Correlation between Edge Roughness of Nanostructures and Backbone Configuration of Polymer Materials

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1. Introduction

As minimum dimensions of integrated circuit decrease, the resolution of lithography is required to approach the dimension of the “molecular sizes”. The reduction of line-edge roughness (LER) in resist patterns is the most important issue in the lithographic techniques, which affect directly the critical dimension (CD) control in the sub-100 nm patterning. The material origin of LER has been investigated vigorously, however still incomplete to date. The effects of the lithographic processes,¹⁾ reactions of polymer molecules as base resin,²⁾ acid diffusion processes,³⁾ etc. have revealed correlation with LER, however those factors have been intricately interwinded each other, giving the total LER in the resist patterns. Configuration of the polymer chain in the base resin, as well as the molecular weight and its distribution of polymers, is one of the most crucial primary factors to determine the roughness, and not only experimental analysis⁴⁾ but also simulations based on the statistical theory of polymer backbone configuration⁵⁾ have been demonstrated. In the present letter, the roughness is discussed

quantitatively in the side-walls of the nanostructures which have been prepared by single particle negative-tone imaging.⁶⁾ The single particle imaging is the powerful tool to give 1-D nanostructures with sub-nm spatial resolutions.⁷⁾ Intrinsic cylinder-like shapes of the nanostructures realize to observe the side walls directly by scanning probe microscopes, reflecting the shape of “polymer molecules”.

2. Method

Polystyrenes and the derivatives were purchased from Aldrich Chemical Co. LTD., or synthesized by anion polymerization technique from doubly distilled corresponding monomers using *n*-butyllithium as an initiator, giving the polymers with monomodal molecular weight distributions with their polydispersity less than 1.2.^{7,8)} The thin films of the polymers on Si substrates were irradiated by several kinds of ion beams from cyclotron accelerator at Japan Atomic Energy Research Institute, Takasaki Research Establishment, and developed by adequate solvents. The sizes and shapes of the nanostructure formed

Figure 1. AFM micrographs of nanostructures based on polystyrene derivatives produced by single particle negative tone imaging. The 1-D nanostructures were collapsed by the development, and observed on the substrate as “lying” wires. Images (a) – (d) were observed in the thin films of PHS, PBrS, PCIS, and PS, respectively after irradiation of 560 MeV $^{129}\text{Xe}^{26+}$ ion beams at the fluence of $1 - 10 \times 10^9$ ions cm^{-2} .

along particle trajectories were observed using a Seiko Instruments Inc. atomic force microscope (AFM).

3. Results

A heavy ion particle impinging on target polymers can release high-density intermediates within a limited area of the ion projectile. Irradiation of the polymers results in a cross-linking reaction along an ion track, forming a cylinder-like structure (nano-wire) for each ion projectile. The non-cross-linked area can then be eliminated by development with an adequate solvent for each polymer, utilizing the change in solubility induced by gelation of the polymers. The nano-wires become completely isolated on Si substrates. Figure 1 shows a series of AFM images of nano-wires on a Si substrate formed in polystyrene (PS), poly(vinyl-phenol) (PHS), poly(*p*-bromostyrene) (PBrS), and poly(*p*-chlorostyrene) (PCIS), respectively. The correlation between the size (radii of the cross section of the nano-wires) and the molecular weight has been investigated precisely, showing clear increase in the radii with an increase in the molecular weight of target polymers.^{6,7)} The averaged sizes of the nano-wires were well interpreted by the theoretical model considering energy distribution in ion track, efficiency of cross-linking reaction, molecular weight, and backbone configuration of the target polymers.

Because of the present technique giving the negative tone of the cross-linked nanostructures without any acid catalytic reactions, the effects of development procedures, acid diffusion, etc. can be eliminated as the factors to cause an increase in the edge roughness of the structures. The values of roughness were defined as the standard deviation (s) of radii of the cross section in the AFM traces. Figure 2 shows the dependence of the values of σ on the degree of polymerization (N) of PS. According to the statistical theory on configuration of polymer chains, gyration radius (R_g) of polymer molecules is determined by following formula considering the impermeable rigid-body approximation;^{7,9)}

$$R_g = aM^\nu = a\left(\frac{N}{M_m}\right)^\nu \quad (1)$$

where M_m denotes the mass of a unit in a polymer chain. The correlation represented in figure 2 is well interpreted by eq. 1, giving the value of index ν as 0.758. The observed value of ν is close to the upper limit of ν : 0.8 which should be observed in case of complete-expanded chains. This is due to

Figure 2. Correlation between estimated values of edge roughness (s) and polymerization degree of PSs. Molecular weights of PSs were ranging from 5.2×10^4 – 1.1×10^6 .

the surface approaching to a rich solvent (toluene for PS) of the polymers during development procedures, and drying without enough shrinking of the molecules.

AFM traces of nano-wires based on the other polymers also estimates the values of σ , giving 2.5, 4.1, 4.3, and 5.3 nm for PS, PCIS, PHS, and PBrS, respectively after the calibration of their molecular weight at 5.0×10^4 according to eq. 1. Backbone configurations of polystyrene derivatives have been investigated precisely in both solution and solid phases. On the basis of the good approximation of expanded-chain model in solution for the roughness estimates, the values of characteristic ratio (C_∞) of the polymer chain in each respective solvent used for the development procedure are given as 10.8, 11.1, 12.0, and 12.5 for PS, PCIS, PHS, and PBrS, respectively.¹⁰⁾ The values of C_∞ show a striking contrast to the values of s , thus this is the case giving the direct experimental evidence of the clear quantitative correlation between edge roughness and backbone configuration of the polymers in the resist materials.

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