Performance of the XR 1541 negative e-beam resist in the e-beam lithography for chosen substrate materials

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In this paper the negative HSQ (hydrogen silsesquioxane) XR 1541 electron beam resist is investigated in terms of its performance in the e-beam lithography for chosen substrate materials, namely for silicon, Ag on Si substrates, and GaAs based heterostructures. The purpose is to discuss its application in the fabrication of periodic structures (lines, pillars or holes). The contrast of the resist which is determined by the nature of the development process, is expressed by the value, calculated from an exposure wedge test. Extracted γ and dose-to-clear numerical parameters for the XR 1541 were γ=3.9 (at 130 μCcm-2) for Si, 2.2 (at 50 μCcm-2) for GaAs and 2.4 (at 85 μCcm-2) for Ag/Si substrate and 40 kV accelerating voltage, respectively. These parameters for the Si substrate but for varying energies of electrons, were as follows: γ=2.5 (at 23.5 μCcm-2) at 20 keV, 4.7 (at 61.5 μCcm-2) at 30 keV, and 3.9 (at 130 μCcm-2) at 40 keV, respectively. Typical achieved periods for the exposed patterns ranged from 500 to 1000 nm, and the minimal diameter of the patterns was cca 100 nm.

Изследване на XR 1541 отрицателен електроннолъчев резист в литография на е-лъч за избраните субстрата материали (Робърт Андок, Ярослава Скринярова, Павол Немец, Анна Бенкурова). *В тази работа негативният HSQ (водород силсескюиоксан) XR 1541 електронно лъчев резист се изследва от гледна точка на ефективността му при електроннолъчева литографията за избраните материали на подложката, а именно за силиций, за Ag върху Si подложка, и за GaAs базирани хетероструктури. Целта е да се обсъди прилагането му в производството на периодични структури (линии, колони или дупки). Контрастът на защитното покритие, което се определя от естеството на процеса на проявяване, се изразява чрез γ стойност, изчислена от тест «експозиция - клин». Извлечените у и «доза-до-изчистване» числени параметри за XR 1541 са у = 3.9 (при 130 μCcm-2) за Si, 2.2 (при 50 μCcm-2) за GaAs и 2.4 (при 85 μCcm-2) за Ag / Si субстрат и 40 кV ускоряващо напрежение, съответно. Тези параметри за субстрата Si, но за различни източници на електрони, са както следва: γ = 2.5 (при 23.5 μCcm-2) при 20 KeV, 4.7 (при 61.5 μCcm-2) при 30 KeV, и 3.9 (при 130 μCcm- 2) при 40 KeV, съответно. Типични периоди постигнати за експонираните рисунъци варират от 500 до 1000 nm, а минималният диаметър на изображенията е 100 nm.*

Introduction

The HSQ XR-1541 resist has been used in e-beam lithography for over 15 years (some of the first articles showing its use in EBL are listed in [1-3]). Since then a number of papers appeared dealing with its high resolution patterning [4-7], for high aspect ratio uses [6, 8], or in bi-layer strategies [9-10]. Our goal in this work was to examine whether the exposition doses applied to and optimized for this resist of a specific thickness depend on the used substrate material.

The performance of the negative e-beam resist HSQ XR-1541 (*Dow Corning*) was investigated by e-beam (resp. EBDW) lithography with respect to its sensitivity for chosen substrate materials, namely for silicon, GaAs based hetero-structures and silicon-silver wafers. The purpose is to discuss the application in the fabrication of periodic structures (lines, pillars or holes, depending on the exposition conditions). According to the manufacturer, the benefits of this resist include high purity, thin films deposition together with excellent line edge roughness [1]. This resist is comprised of hydrogen silsesquioxane (HSQ) resin in a carrier solvent of methylisobutyl-ketone (MIBK) and it functions as a negative tone e-beam resist with reported capability to define features below 10 nm. The exposed areas of the resist are standardly developed by the conventional tetra methyl ammonium hydroxide (TMAH) or KOH and NaOH based developer. The selection of a proper developer is rather important because during the development a negative-tone resist (such as HSQ) heaves in the developer which may in a large extent worsen (increase) the resulting dimensions of the exposed microstructures while worsening the image resolution in the resist. The properties of this heaving depend also on the chemical composition of the polymeric negative resist [11].

