

## Fractal Roughness of Polymers after Lithographic Processing

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The morphology of photoresist polymer surfaces fabricated by lithographic processes is shown to exhibit self-affine behavior for a specific range of scales. The roughness parameters appropriate for the characterization of self-affine surfaces (surface width  $w$ , correlation length  $\xi$  and roughness exponent  $\alpha$ ) are found to depend on the exposure dose (i.e. the solubility) involved in the lithography process and to be correlated. A similar dependence and correlation is extracted from a Monte-Carlo simulation of polymer dissolution, thus indicating the pronounced contribution of the dissolution process to the formation of lithographic roughness. The self-affinity and the correlated behavior of the roughness parameters is a general phenomenon for dissolving polymers of varying solubility and not limited to the lithographic process.

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The continuing success of microelectronics industry in miniaturizing further the circuit elements and devices is largely due to recent advances in lithography. Advanced lithography nowadays achieves the fabrication of nano-features with 30–100 nm dimensions using polymeric-based photoresist materials. At these dimensions the nanometer-scale top and sidewall surface roughness of the fabricated features cannot be ignored, since it can affect their critical dimension and undermine the reliability of the devices. In order to overcome this problem and reduce the roughness of the lithographic surfaces, a lot of effort has been recently devoted to the pinpointing the parameters and process conditions, which cause the formation of roughness.<sup>1)</sup> The motivation of this work is to investigate the kind of lithographic roughness and the collective behavior of the whole set of appropriate roughness parameters (see below), which have attracted much less interest up to now. In addition the systematic study of dissolving polymeric surfaces with different solubility may be of interest in itself.

Surface roughness induced by various surface processes can be classified as one of the following kinds: a) either self-affine fractal scaling roughness characterized by scale invariance under direction dependent length-scale transformations or b) a mound roughness consisting of regular mound structures having a wavelength selection.<sup>2)</sup> The identification of the kind of roughness of a surface is of great importance first for the description of roughness. For self-affine surfaces the best roughness descriptors comprise a three parameters set  $(w, \alpha, \xi)$ , where  $w$  is the surface width (rms roughness, also referred to as  $\sigma$ ),  $\alpha$  the roughness (or Hurst) exponent and  $\xi$  the correlation length, while for mound roughness the mean wavelength of surface morphology has to be included in place of roughness exponent  $\alpha$  which usually tends to 1. Moreover, the kind of roughness of a surface is usually associated with the surface growth processes and, therefore, its specification can reveal the mechanisms responsible for roughness formation. For example, in vapor deposited films, the mound roughness is associated with the existence of an asymmetric step-edge

diffusion barrier (Schwoebel barrier) inhibiting the downhill diffusion of incoming atoms or to shadowing effects when a distribution of the deposition angles is taken into account. No such effects are present in the formation of self-affine surfaces. The development of the latter in both space and time domains has been investigated extensively so that the corresponding scaling exponents are determined and the classification of the surface growth processes in a few universality classes is achieved. However, the vast majority of investigated surfaces have been fabricated through vapor deposition processes, ion bombardment, sputtering, molecular beam epitaxy or plasma etching. Lithography is, in fact, a more complex process and the challenge for this work is to specify and understand the kind of polymer surface roughness that causes as well as the collective dependence of the whole set of roughness parameters on some process conditions. The main findings of the paper can be enumerated as follows: a) the examined polymer surfaces after lithographic processing exhibit self-affine roughness in accordance with previous investigations, ii) the roughness parameters  $(w, \alpha, \xi)$  show a similar behavior when examined versus the exposure dose involved in the lithographic process (the exposure dose is directly related to the solubility of the polymers in aqueous base) and iii) a Monte-Carlo simulation based on the Critical Ionization Model (CIM) for the dissolution step of the lithographic process<sup>3)</sup> is capable of explaining the above roughness behavior.

The lithographic process is, in fact, based on radiation-induced changes in the dissolution rate of thin photoresist films formulated from organic polymers. First, the resist film is spun on a wafer and then exposed to light, electron beam, or other radiation, through a mask containing the pattern appropriate for that particular level of device fabrication. If the photoresist is positive (negative), exposed areas are rendered soluble (insoluble) during the dissolution in a solvent. Thus the mask pattern is transferred on the resist film, which then becomes a stencil protecting the underlying film from attack by the etching process which follows. After etching is complete, the resist film is stripped off by ashing in a second plasma and at the end the initial mask pattern remains printed on the substrate film. It is obvious that the

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main contribution to the roughness of the final printed features- stems from the roughness of resist polymer surfaces, and this is why the understanding of the formation of resist polymer roughness has gained so much interest.

