JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 13, No. 11-12 , November – December 2011, p. 1467 - 1469

Spatial frequency doubling of interference lithographic structure using two-layer chalcogenide photoresist

I. Z. INDUTNYI*, V. A. DAN'KO, V. I. MYN'KO, P. E. SHEPELIAVYI, O. V. BEREZNYOVA
V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41, prospect Nauky, 03028 Kyiv, Ukraine

The low cost method for spatial frequency of the gratings doubling, have been developed. The method combine interference lithography with a spatial frequency doubling, based on vacuum evaporation of two layer $As_{40}S_{30}Se_{30}$-$As_4Ge_{30}S_{66}$ photoresist and wet etching only. Relief parameters and diffractions properties of the obtained structures were studied. This technology can be used for the fabrication of high-frequencies periodic structures on the substrates of the different materials (semiconductors, dielectrics, metals).

(Received June 2, 2011; accepted November 23, 2011)

Keywords: Spatial frequency doubling, Chalcogenide inorganic photoresist, Interference lithography

1. Introduction

High-frequency gratings have many applications in optics, electronics, biotechnology, etc. For manufacture of such gratings most simple and cheap method is interference lithography (IL), or so called holographic lithography [1-3]. Such method allows to receive high-quality and sizable gratings. The smallest period that can be formed by this technique can only approach to λ/2, or λ/2n for immersion interference lithography, where λ is the wavelength of the laser source, n – index of refraction of prism. IL provides an inexpensive method for the fabrication of nano- and microscale periodic structures over large areas and is ideally suited to a large scale manufacturing environment.

As shown in a number of works [4-7], one of the most perspective photoresist for formation of interference relief structures is an inorganic photoresist based on chalcogenide glasses. Such chalcogenide photoresists are characterized by an extremely high resolution (1 nm), vacuum deposition (that allows obtaining homogeneous film of precisely controllable thickness on various surfaces, including the nonplanar ones), sufficient mechanical, thermal and chemical stability. Combining IL and liquid or solid immersion the high-quality holographic gratings were obtained on chalcogenide resist with spatial frequencies up to 6000 and 8000 mm^{-1} [8].

An alternative fabrication technique for manufacture of high-frequency gratings is the "frequency doubling," which doubles the number of lines of a grating [9–11]. However, these techniques based on multiple technological steps, including vacuum deposition, electroless plating, lift-off, wet and reactive ion etching, and others. As a result, frequency doubling process can be lengthy, hence reducing the yield and increasing the cost.

In this work, we present the simplified method for doubling spatial frequency of the periodic structures fabricated using interference lithography. In our process two-layer chalcogenide photoresist As-S-Se / As-S-Ge are used. Compared with previous frequency doubling methods, the present one is based on thermal vacuum deposition, interference lithography and wet etching, only. This simple process can be realized on the substrates of the different materials (semiconductors, dielectrics, metals) and can find a number of applications.

2. Experiment

The samples for our experiments were deposited sequentially onto polished glass and polished (111) silicon substrates using the thermal vacuum evaporation of chromium and chalcogenide glass ($As_4Ge_{30}S_{66}$ and $As_{40}S_{30}Se_{30}$) at the pressure $2 \cdot 10^{-3}$ Pa. The layer thickness was controlled during deposition process by the quartz-crystal-oscillator monitoring system (КИТ-1) and reached 30 nm for the chromium layer, 80-200 nm for $As_4Ge_{30}S_{66}$, and 60-80 nm for $As_{40}S_{30}Se_{30}$ layers. After deposition, the thickness of the films was measured using a MII-4 micro-interferometer.

The prepared samples were exposed by interferential pattern that was generated by an argon laser (wavelength of 488 nm) using the holographic setup assembled by the wave-amplitude division method. The exposure value was near 0.5 J/cm^2. The size of an exposed part of the substrate reached up to 75×75 mm.

After exposure, the samples were chemically treated in non-water alkaline organic solutions [12] (negative etching, i.e. the exposed areas are dissolved more slowly than the unexposed areas) to form a resistive mask in $As_{40} S_{30} Se_{30}$ layer. For etching of $As_4Ge_{30}S_{66}$ layer a weak (less than 0,05 %) water solution of KOH was used. Water solution of HCl was used for etching Cr layer through obtained chalcogenide mask.

The surface patterns of obtained structures were examined with a Dimension 3000 scanning probe microscope (Digital Instruments) in the AFM tapping mode.

Diffraction properties were studied by measuring the spectral $\eta(\lambda)$ (λ is a wavelength) dependence of diffraction efficiency (η) of samples. The diffraction efficiency was taken as the ratio of intensities of the diffracted to the incident beams, and was measured for non-polarized light. Spectral measurements were carried out for the first diffraction order within the range of 400 to 900 nm using the setup for transmission gratings.

