

Megasonic-assisted development of nanostructures

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The effect of high frequency (1 MHz) acoustic agitation (megasonic agitation) on development of electron beam exposed poly(methylmethacrylate) (PMMA) nanostructures is investigated. Test patterns consisting of dense holes, isolated lines, and gratings with high aspect ratios have been used. Compared to conventional dip development, the sensitivity of the development process is increased and the homogeneity of nanopatterns is improved considerably. Furthermore, experiments towards ultimate aspect ratios and resolution of PMMA in the range of 2–3 nm with megasonically assisted development have been carried out. The physical mechanisms for the observed enhanced development performance which is particularly attractive for nanostructuring are discussed. © 2006 American Vacuum Society. [DOI: 10.1116/1.2214709]

I. INTRODUCTION

Acoustic agitation during the resist development process of nanostructures offers decisive advantages over conventional dip development, pushing the limits in the minimum linewidth deep into nanoscale.^{1–3} Moreover, it ensures a highly reliable lithography process⁴ and improves the sensitivity and contrast in positive and negative electron beam resists.^{5,6}

As shown in our previous work,⁷ one of the problems associated with ultrasonic agitation is pattern deformation and destruction of fragile nanostructures with high aspect ratios. To overcome this problem, a more gentle treatment with megasonic agitation in the range of 700 kHz–1 MHz has been suggested, in contrast to ultrasonic systems which typically operate at frequencies between 17 and 100 kHz.

During acoustic agitation, fluid friction at the surface of the sample to be developed induces a thin layer of solution moving slower than the bulk solution. Thus, a characteristic viscous boundary layer is formed with a thickness $\delta = \sqrt{2\nu/\omega}$, where ν is the viscosity of the liquid and $\omega = 2\pi f$ is the acoustic frequency.⁸ This layer acts as a diffusion boundary layer, separating the resist surface from the flow of the developer. Therefore, reducing the thickness δ of this layer is essential for effective resist removal, high developer refresh rates, and developer access to nanostructures. At 1 MHz the thickness of the layer is around 0.6 μm , much smaller than in the ultrasonic case (e.g., 40 kHz \approx 3.8 μm). A more effective development process can be expected therefore.

Several physical processes are associated with high frequency acoustic agitation. They can be assigned to two major classes: (i) direct interaction of the sound field with polymer chain fragments forming the resist and (ii) indirect interaction via the mechanism of acoustic microstreaming.⁹

In the case of direct interaction, periodic forces are exerted directly on resist molecules via the oscillating acoustic

field. During the development process, these oscillating forces can assist exposed polymer chain fragments to overcome intermolecular attachment forces¹ to unexposed resist molecules. In narrow nanoscale structures, where the intermolecular forces limit the resolution decisively, this assisted detachment plays an important role.

The indirect interaction of acoustic agitation is based on cavitation-related mechanisms. Microscopic gas bubbles in the liquid undergo stable large amplitude pulsations or volume oscillations, which in turn cause microstreaming of the liquid.¹⁰ In addition, pressure variations in sound waves moving through the medium give rise to microcavitation. The cavity walls can no longer sustain the compressive forces and implode.¹⁰ The collapsing bubble creates a shock wave in the liquid removing loose as well as embedded polymer chain fragments from the surface by cavitation erosion and acoustic streaming. On the other hand, collapsing bubbles exert local pressures of up to a few kilobars,¹⁰ sufficient to damage even metal surfaces. They are the main reason for pattern deformation and destruction of fragile high aspect ratio nanostructures. With increasing sonic frequencies, however, the bubbles become smaller and denser,¹¹ resulting in gentler but more concentrated transmission of energy to the surface. Therefore, megasonic agitation is expected to provide the same advantages over the conventional dip development as the ultrasonic one does, avoiding however, deformation and destruction of fine nanostructures.

In this article, a megasonic-assisted development process of poly(methylmethacrylate) (PMMA) electron beam resist is investigated and characterized. First, the most commonly used PMMA developers, namely, the solutions of methylisobutyl ketone:isopropanol (MIBK:IPA) in composition 1:3 and water:IPA in composition 3:7 are compared under conditions of megasonic agitation. Next, megasonic-assisted development is studied in comparison with conventional dip development with regard to the reliability of the development process and the sensitivity of PMMA. Finally, results

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on the ultimate aspect ratio and resolution of PMMA using megasonic agitation during development are presented.

