Microsyst Technol (2016) 22:329–336
DOI 10.1007/s00542-014-2389-z

TECHNICAL PAPER

Influence of residual layer on cross-sectional shape of thermal-reflowed photoresist structures

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Received: 18 November 2014 / Accepted: 3 December 2014 / Published online: 13 December 2014

Abstract When photoresist structures are formed by employing various lithography technologies and followed by thermal reflow treatments, the mechanism that transforms the cross-section of a photoresist structure from a rectangular-shape into a circular-shape is seen as an integral constituent of the manufacturing method of microlens arrays. However, in the case, where a residual layer is absent, a photoresist film is completely exposed to the oncoming radiation down to the interface between the photoresist film and substrate. Even in the presence of a residual layer, it has been uncertain to the author if a photoresist structure with a circular cross-sectional shape could be obtained, and be made applicable for the fabrication of a microlens array. The author then executed a set of thermal reflow treatments under various conditions using a positive-tone photoresist AZP4903 known for its capability of forming relatively thick films. As a result, it became clear that the existence of a photoresist's residual layer has large influence on the transformation of the cross-sectional shapes of photoresist structures. These observations can be attributed to whether the bottom surface of a photoresist structure is firmly fixed on a hard substrate, or if it happens to be in contact with a soft photoresist layer which can flow comparatively freely.

1 Introduction

There are two kinds of conventional photoresists used in the semiconductor industries: one is positive-tone resist in which case the resist's irradiated area by lights is removed after its development, and the other is negative-tone resist in which case the irradiated portion of the resist remains present after being developed. In recent years, a high-sensitivity negative-tone photoresist which can form a thick film like SU-8 (Lorenz et al. 1997) series has been developed, and the application of photoresist structures to various devices has spread widely (del Campo and Greiner 2007; Abgrall et al. 2007). This trend has also been observed in the case of positive-tone photoresists. By a binary exposure used in conventional photolithography, a photoresist structure with rectangular cross-sectional shape with vertical sidewalls can be fabricated. Such a structure was used to serve as a masking layer for dry etching of Si substrates (Somekh 1976), and also used in the process of electroforming (Chaudhuri et al. 1998). Moreover, a photoresist structure was used as a component of a grating (Zaidi and Brueck 1988) and microfluidic devices (Thorsen et al. 2001). However, when using photoresist structures for an actual device, the cross-section of the structure may arbitrarily be extended beyond the conventional cross-section of rectangular shape. For example, the process of making sidewalls of photoresist structures, inclined by grayscale lithography technologies, was utilized to develop microelectro-mechanical-systems (MEMS) structures (Waits et al. 2001), MEMS packaging (Morgan et al. 2006), an elastic force motor (Beuret et al. 1994), and a microfluidic device with homogeneous features (Atencia et al. 2007). Moreover, curved sidewalls of photoresist structures formed by multi-steps exposure techniques were applied to a microlens (Che-Ping et al. 2003; Chang and Yoon 2006; Totsu et al. 2006), and to a Fresnel lens (Morgan et al. 2004). In addition, photoresist structures with inclined sidewalls were produced by using a technique that combined binary exposure and optical diffraction (Buraschi et al.

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1989), and focus offset (Mekaru et al. 2010). In a binary exposure without using a special technology, the sidewall tends to stand vertical and the associated photoresist structure maintains a rectangular-shaped cross-section. On the other hand, by applying a thermal reflow treatment as a retrofitted process, the edges of a photoresist structure can be rounded, and its vertical sidewall can be changed to a curved sidewall. A trial production-result of various microlens arrays using this technique was reported (Heremans et al. 1997; Daly 2001; Yang et al. 2004; Roy et al. 2009; Stevens and Miyashita 2010). However, any work on leaned sidewalls of photoresist structures by the thermal reflow treatment has not been reported to the knowledge of the author. When, after completely exposing a photoresist film spin-coated on a substrate, a thermal reflow treatment was applied to it then photoresist structures with curved sidewalls were formed. Thus, after a thermal reflow, the existence of a residual layer might determine the shape of sidewalls. This paper's findings are based on the results of experiments done to explore this hypothesis.