In the following, we present the results from the analysis of the surfaces of a chemically-amplified acrylate-based positive tone photoresist, which has been synthesized at our institute, in order to have control over the composition.<sup>4)</sup> Its composition is typical of 193 nm photoresists, and its imaging is based on the deprotection of tert(butyl methacrylate) units to methacrylic acid upon exposure and bake (the deprotection being catalyzed by photogenerated acid). The protected units are insoluble to aqueous base, while after deprotection they become very soluble. The initial thickness of the resist was 370–390 nm and the concentration of the photoacid generator (PAG) compound was 3% per weight. Both before and after exposure, the resist was baked at 120 °C for 2 min. The resist was exposed to broadband UV radiation for various times (various exposure doses), and post exposure baked. Thus, each dose corresponds to different extent of deprotection and hence different solubility in aqueous base. The resist was partially developed (i.e. the exposure areas were not totally removed) for 15 sec in an aqueous solution of diluted developer (0.013N Tetra Methyl Amonium Hydroxide solution). We examined the topography of the surfaces for various exposure times i.e. different lithographic doses with a Topometrix TMX 2000 Atomic Force Microscope (AFM) microscope in the contact mode and constant force. The scan size of the samples examined was  $2.5 \times 2.5 \mu\text{m}^2$  and the grid lines 300. The measured heights  $z(r)$  of each surface were used for the calculation of the height-height correlation function defined by

$$G(r) = \langle [z(\mathbf{r}_o + \mathbf{r}) - z(\mathbf{r}_o)]^2 \rangle^{1/2} \quad (1)$$

where the inner  $\langle \dots \rangle$  denotes spatial (over  $\mathbf{r}_o$ ) average and the outer  $\langle \dots \rangle$  circular averaging over all  $\mathbf{r}$  with  $|\mathbf{r}| = r$ . From the form of  $G(r)$ , one can extract conclusions about the type of roughness of the surface.<sup>2)</sup> For self-affine surfaces, the behavior of  $G(r)$  is given by

$$G(r) = \begin{cases} r^\alpha, & r < \xi \\ \sqrt{2}w, & r > \xi \end{cases} \quad (2)$$

Figures 1a,b show representative profiles of the Atomic Force Microscope (AFM) resist surfaces and the average height-height correlation functions for three exposure doses. The power law behavior exhibited by these functions for a specific range of scales  $r$  can be clearly distinguished. As explained above, the power law is a hallmark of self-affine surface roughness. By the slope of the linear part (in log-log plot), one can estimate the roughness exponent  $\alpha$ , whereas the correlation length  $\xi$  can be considered as the abscissa of the section of the linear fit of the power law part of  $G(r)$  and its saturated value  $G(r \gg \xi) = \sqrt{2}w$ . The final surface width  $w$  can be estimated from the saturated value of  $G(r)$  or by its definition  $w = \langle [z(r) - \langle z(r) \rangle]^2 \rangle^{1/2}$ . The dependence of these parameters on the exposure dose is shown in Fig. 1(c). Because of the partial development of the resist, one can observe an initial increase peaking to a maximum value and a subsequent decrease of the surface width  $w$  as the exposure dose increases. The same behavior is exhibited by both the roughness exponent  $\alpha$  and the correlation length  $\xi$ .