II. EXPERIMENTAL DETAILS

PMMA with a molecular weight of 950 000 has been chosen in all experiments to achieve a high contrast that determines generally the ultimate resolution of a resist-developer system.¹²

Silicon substrates have been spin coated with PMMA of 950 000 to thicknesses between 50 nm and 3 μm and baked at 170 °C for 16 h prior to exposure.

Electron beam lithography has been performed with a Leica EBPG-5000 TFE system. A pixel size of 5 nm has been used. All exposures have been carried out at 100 kV with a beam current of 120 pA for the resolution tests and of around 1 nA for all other exposures. Estimated spot sizes for these currents have been ~ 5 and ~ 7.5 nm, respectively.¹³ The exposed patterns consist of dense holes, isolated lines, and gratings.

Developments have been carried out with and without megasonic agitation in the same development tool¹⁴ under identical process conditions. The development tool allows automated development of samples of various sizes and geometries. Development parameters such as development temperature, development time, pulse period of the megasonic pulses, and duty cycle of the pulses can be defined prior to the development. After the development a rinse step and nitrogen blow dry step can be included into the process sequence. To generate the megasonic waves, a high frequency excitation voltage is applied to a piezoelectric transducer array, which converts the electrical energy into acoustic energy. For comparison between megasonic-assisted development and development without acoustic agitation the same setup has been used except that the megasonic power has been turned off.

Substrates have been maintained in a fixed position relative to transducer array. The megasonic agitation at 1 MHz has been applied perpendicular to the substrate with the piezoelectric transducers. Its power has been varied between 10 and 100 W providing a power density of up to 5 W/cm². The temperature of the developer has been kept constant at 7 °C for the resolution tests and 20 °C in all other cases. After development, the samples have been blow dried with nitrogen.

To compare MIBK:IPA 1:3 and water:IPA 3:7 solutions as PMMA developers, contrast curves have been generated using $100 \times 100 \mu\text{m}^2$ field exposures. The residual resist thicknesses after development in the respective solution have been determined with a Philips ellipsometer type PZ2000 at a wavelength of 633 nm.

Observations on all samples have been carried out with a high resolution Leo DSM 982 Gemini scanning electron microscope (SEM). Micrographs have been taken with low voltage (500 V) and short acquisition times to avoid resist deformation.

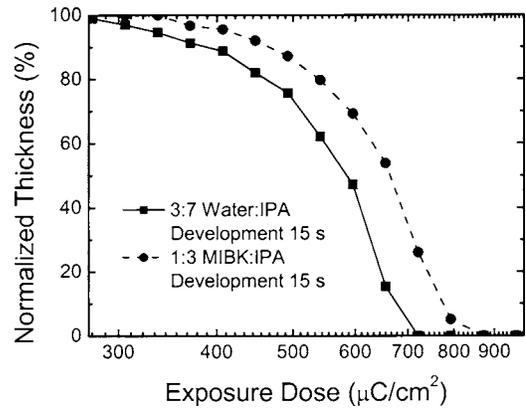


FIG. 1. Contrast curves of megasonically assisted development of 1 μm thick PMMA resist for 15 s at 20 °C with MIBK:IPA 1:3 and water:IPA 3:7 solutions.

III. RESULTS AND DISCUSSION

This section is subdivided into four parts. First, the solutions of MIBK:IPA 1:3 and water:IPA 3:7 are compared as PMMA developers under the conditions of megasonic agitation. Second, investigations on areas of high aspect ratio dense nanoholes are presented. Third, measurements on high aspect ratio lines are shown. Finally, the results of high aspect ratio and ultimate resolution tests are discussed.

A. Comparison of PMMA developers using megasonic agitation

In Fig. 1, contrast curves of megasonic-assisted development of 1 μm thick PMMA resist for 15 s at 20 °C in MIBK:IPA 1:3 and water:IPA 3:7 developer solutions are compared. The process with water:IPA 3:7 shows clear advantages over that with MIBK:IPA 1:3. The values of sensitivity and contrast derived from Fig. 1 in the case of MIBK:IPA 1:3 are 810 $\mu\text{C}/\text{cm}^2$ and 6.2, respectively, whereas in the case of water:IPA 3:7 they are 690 $\mu\text{C}/\text{cm}^2$ and 7.6, respectively. This yields a significant improvement of about 20% in both characteristics. Thus, the better performance of the solution water:IPA as PMMA developer, reported earlier^{3,15} for the cases of conventional dip development and ultrasonically assisted development, has been confirmed also for megasonic agitation during development. Therefore, the solution of water:IPA 3:7 has been chosen as PMMA developer in all further experiments.

