Micropattern Formation of Photosensitive Imide Block Copolymer Thick Films

Sachiko Ito, Hirotaka Osato, Eun-Sil Jung, Katsuya Kikuchi, Shigemasa Segawa, Kazuhiko Tokoro, Hiroshi Nakagawa, Hiroshi Itatani, and Masahiro Aoyagi

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 2, 1–1–1 Umezono, Tsukuba, Ibaraki 305–8568, Japan, 1 PI Research and Development Company Limited (PI R&D Co., Ltd.), 12–5 Torihama, Kanazawa, Yokohama, Kanagawa 236–0002, Japan.

In order to determine the optimal composition for thick films above 10 μm of a photosensitive imide block copolymer/sensitizer composite, we examined the dissolution rates of the exposed and unexposed area, their dissolution contrast and pattern profile during the development of films prepared using a nonprecursor-type imide block copolymer (PI 21-101) with the addition of various sensitizer concentrations of diazonaphthoquinone derivative (THBP-200) from 15 wt% to 50 wt%. The dependence of the dissolution rate on THBP-200 concentration for the films not subjected to the exposing process signifies that the dissolution inhibition above 30 wt% is effective to an alkaline development solution. The dissolution contrast with 30-wt% THBP-200 was found to be 15.4, which is remarkably higher than that with THBP-200 concentrations of 15 wt% and 20 wt% that are the optimal composition for thin films. With the condition of a THBP-200 concentration of 30 wt%, the optimum composition for the present thick films, a good via-hole pattern with a hole size of 20 μm was successfully formed on a film with about 10 μm in thickness.

Keywords: imide block copolymer, thick films and dissolution rate

1. Introduction

Polyimide is one of the most thermally-stable organo-polymeric material, and has a heat-resistant temperature above 400 °C. The polymer has been extensively used in the fields of microelectronics and related technology because of its superior electric characteristics such as high electric insulativity and low permittivity. However, a precursor-type photosensitive polyimide, the current mainstream for photoresists, suffers from its volume shrinkage on heat polymerization after pattern forming. This leads to a serious problem on its application to the interlayer dielectrics of detailed semiconductor LSI devices; namely, severe contraction of the lower polyimide layers in multilayer wiring occurs during the repeated heat treatments.

Itatani, et al. developed a nonprecursor-type solvent-soluble imide block copolymer attained using a catalytic polymerization, and achieved a positive-type pattern formation on it with diazonaphthoquinone (DNQ) sensitizer additive [1,2]. This block copolymer does not require any heat polymerization after patterning, hence no pattern deformation by heating arises. Moreover, the block copolymer is highly stable with respect to chemical environments, and is promising to be applied to high-density-wiring interposer for next-generation packaging technology [3].

Recently, we have successfully devel-
The development mechanism in the photosensitive DNQ/polyimide system is explained as shown in Fig. 1 [6]. The hydrophobicity of DNQ inhibits the dissolution of unexposed area, thus the difference in dissolution rates between exposed and unexposed area, characterized as the dissolution contrast, is expected to be improved by the addition of a greater amount of DNQ. Meanwhile it has been reported an increase in dielectric constant of insulator films due to DNQ-related residues produced by the thermal decomposition of the sensitizer [7], meaning that a smaller amount of DNQ is suitable for avoiding increase of the dielectric constant. We tested the photosensitivity of two types of sensitizers, NT-200 and PC-5 (Fig. 2), and found that the dissolution contrast of the former sensitizer, which has more DNQ groups, is higher than the latter one [5].