2 Experiments

In order to investigate the influence on a cross-sectional shaped structure caused by the existence of a residual layer of photoresist, two kinds of substrates, with the absence, and with the presence of residual layers with two different thicknesses of photoresist films were prepared. Figure 1 shows the experimental procedures employed for the two kinds of substrates. As a preparation step of the substrates, AZP4903 (AZ Electronic Materials), which is one of the positive-tone photoresist that can be spin-coated thickly, was chosen. The photoresist AZP4903 after being taken out of the refrigerator, where it was stored, was warmed up to the room temperature (20 °C). After a 30-min of acclimatization the photoresist was spin-coated on a 4-inch Si wafer (previously sputter-deposited with 10-nm-thick Cr) at rotation speeds of 1,500 and 2,000 rpm to achieve two different film thicknesses. Then in an oven the substrates with the two film thicknesses were prebaked at 110 and 120 °C. The film thicknesses were then measured by a microfigure measuring instrument ET3000i (Kosaka Laboratory) and found to be 20 and 16 µm, respectively. In the case of the thick photoresist film, an internal stress accumulated during the drying process caused the film to become susceptible to the generation of cracks. This issue was solved by allowing the substrate sufficient relaxation time between each process. Laser lithography is known to be a powerful technique to expose a thick photoresist film (Cheng et al. 2002). In the following patterning process, a tabletop micro pattern generator µPG101 (Heidelberg Instruments Mikrotechnik) was used, where 2-mm-length line patterns with their linewidths of 2, 5, 10 and 20 µm were directly drawn with a pitch value of 40 µm. Then, the exposed AZP4903 photoresist was developed for 5 min using a 25 % developer AZ400 K (AZ Electronic Materials), and the sample was then washed with deionized water. Figure 2 shows the relationship between an irradiation energy of laser lights generated from the µPG101 system and the exposure depth of AZP4903 photoresist. In order to expose the 16-µm-thick AZP4903 photoresist completely by a 405-nm diode laser, it turned out that a 7-mW irradiation energy was required. Therefore, when the 20-µm-thick AZP4903 photoresist was exposed under the same conditions, an approximately 4-µm-thick layer remained unexposed. In a following thermal reflow process, the sample was put on a hot plate TH-900 (Asone) heated at 110 or 120 °C; and after

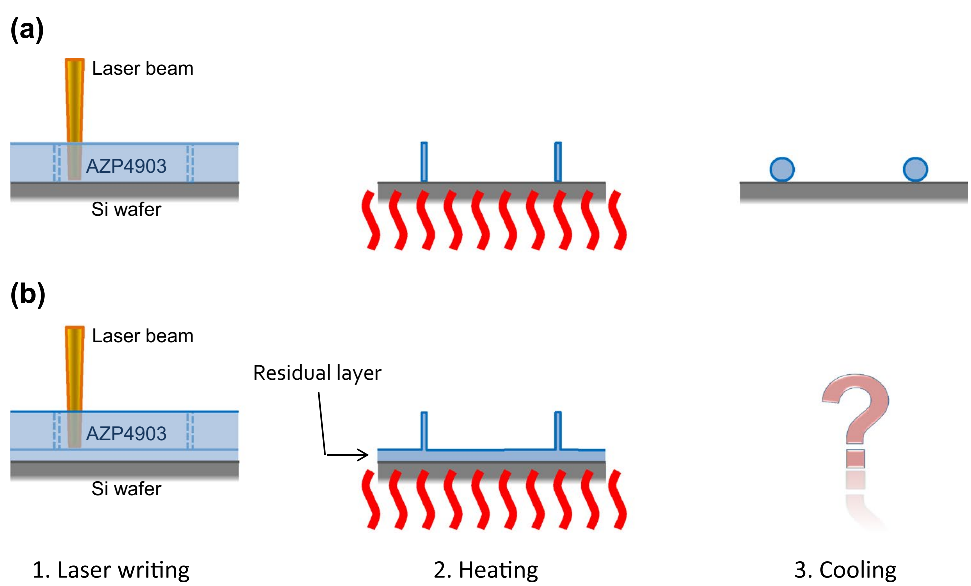


Fig. 1 Process flow combined with laser lithography and thermal reflow treatment in case of: **a** absence and **b** presence of a photoresist's residual layer. The thickness of photoresist was: **a** 16, and **b** 20 µm, respectively