B. High aspect ratio dense nanoholes

In Fig. 2, cross sections of high aspect ratio dense nanoholes exposed in 1 μm thick PMMA resist and developed for 15 s at 20 °C in 3:7 water:IPA without (a) and with (b) megasonic agitation are compared. In both cases, areas of nanoholes have been exposed with identical e-beam doses of $D=63.4 \text{ mC}/\text{cm}^2$. For better illustration, the exposure dose has been chosen so that the features' sidewalls open up into the nanostructures behind, where the designed distance between the holes is only the half of that in the cross-section plane. In this way, a higher contrast between developed and

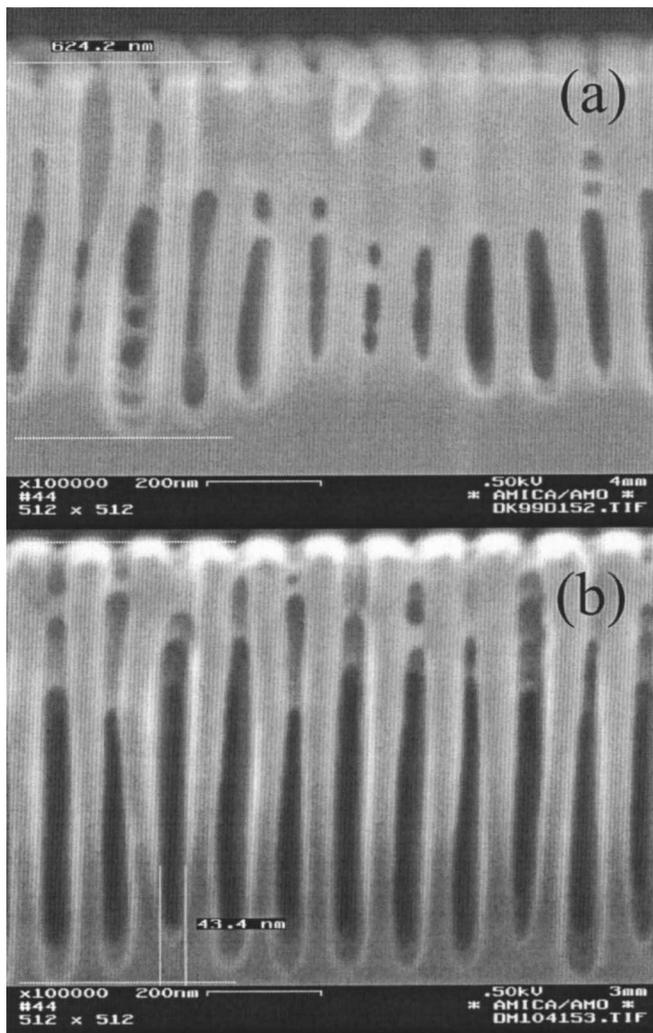


FIG. 2. SEM cross section of a nanohole pattern developed for 15 s at 20 °C without megasonic assistance (a) and with megasonic assistance (b). Exposure dose: 63.4 mC/cm².

undeveloped regions in the SEM images is achieved. Despite some slight deterioration of the samples induced by SEM preparation, it is clearly demonstrated that megasonic agitation results in deeper profiles. Aspect ratios as high as 17 have been achieved in this case. In addition, higher quality and homogeneity of the developed structures have been obtained. Particularly, the uniformity of the depth of the holes has been improved. Furthermore, the larger maximum depth achieved with megasonic development indicates that the sensitivity is increased by acoustic agitation.

A quantitative analysis of similar patterns, exposed identically and developed for a number of different times, is presented in Fig. 3, where the average development velocities with and without megasonic agitation for patterns as in Fig. 2 are plotted as a function of developed depth. The values shown in this figure have been generated by varying the development time from 5 to 45 s, by measuring the resulting developed depths by means of SEM, and by dividing the depths by the respective development times. They represent therefore the average velocities of the development process

