STUDY ON ELECTRON BEAM IRRADIATION SENSITIVE POLYMERS

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1. Introduction

Electron beam lithography (EBL) with a single beam has been used for many years for mask writing and device prototyping in semiconductor manufacture.

In R&D, the polymer based electron beam lithography is one of the most widely applied techniques for the production of nanostructures, for prototyping, production of photomask and imprint mold.

For both, single-beam EBL and multi-beam EBL, resist materials are crucial elements and their performance determines the final results of the structures patterning.

Our aim in this paper is to characterize electron beam irradiation sensitive materials – electron beam resists. Currently used high performance resist materials were selected for this purpose - positive electron beam resists polymethyl-methacrylate (PMMA) A6 (*Microchem*) and AR-P 6200 (CSAR 62) (*Allresist*), and negative electron beam resists SU-8 (*Microchem*) and hydrogen-silsesquioxane (HSQ) (*Dow*). The accuracy of the resist profile and the size of structures are determined by various process parameters, such as solubility rates, dependences of the linewidth on the exposure dose, lithographic resolution, etc. Chemical processes in resists during electron irradiation are desribed to better understand dependence of resist structure dimensions, profiles and line edge roughness on the process parameters. Experimental results on the investigation of process parameters as resist sensitivity, linewidth dependence on the exposure dose and proximity effects are presented and discussed for selected resists.

2. Experimental procedure

Electron beam lithography is based on physico-chemical changes in the resist thin layer [1]. The commonly used resists are polymers dissolved in a liquid solvent with small molecule additives to enhance the lithographic performance of the material.

During the electron beam exposure, the result of inelastic collisions of electrons with the resist is the ionization (secondary electron generation), where an incoming electron provides enough energy to cause an electron to be removed from an atom. In polymers, these lead to many different chemical reactions, which are classified as either chain-scission or crosslinking reactions.

All experiments with resists have been performed using a high-resolution scanning electron microscope (SEM) with field emission Schottky cathode and Gaussian intensity distribution (Inspect F50, FEI) equipped with nanolithography control system Elphy Quantum (Raith) [2] and variable shaped e-beam system ZBA23 (Vistec Electron Beam, GmbH) [3, 4]. In ZBA23, the rectangular shape size can be varied from 50 nm up to 3000 nm in steps of 50 nm. Accelerating voltage was 20 or 40 kV and the beam current density was 1.6 A/cm^2. The resolution of SEM Inspect F50 is 1.3 nm at 30 keV electron energy. The minimal spot and minimal possible beam current of 20 pA at electron energy of 30 keV have been adjusted. Line step size was 13,3 nm and line dwell time 0,0004 ms for the highest resolution.

Each of resists were prepared on silicon substrate by spin coating method. The resist thickness measurements were carried out using the standard profilometry technique (Alphastep). All dimensions measurements were carried out using a high-resolution scanning electron microscope with field emission cathode Quanta 3D (*FEI*). The magnification at least 200 000x was used for linewidth measurements and 300 000x for line edge roughness measurements (LER). LER was evaluated from set of at least 10 linewidth measurements along 1 μm length of the line and at various part of the line. LER was evaluated as the difference of the average linewidth value and maximum linewidth value.

The main resists characteristics of electron beam resists have been obtained from a set of various exposure tests [5] which consists of single lines, periodical line and dot gratings with various dimensions and density.

3. Materials sensitive to electron irradiation

Electron beam resists are crucial for the application of EBL as the ultimate resolution of EBL is set by the resolution of the resist and by the subsequent fabrication process [6], and not by the resolution of electron optical systems which can approach 0.1 nm.

The key features of lithography resist are sensitivity to the exposing radiation, good contrast (differential dissolution speed between exposed and unexposed regions), high resolution capability, exposure/dose latitude, adhesion to substrate, compatibility with standard aqueous developers (TetraMethyl Amonium Hydroxide - TMAH), stability (thermal, environmental, delay - shelf life), resistivity against subsequent technological processes (e.g., reactive ion etching) [1]. The performance characteristics are mainly determined by the base polymer in the resist, but also tools and process conditions.

