Nanofabrication using polymer resist materials

Toshiyuki Yoshimura* and Hiroshi Shiraishi

Central Research Laboratory, Hitachi, Ltd.
Kokubunji, Tokyo 185, Japan
* Electronic mail: yosimura@crl.hitachi.co.jp

Polymer resist materials are utilized in a state-of-the-art semiconductor device fabrication technology to define patterns on substrates. As the integration proceeds, the effects of molecular characteristics cannot be neglected compared with the minimum-feature device sizes. This paper describes several attempts to obtain ultra-small polymer resist patterns that enable nanofabrication. Negative-type resists are used to fabricate gate electrodes and interconnects. By controlling the molecular characteristics of the base matrix polymers of negative-type resists with electron beam exposure, we can suppress the surface roughness of the resist patterns and obtain ultra-narrow line patterns down to ~10 nm. By extending this concept of molecular control, the limit of nanofabrication can be made even smaller. With a uniform electron beam, we can also obtain ultra-small dots of ~3 nm, which can be regarded as polymer micro gels, or possibly the molecules themselves.

1. INTRODUCTION

In semiconductor circuit fabrication, the patterning process is a key step for miniaturizing devices. This process is called "lithography". Polymer resist materials are usually used to define device patterns. After being exposed to energy beams, which include UV, electron beam, X-ray, and ion beam, the solubility of the exposed regions of the resists change in aqueous developer. Polymer patterns are obtained through development procedures. As the integration of semiconductor circuits has advanced, small patterns of ~150 nm are now required. In the near future, fabrication of ultra-small patterns of less than 100 nm -nanofabrication- will be needed to realize more sophisticated ultra-large scale integration (ULSI) and novel devices.

Positive-type resists, in which the exposed regions become more soluble than the unexposed ones, have been used to form the minimum dot structures of ~5 nm in diameter by using a main-chain-secession-type polymer material, polymethyl-methacrylate (PMMA), combined with a finely focused electron beam.[1] Negative-type resists, in which the exposed regions become less soluble than the unexposed ones, are used to define gate electrodes and interconnects in ULSIs.

As the minimum feature sizes decrease, the molecular characteristics of the resist materials have become significant with respect to the device sizes. For example, ultra-small edge roughness in the fabricated resist patterns cannot be ignored in miniaturized devices, because the fluctuations in the device size induced by the roughness will degrade the circuit performance. We call this roughness "nano edge roughness".[2,3] We think it is critical to reduce the nano edge roughness by means of molecular control in future ULSI fabrication. In this paper, we will elucidate nanofabrication approaches that use negative-type polymer resist materials combined with electron beam lithography from the standpoint of molecular control of base matrix polymers.

2. EXPERIMENTS

The negative-type electron beam resists used here were conventional two-component azide-phenol-resin-based resists.[4,5] We used two types of resins as base matrix polymers; polyvinylphenol and cresol novolak, whose molecular-weight distributions were controlled. The polymers were fractionated by using a precipitation method with xylene and methylisobutylketone solutions.[6] All the resins here were mixed with the same concentration (17 wt.%) of the crosslinker, 3, 3'- diazidodiphenylsulfone. The molecular-weight distributions of the base matrix polymers were measured by gel permeation chromatography (GPC).

The resist films must be thin to achieve high resolution.[7] It is thought that the resolution can be improved by using thin resist films on account of reduction of the forward scattering in electron beam lithography. Si wafers were treated with hexamethyl disilazane vapor at 100°C for 60 s. Very thin resist films of ~20 nm were obtained by spin-coating the resist solution onto Si wafers, followed by soft baking at 80°C for 90 s.

For the nano-line fabrication, we used a finely focused electron beam of a scanning electron microscope (SEM, S-900, Hitachi) at an acceleration voltage of 30 kV. The beam diameter was assumed to be ~0.8 nm. For nano-dot fabrication, we used a uniform electron beam of a shaped-beam-type direct writing machine (HL-750D, Hitachi) at an acceleration voltage of 50 kV. The beam size was 2 μm x 2 μm.

It has been thought that a finely focused electron beam is necessary for nanofabrication. This approach was applied for the nano-line fabrication. A uniform electron beam can also be regarded as a flux of ultra-fine beams of individual electrons. Each electron causes resist reactions, for example, crosslinking in negative-type resists in the secondary electron range.[8] We also applied this approach for nano-dot fabrication. Fabricated resist patterns represent a composite of the resist reactions, and the resist pattern induced by a single electron might appear as a polymer nano-dot. The resolution limit of polymer resists can also be investigated by this method. We call this process "single electron patterning technology (SEPT)", even though dots may actually be created by more than one electron.