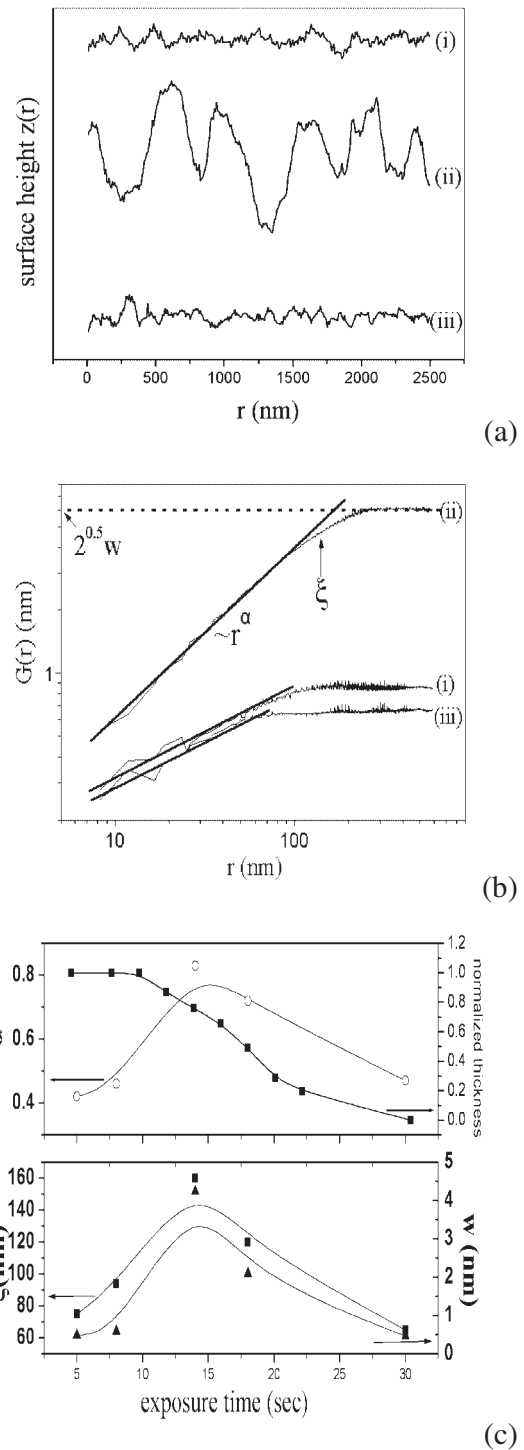


Fig. 1. a) Profiles of the Atomic Force Microscope (AFM) resist surfaces for low (i), intermediate (ii) and high (iii) exposure doses, b) the corresponding average height-height correlation functions  $G(r)$  and c) the roughness parameters ( $w, \xi, \alpha$ ) vs exposure dose as well as the normalized remaining thickness of the resist after dissolution.

The effect of the exposure dose on surface width of a positive tone resist has also been investigated by other researchers<sup>5-8)</sup> who proposed various models for explanation of the experimental data. Very little has been said, however, on the self-affinity of lithographic surfaces, and the remaining two parameters, namely  $\xi$  and  $\alpha$ : He and Cerrina<sup>5)</sup> comment on the fractality of roughness and show limited data for the variation of fractal dimension  $D$  (related to roughness exponent,  $D = 3 - \alpha$ )<sup>2)</sup> with dose, while Yama-

guchi *et al.*<sup>8)</sup> present data on a long scale correlation length for a limited range of doses. Our group has also presented the fractality, and the dependence of surface width and fractal dimension versus dose for negative tone photoresists.<sup>9)</sup> Here, we show that the CIM model is capable of interpreting the experimentally observed self-affinity of the lithographic surfaces and the correlated behaviour of the roughness parameters.

CIM emphasizes on the ionization of the acidic groups of the resist by the hydroxide of the developer and it proposes that a critical fraction of the repeating units on each polymer chain must be ionized for dissolution of the chain to occur.

Our simulation uses a 2-D grid for the polymer matrix on which polymer chains are inserted through self-avoiding walks with necessary sharing, providing thus the minimum entanglement between chains. The polymerization length is chosen constant and quite small (10 monomers per chain) to facilitate the calculations and since it is quite smaller than that of real polymer smaller correlation lengths are expected too. A fraction  $f_v = 10\%$  of the grid cells is keeping void (without monomers) while the size of the grid cell is considered 1 nm. The polymer chains are, in fact, made of blocked (protected and insoluble) and unblocked (deprotected and soluble if ionized) monomers. The exposure dose with the post-exposure bake is represented in the simulation through the fraction of unblocked monomers  $1 - f_b$ .

At each step of the dissolution process, the unblocked monomers in contact with the solvent are ionized and the polymer chains with ionized monomers larger than a critical fraction (0.5 in our simulation) are dissolved and taken out of the polymer film.

To be in accord with the partial development in experiments, we stop the simulation procedure (i.e. the dissolution process) after a time period defined as the time at which the resist loss becomes the 80% of the initial resist thickness in case all the monomers are unblocked. The dimensions of the polymer matrix are accordingly chosen to be  $300 \times 1024$  (thickness  $\times$  width). The output of the simulation is the profile of the interface between the resist and the developer solution after the dissolution time has elapsed. The roughness of this profile is analysed through the calculation of the height-height correlation function  $G(r)$ . Figures 2(a), 2(b) show respectively representative profiles and the average  $G(r)$  over many runs of the simulator (more than 50) for three exposure doses. The power law behaviour for small  $r$  clearly demonstrates the fractal self-affine character of the surfaces. Through these functions the values of the roughness parameters can be estimated and their dependence on the  $1 - f_b$  is depicted in Fig. 2(c). The qualitative similarity with the experimental results of Fig. 1(c) is apparent. However, you can notice that the simulation indeed predicts clearly smaller correlation lengths in accordance with the aforementioned expectations.