Experiment and discussion

EBDW lithography experiments

Before the resist coating the surface of the wafers was activated in HF:H_2O 1:10 solution for ca 10-20 sec followed by standard ACE / IPA / N_2 cleaning and drying. After the spinning the resist layer was prebaked on a hotplate for 2 min at 170°C in order to get high contrast and a good reproducibility. The resulting thickness of the dry resist was between 150 and 170 nm. The exposure was done using ZBA 23 (currently Vistec, Ltd.) variably shaped e-beam pattern generator with 20 and 40 keV energy of electrons. Experiments with 30 keV energy of electrons were carried out previously on ZBA 10 pattern generator. A standard and optimized exposure process was chosen where the resist shows the highest contrast: 500 W / 5 min substrate cleaning in O_2 plasma; resist spin-coating at 1200 rpm; EBDW lithography; resist development at 21°C for 120 sec in the AZ326 MIF (*Microchemicals*) developer, and final rinse in DEMI H_2O for 10 sec. Subsequently a post-exposure bake at 350°C in N_2 atmosphere took place. Optimal doses depend upon beam energy, desired resolution and film thickness. In order to eliminate possible organic residuals on the wafers a soft descumming was performed in oxygen plasma at 1 Pa, 150 W, -180 V U_{SB} and 60 sec.

As variable energy e-beam lithography allows to control electrons penetration depth in HSQ, we carried out several tests with different exposure doses ranging from 200 to 1600 μCcm^{-2} and beam current between 0.8 – 1.6 Acm^{-2}. But area doses from ca 250 to 600 μCcm^{-2} have shown to be sufficient for this purpose. As has been shown, optimal doses in general depend upon beam energy, desired resolution, and film thickness. Using e-beam energies from the mentioned interval, we have achieved typical periods for the exposed patterns from 500 to 1000 nm, and the minimal achieved diameter of the patterns was cca 100 nm. In our experiments we have used exposure doses smaller than nominal ones (i.e., a soft under-exposition) which resulted in thinner patterns (pillars), while for higher exposure doses (over-exposition) the pillars were merged leading to formation of holes in the resist material.

To extract the main numerical lithographical parameters, some exposure tests have been used. The exposure wedge (EW) test was analyzed to extract the dose-to-clear and the contrast numerical value from the characteristic curve, and to extract the contrast γ value of the resist for optimized resist pre- and post- exposure process parameters.

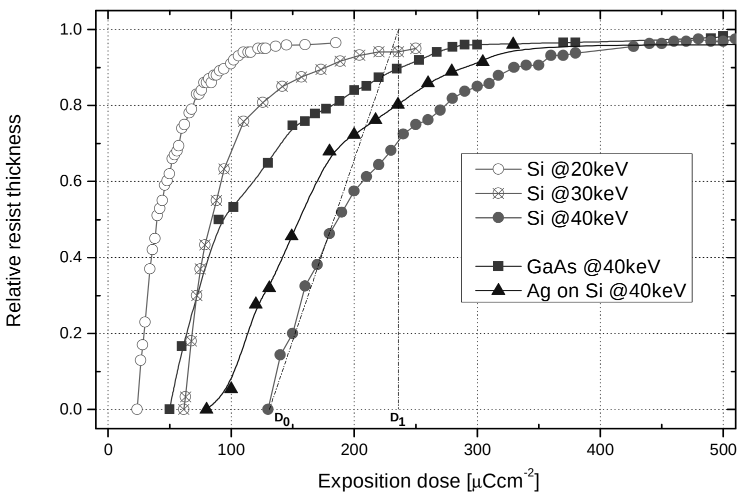

Fig. 1. Characteristic curves for the HSQ XR 1541 resist on Si, GaAs based heterostrucure and Ag/Si substrates at 40kV accelerating voltage. Evolution of the charactericțic curves for Si substrate at 20, 30 and 40 kV accelerating voltage, respectively.

Process homogeneity can also be controlled using EW test patterns exposed at various locations over the whole substrate. The measurements on EW tests were carried out using the standard profilometry technique (Talystep, Alphastep). The exposure test ET served to extract the main numerical lithography parameters from the experiment and consisted of isolated lines and gratings exposed by increasing doses. Observation and measurement of the test structure's special details enabled us to determine the influence of the proximity effects on the resulting pattern deformation. The contrast of the resist is determined by the nature of the development process and the contrast γ value, calculated from an EW test (Eq. 1), represents the differential dissolution speeds between exposed and unexposed regions of the resist:

$$\gamma = \frac{1}{\log\left(\frac{D_1}{D_0}\right)} \text{, or } \gamma = \frac{d\ln r}{d\ln E} \tag{1}$$

where D_0 is the extracted dose-to-clear value and D_1 is the dose at which the resist begins to be removed (for a positive process; such as e.g. PMMA) or cross-linked (for a negative process; e.g. XR 1541) [12]; in an equivalent expression r represents the dissolution rate from an exposure dose E [13].

