Materials Science in Semiconductor Processing 66 (2017) 26–32

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Dynamic behavior in self-assembly process of cylindrical phase PS-*b*-PMMA block copolymer

M. Loucif Seiad[a,b,c,e,*], V.K. MKuppuswamy[a], Y. Cao[d], R. Gronheid[a], M. Ferhat[f]

[a] *imec, Kapeldreef 75, B-3001 Leuven, Belgium*
[b] *KACST-Intel Consortium Center of Excellence in Nano-manufacturing Applications (CENA), Riyadh, Saudi Arabia*
[c] *Centre de Développement des Technologies Avancées, DMN, BP N°17 Baba Hassen, 16303 Algiers, Algeria*
[d] *EMD Performance Materials Corp., 70 Meister Ave., Somerville, NJ 08876, USA*
[e] *Semiconductor and Functional materials laboratory, University Amar Telidji of Laghouat BP 37G, Ghardaïa Road, 03000 Laghouat, Algeria*
[f] *Department of Physics, The University of the West Indies, Mona Campus, Kingston 7, Jamaica*

ARTICLE INFO

Keywords:
Block copolymer
Self-assembly
Microphase separation
Cylindrical phase
Dynamics

ABSTRACT

Self-assembly through phase separation in block copolymers (BCPs) thin films represents an attractive route to create spontaneously ordered patterns at the sublithographic range. The cost effectiveness, the fast parallel processing time as well as the compatibility with the standard microelectronics technologies make it among the most promising techniques to meet the ever challenging feature size requirements in nanotechnologies. In the present work, we investigate the behavior of cylinder forming poly (styrene-b-Methyl-Methacrylate) PS-b-PMMA self-assembly on a chemically neutralized 300 mm Silicon wafer. The effects of the process parameters such as the annealing temperature and time, the film thickness, and the BCPs periodicity on the holes formation after PMMA removal were studied in systematic fashion using statistical analysis of the Critical Dimension- Scanning Electron Microscope (CD-SEM) images,focusing mainly on the Critical Diameter (CD) and circularity of holes. In particular, it was found that both (CD) in the narrow range of 10–15 nm and a hole circularity of (0.8–0.9) in excess of 96% can be achieved on the whole wafer under appropriate processing conditions. The obtained results were correlated to the self-assembly process and shed some light on the dynamic of the phase separation process of BCPs. The level of reproducibility and control achieved on a 300 mm silicon wafer, hold a promise for future applications in nanotechnology.

1. Introduction

Self-assembling (S-A) soft materials have realistic potential for manufacturing nanodevices at future technology nodes. BCPs are a class of self-assembling materials that segregate on nanometer length scales, making them ideal for emerging nanotechnologies [1–3], including many applications in nanotemplating [4–8]. These applications require the use of BCPs in thin film geometries (< 100 nm thickness), where self-assembly is strongly influenced by different parameters. The simplicity and cost-effectiveness of the spontaneous BCP self-assembly process is attractive and holds promise for applications in nanolithography [9–12], with demonstrated capabilities in the fabrication of nanoscale devices [1]. Specifically, the use of cylindrical phase BCPs has been demonstrated for printing the capacitor layer of dynamic access memory devices [13–15]. PS-*b*-PMMA is a promising choice for nano-lithographic applications since the surface energies at the PS/air and PMMA/air interface are nearly equal under typical thermal annealing conditions [16]. This allows for easy and therefore low-cost processing. Moreover, the nanodomains of PMMA can be degraded by radiation and then removed with an organic solvent leaving PS as etch mask. Many researches have contributed to provide an understanding of block copolymer self-assembly, beginning with the characterization of bulk morphologies using the Flory-Huggins interaction parameter (χ), degree of polymerization (N), volume fractions (f) and chain architecture [17].

In thin films, where the interfaces strongly affect the final nanoscale morphology, commensurability between the film thickness (t) and the natural period (L_0) along with polymer-surface interactions can influence both the morphological symmetry and the orientation [18]. Several studies based on the ordering kinetics and morphology evolution in BCP materials have been described during the past. Perpendicular orientation of the nanodomains in cylindrical morphologies can be achieved by different methods such as surface modification, strong electric field, and solvent annealing. Important progress has been

* Corresponding author at: Centre de Développement des Technologies Avancées, DMN, BP N°17 Baba Hassen, 16303 Algiers, Algeria.
E-mail address: mloucif@cdta.dz (M. Loucif Seiad).

http://dx.doi.org/10.1016/j.mssp.2017.03.035
Received 29 November 2016; Received in revised form 25 February 2017; Accepted 30 March 2017

reported in the literature to reduce the annealing time necessary for the BCP to self-organize. Short processing times were obtained by Welander et al. [19] using thermal processes performed on hot plates. However, the behavior of the morphology of BCP S-A in the very early stages of annealing (first few seconds) has not been reported yet, due to the impossibility to control the thermal energy transferred to the sample. Ferrarese Lupi et al. [20] and Jacobs et al. [21] proposed a new technological approach able to overcome those limitations, using a rapid thermal processing machine (RTP) and a laser spike annealing (LSA) respectively, to decrease the annealing time and improve the quality by reducing the defects concentration. The hole formation was also studied over the past. Guarini and Andreozzi [22,23] investigated the influence of process parameters on the self-assembly process for PS/PMMA System, focusing on the distribution of the pore diameters, and the pore spacing across the film. In this article we investigate the dynamics of BCP S-A, using an in-plane analysis technique (CD-SEM) by following the evolution of the critical dimension (CD) and the hole circularity in the finale template as function of the processing parameters, which to the best of our knowledge has not been reported so far.