The exposed resists were developed using tetramethylammonium hydroxide-based solutions, and rinsed with deionized water. These fabricated resist patterns were also observed with the S-900. The microscopic surface characteristics were observed with an atomic force microscope (AFM, Nano Scope II, Digital Instruments).

3. RESULTS AND DISCUSSION

3.1. Nano-line fabrication

The molecular-weight distributions of two of the base matrix polymers measured by GPC are shown in Fig. 1.[2] The weight-average molecular weights (M_w) of both resins are almost identical (~6,000), whereas the polydispersity (M_w/M_n) of
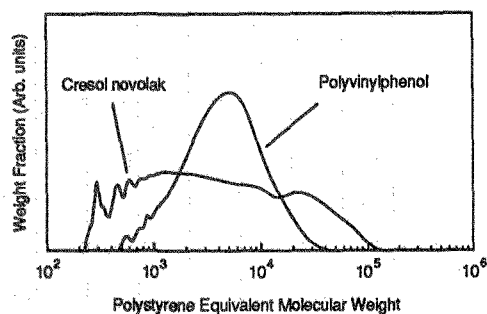

Figure 1. Molecular weight distributions of the base matrix polymers measured by GPC.

polyvinylphenol (1.9) is significantly smaller than that of cresol novolak (4.0). This means that both polymers have an almost equivalent average molecular size, but that the polyvinylphenol-based resist contains polymers with a smaller size distribution.

Figure 2 shows the surface roughness of the large exposed regions. The roughness corresponds to the nano edge roughness. It is evident that the surface roughness can be reduced by using a base matrix polymer with a smaller M_w. We also found that polyvinylphenol-based resists exhibited less surface roughness than cresol-novolak-based resists with equivalent molecular-weight-distribution characteristics. We believe this is due to a difference in the rigidity in the main chain of the polymer.[3] Polyvinylphenol is expected to be less rigid than cresol novolak on account of steric hindrance because the side chain contains aromatic rings.[9]
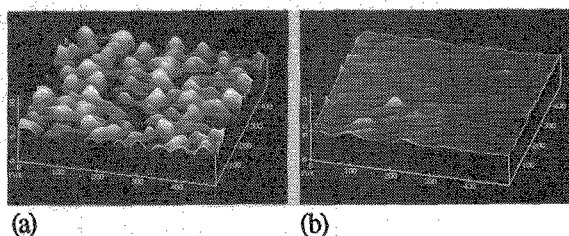

(a)   (b)

Figure 2. AFM images of resist surfaces: (a) Cresol-novolak-based with a large M_w (5,300), and (b) Polyvinylphenol-based with a small M_w (2,300).

The narrowest nano-line ever obtained using a negative-type resist of ~10 nm is shown in Fig. 3. This was obtained with a polyvinylphenol-based resist.[2] The approach of molecular control of base matrix polymers has recently been extended to much smaller molecules.[10]
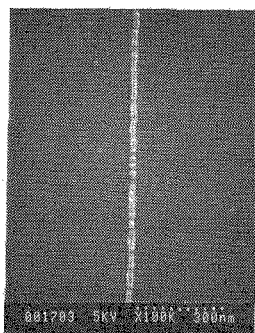
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Figure 3. SEM image of a nano-line of ~10 nm.

3.2. Nano-dot fabrication

We chose two types of cresol novolak for the base matrix polymer. Both resins had almost identical M_w (~5,000), but M_w/M_n of each resin was different: the value for cresol novolak A was 4.0 and that of cresol novolak B was 1.4. We used cresol novolak in this experiment, because we expected the effect of its molecular characteristics would be larger than polyvinylphenol.

In the measurement of the sensitivity characteristics, the electron beam doses for the macroscopically 0% remaining film thickness (D_0) under identical conditions were almost the same. We expected that very small dot patterns could be obtained by selecting electron beam doses near D_0, because there are few crosslink reactions near D_0.

Fabricated dot structures made using the resists are shown in Fig. 4, where the minimum feature dot size is 3 to 5 nm.[11] A larger distribution of dot sizes is clearly seen for the cresol-novolak-A-based resist than for the cresol-novolak-B-based resist.