In the present work, we adopted THBP-200 as a sensitizer, which consists of benzophenone skeleton similarly to NT-200 but is a dissolution inhibitor stronger than that [8], and examined dissolution rates of exposed and unexposed area on thick films (about 10 μm) of nonprecursor-type imide block copolymers containing various THBP-200 concentrations from 15 wt% to 50 wt% in order to improve resultant hole-shape pattern profiles.
2. Experiments

Fluorine containing polyimide (PI 21-101, supplied from PI R&D Co., Ltd.) was synthesized through a single step polycondensation reaction between dianhydrides and diamines with γ-valerolactone/pyridine catalyst in NMP/toluene mixture at 180 °C, to which different concentrations (15, 20, 30, 40 and 50 wt%) of sensitizer (THBP-200, from Tokyo Gosei Kogyo Co., Ltd.) were added after the polymerization (Fig. 2). The obtained composites were dissolved into N-methyl-2-pyrrolidone (NMP) so that the polymer concentrations range from 16.5 wt% to 19.5 wt%. The solutions were stirred for 30 min and then degassed for 30 min at room temperature, and thus photosensitive THBP-200/PI 21-101 solutions were obtained.

The polymer solutions were spincoated on 3-inch silicon wafers with covering of DC-sputter-deposited Al, where the material of Al was chosen by comparing the film adhesivity to wafers without and with three types of covering materials, that is, DC-sputter-deposited Al and Nb and a spincoated silane-coupling reagent. For preventing the constituents from degassing out by heating, the samples were prebaked by a step-by-step heat treatment at 60 °C for 10 min and at 100 °C for 10 min. The resultant film thickness ranged from 13 μm to 19 μm.

The spincoated films were exposed with an exposure dose of 4000 mJ/cm² and Focus 0 using a g-line stepper (Stepper 1700-842, Ultratech). G-line was confirmed to be highly transparent for the present system (Fig. 3). The exposed films were developed by dipping in A0 solution (ethanolamine/NMP/H₂O = 1/1/1 by weight) at 40 °C (Fig. 1). We note that 2.38-% TMAH solution, conventional for photoresists, is not suitable for the film development [5]. After the development, the film was rinsed by pure water two times at 40 °C and room temperature. Postbaking was done at 150 °C for 30 min and 300 °C for 30 min, during which temperature was gradually increased to promote smooth degassing of nitrogen caused by the thermal decomposition of THBP-200.

The film thickness was measured at the time before and after the development of films and after the postbaking using the profilometer (α-step 500 Ten-cor). Dissolution rates for the exposed and unexposed area on the films were determined by measuring film thickness with a variation of development time.

3. Results and discussion

Figure 4 shows variations of the film thickness without exposing as a function of dipping time. The thickness for all films linearly decreased with increasing dipping time up to 10 min. The decrement of thickness per minute less than 8 min was weakened as THBP-200 concentration increased, clearly showing the dissolution inhibition effect of THBP-200. With further increasing dipping time above 10 min the reduction rate became several times of magnitude larger than the rate below 10 min for...
each sample with a THBP-200 concentration above 20 wt%. This suggests that a good pattern formation in the present THBP-200/PI 21-101 system demands a development time less than 10 min.

The absolute film thickness of the exposed area cannot be measured directly by the profilometer due to the thickness reduction of the unexposed area. Thus the thickness of the exposed area was deduced from the difference between the development depth and film thickness after the development. The variation of the deduced film thickness after the exposing and development is shown in Fig. 5 as a function of development time. The thickness linearly decreased with increasing development time, the slope of which significantly became steeper as THBP-200 concentrations increased. The dissolution rate of the exposed area was evaluated by the slope of the plot before the complete resolving.

In Fig. 6 are shown the variation of the dissolution rates for the unexposed and exposed area and their dissolution contrast as a function of THBP-200 concentrations. The dissolution rate for the unexposed area decreased with increasing THBP-200 concentration; especially, it rapidly reduced from 15 wt% to 30 wt%, and beyond that it kept an almost constant value about 300 nm/min indicative of the effective dissolution inhibition by the DNQ group of THBP-200. In contrast, the dissolution rate for the exposed area linearly increased with increasing THBP-200. Meanwhile the dissolution contrast shows an exponential elevation with increasing THBP-200 concentration, signifying that an increased THBP-200 concentration is appropriate in terms of improving the resolution.