Figure 1 shows relative resist thickness dependence of the HSQ XR 1541 resist as a function of exposure dose for three different substrates, namely for silicon, GaAs based hetero-structure and thin Ag on Si substrate at 40kV accelerating voltage. For silicon substrates the resist becomes cross-linked at the dose of 230 μCcm^{-2} (for Ag on Si substrates a little bit smaller dose), while for GaAs substrates which are more sensitive, this dose is 140 μCcm^{-2}. This corresponds to different densities of the two materials, for GaAs the density being more than twice the value of silicon (2330 kgm^{-3}).

For comparison, a development of the relative resist thickness dependence on exposure dose is plotted for a Si substrate at three different accelerating voltages, i.e. at 20, 30 and 40 kV, respectively. For silicon the resist is crosslinked already at 60 μCcm^{-2} (20 kV), at 100 μCcm^{-2} (30 kV), and at 235 μCcm^{-2} (40 kV). A rather large difference between these dependencies for Si substrate can be seen between 20 – 40 keV electron energies. While XR 1541 resist is very sensitive at 20 keV and can be used, e.g., for large areas exposition, large-area gratings for nanophotonics etc., on the other hand it shows a better resolution at 40 keV.

Extracted dose-to-clear (D_0) and γ numerical parameters for the XR 1541 were as follows: γ=3.9 (at D_0=130 μCcm^{-2}) for Si, 2.2 (D_0=50) for GaAs and 2.4 (D_0=85) for Ag on Si substrate and 40 kV accelerating voltage, respectively. It can be seen that GaAs and Ag on Si substrates have a similar γ value and about twice that value has been calculated for a Si substrate at the same energy of electrons (40 keV). On the other hand, if we compare the dose-to-clear and γ parameters for the same Si substrate but for different energies of electrons, the calculated values are as follows: γ=2.5 (at D_0=23.5 μCcm^{-2}) at 20 keV, 4.7 (D_0=61.5) at 30 keV and 3.9 (D_0=130) at 40 keV, respectively.

GaAs as substrate material

Our goal was to achieve 1:1 ratio pillars *vs.* spaces. In order to find an optimal exposure dose, we made series of experiments where we changed the exposure dose (from 200 – 1600 μCcm^{-2}) together with the input pillars *vs.* spaces ratio within the required period of structures. An array of dots was exposed in a meander-like manner with intention to achieve exposition in a circular area of a diameter of 80 μm.

For 900 nm period (Fig. 2) of structures (theoretical input pillars diameter 300 nm, space 600 nm) we used exposure doses between 200 – 800 μCcm^{-2}. For lower exposure doses (200 μCcm^{-2}) this ratio was 1:2 and for 400 μCcm^{-2} doses the ratio changed to 2:1. The optimal dose for our required structures was in this case 280 μCcm^{-2}.

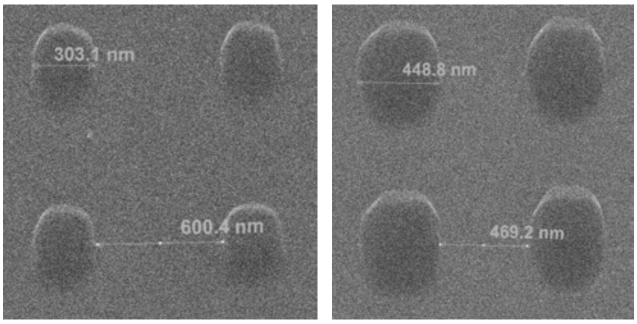

Fig. 2. A 900nm (300/600nm pillars vs. spaces) period of structures in the HSQ XR 1541 resist (after exposure and development) on a GaAs heterostrucure. The influence of the exposure dose for the ratio pillars vs. spaces. Left: Exposure dose 200 μCcm^{-2} (ratio 1:2 for pillars vs. spaces). Right: Optimal exposure dose 280 μCcm^{-2} (ratio 1:1).

A somehow different situation was for a theoretical input ratio 200/700 nm for which we used the exposure doses between 400 – 1600 μCcm^{-2}. The optimal value was achieved at ca 490 – 530 μCcm^{-2}. Further exposure dose increase led to a significant merging of the pillars and to creation of holes between the pillars.