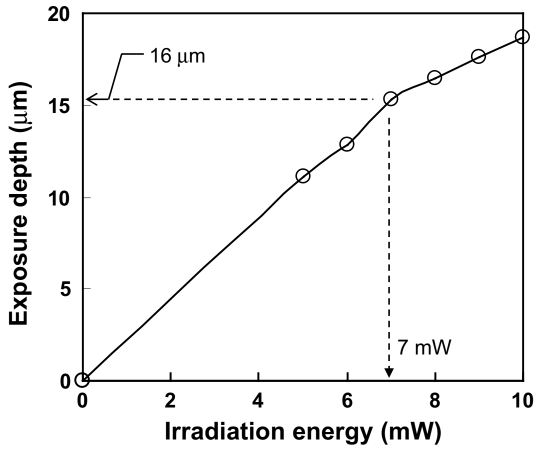


Fig. 2 Relationships between irradiation energy and exposure depth of AZP4903 photoresist

Table 1 Experimental conditions

Process	Material	Parameter	Condition
Spin-coating	AZP4903	Thickness	16, 20 µm
Pre-baking #1 (oven)		Temperature	100 °C
		Time	15 min
Pre-baking #2 (oven)		Temperature	120 °C
		Time	5 min
Laser exposure		Exposure energy	7 Mw
Development	AZ400k + DW (1:3)	Temperature	RT
		Time	5 min
Reflow (hot plate)		Temperature	110, 120 °C
		Time	30, 60, 90 s

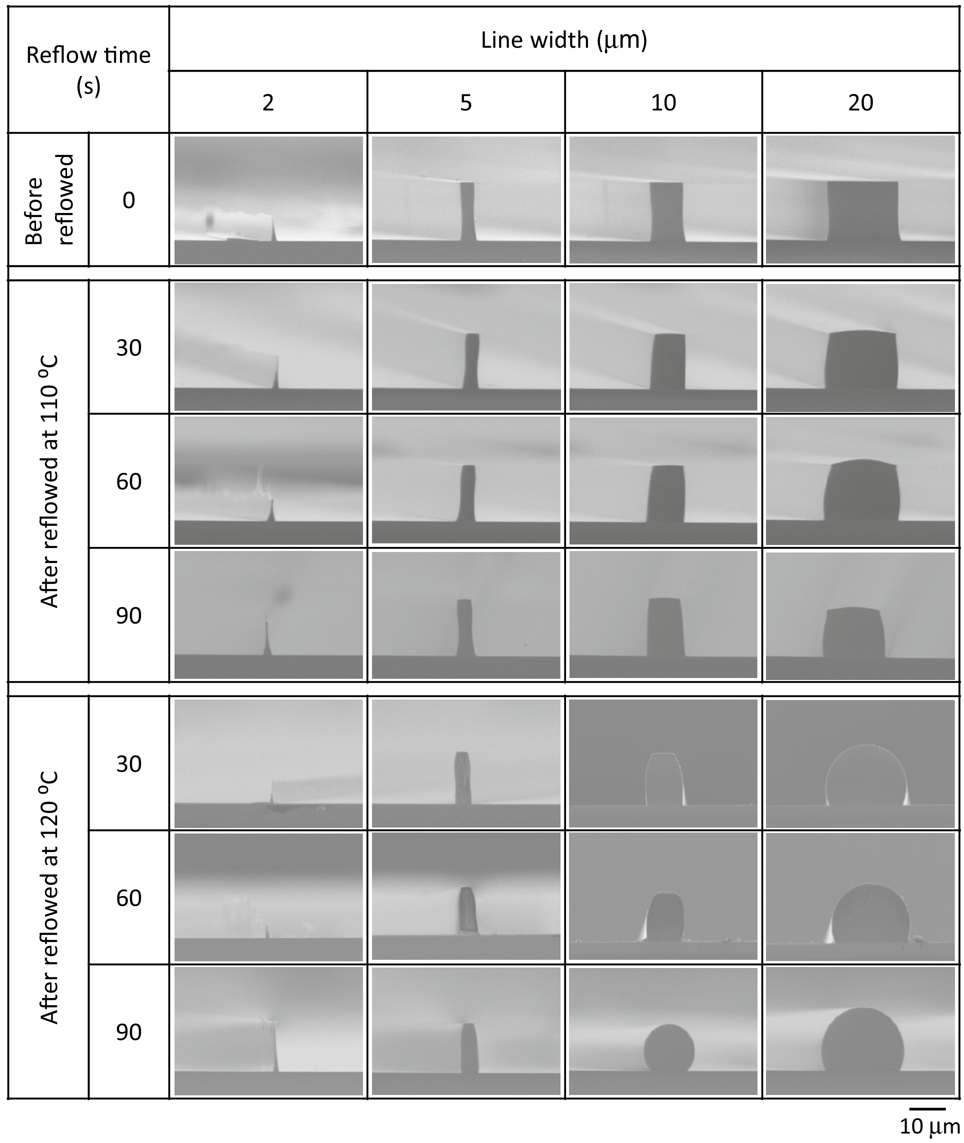
a predetermined period, the sample was removed from the hot plate. As the last step, the sample was cleaved by hand in an orientation perpendicular to the line patterns; and after a 10-nm-thick Pt sputter-deposition for the prevention of charge-buildup at the cross-section, it was observed by a scanning electron microscope (SEM). Table 1 shows the details of experimental conditions.