For improving both sensitivity and resolution of photoresists using the abhorrent inhibition-enhancement effects on dissolution with the DNQ photoreaction, important factors are to enlarge the dissolution contrast, to rise the dissolution rate of the exposed area per exposure dose, and to heighten the rate itself. Although increasing DNQ concentration in the photoresists intensifies their dissolution contrast due to the effective dissolution inhibition,
the total light absorption of the concentrated DNQ is simultaneously intensified, hence the overall photosensitivity is reduced, as evidenced in other photosensitive systems such as Novolak [9] and poly-benzoxazol [10]. However, for the present system, both dissolution contrast and photosensitivity were enhanced with increasing THBP-200 concentration. It has been reported that similar results are obtained for a DNQ-introduced polyamic acid derivative photosensitive polyimide [11].

Figure 7 shows the variation of the reduction in thicknesses due to the development and postbaking processes for the THBP-200/PI 21-101 polyimides as a function of THBP-200 concentration, which were resolved with the condition of a 4000-mJ/cm² exposure dose and each optimum development time (T_{op} = 10, 7, 5, 3 and 3 min for 15, 20, 30, 40 and 50 wt%, respectively). Suppressing the reduction in film thickness during each process is particularly important for a good pattern formation. Although the reduction during the development was effectively suppressed by the addition of THBP-200, it linearly increased with increasing THBP-200 concentration during the postbaking. This suggests increased thermal decomposition of DNQ during the postbaking, which can occur around 70°C as well as its photoreaction and proceeds more as temperature rises above 140 °C [12], followed by removing nitrogen gas from the film (no bubbling up was observed on the account of the step-by-step temperature elevation). For the application to interlayer dielectrics a smaller reduction in thickness during postbaking is desirable, because of the collateral thickness reduction of the lower layer polyimide by postbaking of the upper layer. As the result, the thickness reduction during the postbaking was greater than that during the development for THBP-200 concentrations above 30 wt%. Interestingly, the total reductions in thickness through both development and postbaking were almost the same for THBP-200 concentrations.
of 30 wt%, 40 wt% and 50 wt%.

SEM images of 20–35-μm via holes are shown in Fig. 8, obtained for the films with 20–50 wt% of THBP-200 concentrations. As one can see, the sidewall angle of via holes for THBP-200 20 wt% is small (about 60°) due to the low dissolution contrast. No large variation in shape for the 30-wt%-THBP-200 film was observed in the range of $T_{op} \pm 1$ min. In contrast, for 40 wt% and 50 wt% not only the patterns were partly unresolved at two minutes of development time ($T_{op} - 1$ min), but also the via-hole sizes were significantly changed at 4 min (over development time, $T_{op} + 1$ min). These results show that the via-hole change in size with increased development time is enhanced with increasing THBP-200 and conclude that the optimum THBP-200 concentration is 30 wt% by considering its advantageous process margin in terms of the development time. At the THBP-200 30 wt%/Pl 21-101 composition, good via-hole patterns with a sidewall angle of about 71 degrees were obtained for a film with about 10 μm in thickness (measured after postbaking).

4. Conclusion

The dissolution rates of the exposed and unexposed area during the development process for the imide block copolymers with various THBP-200 concentrations from 15 wt% to 50 wt% were examined. The dissolution rate of the unexposed area above 30 wt%-THBP-200 concentration was around 300 nm/min, signifying that the dissolution inhibition is effective to the alkaline development solution. Both dissolution rate of the exposed area and dissolution contrast were increased with increasing THBP-200 concentration. However, the increased THBP-200 concentration also induced greater reduction of the film thickness. In addition to this, the via-hole size change became remarkable around the optimum development time, which seriously influences the resolution of the via-hole patterns. Therefore we concluded that a THBP-200 concentration of 30 wt% is most appropriate for the application to films thicker than 10 μm. With this optimum composition, a good via-hole pattern with a hole size of 20 μm was successfully formed on a film with about 10 μm in thickness.

5. References