The correlated dependence of the roughness parameters on the exposure dose we observe and predict can be appreciated as follows. At low exposure doses (few unblocked monomers) the developer cannot penetrate into the bulk polymer and thus, removes chains from the neighbourhood of the randomly distributed unblocked monomers located uncorrelated on the surface. The resulting surface has no important vertical roughness (small  $w$ ),

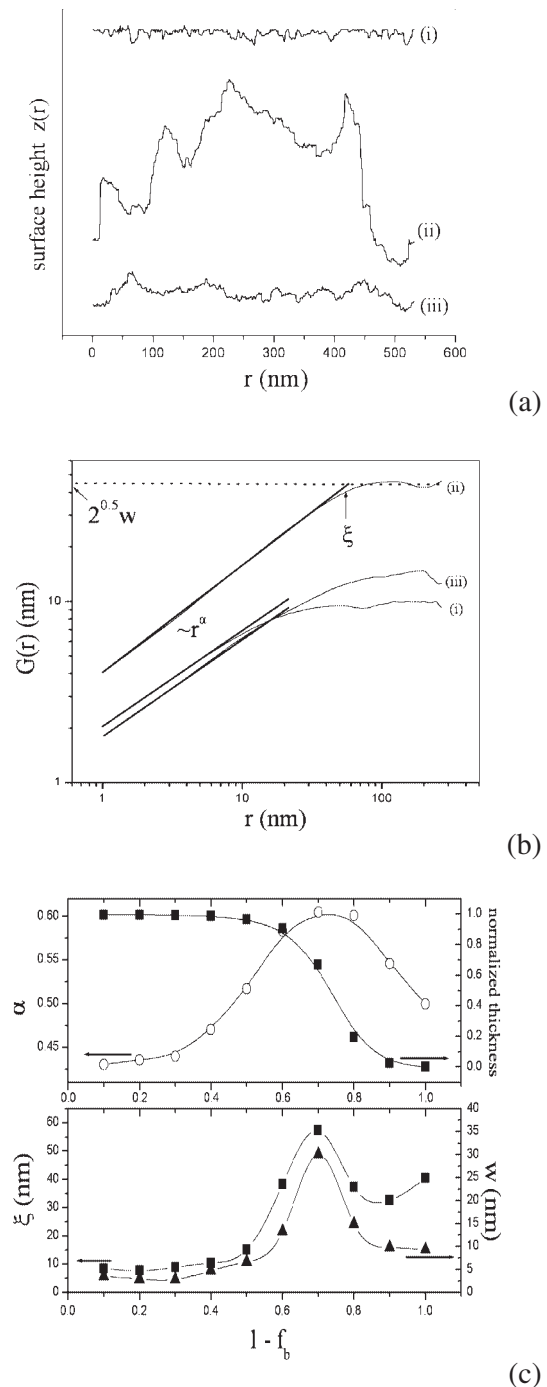


Fig. 2. a) Profiles from the simulation for low (i), intermediate (ii) and high (iii) exposure doses, b) the corresponding average height-height correlation functions  $G(r)$  and c) the roughness parameters ( $w, \xi, \alpha$ ) vs exposure generated methacrylic acid content ( $1 - f_b$ ) as well as the normalized remaining thickness of the resist after dissolution.

limited to short distance correlations (small  $\xi$ ) and important relative contribution of high frequency roughness (small  $\alpha$ ). As the dose increases, the probability the developer to find “tunnels” to penetrate into the polymer also increases, giving rise to surfaces with pronounced low frequency modulations (valleys and mountains) and therefore elevation of the roughness parameters ( $w, \xi, \alpha$ ). At high doses, the “tunnels” of penetration becomes so dense that the polymer chains are removed homogeneously from the whole polymer surface. The final surface morphology is similar to that at

low doses, without valleys and mountains and therefore with decreased roughness parameters.

In conclusion, it was shown for a particular resist that lithography induces fractal self-affine roughness on the fabricated resist polymer and that the roughness parameters depend in a correlated way on the exposure dose/solubility of the polymer. The same roughness behavior was demonstrated by a Monte Carlo simulation of the dissolution process revealing the generality of the findings and the pronounced contribution of the dissolution process and the resist solubility on the resist roughness formation.

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