We postulate that this difference between the two resists reflects the molecular-weight dis-

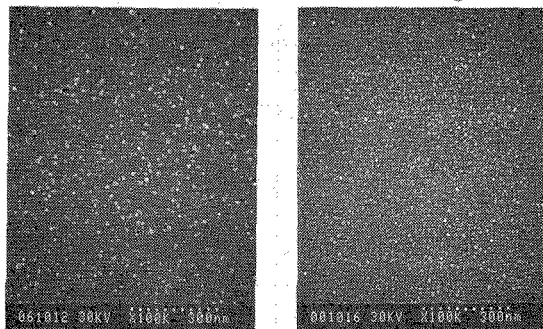(a)   (b)

Figure 4. SEM images of fabricated nano-dots: (a) Cresol-novolak-A-based resist, and (b) Cresol-novolak-B-based resist.

tributions of the base matrix polymers. The density of the dots decreased at smaller electron doses, and large island structures appeared at larger electron doses as shown in Fig. 5. There were no patterns in the unexposed regions. Therefore, we conclude that the dots are not development residues. The dot density (~10^{10}/cm^2) is much smaller than the incident electron density (~10^{13}/cm^2). Electrons injected onto the resist surface are assumed to obey the Poisson distribution. We think the smaller dot densities were due to resist-reaction probabilities, the adhesion characteristics of the polymers to the substrates, distributions of crosslinked sites, and nonuniformities of the incident beam.
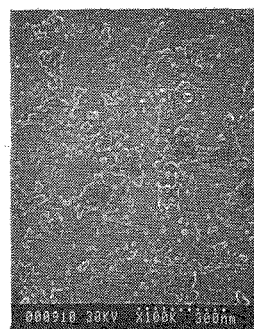

Figure 5. SEM image of fabricated nano-dots with islands (Cresol-novolak-A-based resist).

AFM surface images of the same samples are shown in Fig. 6. As seen in Fig. 4, the cresol-novolak-A-based resist sample contains nano-dots with a larger size-distribution, whereas the cresol-novolak-B-based resist sample exhibits a more uniform distribution of nano-dots.[11] Note that the dot sizes shown by AFM do not correspond with the SEM results shown in Fig. 4. We think this is due to the finite radius of the AFM tip.[12] The tip radius is thought to be larger than 20 nm, so patterns smaller than this value are shown to have a larger morphology than their actual sizes.

When the base matrix polymer molecules are assumed to be entangled coils, the effective diameter of each molecule is proportional to the square root of its molecular weight.[13] The molecular size of cresol novolak with M_w ~5,000 is estimated to be ~3 nm by taking the monomer size of the cresol novolak (~0.5 nm) into account. It is well known that polymers crosslink to form micro gels of a few molecules before forming gels which theoretically consist of an infinite crosslinking network.[14]
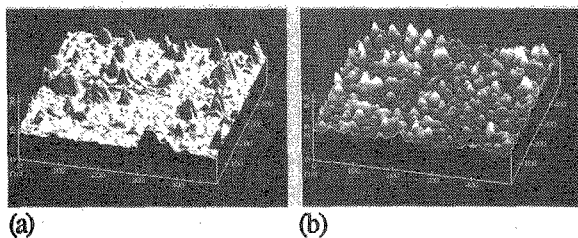
Figure 6. AFM images of fabricated nano-dots:
(a) Cresol-novolak-A-based resist. (b) Cresol-novolak-B-based resist.

Therefore, the patterns seen in Fig. 4 can be explained as micro gels of cresol novolak molecules induced by electron beam exposure, or possibly, the molecules themselves.

We applied X-ray photoelectron spectroscopy (XPS) to investigate the surface conditions of the substrates. A nitrogen N_{1s} peak was clearly detected in the sample with the dot structures, where nitrogen was contained only in the crosslinker. This peak was attributed to the crosslinker combining with the resin molecules on the Si surface. However, there was no nitrogen peak for the reference Si wafer sample. Consequently, we have confirmed that the nano-dot structures are made of micro gels of the cresol novolak molecules, or possibly the molecules themselves combined with the crosslinker.

4. CONCLUSION

We fabricated ~10-nm nano-line patterns using a negative-type polymer resist combined with a finely focused electron beam. Ultra-small edge roughness in the fabricated resist patterns (nano edge roughness) was suppressed by using a less rigid base matrix polymer, polyvinylphenol. Negative-type polymer resists, which consisted of cresol novolak resins and crosslinkers, were used with a uniform electron beam for experiments on the resolution limit of polymer resist materials. Nano-dot structures of ~3 nm in diameter were successfully obtained. The uniform electron beam can be considered to be a flux of ultra-fine beams of individual electrons. We call this method "single electron patterning technology (SEPT)". The nano-dots appear to be micro gels of resist molecules, or possibly the molecules themselves, and XPS analysis confirmed that they were made of the resist material.

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