Similar results have been achieved also for the period of 700 nm. We have chosen a 200/500 nm theoretical ratio between pillars and spaces with exposure doses varying between 200 – 800 μCcm^{-2}, and for theoretical pillars *vs* spaces ratio 100/600 nm the exposure doses varied between 400 – 1600 μCcm^{-2} (Fig. 3). We have found out that for the theoretical input ratio 100/600 nm the optimal exposure dose for achieving 1:1 ratio was within the interval of 800 – 820 μCcm^{-2}, and for 200/500 nm ratio the optimal value came out to be 240 μCcm^{-2} (Fig. 4), respectively.

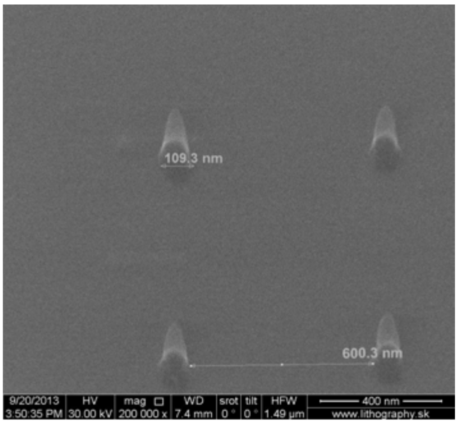

Fig. 3. A 700 nm (input ratio 1:6) period of structures in the HSQ XR 1541 resist on GaAs heterostructure. An example of a low exposure dose used (400 μCcm^{-2}).

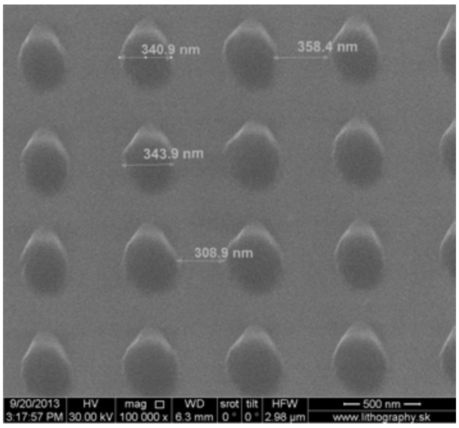

Fig. 4. Example of an optimal exposure dose (240 μCcm^{-2}) with input ratio 1:6 of pillars vs splaces for achieving the desired ratio 1:1.

For 600 nm period (Fig. 5) of the structures (theoretical input values: 100 nm pillars diameter, 500 nm space) we have tested the doses from 200 to 800 μCcm^{-2}. We have found out that at 360 μCcm^{-2} the exposure dose is sufficient. The exposure doses below that value turned out to be insufficient as total resist change occurred and after its development the exposed part of the resist was washed away. Reproducible results have been achieved at exposure doses in the interval from 400 to 800 μCcm^{-2}, while by increasing the value of the exposure dose the pillar *vs* space ratio shifted in favour of the pillars. At lower exposure doses this ratio was 1:5 and, on the other hand, at high doses it changed to 3:1. Additional increase of the exposure doses has led to overexposition of the pillars, which means that the pillars merged leaving only holes between the neighboring pillars (this ratio remains 6:1).

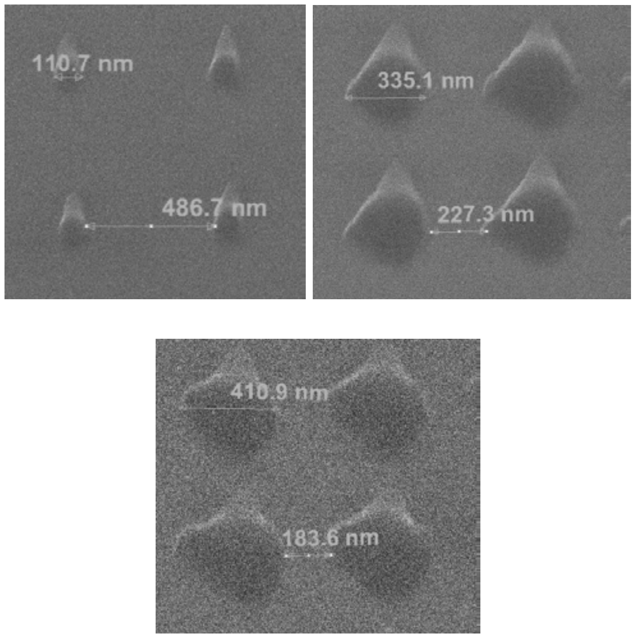

Fig. 5. 600 nm periods of structures in the HSQ XR 1541 resist on GaAs substrate. Above left: pillars vs spaces ratio 1:5; right: ratio 3:1; below: overexposure of the pillars, ratio 6:1.

