

PHOTOLITHOGRAPHIC STRUCTURING WITH EVAPORATED INORGANIC PHOTORESIST

B. Mednikarov*, M. Sahatchieva

Central Laboratory of Photoprocesses – Bulgarian Academy of Sciences
Acad. "G. Bonchev" str. Bl 109, Sofia, Bulgaria

A photolithographic material based on vacuum evaporated layers of the chalcogenide semiconductor As_2S_3 and a technology for the creation of precise photolithographic images on different substrates is developed in the Central Laboratory of Photoprocesses (CLF) at the Bulgarian Academy of Sciences (BAS). The photoresist has several advantages over the classical organic photolithographic materials. Here, the possibility of getting precise microstructures on chromium and AlN layers as well as on glass substrates by means of the evaporated photoresist is shown.

(Received April 25, 2005; accepted May 26, 2005)

Keywords: Photolithography, Inorganic photoresist, Microstructures, As_2S_3 , AlN, Glass

1. Introduction

Methods based on photolithographic techniques for creating images with complex topography and fine structures are well known and have been widely used in practice for a long time. Any particular practical purpose requires an *ad hoc* development and application of a positive or negative working photoresist. The deposition on the substrate is carried out by spin, spray, roll or dip coating. The working layer thickness is within 0.5-1.0 μm . Regardless of the enormous diversity and the specific characteristics of all well-known photoresists, the procedure comprising coating and processing is a multistage one and in some cases rather sophisticated. Moreover, photolithography based on conventional photoresist systems, due to the relatively great thickness of the resist layer, requires expensive devices for the reproduction of submicron structures by exposure with electrons, X-rays or at least deep UV.

There is a large number of investigations [1-5] directed to the creation of photosensitive coatings, whereby the deposition on the substrate is performed by vacuum evaporation and condensation. All they use photodoping of Ag in the chalcogenide glass and had been carried out on a laboratory scale, without any practical application.

The inorganic photoresist based on As_2S_3 and developed in the Central Laboratory of Photoprocesses [6-8] is an amorphous vacuum evaporated chalcogenide, which changes its solubility in alkaline solutions on irradiation with actinic light ($\lambda \leq 500 \text{ nm}$) and has an excellent resistance to most acids. The coating method by vacuum evaporation reveals new application possibilities and simplifies the procedures in comparison to the traditional liquid resist technologies [9-11].

2. Experimental

The obtaining and processing of the evaporated inorganic photoresist (EPhR) are illustrated in the scheme bellow. On appropriately cleaned glass substrates, any kind of layers (metal, Me_xO_y , Me_xN_y), which should be structured, can be deposited by vacuum evaporation and condensation. On

* Corresponding author: bormed@clf.bas.bg

them, in the same or in a subsequent vacuum cycle, a layer of EPhR, 90-100 nm thick, is deposited by thermal evaporation. After exposure through a desired mask (contact or projection), structural changes occur in the photoresist, which make the illuminated area soluble in alkaline solutions, while the unexposed one does not change at all (Fig. 1). Thus, one obtains a direct positive image in the photoresist layer. The next step is etching of the layer beneath the EPhR with suitable solutions (usually, oxidizing acid solutions). The photoresist is stable in these solutions and does not undergo any changes. Finally, after removing the unexposed photoresist in 5% NaOH, one obtains a direct positive image in the working layer.

The image quality strongly depends on the quality of the “master” mask. Nevertheless, with precise adjustment of exposure and development, one can correct the size of the structures (“line-space”) in the desired direction.