3 Results and discussion

The SEM images of the cross-sectional shapes of the AZP4903 photoresist structures in cases of absence, and presence, of the residual layer are shown in Figs. 3 and 4, respectively. In both cases, photoresist structures with a linewidth of 2 µm were destroyed when the sample was cleaved by hand, and they could no longer be used for accurate observation. Therefore, the 2-µm-wide patterns were removed from the evaluation. In the case where the residual layer was absent as shown in Fig. 3, if a reflow time became long, the upper edge of photoresist structures became rounded regardless of the linewidth. The speed of deformation was fast when a reflow temperature was high. Especially, when the 20-µm-wide photoresist structure was heated at 120 °C for 30 s, the cross-sectional shape changed from its rectangular shape to a circular shape. Moreover, in the case with a linewidth of 10 µm, the cross-sectional shape changed into a perfect circle by a thermal reflow treatment for 90 s at 120 °C. Thus, it turned out that the transition of the cross-sectional shape is greatly dependent on the pattern's linewidth under the same thermal reflow conditions. On the other hand, in a case of a presence of the residual layer as shown in Fig. 4, a trend that vertical sidewalls inclined gradually was observed after the thermal reflowing. However, this phenomenon was observed only when the thermal reflow temperature was 110 °C. Even when the sample was heated at 120 °C for only 30 s, photoresist structures got buried into the residual layer and it became impossible to discern any trace of them when the thermal reflow time became long.

The cross-sectional SEM images of patterns 'features in Figs. 3 and 4 relating to the features'upper width, bottom width, and height at various reflow temperatures and reflow times are shown in Figs. 5, 6 and 7 respectively. In these figures, data in a case where the residual layer was absent is shown plotted in figures (a); and the data in the other case where the residual layer was present is shown plotted in figures (b). The upper width of photoresist structures with a circular cross-sectional shape is indicated as 0 µm in Fig. 5a. When some samples were cleaved by hand, there was a case where a cleaved surface appeared inclined to the line patterns by several angles. For this reason, the maximum error for measurement on the widths and the height of patterns using cross-sectional SEM images was estimated to be as 0.14 %. The measured linewidths of the photoresist structures whose designed widths were 5, 10 and 20 µm were found to be 4.0, 9.0 and 19 µm, respectively. When the thermal reflow temperature was 110 °C, any noticable change was not observed except for the pattern with a designed linewidth of 20 µm. However, when the thermal reflow temperature was raised up to 120 °C, the speed of deformation was different; whereas when the thermal reflow time was increased, a tendency for the upper width to decrease was observed. On the other hand, in Fig. 5b, the 5-, 10- and 20-µm designed-width patterns became still narrower to 3.1, 8.4 and 18.7 µm, respectively. Although a temporary depression was seen when the thermal reflow time was 30 s, the tendency for the upper width to also spread was observed with an increase in the thermal reflow time. That is, an opposite tendency was revealed by the existence of the residual layer. In the bottom width as shown in Fig. 6, a still bigger difference was observed compared with the upper width. In the case where the residual

