High-Sensitivity and High-Resolution Contact Hole Patterning Enhanced by an Optimized Developer

H. Shimada, S. Shimomura, K. Hirose, M. Onodera and T. Ohmi

Department of Electronics, Faculty of Engineering, TOHOKU University Aramaki Aza-Aoba, Aoba-ku Sendai, 980 Japan, Phone:022(224)2649, Fax:022(224)2549

We have determined that high-sensitivity and high-resolution contact hole resist patterning can be achieved by using an optimized combination of developer, added surfactant and ammonium chloride salt. The addition of surfactant improves the wettability of the developer and promotes resist dissolution. The presence of ammonium chloride salt protects the sidewall of the contact hole resist pattern. The optimal developer can form contact hole patterns smaller than the illumination wavelength of the stepper without phase shifting technology.

1. INTRODUCTION

Developments in photoresist materials and exposure systems have made it possible to achieve fine photoresist patterns for semiconductor device fabrication. Advanced Novolac-based resists^{1,2)} and chemically amplified resists^{3,4)} have been proposed for i-line and KrF excimer lithography, respectively. Recently, phase-shifting mask technology⁵⁻⁸⁾ and the steppers with innovative illumination systems9,10) are being developed to improve the resolution and the depth of focus of resist patterns. Although line and space (L&S) resist patterns have been extensively evaluated at the research level, failures of contact hole (CH) resist patterns still often occur in production. Since the resolution capability of CH patterns is lower than that of L&S patterns, the exposure energy for CH patterns is required to be two or three times higher. The purpose of this paper is to overcome this problem by presenting the high performance formation of CH patterns by using a developer which contains surfactant and ammonium salt.

2. EXPERIMENTAL

The pre-bake (90°C/90s) thickness of the Novolac-based resists was 1.26 μ m. We employed g-line and i-line stepper systems (FPA-1550MII,MIVW, FPA-2000i : Canon) and evaluated CH patterns larger than 0.3 μ m. After exposure, the samples were post-exposure baked (110°C/90s). Next, the wafers were developed in 2.38wt% tetramethylammonium hydroxide (TMAH) aqueous solutions for 70 seconds and then rinsed in ultrapure water for 60 seconds; two TMAH solutions (TMAH-1, TMAH-2) and one surfactant were examined. The TMAH-2 solution included a tetramethylammonium chloride (TMAC) concentration

of approximately 25ppb. The surfactant, a nonionic hydrocarbon type, was added to the developers in concentrations ranging from 0ppm to 200ppm. Crosssections of the CH patterns were observed by scanning electron microscope (SEM). In order to evaluate the development characteristics of the CH resist pattern of various developers, the threshold exposure energy of contact hole (E_{TC}), the exposure energy necessary for the bottom of contact hole to reach the substrate, was determined.

3. RESULTS AND DISCUSSION

Figure 1 shows the cross-sectional SEM views of $0.8\mu m$ to $0.6\mu m$ CH patterns formed by developer without surfactant (TMAH-1). When the exposure dose of $220mJ/cm^2$ (fig.1(a)) is supplied, the $0.8\mu m$ CH pattern is precisely clear, but the others are under exposed. In the case of $280mJ/cm^2$ (fig.1(b)), the $0.7\mu m$ CH pattern is good, but the others are failures. This



Fig.1 Contact hole pattern profiles formed by developer without surfactant under the following exposure conditions: (a) 220mJ/cm², (b) 280mJ/cm²





(b) TMAH-2+Surfactant

Fig.2 Relationship between threshold exposure energy (E_{TC}) and additional amount of surfactant for 0.6µm, 0.7µm and 0.8µm contact hole patterns by using (a) TMAH-1 + surfactant and (b) TMAH-2 + surfactant.



Fig.3 Cross-sectional SEM images of contact hole resist patterns of sizes $0.6\mu m$, $0.7\mu m$ and $0.8\mu m$, formed by a gline stepper (NA=0.43) and the following developers: TMAH-2, TMAH-1 + 200ppm surfactant, and TMAH-2 + 200ppm surfactant.

data says that it is impossible to form CH patterns larger than $0.6\mu m$ under same exposure condition except by using a reticle with bias sizing. This effect is considered to be caused by the poor wettability¹¹) of developer.

However, if 200ppm surfactant is added to developer, the contact angles of developer on the unexposed and exposed resist decrease by 33.5° and 22.4°, respectively. Figures 2(a) and (b) show the E_{TC} as a function of the concentration of surfactant added to TMAH-1 and TMAH-2, respectively. For the developers without surfactant, the E_{TC} s of various contact hole sizes are very different. As the amount of surfactant in TMAH-1 increases in fig.2(a), the E_{TC} s decline, but the initial difference of the E_{TC} s of various hole sizes does not reduce. However, in the case of TMAH-2 (fig.2(b)), as the amount of surfactant increases, the E_{TC} decreases *and* the E_{TC} difference between varying pattern sizes becomes lower. It is

confirmed that CH patterns as small as $0.6\mu m$ can be formed under the same exposure condition and that TMAH-2 + surfactant enhances the resist resolution of CH patterns.

Figure 3 exhibits the SEM micrographs of $0.8\mu m$ to $0.6\mu m$ CH patterns using the differing developers. While patterns smaller than $0.8\mu m$ could not be obtained by using developer without surfactant, the addition of 200ppm surfactant allows the formation of CH patterns down to $0.6\mu m$. The results of TMAH-1 + surfactant show walls of CH patterns with curved profiles, but the CH walls obtained by TMAH-2 + surfactant are straight. It is therefore suggested that the addition of surfactant improves the wettability of the developer and promotes the resist dissolution, and that the existence of chloride provides an inhibition effect¹², which prevents the resist dissolution of the CH sidewall.

Figure 4 presents the SEM micrographs of 0.4µm CH patterns exposed by a g-line stepper as a function



Fig.4 SEM images of $0.4\mu m$ contact holes as a function of exposure energy. Patterns were formed by a g-line stepper (NA=0.55) and the following developers: TMAH-2, TMAH-1 + 200ppm surfactant, and TMAH-2 + 200ppm surfactant.



No Surfactant



TMAH-1 Surfactant



TMAH-2 1.0μm

Fig.5 SEM images of $0.35\mu m$ contact holes patterned by an i-line stepper (NA=0.52) and following developers: TMAH-2, TMAH-1 + 200ppm surfactant, and TMAH-2 + 200ppm surfactant. Exposure energy: 279mJ/cm^2

of exposure energy for different developers. In the case of TMAH-2 + surfactant, the resist sensitivity is much higher, and the exposure latitude is much greater. Figure 5 shows 0.35μ m CH pattern profiles of various developers, exposed by an i-line stepper. Accurate 0.35μ m CH patterns can be resolved by using TMAH-2 + surfactant. We have also confirmed the formation of 0.3μ m CH patterns by TMAH-2 + surfactant.

4. SUMMARY

We have found that developer including surfactant and ammonium salt enhances the resist performance: high-sensitivity and high-resolution of contact hole patterning. Due to the additional surfactant to the developer, its wettability becomes good and resist dissolution in narrow spaces is promoted. The presence of ammonium chloride salt in the developer prevents the dissolution of the sidewall of the contact hole pattern. By matching resist materials with this optimized developer, we can achieve ultrafine contact hole patters as well as line and space patterns.

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