3. Results and discussion

The frequency doubling process starts with a sequential thermal vacuum deposition on a substrate of three layers (Fig. 1, a): Cr (layer thickness was 30nm), $As_4Ge_{30}S_{66}$ (150 nm) and $As_{40}S_{30}Se_{30}$ (80 nm). Top $As_{40}S_{30}Se_{30}$ layer is light-sensitive (photoresist) and can be used for recording of interference pattern and formation of first lithographic mask (Fig. 1, b) as a grating of parallel lines. Selective non-water etchant [12] on the basis of amine solution is characterized by good selectivity for $As_{40}S_{30}Se_{30}$ layer (value of selectivity, that defined by the solubility ratio of exposed and nonexposed film areas, achieves 13), and almost does not dissolve $As_4Ge_{30}S_{66}$ layer, both exposed and unexposed. The width of grating lines was controlled by the time of selective etching of $As_{40}S_{30}Se_{30}$ layer so that the gap between the mask lines is about half of the final grating period.

Second, thicker $As_4Ge_{30}S_{66}$ layer almost is not sensitive to light, but dissolves in weak aquatic solution of KOH. This etchant is actually neutral for $As_{40}S_{30}Se_{30,}$ not dissolving neither exposed nor unexposed $As_{40}S_{30}Se_{30}$ films [13]. At the same time $As_4Ge_{30}S_{66}$ layer dissolves with high speed that gives possibility to form on this two-layer chalcogenide structure more deep relief with the "mushroom" form of grooves (Fig. 1, c). The width of the grooves in their bottom part (near Cr layer) was also controlled by the time of $As_4Ge_{30}S_{66}$ etching and was equal to gap between "mushrooms".

In the next step (Fig. 1, d), additional resistive layer (5) was evaporated onto the sample at an incident angle normal to the substrate (in our case it was the same $As_{40}S_{30}Se_{30}$ photoresist). Then Cr layer was wet etched using water solution of HCl (Fig. 1, e).

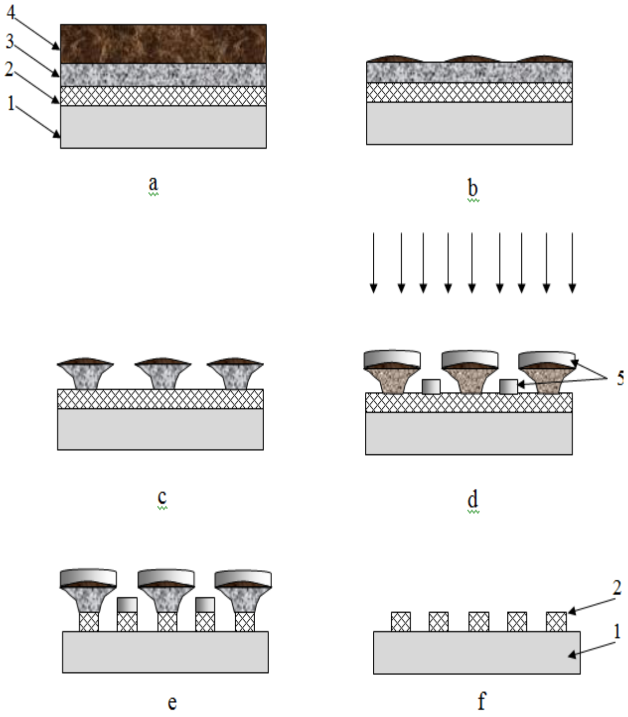

Fig. 1. Process of spatial frequency doubling: (a) deposition of the three-layer structure (2 – Cr, 3 - $As_4Ge_{30}S_{66}$, 4 - $As_{40}S_{30}Se_{30}$) onto substrate (1); (b) formation of the lithographic mask (using IL onto $As_{40}S_{30}Se_{30}$ photoresist) as a grating of parallel lines; (c) wet etching of $As_4Ge_{30}S_{66}$ layer; (d) evaporation of additional resistive layer (5); (e) wet etching of Cr; (f) removing of both chalcogenide by concentrate KOH solution.

Finally, the remaining $As_4Ge_{30}S_{66}$ and $As_{40}S_{30}Se_{30}$ are removed using concentrate KOH solution (Fig. 1, f). As a result of our frequency doubling process we have obtained a periodic Cr pattern which has doubled (as to the first interference lithographic mask) spatial frequency.

Fig. 2 shows the AFM image of obtained Cr pattern. During deposition of the additional resistive layer (step (d) on Fig. 1) part of the sample was screened. After etching we have obtained onto the same sample both initial grating with spatial frequency 769 mm^{-1}, and grating with double frequency – 1538 mm^{-1}. Fig. 2 shows area on the interface between these two parts of the sample.

By varying the etching time in the fabrication cycle we can form periodic structures with different line-width.

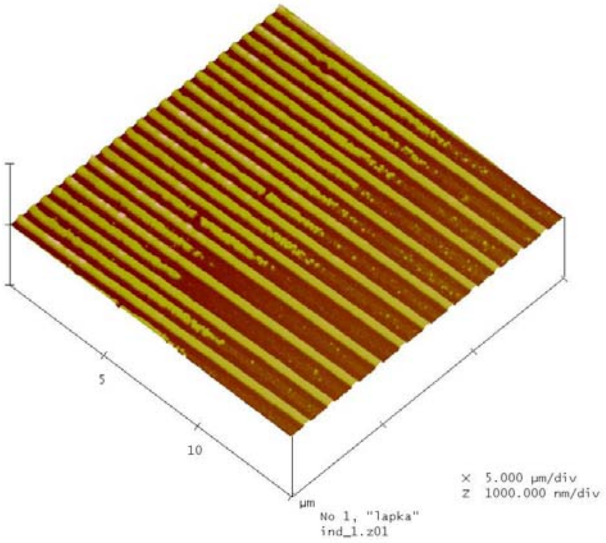

Fig. 2. AFM image of Cr grating: right part of the picture – original grating formed by IL method, left part – IL and frequency doubling.