Fig. 3 Cross-sectional SEM images of AZP4903 photoresist structures in the absence of residual layer before and after the thermal reflow treatment at 110 or 120 °C. SEM observation was performed after Pt sputter deposition on the sample



layer was absent (Fig. 6a), each bottom width before the thermal reflow treatment in the cases of the designed width 5, 10 and 20 µm was measured as 4.9, 10.1 and 20.3 µm. The bottom widths of the photoresist structures after the thermal reflow also maintained the almost same values. On the other hand in the case where the residual layer existed (Fig. 6b), a transition of the bottom widths of the designed 5-, 10- and 20-µm-wide photoresist structures started from the values, as measured actually before the thermal reflow, and were 6.6, 14.2 and 24.1 µm, respectively; and whereas the thermal reflow treatment was advanced at 110 °C, the bottom width increased to 24.6, 30.2 and 43.8 µm, and spread up to a maximum of 3.7 times the original values. Furthermore, when the sample was heated at 120 °C, after the bottom width was spread rapidly up to a maximum of 2.8 times of the original value before the reflow, measurement of the bottom width became impossible. In a transition of heights of photoresist structures in which the residual layer was absent as shown in Fig. 7a, a set of three parameters were to be looked at. The height of photoresist structures with a designed width of 5 and 10 µm heated at 110 °C hardly changed, but became low to 12.7 µm by heating at 120 °C. On the other hand, in the pattern with a designed width of 20 µm, a tendency of a slight increase from the original value as roughly 16 µm was observed without being dependent on the thermal reflow temperature. Although a remarkable reduction was seen before and after the thermal reflow in the case where the residual layer was present as shown in Fig. 7b, the influence by the extension of the thermal reflow time was small after being heated at 110 °C. However, when the thermal reflow temperature was 120 °C, the height decreased to one-sixth of the original value before the reflow and then became incapable of measurement. In consideration of these measurement