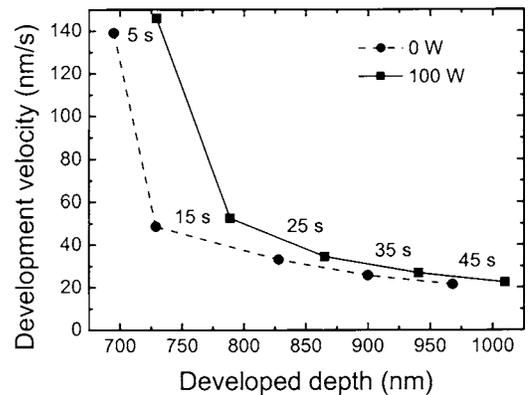


FIG. 3. Average development velocity at 20 °C as a function of developed depth for conventional dip development (0 W) and megasonic-assisted development (100 W). Exposure dose: 74 mC/cm².

from its start to its end. In both cases more than 2/3 of the total resist thickness has been developed during the first 5 s. After this time, the development process is slowed down rapidly and only about 1/3 of the total resist thickness is developed in the remaining 40 s.

These results suggest that two phases of the development process of high aspect ratio nanostructures can be distinguished. Down to a certain critical depth (about 700–750 nm in our case), the development rate remains fairly constant on the level pertinent to the development of large structures without space boundary limitations (not shown in Fig. 3). Here, the development process is governed by the disentanglement of the polymer molecules. The duration of this first phase is less than 5 s and since there is no way to obtain reliable data for such short development times with our tool, the accurate pinpoint of the time and depth where the transition between the two phases occurs is not possible.

In the second phase (presented in Fig. 3), i.e., for higher depths, the development velocity decreases almost exponentially reaching a certain saturation level much lower than that in the first phase. Here, the space boundary conditions in the deep nanoholes start playing an important role and development is mainly limited by developer transport and removal of resist fragments. As a result, the duration of the second phase is significantly greater and the development of the last 250–300 nm of the resist takes, in our case, more than 40 s. Therefore, the second phase dominates the total development time.

The results presented in Fig. 3 demonstrate that at least two effects are achieved with the application of the megasonic agitation: (i) the transition between the two phases is shifted to greater depths and (ii) the development velocity in the second phase is increased. As a consequence, the total development time of certain structures is reduced and parasitic resist swelling, known to limit the resolution and to cause pattern distortion,¹⁶ is suppressed.

C. High aspect ratio lines

Contrast curves obtained from structures with large feature sizes are generally employed to determine the resist dis-

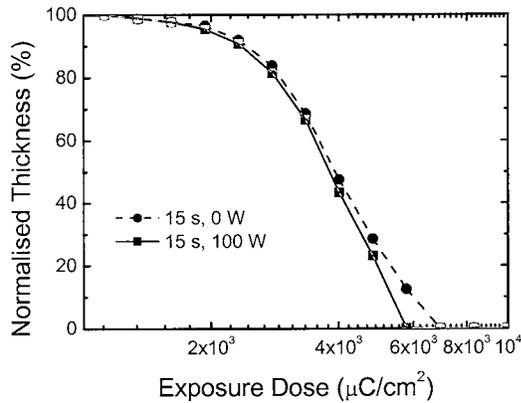


FIG. 4. Normalized residual resist thickness of line structures vs e-beam exposure dose for conventional dip development (0 W) and megasonic-assisted development (100 W). Development time: 15 s at 20 °C.

solution characteristics as a function of exposure dose. These contrast curves are, however, not applicable to small feature sizes or structures with high aspect ratio, because other physical mechanisms, such as intermolecular forces, reduced rates of developer refreshment, and transportation of dissolved resist fragments, gain increasing influence. In this subsection therefore only structure dependent contrast or sensitivity values are considered. Instead of the commonly used square pads, the pattern of interest has been exposed with the proper dose variation and the residual resist thickness at every dose value has been measured by means of SEM on the actual structures to be studied.

In the next step, the contrast curves obtained with and without megasonic agitation are compared. In Fig. 4 the normalized residual resist thickness versus e-beam exposure dose is plotted. A test pattern of narrow lines with a linewidth of around 40 nm and a pitch of 2 μm has been exposed in 1 μm thick PMMA resist and subsequently developed for 15 s in 3:7 water/IPA at 20 °C either with or without megasonic agitation.

While the clearing dose, i.e., the minimum dose required for complete development, for conventionally developed samples is around 6.9 mC/cm^2 , an exposure dose of only 5.8 mC/cm^2 is needed to fully develop the lines with acoustic agitation. This corresponds to an improvement in sensitivity of nearly 20%, attributed to the extra energy provided by the megasonic agitation. The increased sensitivity leads again, as in the case of dense nanoholes, to shorter development times with the advantages discussed above.