One of the first materials developed for e-beam lithography was **polymethyl methacrylate (PMMA)** [7]. It is a widely used organic resist with important applications in nanolithography for nanostructure pattern transfer. PMMA resists with molecular formula [$CH_2C(CH_3)$ (CO_2CH_3)] are polymers dissolved in either chlorobenzene, or safer anisole solvent. Standard PMMA products are formulated with 495,000 and 950,000 molecular weight (MW), and custom MW products are ranging from 50,000 - 2.2 million MW [8].

In PMMA, the exposure induces the scissions of the chain of methacrylic monomers that constitute the resist material. The main chain-scission reaction is shown in Fig. 1.

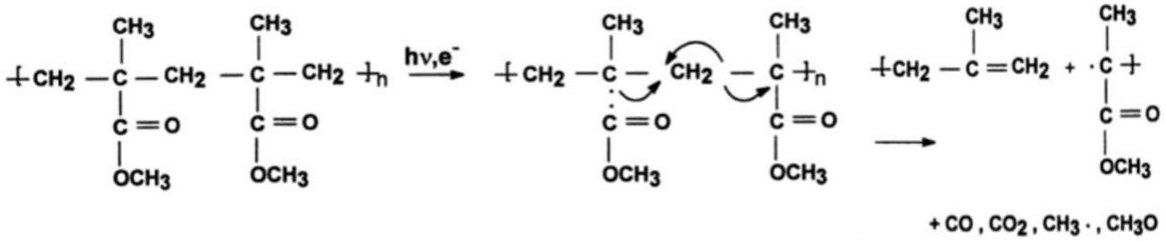


Fig. 1 *Chemistry of PMMA reaction [9]*

Advantages of PMMA positive electron beam resist include the large range of molecular weight (50,000–2.2 million), the ultimate resolution (less than 10 nm), high contrast, uniform resist coating, long shelf life and good adhesion to most substrates. The main disadvantages are low sensitivity and poor dry etch resistance.

AR-P 6200 (CSAR 62) (*Allresist*) is based on styrene acrylates and is dissolved in the solvent anisole [10, 11]. The main components of the resist are poly(α-methylstyrene-co-methyl chloroacrylate), an acid generator and the solvent anisole [10].

The chlorine atoms support breaking of the polymer chain during irradiation by electrons. In addition, a halogen-containing acid generator enhances this effect. The introduction of further reactive halogens accelerates the attack on the polymer chain even

more. The improved plasma etch resistance results from the introduction of aromatic substituents such as e.g. phenyl, naphthyl or anthracyl groups into the polymer.

In comparison with PMMA resists, the AR-P 6200 (CSAR 62) is characterised by a higher sensitivity and substantially improved plasma etch resistance.

SU-8 negative resist (*Microchem*) is a chemically amplified, epoxy based negative UV-photoresist [12]. However, capabilities of SU-8 as negative e-beam lithography resist have been discovered [13].

Advantages of this resist are very high sensitivity and good dry etch selectivity. The main disadvantages are low resolution and poor line edge roughness. The properties of epoxy-novolack Epon SU-8 are low molecular weight, good solubility, high transparency, glass and film formation, low glass transition temperature (Tg), an excellent chemical resistance and good biocompatibility.

