such a mask, obtained by scanning electron microscopy (SEM). The photograph demonstrates a high chemical contrast, that is, the ratio of the dissolution rate of the resist areas that received the minimum exposure dose to the dissolution rate of the areas with the maximum exposure, which is

manifested in a slight decrease in the mask thickness after development and a high aspect-ratio (vertical edge on the cross section of the mask), a feature useful for practical applications.

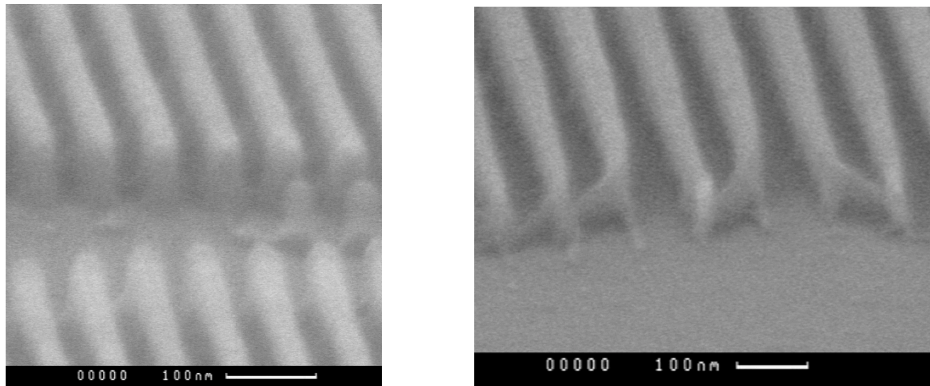
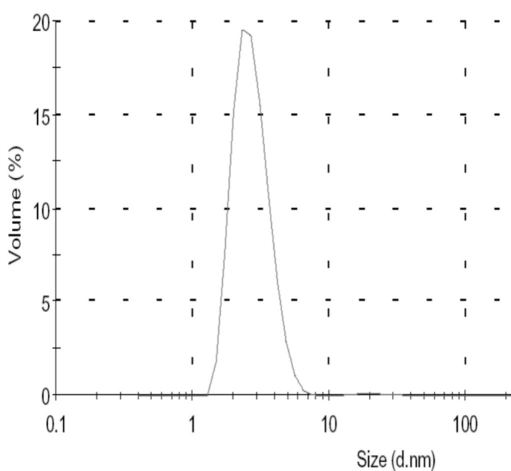


Fig. 2:

Figure 2(b) shows an edge of the mask. During exposure, there was a boundary of the interference field, where the radiation intensity gradually decreased to zero. As a result, after development, the width of the lines of the mask also gradually decreased as it approached the edge and at the very edge was less than 10 nm in cross section. At the same time, visible defects such as punctures and irregularities on the edge were not observed, which suggests that it is possible to obtain masks with an element size of about 10 nm based on such a resist.

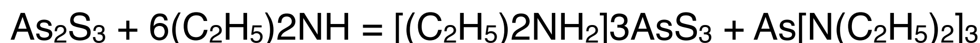


The developer solution after processing the exposed samples was investigated by dynamic light scattering (DLS) using a Zetasizer Nano Z device from Malvern Instruments. In these measurements, tiny particles were found in the developer that were absent in the solution before the samples were developed. The obtained particle size distribution is shown in Fig. 3.

Fig. 3:

The graph shows that particles with a characteristic size of about 3 nm dominate and their size distribution is close to monodisperse. What can such particles be? M.D. Mikhailov et al. [15] argued that a chalcogenide glassy film

can be considered as an inorganic polymer, the structural units of which are AsS_4, $As_2S_{3/2}$ and sulfur rings S_n. During exposure, as a consequence of rearrangement of chemical bonds due to the excitation of LPs, the degree of polymerization increases. When the film is dissolved in an organic alkali solution in accordance with the reaction



$$As_2S_3 + 6(C_2H_5)2NH = [(C_2H_5)2NH_2]3AsS_3 + As[N(C_2H_5)_2]_3$$

reaction products are formed that also consist of structural units such as AsS_4, $As_2S_{3/2}$, the bonds between which were broken [15]. Fragments of the polymer structure of the unexposed film pass into the solution, in contrast to the undissolved structural units of the exposed polymerized areas.

Of interest is a very uniform particle size distribution in the solution. The characteristic particle size of these structural fragments determines the surface roughness after contact with the developer and the roughness of the mask edge. This size allows one to estimate the graininess of a photosensitive sensitive material and its ultimate resolution. Based on the data obtained, we argue that the ultimate roughness of the mask edge can be about 3 nm. The value of 3 nm approximately corresponds to the so-called intermediate-range order in glasses [16], i.e. the distance at which the structure “forgets” about the coordination of atoms in neighboring regions. This “loss of memory” is due to a rather small energy cost of bond angles variation for two-fold coordinated chalcogen atoms. It can be assumed that additions to the CGS of elements capable of interacting with lone-pair electrons, such as transition metal atoms, will locally increase the coordination number, leading to the formation of fragments centered on such atoms, which should manifest itself in a change of the characteristic dimension of the intermediate-range order.

It should also be borne in mind that films used as a resist were as-deposited films, i.e. films with local deviations from stoichiometry. Therefore, it cannot be ruled out that the size of the structural fragments passing into the solvent is determined by the characteristic parameters of local nonstoichiometry. It is interesting to note that the introduction of transition metal atoms into phase-change chalcogenides significantly reduced the crystallization times, which was due to the appearance in the amorphous phase of highly coordinated fragments based on transition metal atoms, the local structure of which does not change during crystallization [17]. It can be assumed that in the case of chalcogenide glasses, doping with transition metals will also lead to the formation of such highly coordinated fragments due to the formation of chemical bonds between the LPs of the chalcogen and unfilled d-orbitals of

transition metals. The formation of such fragments, on the one hand, can lead to an undesirable decrease in sensitivity and chemical contrast, while, on the other hand, it should result in a decrease in the characteristic size of intermediate-range ordering, and hence lead to an increase in the resolution of the resist.

In addition to the high resolution, inorganic resists based on chalcogenide glasses have a number of other characteristics that can be useful for practical applications. These include:
- the possibility of applying a uniform thin layer on nonplanar and curved substrates due to deposition in a vacuum, in contrast to the centrifuge deposition of traditional resists;
- the possibility of dry development using reactive ion etching;
-high stability in acidic media and oxygen plasma, which makes it possible to use inorganic resist based on chalcogenide glass as a sensitive layer of multilayer masks.

Finally, we note that chalcogenide-based resists may be of special interest for use with two-dimensional chalcogenide materials that are now at the forefront of semiconductor research, such as topological insulators (Sb_2Te_3, Bi_2Se_3 etc), transition metal dichalcogenides (e.g. MoS_2), two-dimensional InSe, etc [18-20]. There is every reason to believe that with the progress of nanoelectronics based on two-dimensional chalcogenides, high-resolution resists based on chalcogenide glasses will find an even wider practical application.

4. **Conclusion**

This paper demonstrates the possibility of using a chalcogenide glass resist for exposure with synchrotron radiation in the EUV range. The resulting high resolution and contrast, the sensitivity comparable to the sensitivity of traditional resists based on organic polymers, make it possible to consider a photoresist based on As_2S_3 chalcogenide glass, possibly doped with other elements, promising for use in lithographic processes with increased requirements for resolution.

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