2. Material and methods

2.1. Materials

A brush copolymer (AZEMBLY™ NLD-173) was used as an underlayer and two different BCPs P(S-*b*-MMA) (AZEMBLY™ PME-633 and AZEMBLY™ PME-585) with different periodicity (29 nm, 37 nm respectively) and viscosities. Both BCPs with approximately 70% PS volume fraction (obtained from Merck) were used as received.

2.2. Microphase separation process

2.2.1. Substrate neutralization

All processes used in this study were performed at IMEC on a TEL CLEAN TRACK ACT™ 12 system. Which incorporates four separate high-performance application modules: i) coating, ii) annealing, iii) exposure and iv) development. The tool provides sophisticated control and reproducibility in the photomask manufacturing process to meet the needs of advanced industry requirements. The underlayer (AZEMBLY™ NLD-173) was used in order to neutralize the substrate surface. It is a random co-polymer of PS-*r*-PMMA with a terminal functional group that grafts to the substrate on thermal anneal. An amount of 3 ml was spin coated at 1500 rpm and annealed under nitrogen atmosphere at 250 °C for 60 s. The ungrafted brush molecules were removed with organic solvent rinse. Final grafted brush thickness was measured around 7 nm.

2.2.2. BCPs coating

Thin films were obtained by spin-coating BCPs solutions onto previously neutralized Si wafers. The films were annealed at 240 °C for 600 s under nitrogen atmosphere to promote the self-assembly of the PMMA cylinders in the PS matrix. Then, they were exposed to deep ultraviolet radiation (DUV) in order to cross-link the PS and degrade the PMMA blocks respectively. The PMMA cylinders were selectively removed after exposure and solvent rinse.

2.3. Characterizations

An ellipsometer (KLA Tencor, ALERIS) was used to measure the polymeric film thickness. The film morphology of the polymeric films after anneal and PMMA removal was studied using a Critical Dimension Scanning Electron Microscope (CD-SEM) (Hitachi CG-4000).

2.4. Statistical analysis

First, a visual inspection of a large area of the wafer was performed in order to confirm the homogeneity of the obtained patterns. After that, a collection of representative SEM images were taken at different magnification level (x100k, x200k and x400k) in different location (top, bottom, center, right and left) in order to have an overview about the global surface. This procedure was repeated at least on three wafers from each processing condition presented in this paper to insure the reproducibility of the results and collecting by the way a considerable number of images per step, yielding a reliable statistical analysis study. On the basis of the measured (C and CD) values, we calculated the circularity distribution in the polymeric template for each process condition. As an example, we present in Table 1, the typical statistical analysis results obtained for AZEMBLY™ PME-633 annealed at the optimum process condition.

Table 1
Typical statistical analysis of the pore shape (cylinder diameter (CD) and circularity (C) for AZEMBLY™ PME-633 at 30 nm film thickness annealed at 240 °C.

t (s)	$\mathbf{C}_{(\mathrm{Average})}$	$\mathbf{C}_{(\mathrm{STDEV})}$	$\mathbf{CD}_{(\mathrm{Average})}$ (nm)	$\mathbf{CD}_{(\mathrm{STDEV})}$ (nm)
5	0.52210	0.23576	12.87871	3.42549
10	0.75164	0.09991	12.31959	1.09041
30	0.75388	0.08703	12.31630	0.85287
300	0.81084	0.05929	12.12844	0.86822
600	0.83855	0.04494	11.97520	0.81724

The details of the procedure allowing the determination of the C and CD values starts from the top-down SEM images, where the pores seen on the surface were identified as cylinders in the PS matrix. SEM images analysis software was used to determine the size and the spatial distribution of the pores in the PS matrix. The schematic diagram shown in Fig. 1, illustrate the steps followed in this methodology. Initially the wafers morphologies were captured with the required top-down SEM images, which contain several numbers of pores (~130) with respect to the applied magnification (x400k). In those images, noise smoothing filter was applied. Then, image binarization was obtained using the Otsu's method of thresholding [24,25], allowing the detection of inner edges of the pores. The best fitted circle to these points was defined and the coordinates of the center and the radius were deduced. Finally, the diameter and the circularity of pores were calculated. The Matlab Algorithm used, calculate the hole circularity (C) according to (1):

$$C = \frac{4\Pi a}{p^2} \tag{1}$$

where, a and p are the hole area and the hole circumference respectively. According to this formula, a perfect circle is achieved for C = 1 and lower values of C quantifies mathematically the deviation from the perfect circularity.

3. Results and discussion

3.1. Effect of annealing time

The effect of annealing time on the formation of ordered templates was investigated by heating the wafers at 240 °C for different lengths of time. Fig. 2 shows SEM micrographs obtained for PS-*b*-PMMA film at 30 nm thickness for annealing times of 0, 5, 10, 30, 300 and 600 s. As shown, the developed template remains irregular and the presence of defects within the film was observed during the annealing process. Some of these defects correspond to the presence of cylinders oriented parallel to the substrate. Fig. 2(a) shows the template quality after spin coating. We observed a homogenous film without appearance of any cylinders (parallel or perpendicular orientation). The film is in the disordered phase. Fig. 2(b) shows clearly a large number of defectives cylinders. They appear darker than the matrix containing perpendicular cylinders. This indicates the beginning of the micro-phase separation during the annealing process (Fig. 2(b) to (f)).