Fig. 3 shows the spectral dependences of diffraction efficiency for Cr gratings presented on Fig. 2. Curves 1 and 2 correspond to the initial grating and grating with double frequency. These gratings were formed onto glass substrate and spectral η measurements were carried out in transmittance mode. As it is evident from the figure, the useful wavelength range of high-frequency grating is shifted to short wavelength and cover all visible spectral range. The initial, low-frequency grating most effectively cover the wavelength range in visible and IR spectral range (0,45 – 1,0 mkm).

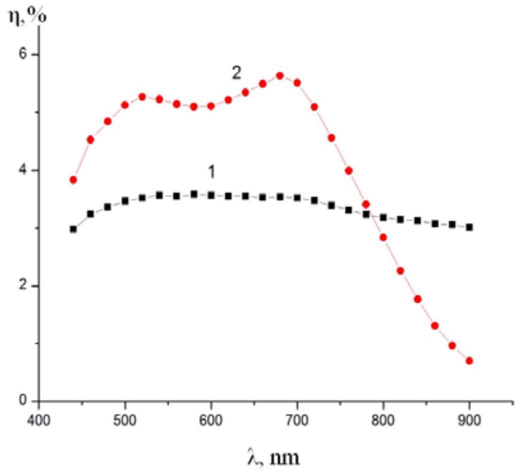

Fig. 3. Spectral dependence of the diffraction efficiency η for non-polarized light: curve 1 - initial grating with spatial frequency 769 mm^{-1}, 2 - with double frequency – 1538 mm^{-1}.

4. Conclusions

We have shown that the two-layer chalcogenide photoresist can be applied in the frequency doubling process which doubles the number of lines of a grating fabricated by interference lithography. The developed fabrication process involves only IL, vacuum evaporation and wet etching, which are all low-cost processes. In addition, this process can be realized on any substrate, including semiconductor and dielectric one. The developed frequency doubling technique can find a number of applications, particularly in the field of subwavelength optical devices, or optical sensors.

References

[1] Z. Yu, L. Chen, W. Wu, H. Ge, S. Y. Chou. J. Vac. Sci. Technol. **B21**, 2089 (2003).
[2] T. Geppert, S. L. Schweizer, U. Gosele, R. B. Wehrspohn. Appl. Phys. **A 84,** 237 (2006).
[3] D. A. Gish, M. A. Summers, M. J. Brett. Photonics and Nanostructure – Fundamentals and Applications **4**, 23 (2006).
[4] I. Z. Indutnyy, M. Popescu, A. Lorinczi, F. Sava, V. I. Min'ko, P. E. Shepeliavyi, J. Optoelectron. Adv. Mater. **10**, 3188 (2008).
[5] V. I. Min'ko, P. E. Shepeliavyi, I. Z. Indutnyy, O. S. Litvin, Semiconductor Physics, Quantum Electronics and Optoelectronics **10**, 5 (2007).
[6] I. Z. Indutnyy, M. T. Kostyshyn, I. P. Kasjarum et al., Photostimulated Interactions in Metal-Semiconductor structures, Kyiv, Naukova Dumka, 240, 1992.
[7] I. Z. Indutnyi, A. V. Stronski, S. A. Kostioukevich et al., Optical Engineering **34**, 1030 (1995).
[8] V. A. Dan’ko, I. Z. Indutnyi, V. I. Min'ko, P.E. Shepeliavyi, Avtometrija (in Russia) **46**, 103 (2010).
[9] D. C. Flanders, N. N. Efremow, J. Vac. Sci. Technol. B **1**, 1105 (1983).
[10] Bo Cui, Zhaoning Yu, Haixiong Ge, Stephen Y. Chou, Appl. Phys. Lett. **90**, 043118 (2007).
[11] Zhaoning Yu, WeiWu, Gun-Young Jung, D. L. Olynick, J. Straznicky, Xuema Li, Zhiyong Li, William M. Tong, J. A. Liddle, Shih-YuanWang R. Stanley Williams, Nanotechnology **17,** 4956 (2006).
[12] I. Z. Indutnyi, S. A. Kostjukevich, P. E. Shepeliavyi, Pat. 2008285 Russian Federation, Publ. № 4, 1994.
[13] I. Z. Indutnyy, M. Popescu, A. Lorinczi, F. Sava, V. I. Min'ko, P. E. Shepeliavyi, V. A. Dan’ko, J. Optoelectron. Adv. Mater. **11**, 1967 (2009).

---

*Corresponding author: indutnyy@isp.kiev.ua