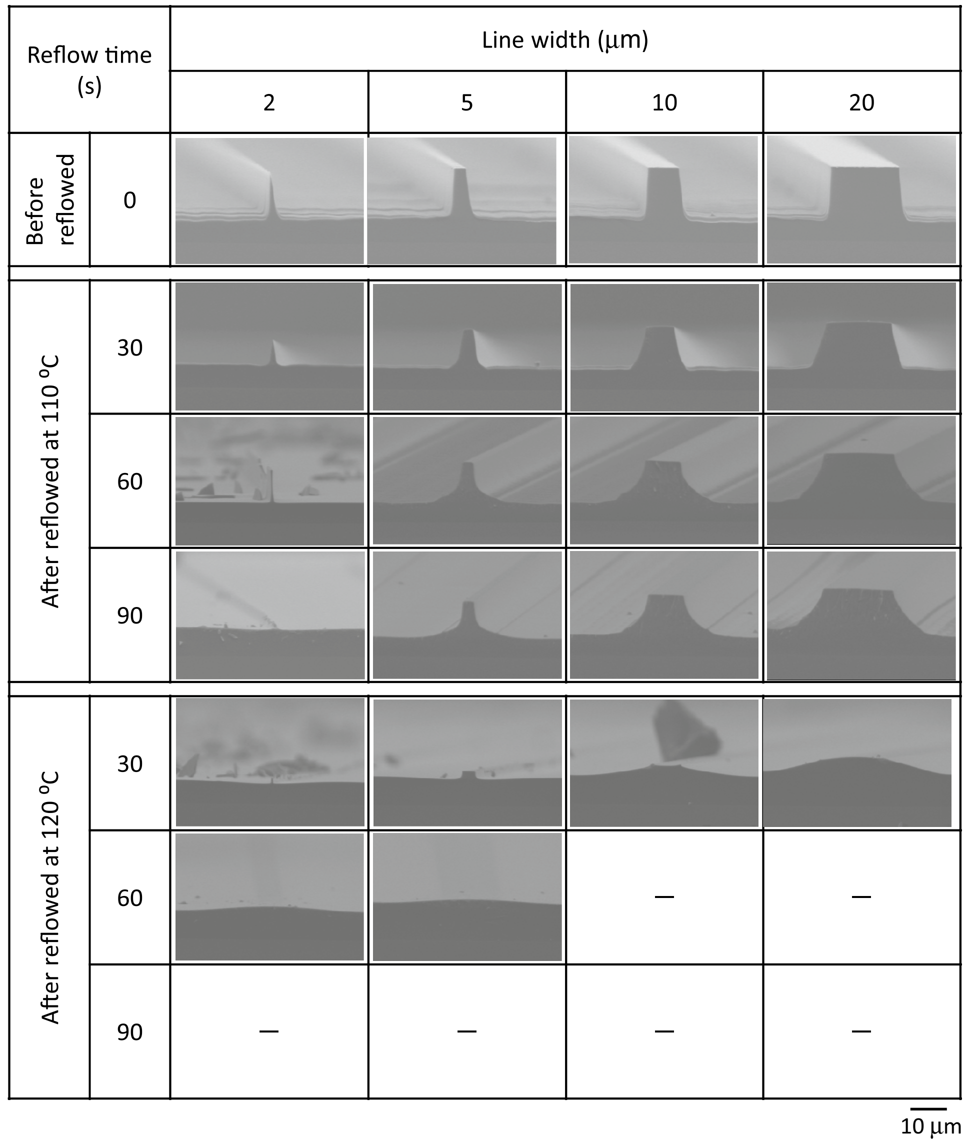


Fig. 4 Cross-sectional SEM images of AZP4903 photoresist structures in the presence of residual layer before, and after the thermal reflow treatment at 110 or 120 °C. In the case where the samples were heated at 120 °C for 60 and 90 s, any photoresist structure could not be observed. SEM observation was performed after Pt sputter deposition on the sample

results, the author made estimation of the influence that the thermal reflow treatment has on the cross-sectional shape of photoresist structures. One of the main ingredients of a conventional positive-tone photoresist is polymethyl methacrylate (PMMA), of which the glass transition temperature is known to be 105 °C (Ashby 2005). A photoresist when heated to more than its glass transition temperature, is softened and behaves like a liquid. When the residual layer was absent as shown in Fig. 8a, the photoresist structures were crushed under their own weights. Since the bottom surface and the substrates were stuck firmly, photoresist could not flow and spread on the substrate's surface at an initial stage. Then, the cross-sectional shape approached to form a circular shape so that the surface tension of softened photoresist could be minimized. On the other hand, when the residual layer was present as shown in Fig. 8b, the bottom surface of photoresist structures was in contact only with the residual layer, and thus the contact position was comparatively free from the substrate. Therefore, photoresist structures gradually collapsed under their weights, and finally got buried into the residual layer. In this phenomenon, the bottom width of the photoresist structure was spread while the upper width was barely changed, resulting in the formation of a trapezoidal shaped cross-section with inclined sidewalls. Figure 9 shows the result of plotting the inclined angles of the sidewall of the photoresist structures measured from the cross-sectional SEM images of Fig. 4. Although the inclined angle was of several degrees before the advent of the thermal reflow, the value slightly increased by heating at 110 °C with an increase of the thermal reflow time. From these results, it became clear that a flowing of the softened photoresist was enhanced and followed by the formation of inclined sidewalls in the case with a presence of the residual layer under the bottom of photoresist structures.

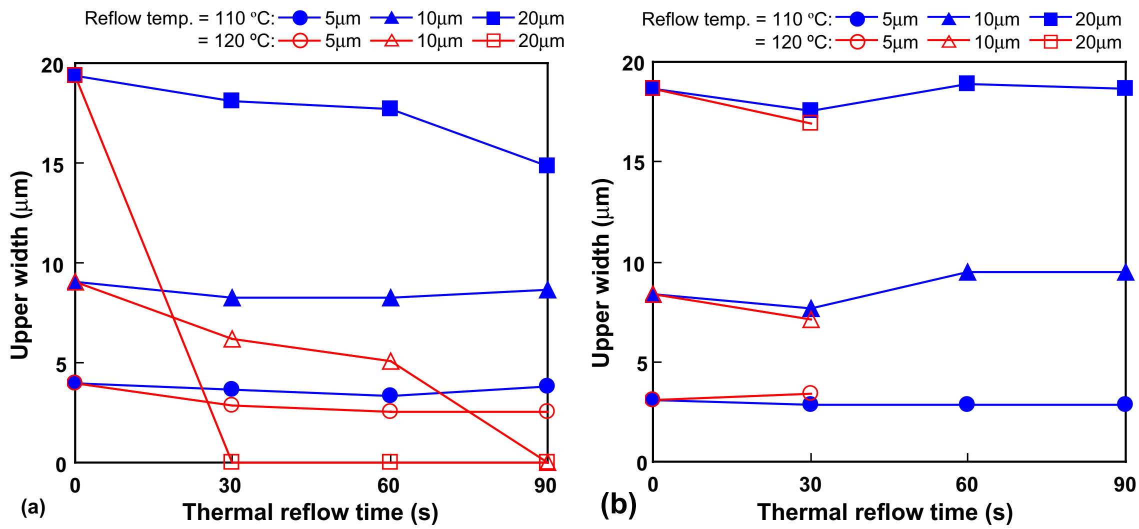


Fig. 5 Relationships between thermal reflow time and upper width in the cases of: **a** absence and **b** presence of AZP493 photoresist's residual layer

