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Effect of Development Time on Polymer Phase Separation in a PMMA Resist

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Abstract

Developer composition type and development technique are known to influence surface and edge roughness in polymethylemethacrylate (PMMA); and it is during development, we believe, that the result is most influenced by the phase separation into polymer-rich and polymer-poor regions. This polymer phase separation is more prominent in a weaker developer and low temperature. In this paper, we investigate the effect of development time on the extent of polymer phase separation in an exposed PMMA developed in a standard developer *i.e.* 1:3 MIBK:IPA at 20 °C and rinsed in pure IPA for 30 sec. The polymer phase separation is found to increase with the development time.

Key Words: e-beam; surface roughness; PMMA; phase separation; develop time.

1. Introduction

In sub-100 nm devices, Line Edge Roughness (LER) of lithographically defined features is the most important issue. In 2001, the International Technology Roadmap for Semiconductors (ITRS) highlighted the difficulties in controlling LER as a major roadblock to future progress [1]. In recent years, LER has been the subject of many investigations. The primary focus has been on the causes of roughness, such as the degree of mixing of the resist components [2], ariel image quality including mask roughness [3] and shot noise during photochemical processes [4]. It was found that higher ariel image contrasts leads to lower LER [5]. So far, little work has been done on the origin of line width fluctuation.

Negase et al [6] reported that the roughness was not caused by one polymer, but by an aggregate of several polymer molecules with a typical size of about 30 nm [6, 7]. They claim that polymers surrounding these aggregates dissolve faster than the aggregates, because the density of aggregates is larger compared to surrounding polymers [8] and hence, as the resist dissolves, the aggregates shape appears on the pattern edge or surface. The changes in the shape and size of these aggregates are also reported by changing the resist layer thickness and its affect on LER [9].

Recently, we reported that the roughness in conventional positive resist PMMA and chemically amplified resist UVIII is caused by polymer phase separation into polymer-poor and polymer-rich regions during the development step [10, 11]. It was also shown that the polymer phase separation can be reduced through the use of a stronger developer, and ultrasonically-assisted development. In all cases the trend in the variation of roughness was similar: roughness increases with the increase of dose and reaches its maximum value at dose near to clear, then decreases. The reduction in roughness due to the use of ultrasonically-assisted development is explained on the basis of reduction in viscosity due to shear thinning and availability of fresh developer at the resist-developer interface due to micro streaming.

Namatsu *et al.* [12] showed that the sidewall morphology is similar to the lightly exposed film surface. This is because the pattern sidewall is exposed by the tail of the electron beam profile. Such an exposure has the same effect as exposing the film surface at a low dosage. From a scaling analysis [5], it was shown that line width fluctuation and the surface roughness have the same origin.

In this work, we extend the previous study of polymer phase separation for short fix time of 30 sec to variable times from 30 sec to 1.5 hours, in order to see the influence of viscoelastic phase separation on the development time.

2. Experiment

High molecular weight (950 k) PMMA was spin coated onto 5 mm × 5 mm chips at a speed of 5000 rpm and post-application baked (PAB) at 180 °C for 1 hour giving a resist thickness of about 900 nm. The substrate used was unoxidised silicon. Large area (40 μm × 60 μm) exposures, using a dose matrix of 10 μC/cm^2 to 600 μC/cm^2 with an increment of 10 μC/cm^2, were carried out using a low resolution electron beam system with a beam diameter of 250 nm and a beam voltage of 50 kV. Samples were then developed with 1:3 MIBK:IPA at 20 °C for variable times from 30 seconds to 14 hours followed by a rinse in IPA for 30 seconds and then blown dry with nitrogen. The thickness of resist removed from the exposed region after development was measured using a Veeco DEKTAK surface profile measuring system. Images of developed resist regions were also obtained using a powerful optical microscope and a non-contact mode AFM. Under ideal conditions, the cantilever tip of the AFM does not touch the sample surface in this mode and so is less invasive for the imaging of soft materials, such as polymers. Although the AFM is capable of atomic-scale resolution with nearly flat surfaces, the images of samples with steep topography are distorted in the horizontal direction by the influence of the tip size and shape. As the smallest commerciallyavailable tip size is about 10 nm, the distortion will be at this size or greater. To perform accurate measurements, it is necessary to know the shape and size of the AFM tip; however, it is impractical to measure every tip size and shape before and after imaging. In this study we do not attempt to correct the experimental AFM images for this type of distortion because the size scale of our features are an order of magnitude greater than the size of the tip.

