Megasonic-assisted development of nanostructures: Investigations on high aspect ratio nanoholes

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The influence of megasonic agitation on the development of nanostructures with high aspect ratio is investigated thoroughly. The improvements in homogeneity, depth, and quality of nanostructures are related to specific interactions of the sound wave with the resist and developer. Two phases in the development process are operative. The specific role of microstreaming providing physical supply of fresh developer is identified and the reduction of viscosity by megasonic interaction is derived. The advantage of megasonic agitation as a nondestructive development of high aspect ratio nanostructures is demonstrated. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1819986]

Ultrasonically assisted development of nanostructures has been reported to overcome limitations in the minimum linewidth.[1–3] Moreover, it ensures a highly reliable lithography process[4] and improves the sensitivity and contrast in positive and negative electron beam resists.[5,6] There is, however, a major problem with ultrasonically assisted development. The patterns deform and especially fragile nanostructures are destroyed. To overcome this problem, a more gentle treatment with megasonic agitation (~1 MHz) is proposed in this letter.

Principally, the development of a resist is limited by the reactions at the interface resist-developer and by the transportation of the polymer fragments dissolved.

Polymer dissolution occurs in two main steps. During the initial stage, the solid polymer starts swelling due to developer influx and simultaneously transforms into a gel-like phase. As the chains disentangle, they move out of the gel-like phase to the liquid solution. The net rate of movement of this gel–liquid interface, l, can be described as[7]

$$\frac{dl}{dt} = D_m \left.\frac{\partial \phi_s}{\partial x}\right|_{x=l} - k_d. \tag{1}$$

The first term on the right-hand side presents the developer ingress leading to swelling. The second term describes the subsequent chain disentanglement with the rate k_d of the polymer chains from the gel–liquid interface. ϕ_s represents the developer volume fraction at the interface and D_m is the coefficient of the mutual diffusion of the polymer and the solvent. The disentanglement rate and with it the development process for high aspect ratio nanostructures falls into two sections. The first one is the phase of the *quasi-instantaneous* dissolution. In this phase the disentanglement rate k_d remains fairly constant on high level, since effective fresh developer is supplied in sufficient amount at the gel–liquid interface. This phase of high development velocity is therefore limited by the diffusion rate of the developer into the polymer and the disentanglement rate k_d. As developed depth increases, boundary conditions change and the supply of fresh developer is reduced. Therefore, the disentanglement rate k_d drops exponentially to a certain saturation level in nanostructures with high aspect ratio.

Since the disentanglement rate k_d is inversely related to the reptation time,[8] direct interaction of the sound field with the polymer leading to a reduction of the reptation time should increase the disentanglement rate. An even more distinct enhancement by acoustic agitation is expected in the second phase. In this phase, the development is slowed down significantly in high aspect ratio nanostructures. The main reason is the less effective developer at the gel–solvent interface after critical development time and depth. This reduced developer efficiency is caused by limitations in the transport of dissolved polymer fragments. Here, acoustic agitation enables better refreshment of the developer, leading to enhanced development characteristics.

The physical processes associated with high frequency acoustic agitation are based on two major principle classes: (i) the direct interaction of the sound field with resist particles and (ii) the indirect action via the mechanism of acoustic microstreaming.[9] In the former, periodic forces are directly exerted on resist molecules via the oscillating acoustic field. During development, these oscillating forces might help the particles to overcome the attractive attachment forces and to free them more easily. Intermolecular forces limit the resolution especially in narrow features, since these forces may prevent exposed molecules that are attached to unexposed resist particles from being dissolved into the developer solution.[1]

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The indirect action of acoustic agitation is based on cavitation-related mechanisms. The most important indirect phenomenon with regard to this study is the acoustic microstreaming. Microscopic gas bubbles in the liquid undergo stable large amplitude pulsations, which in turn cause movements of the liquid.[10] When acoustic agitation is applied to a developer liquid, a characteristic viscous boundary layer is formed. The thickness of this boundary layer δ is estimated as $\delta=\sqrt{(2\nu/\omega)}$, where ν is the viscosity of the liquid and $\omega=2\pi f$ the acoustic frequency. The fluid friction at the surface of the sample to be developed causes a thin layer of solution to move more slowly than the bulk solution, thus shielding the resist surface from the flow of the bulk solution. The thinner this boundary layer is the more effective the resist particle removal, the higher the developer refresh rates, and the more fresh developer accesses the nanostructures. At 1 MHz the thickness δ is around 0.6 μm, much smaller than in the ultrasonic case (40 kHz, $\approx$3.8 μm).

In this letter we report on a careful comparison of nanostructures developed with and without megasonic agitation. The specific advantages of megasonic-assisted development are addressed and supported by a series of dedicated experiments.