Similar measurements have been performed on structures with various feature sizes to detect possible dependencies of the improvements caused by the acoustic agitation over the conventional dip development on linewidth. The samples have been processed in the same way as the ones used for generating Fig. 4. For every feature size, the highest increase in development depth at a certain exposure dose has been determined and summarized in Fig. 5, where the maximum measured percentage increase in developed resist depth of megasonic-assisted development, compared to conventional dip development, is plotted as a function of the linewidth.

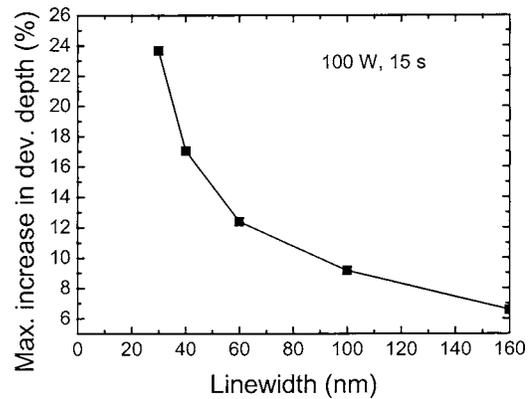


FIG. 5. Maximum percentage increase in the developed depth of lines developed with megasonic agitation vs conventionally developed lines as a function of linewidth.

Resist depths after exposure and development have been measured again on cleaved samples by means of SEM. A significant increase of the percentage improvement in developed depth with decreasing feature size has been found (see Fig. 5). These results demonstrate that high frequency acoustic agitation is especially effective for structures with small feature sizes. For linewidths of 30 nm the maximum improvement in developed depth is nearly 24%.

D. High aspect ratio and ultimate resolution tests

For many years PMMA has remained the positive resist of choice for ultrahigh resolution electron beam lithography. Therefore, it is worth estimating the limits of this resist in respect to antireflection (AR) and resolution with the improved megasonically assisted development process. Standard metrics for the resolution of patterning processes are linewidths and grating periods. Some examples demonstrating the ultimate AR and resolution achieved in this work are presented here.

In Fig. 6, a micrograph of a high aspect ratio isolated trench in 2 μm thick PMMA exposed to an e-beam dose of $D=11.98$ mC/cm^2 is shown. The sample has been developed for 50 s with megasonic agitation. The developer temperature has been kept at 7 °C to increase the contrast¹⁷ and consequently the resolution. The calculated aspect ratio of the structure in Fig. 6, defined as the ratio of developed resist thickness to the maximum width of the exposed line, is higher than 20, demonstrating that high frequency acoustic agitation clearly leads to extremely high aspect ratios. The results presented in Fig. 6 stimulate the interest to explore the resolution limits in this work.

In Fig. 7, a SEM image of a grating with a period of 30 nm and linewidths below 5 nm is shown. The grating has been exposed in 50 nm PMMA and developed for 15 s at 7 °C in 3:7 water/IPA with megasonic agitation. After development, it has been coated with a thin layer of evaporated Cr to avoid resist deformation and sample charging during microscopy. These results demonstrate that even at such extremely small linewidths, aspect ratios above ten can be achieved with megasonically assisted development.

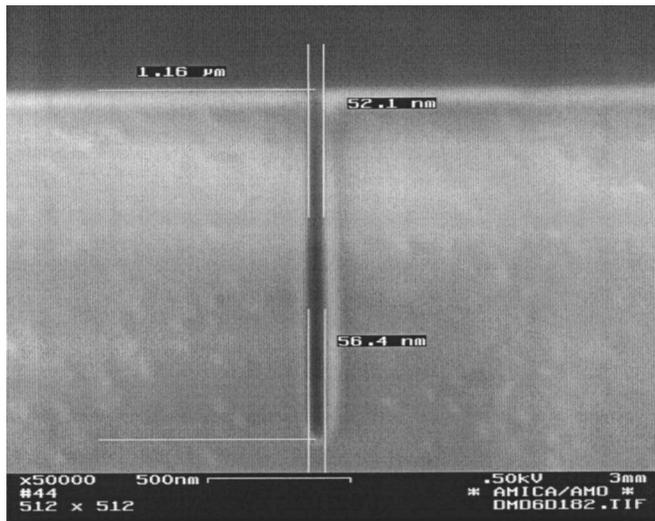


FIG. 6. SEM cross section of a high aspect ratio line developed for 50 s at 7 °C with megasonic assistance. Exposure dose: 11.98 mC/cm².