3. Results and Discussion

Entanglement makes a large contribution to the free energy of polymer solutions, and this leads to a double minimum in the Gibbs free energy curve (compared to the usual single minimum case), when the temperature is low, or the polymer molecular weight is high, or the compatibility between the polymer and the solvent is small; see Figure 1(a). Polymer-solvent compatibility may be controlled through developer composition, usually a solvent/non-solvent binary mixture for conventional resist, and is characterized by the chi parameter χ [10]. Developers consisting of a mixture of MIBK (solvent) and IPA (non-solvent) have been used widely with PMMA resist. In this case, χ can be varied from about 1.25 with a strong developer (1:1 MIBK:IPA) to about 1.75 with a weak developer (1:4 MIBK:IPA). For a given developer mixture (χ value) a phase diagram can be constructed; see Figure 1(b) [13]. For temperatures above a critical value C, all polymer-solvent mixtures are homogeneous and stable and thus gives a single minimum. However, the region below the curves indicates unstable polymer-solvent mixtures, which can lower the free energy of the solution by phase separation. Resist development is usually conducted at a fixed temperature (in the case under study the development temperature 20 °C), which is well below the critical value C.

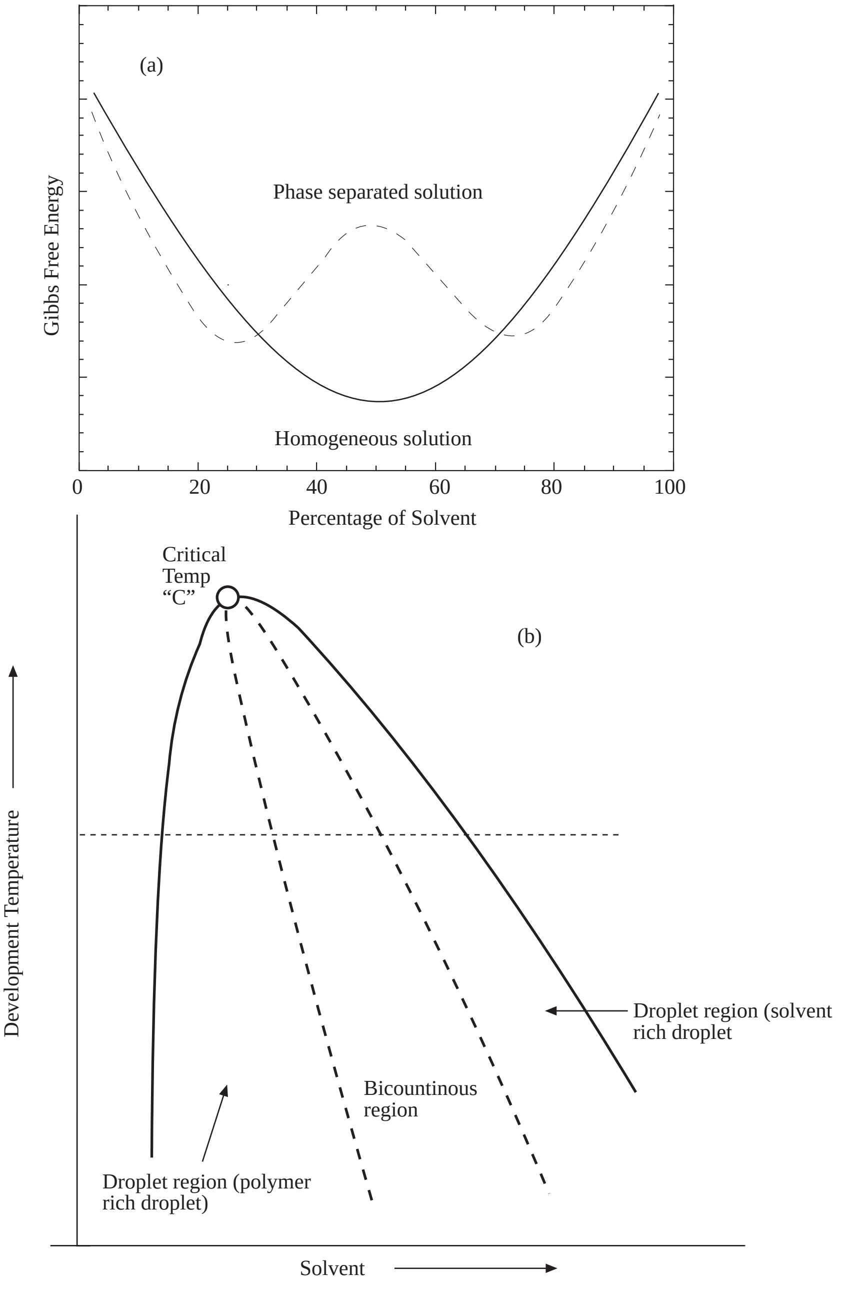

Figure 1. Schematic Gibbs free energy diagram for polymer-solvent mixtures as a function of solvent fraction. For development in a stronger developer, a homogeneous solution is the stable case; but in a weaker developer, the solution obtains a minimum Gibbs free energy when it phase-separates into polymer-rich and polymer poor-regions. (b) Schematic phase diagram for a single polymer molecular weight and developer solvent compatibility χ. The critical temperature C is indicated, together with the bi-countinous (region under the broken line) and droplet (region under the continuous line) curves. The development temperture is indicated by the horizontal broken line.