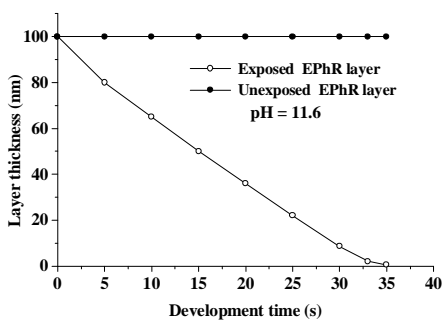
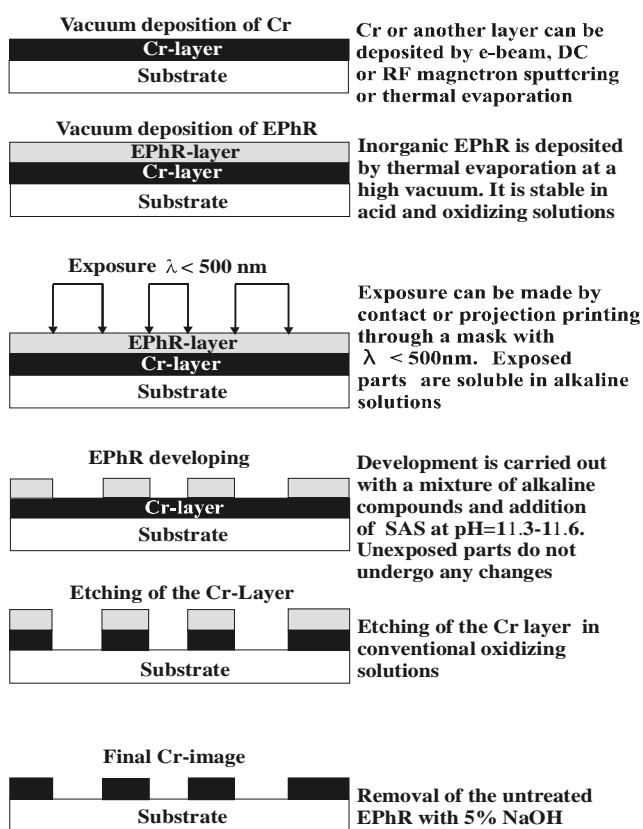


Fig. 1. Changes in the thickness of the exposed EPhR layers with time of development at pH = 11.6. For the time of complete dissolution of the exposed area, the unexposed part does not undergo any changes.

The advantages of the evaporated photoresist can be summarized as follows:

- extremely high resolution and acuity;
- thin and uniform dry layer produced by vacuum deposition under clean conditions;
- rotational symmetry of the substrates not required;
- prebaking and postbaking unnecessary;
- 30-50% broader exposure and processing latitude [9] which, under constant working conditions, ensures the accurate reproduction of details of both submicron and a few micron dimensions;
- fireproof;
- no highly toxic solvent vapors, as in the case of the liquid resist;
- non-toxic aqueous solutions secure rapid processing;
- good adhesion to Cr, Ni, Ag, glass, Al, Si, SiO₂, Si₃N₄, DLC, *etc.*

After development and etching, the remaining photoresist is completely removable from the substrate.

Fig. 2 shows the structures obtained on Cr layers with optical density $D_{opt} = 3.0$ (100-110 nm thick) deposited on glass substrates. The procedure follows the steps described in the scheme above.

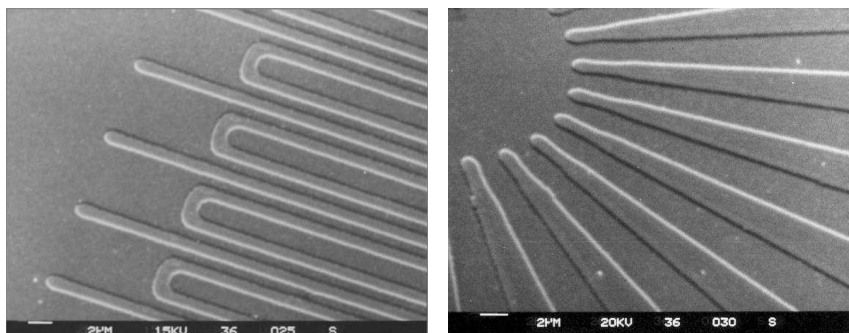


Fig. 2. SEM pictures of contact printing test masks on As₂S₃/Cr layers after etching of the chromium layer. Space-line dimension 1 μm.