In our experiments, electron beam lithography has been performed at 100 keV with a Leica EBPG-5000 system. Silicon substrates have been spin coated with a thick (up to 1.2 μm) poly(methylmethacrylate) (PMMA) layer of 950k molecular weight. PMMA-950k has been taken to achieve a high contrast, which generally determines the ultimate resolution of a resist-developer system.[11] The exposed pattern is a field of dense holes. The holes have diameters down to 30 nm. Developments have been carried out with and without megasonic agitation in the same development tool[12] using a composition of 7:3 isopropanol:water (IPA:H_2O) at a constant temperature of 20 °C. The megasonic agitation (1 MHz) generated by piezoelectric transducers has been applied perpendicular to the substrate with a power density of up to 5 W/cm^2.

In Fig. 1 cross sections of high aspect ratio nanoholes developed for 15 s with conventional dip development (a) or megasonic agitation (b) are compared. In both cases the same e-beam dose of 63.4 mC/cm^2 is applied. For better illustration, it is chosen so that the features sidewalls open up into the nanostructures behind, where the designed distance between the holes is only half of that in the cross-section plane. In this way, higher contrast between the developed and undeveloped regions on the scanning electron microscope (SEM) images is achieved. It is clearly demonstrated that megasonic agitation results in deeper profiles. In addition, a higher quality and homogeneity of the developed high aspect ratio structures are achieved. Particularly, the uniformity in the depth of the holes is improved. The maximum depth achieved indicates that the sensitivity is increased by acoustic agitation.

In Fig. 2, the thickness of the resist remaining after development of the nanoholes is plotted as a function of the exposure dose. The samples have been developed either with or without megasonic agitation for a constant time of 5 s. The developed resist depth is determined with SEM (see Fig. 1). The plot shows the average of multiple measurements on different samples for better statistics. It becomes apparent that during the initial phase, k_d remains nearly constant due to unlimited developer exchange. There is no remarkable impact of acoustic agitation. With increasing depth a pronounced megasonic effect becomes operative. The splitting of the two curves in Fig. 2 indicates that agitation leads to a lower decrease of the disentanglement rate in high depths. A reduction of the clearing dose by 10% through megasonic agitation can be observed.

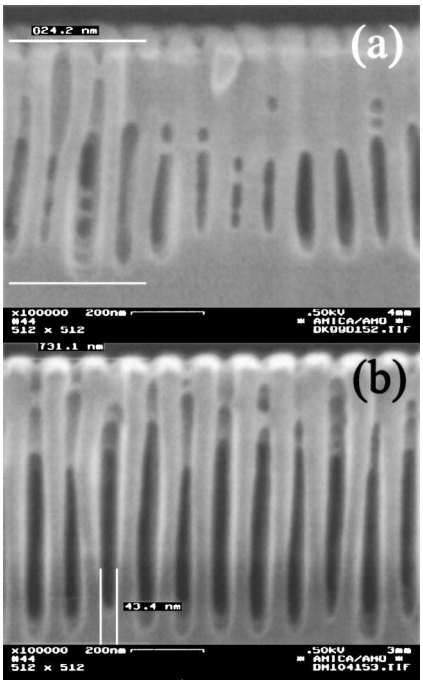

FIG. 1. SEM cross section of a nanohole pattern developed for 15 s without megasonic assistance (a) and with megasonic assistance (b).

As a consequence of this increase in sensitivity, the development time of certain structures is reduced leading to lower resist swelling. Swelling is known not only to limit the resolution but also to cause pattern distortion.[13] Shorter development times are therefore essential for reliable process control on the nanoscale.

In Fig. 3 the depth of the developed nanoholes is plotted versus development time, again for the case with and without acoustic agitation (keeping all other exposure and development parameters, including developer temperature, constant). The exposure dose was 74 mC/cm^2. The depth of the nanoholes for different development times is again determined by SEM analysis. The data in Fig. 3 are average values of different samples with error bars for minimum/maximum val-

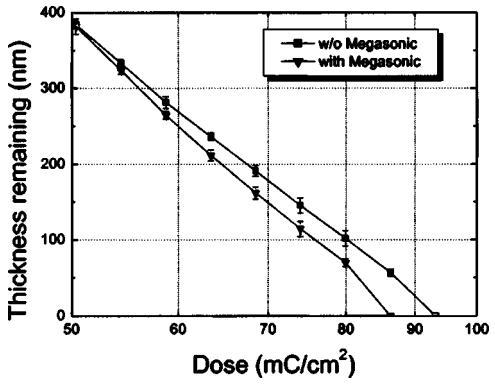

FIG. 2. Dependencies of the remaining PMMA resist thickness on the exposure dose for development with and without megasonic assistance for 5 s. Initial resist thickness ~900 nm.