During development, the dissolution process results in the polymer fraction in the solution at the resist layer changing from 1 to zero. But in doing so, the polymer fraction must cross the region under the two curves, where the mixture is subject to phase separation. This phase separation is driven by the gain in free energy, but the rate at which this can take place is limited by the high viscosity of the polymer solution due to the viscoelastic behaviour where the polymer concentration is above a few percent. The characteristics of this type of phase separation in viscoelastic media have been modelled in two dimensions by Tanaka [13]. Phase separation in the spinodal region results in a bicontinuous division of the mixture into polymer-rich and polymer-poor phases, with a coarsening of the size scale with time. This polymer phase separation results in surface and line edge roughness in e-beam or optically defined features in polymeric resist. Although the "infinite" reservoir of pure solvent in the developer, well away from the resist surface, would eventually dissolve all parts of the exposed polymer, the delay in dissolution of the polymer rich phase results in some regions being left behind at the end of the development time. These regions are indistinguishable from the unexposed resist and appear as roughness. As the exposure dose is varied, the viscosity, and the dynamics of the phase separation of the mixture, are modified. With increasing exposure dose, the molecular weight of the polymer is reduced (in a positive resist process), so reducing the gain in free energy due to phase separation. But at high molecular weight the polymer-solvent mixture is highly viscous so that phase separation is slow. Together, these two effects lead to a bell-shaped extent of the RMS surface roughness with varying dose, as shown in Figure 2. The sample in this case is developed with 1:3 MIBK:IPA at 20 °C and rinsed in IPA for 30 sec. The RMS surface roughness is maximum at a point of maximum phase separation and is happening in a bi-continuous region.