It can be seen from Figure 5, by increasing the exposure dose, how the ratio pillars *vs* spaces (holes) changed in favour of the pillars. The optimal doses for the 1:1 ratio were in the interval 570 – 590 μCcm^{-2} (for theoretical ratio 100/500 nm). For the theoretical ratio 200/400 nm the exposure dose was about 300 μCcm^{-2}

For 500 nm period (Fig. 6) of the structures (desired input ratio: 100 nm pillar diameter, 400 nm space) we have tested the exposure doses from 200 to 800 μCcm^{-2}.

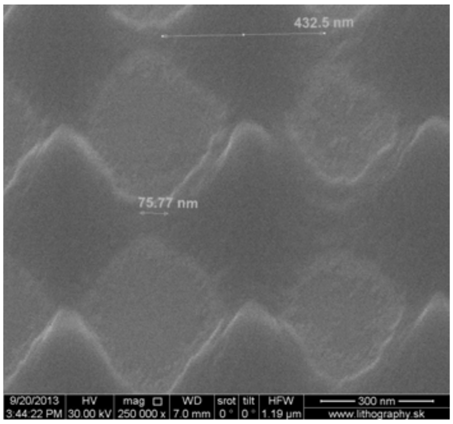

Fig. 6. Creation of holes in the HSQ XR 1541 resist by overexposing of pillars.

Optimal exposure dose for this configuration appeared to be ca 280 μCcm^{-2}. At this period (and lower) yet a small increase of the exposure dose significantly changes the desired ratio. For example, at dose increase in 30 μCcm^{-2} a clear increase of the pillars dimension occurs that leads to touching (or merging) of the pillars and to formation of holes (Fig. 6). It is thus important to choose a fine scaling of the exposure doses.

Si as substrate material

For Si substrates we have tested exposure doses for 1D structures with theoretical ratio of line/space equal 300/700 nm. The required real ratio of structures was 1:1. Exposure doses from 250 – 600 μCcm^{-2} were used. Table 1 is a summary of used exposure doses *vs.* achieved line/space dimensions.

Table 1.

1D structures line/space theoretical ratio 300/700 nm on Si substrate.

Exposure dose [μCcm^{-2}]	1D structures line/space [nm]
260	160 / 840
300	240 / 760
340	310 / 690
420	370 / 630
460	400 / 600
500	420 / 580
540	450 / 550
600	500 / 500

Optimal doses for the required ratio line/space were in the interval 540 – 600 μCcm^{-2}. Figure 7 shows the influence of increasing exposure dose on increasing ratio line/space up to the ratio of 1:1.

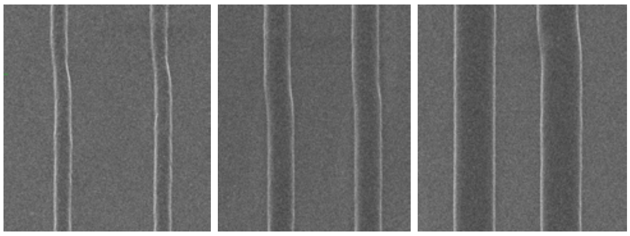

Fig. 7. A micron period of structures in the HSQ XR 1541 resist on a Si substrate. Left:160 / 840 nm lines/spaces (at 260 μCcm^{-2}); middle: 310 / 690 nm (at 340 μCcm^{-2}); right: 500 / 500 nm (at 600 μCcm^{-2}).

Similar tests have been done for 2D structures in the interval of doses from 280 – 800 μCcm^{-2}. For the ratio pillars *vs.* spaces equal 1:2 the doses close to 760 μCcm^{-2} were needed (theoretical ratio 300/600 nm).