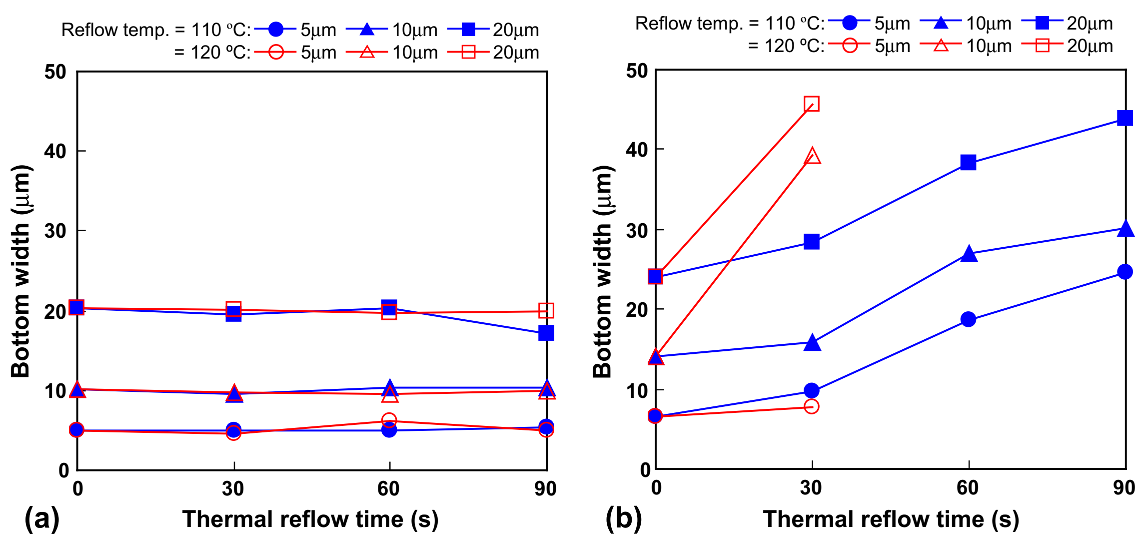


Fig. 6 Relationships between thermal reflow time and bottom width in the cases of: **a** absence and **b** presence of AZP493 photoresist's residual layer

4 Summary

Chromium sputtered Silicon substrates (Cr/Si) spin-coated with photoresist AZP4903 with different thicknesses were prepared, and patterns with the designed widths of 2-, 5-, 10- and 20-µm were drawn on them using laser lithography. By optimizing the irradiation energy of the laser beam, two kinds of samples, one with residual layer present and the other with residual layer absent were produced. Using these samples, the influences of thermal reflow treatments on the cross-sectional shapes of photoresist structures were investigated, that exhibited large difference between the two kinds of samples. In the case where the residual layer was absent, pattern edges became round with an increase in the thermal reflow time, without causing any change in the linewidth, because the bottom surface of photoresist structures remained fixed on the substrate. Especially, in the case of large linewidths, the cross-sectional shape of the photoresist structures changed from rectangular to circular as governed by the structure's own weight and the surface tensions involved in the process. On the other hand, in the case where the residual layer was present, although the upper width of the photoresist structures did not change with an advancement of thermal reflowing, the bottom