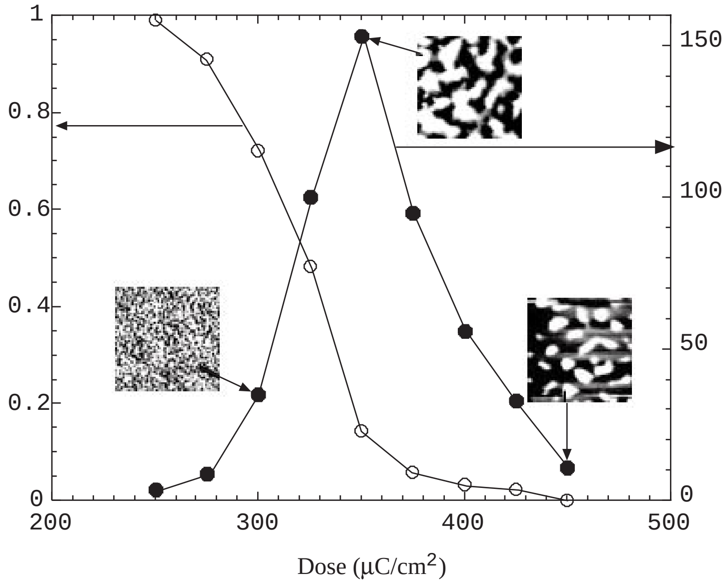

Figure 2. Normalized RMS surface roughnes vs dose for 30 sec development in 1:3 MIBK:IPA at 25 °C followed by 30 seconds rinse in IPA. The reason for the bell-shaped trend of RMS roughness as a function of dose is explained in the text. The inset shows the AFM images in a granular (polymer-rich droplet), bi-continous and again granular (solvent-rich droplet) regions.

Figures 3a and b show optical images of samples developed in 1:3 MIBK:IPA for 1.5 min and 1.5 hour respectively. The images clearly reflect the predication of Figure 1b *i.e.* passing from granular to bi-continuous and again granular. The only difference between Figure 1b and Figure 3 is that, in the former, the boundaries are defined as a function of the amount of solvent, whereas in Figure 3 the boundaries are marked by the dose received. As the molecular weight of the polymer is a function of dose and the solubility of exposed poylmer is a function of molecular weight, increasing dose is directly related to the fraction of solvent in the solution. From the comparison of Figures 3a and b, it is clear that, it is not only the shift of the boundaries between the different regions towards the lower dose, but also the degree of phase separation increases in the granular as well as bi-continuous region with the increases of development time. This fact is more clearly visible in Figure 4a–e. The reason for the lateral increase in the polymer rich and polymer poor regions with increase of development time is associated to the kinetic and thermodynamics polymer solutions [14].

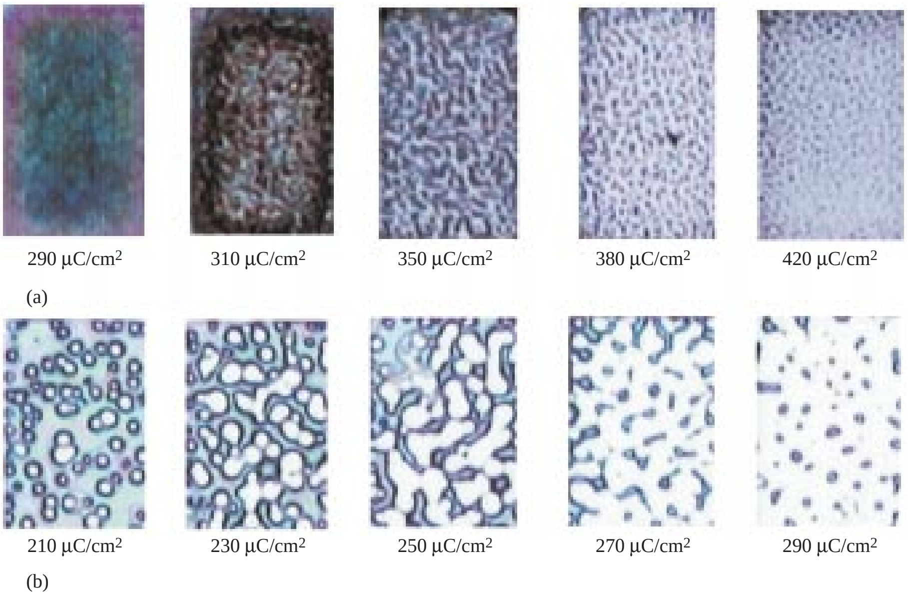

Figure 3. Optical images (a) 30 sec and (b) 1.5 hours developed in 1:3 MIBK:IPA at 20 °C and rinsed in IPA for 30 sec. Although the samples show increasing granular, bi-countinous and again granular structure with increase in dose, the phase separation is more prominent for longer development time.