Conclusions

In our work we have tested the XR 1541 e-beam HSQ resist and the influence of the used substrate materials in order to obtain optimal exposure dose for patterning of two-dimensional structures (lines, pillars) with the periods of 500 – 900 nm. For heterostructuers on GaAs optimal exposure doses for the pillars period of 1000 nm was 280 μCcm^{-2} (for theoretical ratio 3:6). However, for the ratio 1:1 of pillars/spaces this exposure dose increased to 490 – 530 μCcm^{-2}. This is caused by the fact that we had to overexpose the area with pillars in order to achieve the resulting ratio 1:1. From the practical reason we have chosen the lower exposure dose obtained for the theoretical period of pillars equal to 300 / 600 nm. Similar results have been achieved also for 700 nm period at theoretical ratio 200 / 500 nm. Optimal exposition dose in this case was 240 μCcm^{-2}. On the other hand, for theoretical ratio 100 / 600 nm the exposure dose increased to 800 – 820 μCcm^{-2}. For 600 nm period the optimal dose was 300 μCcm^{-2} and for 500 nm period the optimal dose was 280 μCcm^{-2}.

In comparison to GaAs substrate for which at the theoretical ratio 300 / 600 nm only an exposure dose of 280 μCcm^{-2} would be sufficient to achieve the desired ratio 1:1, in the case of a silicon substrate the dose of 760 μCcm^{-2} is required (at theoretical ratio 1:2). Such a difference in exposure doses for the two substrates is probably caused by a different reflexion of the used substrate materials.

Acknowledgments

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REFERENCES

[1] Dow Corning Material Data Sheet, www.dowcorning.com/electronics

[2] H. Namatsu, Y. Takahashi, K. Yamazali, T.Yamaguchi, M. Nagase, Three-dimensional siloxane resist for the formation of nano-patterns with minimum linewideth fluctuations. J. Vac. Sci. Technol., B 16, 1998, pp.69-76.

[3] H. Namatsu, F. Yamaguchi, M. Nagase, K.Yamazali, K. Kurihara. Nanopatterning of a hydrogen silsesquioxane resist with reduced linewidth fluctuations. Microelectron. Eng. 41/42, 1998, pp.331-334.

[4] B. E. Maile, W. Henscheld, H. Kurz, B. Rienks, R. Polman, P. Kaars. Sub-10 nm linewidth and overlay performance achieved with a fine-tuned EBPG-5000 TFE electron-beam lithography system. Jpn. J. Appl. Phys. 39, 2000, 6836.

[5] L. Mallard, C. Cunge, S. Tedesco, B. Dalzotto, J. Foucher. HSQ hybrid lithography for 20 nm CMOS device development. Microelectron, Eng. 61/62, 2002, pp.755-761.

[6] St. Trellenkamp, J. Moers, A. van der Hart, P. Kordos, H. Luth. Patterning of 25 nm-wide silicon webs with an aspect ratio of 13. Microelectron. Eng. 67/68, 2003, pp.376-380.

[7] M. J. Word, I. Adesia, P. R. Berger. Nanometer-period gratings in hydrogen silsesquioxane fabricated by electron beam lithography. J. Vac. Sci. Technol., B 21, 6, 2003, L12-L15.

[8] T. Wahlbrink, D. Kupper, Y.M. Georgiev, et al.. Supercritical drying process for high aspect-ratio HSQ nano-structures. Microelectronic Engineering 83, 2006, pp.1124-1127.

[9] W.-S. Chen, P.-S. Chen, H.-W. Wei, F.T. Chen, et al.. Substrate and Underlayer Dependence of Sub-32 nm E-beam HSQ Pillar Patterning Process for RRAM Application. Proc. of SPIE Vol. 8325, 2012, 83250V.

[10] W.-S. Chen, P.-S. Chen, H.-W. Wei, F.T. Chen, et al.. Transfer Optimized Dry Development Process of Sub-32 nm HSQ/AR3 BLR Resist Pillar from Low-K Etcher to Metal Etcher. Proc. of SPIE Vol. 8328, 2012, 83280P.

[11] I. Kostič, A. Benčurová, A. Konečníková, P. Nemec, A. Ritomský, E. Koleva, K. Vutova, G. Mladenov. Study of electron beam resists: negative tone HSQ and positive tone SML300. Elektrotechnika i elektronika E+E: Eleventh International Conference on Electron Beam Technologies, vol. 49, 2014, no. 5-6.

[12] S.A. Campbell. The Science and Engineering of Microelectronic Fabrication. New York, Oxford: Oxford University Press 2001.

[13] A. Liddle et al. Resist Requirements and Limitations for Nanoscale Electron-Beam Patterning. Mat. Res. Soc. Symp. Proc. 739, 19, 2003, pp.19-30.

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