Figure 8 presents an array of dense nanoholes in PMMA with diameters of around 6 nm and a pitch of 20 nm. The resist thickness and the development process are the same as for the grating in Fig. 7.

The grating structure and the dense holes shown in Figs. 7 and 8 represent features on the verge of ultimate resolution using conventional electron beam exposure of PMMA. In addition to the small spot size of the low current (120 pA) finely tuned electron beam and the low developer temperature, the megasonic agitation during development has been demonstrated as decisive for achieving these outstanding results.

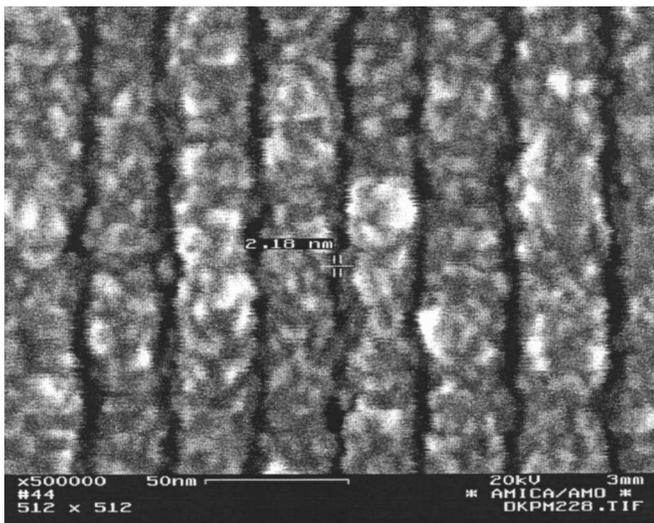


FIG. 7. SEM micrograph of a grating with a pitch below 30 nm and line-width down to 2–3 nm in 50 nm PMMA resist. The sample has been coated with a thin layer of Cr to avoid static.

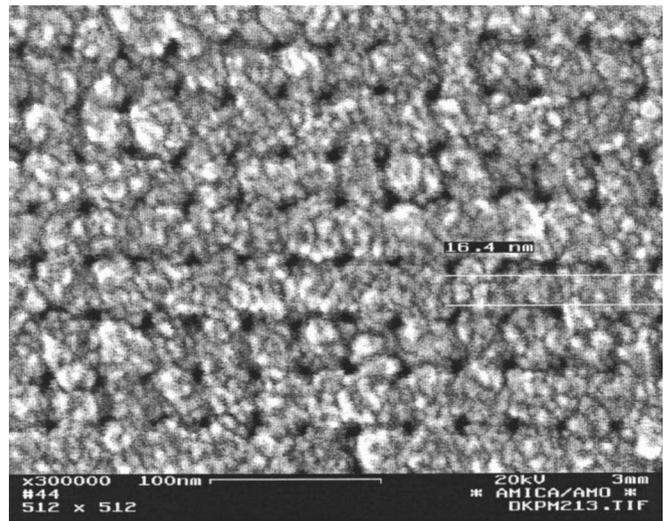


FIG. 8. SEM micrograph of an area of nanoholes with a pitch of 20 nm and diameter of ~6 nm in 50 nm PMMA. The sample has been coated with a thin layer of Cr to avoid static.

IV. CONCLUSIONS

Megasonic-assisted development of nanostructures has been investigated in this work. Two PMMA developers, MIBK:IPA 1:3 and water:IPA 3:7, have been compared using high frequency (1 MHz) acoustic agitation and the superior performance of the latter has been confirmed. Furthermore, megasonic agitation has been demonstrated to enhance the development characteristics in high aspect ratio and narrow nanostructures. In particular, it has been shown that megasonic-assisted development of PMMA has distinguishing advantages over conventional dip development, because the development rate of high aspect ratio nanoholes and nanolines is improved, reducing the development time decisively. The reasons for these improvements are believed to be boundary layer minimization, acoustic microstreaming, and direct interaction of the sound field with the polymer chain fragments leading to lower viscosity of the polymer/solvent mixture and reduced intermolecular forces within the structures. Finally, megasonic agitation helps to reduce the minimum obtainable grating periodicity in PMMA to below 30 nm and feature sizes to below 5 nm.

ACKNOWLEDGMENT

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