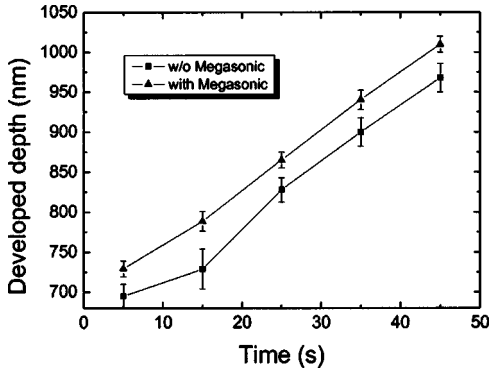

FIG. 3. Developed depth as a function of development time for conventional dip development (w/o megasonic) and megasonic-assisted development.

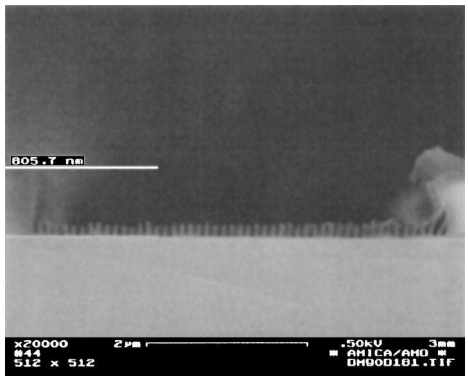

FIG. 4. SEM cross section of a nanohole pattern developed for 15 s with ultrasonic agitation.

ues. Figure 3 confirms conclusively that the development process is governed by two regimes. Within the first 5 s already more than 2/3 of the resist (>700 nm) are developed. This first phase (<5 s) is characterized by a high and nearly constant disentanglement rate k_d. These results are in good agreement with PMMA development rate data obtained by Raptis *et al.*[14] in a case without space boundary limitations. However, since there is no way to obtain reliable data for development times below 5 s with our tool, accurately pinpointing the time and depth/aspect ratio where the transition from fast initial to slow final process occurs is not possible. In the second phase, i.e., in higher depths, the development proceeds at a much lower rate, mainly limited by developer transport. In this phase, a new equilibrium between the supply of fresh developer and the removal of dissolved resist particles is established. The development rate remains fairly constant for the time range studied and the development process proceeds almost linearly with time. These results are in a good agreement with the linear solutions of the transport equation in the time–position plane.

In Fig. 3 it becomes apparent that megasonic agitation increases the development velocity compared to conventional dip development. The deeper the structures the longer the times required for developments. In deep structures particularly, the developer refreshment is limited. The slope in Fig. 3 confirms that the development in our case is transport and reaction limited in both cases. In conventional dip development as well as in megasonically assisted development, the concentration of the polymer dissolved in the developer close to the exposed regions of the sample increases with time. High polymer concentration increases viscosity that is related to entanglement effects between the polymer molecules.[15] The increased viscosity prevents the polymer from being removed from the surface of the resist and, therefore, slows down the development process. The viscosity in the developer/polymer mixture appears to be reduced by acoustic agitation, due to a lower interaction of resist molecules in the solution. In addition, microstreaming provides fresh developer at the surface of the developing structures more effectively. Another important megasonic contribution is the weakening of intermolecular forces between exposed PMMA molecules and unexposed resist molecules[1] due to direct interaction of the sound field with the particles. In particular, narrow nanostructures are therefore developed faster.

Finally, one of the most important advantages of megasonic compared to ultrasonic-assisted processing is demonstrated. Attempts to develop structures, processed identically as those in Fig. 1, by ultrasonic agitation (38 kHz) end in their heavy destruction (see Fig. 4). Obviously, excessive cavitation damage prohibits the development of fragile nanostructures with ultrasonic assistance. The higher frequencies associated with megasonic agitation sufficiently eliminate cavitation damage of nanostructures.

In conclusion, two phases of the development process of high aspect ratio nanostructures are identified. Down to a critical depth, the disentanglement rate k_d remains fairly constant, whereas afterwards it decreases exponentially to a certain saturation level. The influence of high frequency acoustic agitation (1 MHz) on the disentanglement rate within the two regimes is investigated. In comparison with conventional dip development, acoustic agitation is shown to slightly increase the disentanglement in the first phase and significantly in the second phase. As a consequence, faster resist development of high aspect ratio nanoholes is obtained and a higher developing homogeneity is achieved without the destructive influence of ultrasonic agitation.

In this way, megasonically assisted development offers distinguishing advantages over conventional dip development and over ultrasonic-assisted development.

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