On top of the Cr layer, a 90 nm film of EPhR-As₂S₃ with purity 5N is deposited in vacuum by thermal evaporation. The contact printing is made through a test mask vacuum pressed to the sample. The light source is a mercury high-pressure lamp with intensity 80 mW/cm² in the exposure plane. The exposure time is directly proportional to the As₂S₃ layer thickness and in this case is 10 s. After illumination, development of the samples takes place. The developer consists of Na₂CO₃, Na₃PO₄ and a definite quantity of surfactant (SAS) [6,7]. The development is carried out at pH = 11.3-11.6 for 2-3 min. After rinsing in deionized water, etching of the Cr layer through the already obtained photoresist mask is performed. It should be noted that the As₂S₃ layers exhibit a strong resistance to a large number of acids and oxidizing solutions. The etchers are conventional oxidizing solutions, such as [(NH₄)₂Ce(NO₃)₆+HClO₄+H₂O)] or [Ce(SO₄)₂ +HNO₃+H₂O]. The etching time depends on the Cr layer thickness and in the present case it is about 40-50 s. Finally, after stripping the photoresist mask in 5% NaOH, the chromium image is ready.

Thanks to their outstanding properties (high electrical resistivity (10¹¹-10¹³ ohm.cm), high thermal conductivity [13], high hardness (11-15 GPa), wide band gap (6.0-6.2 eV) [14], high velocity of acoustic waves) AlN layers are a very promising candidate for a variety of technological applications: surface passivation of thin films, barrier layers [15,16], in microelectronics [17], in a variety of surface acoustic wave (SAW) devices [18,19]. This determines the necessity of structuring of the AlN layer using either dry (physical) [20,21] or wet (chemical) etching [22,23]. Dry etching (RIE) is a very expensive method and creates problems with the etching selectivity through resist masks, controlled undercutting is difficult to attain [24], surface irregularities are formed due to the undesired deposition of the products of etching on the material below the AlN layer [25]. For a resist mask in wet etching, thick layers of photoresist lacquers, such as *Hunt 1182* [26], *Shipley* or *Apiezon wax* [24] are commonly used. The etching solutions are usually H₃PO₄ [27], buffered HF [24,25] or

KOH. Normally, the etching temperature is high (60-80°C), which creates inconveniences during processing.

For structuring of AlN layers with EPhR, we have applied the following two-stage technique. On cleaned substrates, an AlN layer (70-100 nm thick) is deposited by reactive RF sputtering. On top of this layer, a thin (50-80 nm) chromium film (insoluble in alkaline solutions) is coated, followed by a 100 nm film of EPhR (insoluble in oxidizing acid solutions). Then, exposure through a suitable functional mask, development of the EPhR (alkaline developer pH = 11.6) and etching of the Cr layer are performed. Through the open windows in the EPhR and the Cr layer, the AlN film is structured with 10% NaOH at 23°C. At this treatment the unexposed layer of EPhR dissolves and the remaining mask of chromium layer prevents the undesired dissolution of the functional shape of AlN structures. Finally, the protective Cr layer on the AlN structures is removed by a standard chromium etcher and one obtains a structured AlN layer (Fig. 3). In this case, the two-step technique is required because the As_2S_3 photoresist is soluble in NaOH while the Cr layer is not. On the other hand, direct photolithography (AlN + EPhR) by etching with H_3PO_4 at high temperature is inconvenient.

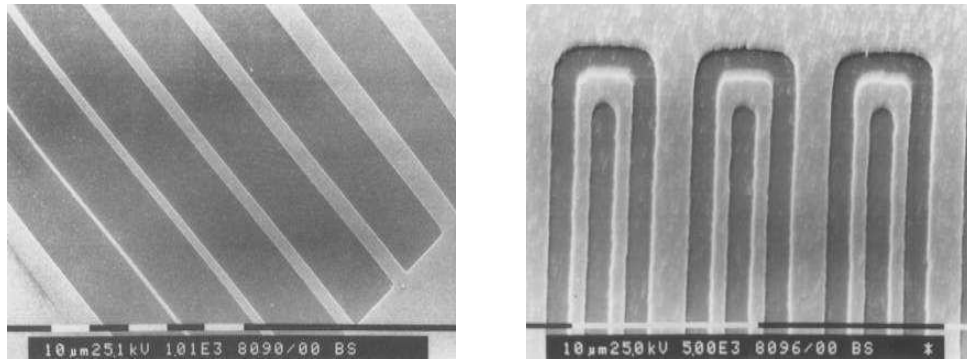


Fig. 3. SEM pictures of structured AlN layers with EPhR. Etching is made with 10% NaOH at 23 °C at a rate of 75 nm/min. The minimal size of the structures is 0.8-1.0 μm.