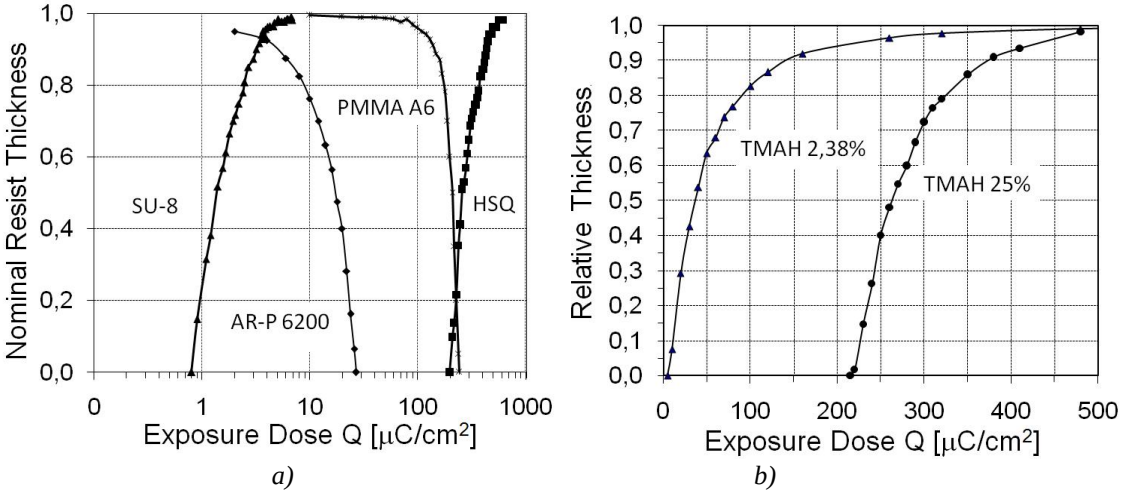
Hydrogen Silsesquioxane (HSQ) (*Dow*) is used as a high-resolution resist with resolution down below 10 nm half-pitch [15]. On the other hand, as inorganic resist material, it is interesting as masking layer in reactive ion etching (RIE). It is inorganic compounds with the chemical formula $[HSiO_{3/2}]_{2n}$ [16]. Silicon atoms sit at the corners of a cubic structure. Each silicon is bonded to a hydrogen atom and bridges 3 oxygen atoms.

The use of HSQ as a negative tone resist for electron beam lithography (EBL) was published in [17]. They suggested that the silicon hydrogen bonds (which are weaker than SiO bonds) are broken during e-beam irradiation and converted to silanol (Si–OH) groups in the presence of absorbed moisture in the film.

Sub-10-nm lines in HSQ were successfully achieved when using very small spot sizes and acceleration voltages of 100 keV [18, 19].

4. Results and discussion

A comparison of sensitivity and contrast curves (normalized resist thickness vs. exposure doses) of PMMA, AR-P 6200 (CSAR62), SU-8 and HSQ resists is shown in Fig. 2a. The resist thickness prepared on silicon substrate was 600 nm, and energy of electrons was 40 keV for all resists. The sensitivity of positive resist AR-P 6200 (CSAR62) was measured 27 μC/cm^2 and is significantly higher when compared to PMMA value of 245 μC/cm^2. The sensitivity of negative resist SU-8 of the value 0,8 μC/cm^2 is very high when compared to negative resist HSQ of the value 200 μC/cm^2 and both positive resists.