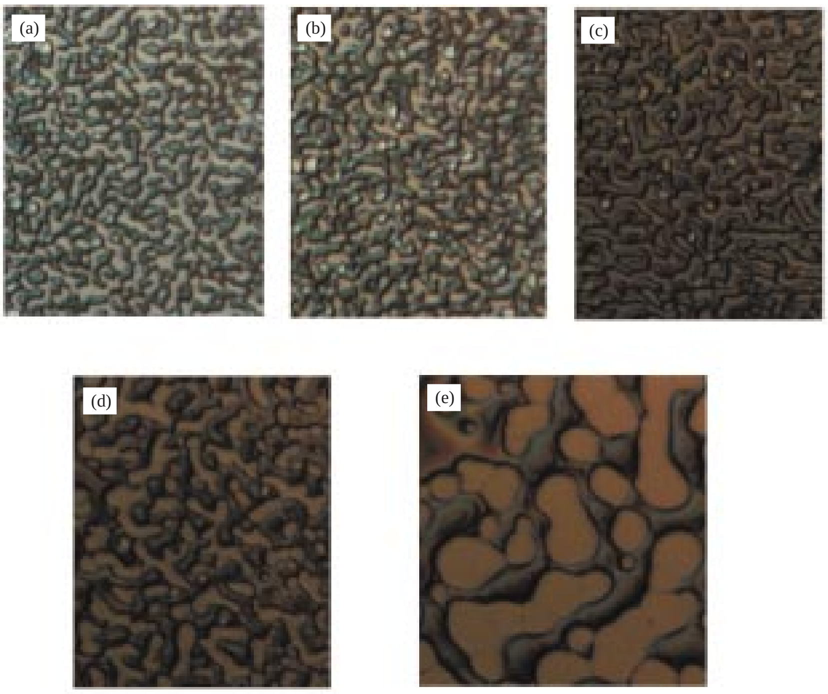

Figure 4. Optical images of the bi-countinous regions for (a) 30 sec, (b) 90 secs, (c) 9 min, (d) 30 min and (e) 90 min, developed in 1:3 MIBK:IPA at 20 °C and rinsed in IPA for 30 sec. The phase separation increases with the increase of development time.

4. Conclusions

The process of polymer phase separation is unlike the law of diffusion in which the motion is from higher concentrated region to lower concentrated region; the passage of time results in homogeneous solution, where the polymer move from polymer poor region to polymer rich region. The two dimensional modeling of phase separation in polymer solution by Tanaka [13] is verified experimentally, showing the increase in polymer phase separation with the passage of time.

References

[1] http://public.itrs.net

[2] D. McKean, R. Allen, P. Kasai, U. Schaedeli and S. MacDonald, *Proc. SPIE*, **1672**, (1992), 94.

[3] M. Yoshizawa and S. Moriya, *Proc. SPIE*, **3997**, (2000), 301.

[4] W. Henke and M. Torkler, *J. Vac. Sci. Technol.*, **B17**, (1999), 3112.

[5] J. Shin, G. Hen, Y. Ma, K. Moloni and F. Cerrina, *J. Vac. Sci. Technol.*, **B19**, (2001), 2890.

[6] M. Nagase, H. Namatsu, K. Kurihara, K. Iwadate, K. Murase and T. Makino, *Micro. Electron. Eng.*, **30**, (1996), 419.

[7] T. Yamaguchi, H. Namatsu, M. Nagase, K. Yamazaki and K. Kurihara, *Appl. Phys. Lett.*, **71**, (1997), 2388.

[8] T. Yamaguchi, H. Namatsu, M. Nagase, K. Yamazaki and K. Kurihara, *Mater. Res. Soc. Symp. Proc. SPIE*, **3333**, (1998), 830.

[9] K. Kanzaki, T. Yamaguchi, M. Nagase, K. Yamazaki and H. Namatsu, *Jpn. J. Appl. Phys.*, **41**, (2002), L1342.

[10] S. Yasin, D.G. Hasko, M.N. Khalid, D.J. Weaver and H. Ahmed, in press for *J. Vac. Sci. Technol*, 2004.

[11] S. Yasin, M.N. Khalid, D.G. Hasko and H. Ahmed, Presented in MNE 2003.

[12] H. Namatsu, M. Nagase, T. Yamaguchi, K. Yamazaki and K. Kurihara, *J. Vac. Sci. Technol.*, **B16**, (2001), 3315.

[13] H. Tanaka, *J. Phys. Condens. Mattter*, **12**, (2000), R207.

[14] D.G. Hasko, S. Yasin and A. Mumtaz, *JVST.*, **B18**, (2000), 3441.