Structuring of glass substrates is applied for the obtaining of phase optical elements widely used in optics. This is usually achieved by scribing and dry or wet etching. Here, the possibility of glass structuring by EPhR-lithography is shown, using again a two-stage technique.

On suitably cleaned soda-lime glass (SLW), commonly used for optical masks, a chromium layer is deposited, followed by an EPhR layer. After exposure and development of the EPhR, etching of the chromium layer is performed in order to obtain a new Cr mask through which etching of the glass plate is possible. The etching solution is buffered HF ($NH_4F + H_2O + HF$) or a mixture of $HF + HNO_3 + H_2O$. Depending on the composition and concentration, one can obtain a different etching depth, which is directly proportional to the etching time (Fig. 4).

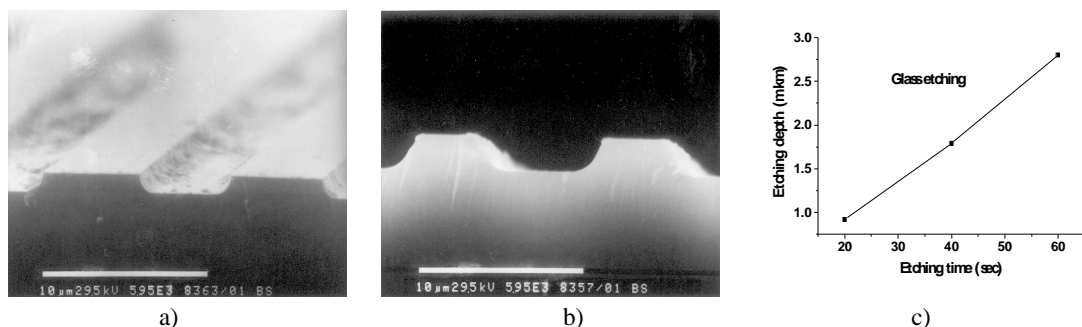


Fig. 4. SEM pictures of structures in glass obtained by EPhR. $T_{\text{line-space}} = 11 \mu\text{m}$: a) time of etching 20 s at room temperature, etching depth 0.92 μm; b) time of etching 40 s, etching depth 1.80 μm; c) time dependence of the etching depth.

Chemical etching is isotropic and expands the spaces between the lines proportionally to the depth of etching. Since the observed correlation is strong, one can design the “master” mask taking into account this feature and correct the “line-space” dimensions.

3. Conclusions

The present work shows the possibility of obtaining accurate photolithographic structures by means of EPhR-As₂S₃. Taking into account its specific features (see below) it can be concluded that this material can find wide application in photolithography.

- spectral region: $\lambda < 540$ nm;
- sensitivity: 80 mJ/cm² ($\lambda = 365$ nm) [12]; for electrons: $1.3 \cdot 10^{-4}$ C/cm² at 7.5 kV; for Ar⁺ laser: 220 mJ/cm² ($\lambda = 488$ nm) [10]; layer thickness 80-100 nm;
- exposure latitude: $\pm 30\%$ [9];
- development latitude: $\pm 50\%$;
- edge sharpness and acuity better than 0.1 μm depending on the quality of the master provided by the customer;
- minimal width of the structures: down to 0.8 μm at contact printing through test mask; 0.3 μm ($\lambda = 436$ nm) at projection printing; 0.1 μm (electron beam);
- shelf life of the exposed and unexposed material - over 6 months.