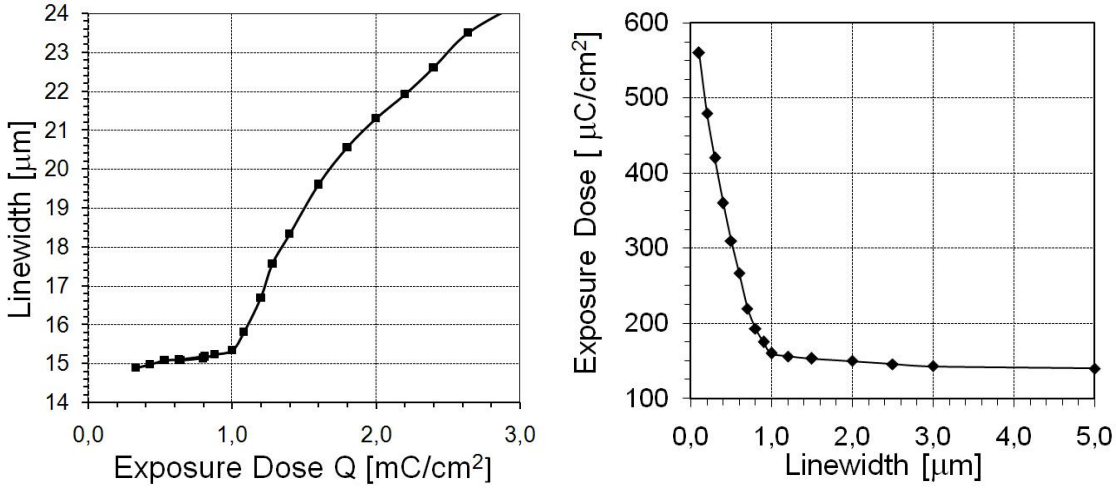


a) *b)*

Fig. 2 *Sensitivity and contrast curves of PMMA, AR-P 6200 (CSAR62), SU-8 and HSQ e- beam resists. The resist thickness was 600 nm, Si substrate, energy of electrons 40 keV (a). Sensitivity and contrast curves for the HSQ negative tone resist developed during 30 sec in TMAH with two concentrations 2,38% and 25% (b).*

Lithographic parameters are depending on the development process. The influence of various development process conditions on the resist sensitivity and contrast were investigated. Fig. 2b shows the sensitivity and contrast curves for HSQ resist after development for 30 sec in two TMAH developer concentration: 2.38% (solution in H_2O) and 25%. The obtained sensitivity is remarkable higher at 2.38 % TMAH concentration.

The linewidth dependence on the exposure dose is demonstrated on Fig. 3a. A single line of 15 μm linewidth was exposed in 50 nm thin HSQ negative resist on silicon substrate at 40 keV electron energy. As seen, the dependence is strongly non-linear. There is a nearly linear part within the exposure dose 0,3 – 1,0 mC/cm^2. In this case, the main contribution to the resist image formation comes from forward scattered electrons and the contribution of backscattered electrons is low. The linewidth starts to grow sharply over the exposure dose 1,0 mC/cm^2 as the contribution of backscattered electrons becomes significant. The radius of backscattered electrons influence is about 15 μm at 40 keV.



a) *b)*

Fig. 3 *The linewidth vs. the exposure dose of single line (15 μm) in the case of 50 nm thin HSQ negative resist on Si substrate for 40 keV electron energy (a). The exposure dose vs. the linewidth for single lines in the case of 350 nm thin PMMA E2041 positive resist on Cr/Quartz substrate for 20 keV electron energy (b).*

To determine the influence of electron scattering on the structures patterning, the line test consisting of lines with a set of various dimensions and exposure dosis was exposed and analysed. Dependence of the linewidth on the exposure dose was measured for various process parameters (type of resist, resist thickness, substrate material, electron energy, development process). In Fig. 3b is shown the case of 350 nm thin PMMA E2041 positive resist on Cr/Quartz substrate, 20 keV electron energy, developer MIBK:IPA (1:3), and development time 60 sec. Below one micrometer linewidth, the exposure dose is increasing sharply with the line scaling to nanometer dimensions.

5. Conclusions

There is a large number of parameters affecting the EBL process in a complex, interacting fashion. A precise control of these parameters requires systematic understanding of the limiting factors involved in both the electron-resist interaction and in the polymer dissolution (development), as well as the corresponding interplay of the numerous process control parameters including the accelerating voltage, exposure dose, materials and development conditions. The main resists characteristics of selected electron beam polymer resists PMMA, AR-P 6200 (CSAR62), SU-8 and HSQ deposited on silicon substrate were investigated experimentally with focus on resist sensitivity and contrast, and dependence of

linewidth on the exposure dose. A comparison of sensitivity and contrast of selected resists was performed. The influence of various development process conditions on the resist sensitivity and contrast were investigated. Dependence of the linewidth on the exposure dose was measured for various process parameters (type of resist, resist thickness, substrate material, electron energy, development process).

6. Acknowledgement

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