The EPhR is very suitable for the mass production of encoder gratings, scales, reticules, *etc.*

References

- [1] R. W. Hallman, G. Wurtz, US Pat. No.3,762,325 Oct.17, 1973.
- [2] T. I. Shirakawa, I. Shimizu, H. Kokado, E. Inoue, Phot. Sci. Eng., **19**, 139 (1975).
- [3] M. S. Chang, J. T. Chen, Appl. Phys. Lett., **33**, 892 (1978).
- [4] A. Yoshikawa, O. Ochi, H. Nagai, Y. Mizushima, Appl. Phys. Lett., **29**, 677 (1976).
- [5] J. I. Masters, G. M. Goldberg, J. M. Lavine, IEEE, v.EDL-1, 61 (1980).
- [6] I. Konstantinov, B. Mednikarov, M. Sachatchieva, A. Buroff, US Pat.No.4458008/03.07.1984.
- [7] I. Konstantinov, B. Mednikarov, M. Sachatchieva, A. Buroff, US Pat.No.4499173/12.02.1985.
- [8] I. Konstantinov, B. Mednikarov, M. Sachatchieva, A. Buroff, EP Pat.No.0034490/02.10.1985.
- [9] B. Mednikarov, Solid State Techn.,v.**27**, No.5, p.177, May 1984.
- [10] A. G. Poleshchuk, E. G. Churin, Yu. I. Yurlov, B. Mednikarov, Jour. Imag. Sci. **30**(3),132 (1986)
- [11] B. Mednikarov, A. G. Poleshchuk, E. G. Churin, Autometria, No.4, 87-93 (1993).
- [12] M. A. Sachatchieva, B. Mednikarov, J. Inf. Recording, **23**, 337-346 (1996).
- [13] S. Stritc, H. Morkoe, J. Vac. Sci. Technol. B **10**, 1237 (1992).
- [14] E. I. Bienk, H. Jensen, G. N. Pedersen, S. Sorensen, Thin Solid films, **230**, 121 (1993).
- [15] D. Zanghi, A. Traverse, F. Petroff, et al., J. Appl. Phys. **89**, 6329 (2001).
- [16] S. Manish, H. N. Janice, C. A. Thomas, X. W. Shan, Appl. Phys. Lett. **77**, 2219 (2002).
- [17] M. Park, J-P. Maria, J. J. Cuomo et al., Appl. Phys. Lett. **81**, 1797 (2002).
- [18] F. Engelmark, G. Fucntes, I. V. Katadgiev, A. Harsla, U. Smith, S. Berg, L., Vac. Sci. Technol. **18**, 1609 (2000).
- [19] M. Penza, M. F. De Ricardis, L. Mirengi, M. A. Tagliente, E. Verona, Thin Solid Films **259**, 154 (1994).
- [20] I. Adesia, A. Mahajan, E. Andideh, M. Asif-Khan, D. T. Olsen, J. N. Kuznia, Appl. Phys. Lett., **67**, 2777, (1993).
- [21] H. Lee, D. B. Oberman, J. S. Harris Jr, Appl. Phys. Lett., **67**, 1754, (1995).
- [22] T. Y. Sheng, Z. Q. Yu, G. J. Collins, Appl. Phys. Lett., **52**, 576, (1988).
- [23] J. R. Mileham, S. J. Pearton, C. R. Abernathy, J. D. MacKenzie, R. J. Shul, S. P. Kilcoyne, Appl. Phys.Lett. **67**, 1119, (1995).
- [24] C. B. Vartuli, S. J. Pearton, J. W. Lee et al., J. Electrochem. Soc., v.**143**, No.11, 1996.
- [25] D. Meier, J. Przybycz, J. Kang, IEEE Transactins on Magnetics, **27**, 3121, (1991).
- [26] S. J. Pearton, C. R. Abernathy, F. Ren et al., J. Vac. Sci. Technol. A **11**(4), Jul/Aug 1993.
- [27] L. Huang, Xiao-Dong Wang, K. W. Hips et al., Thin Solid Films, **279**, 43-48, (1996).