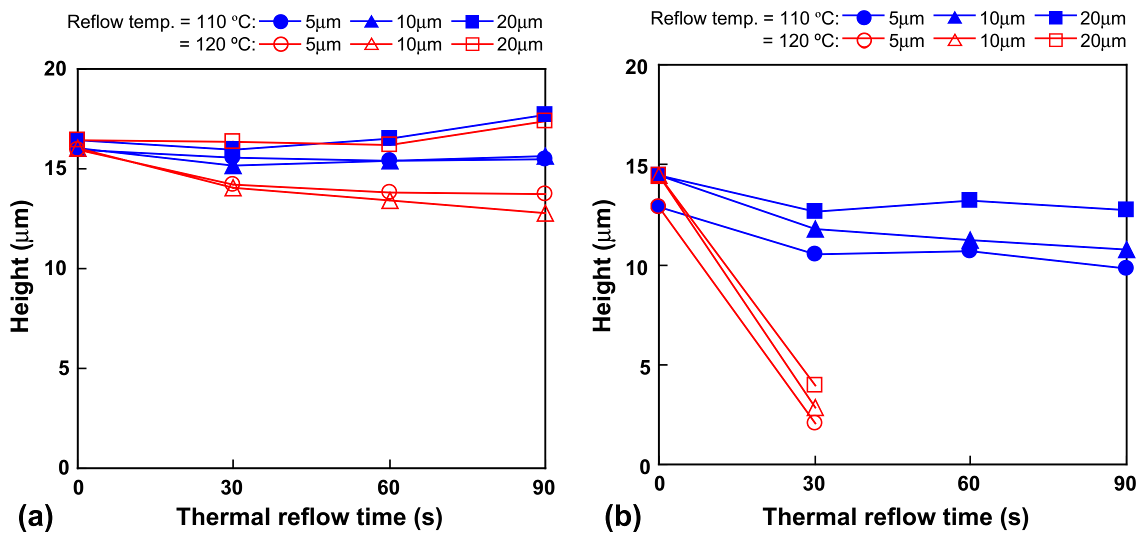


Fig. 7 Relationships between thermal reflow time and height in the cases of: **a** absence and **b** presence of AZP493 photoresist‘s residual layer

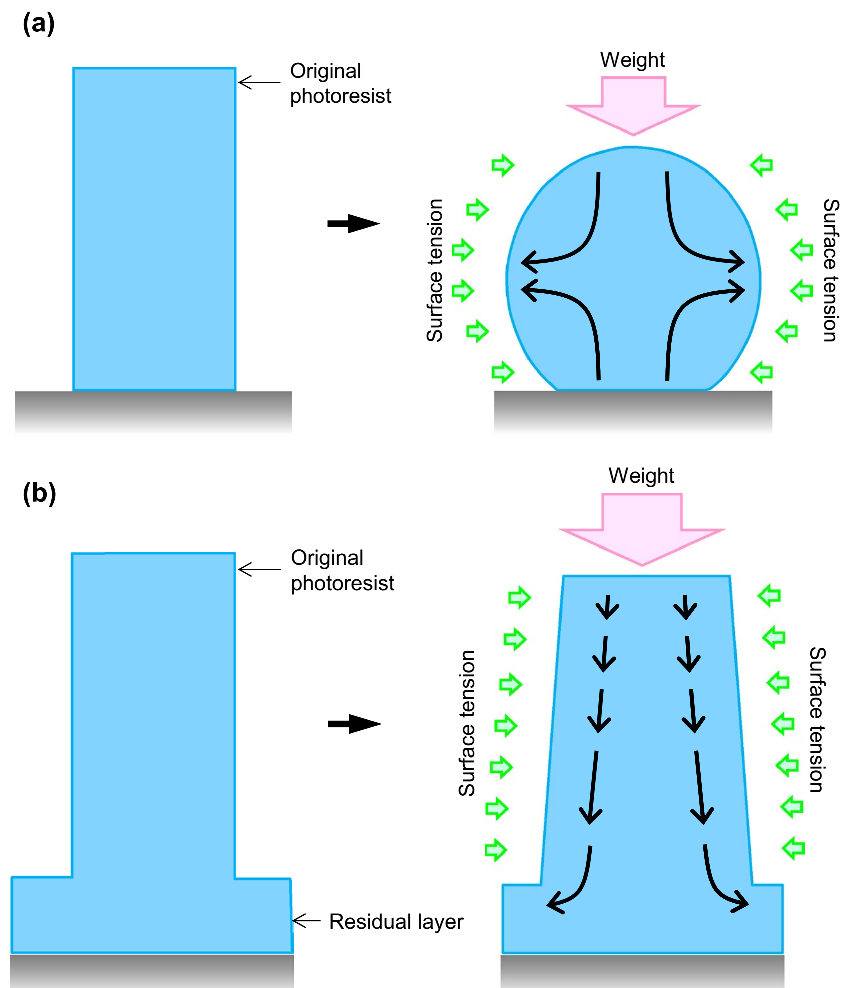


Fig. 8 Illustrations of photoresist structures in the case of: **a** absence and **b** presence of residual layer during the thermal reflow treatment

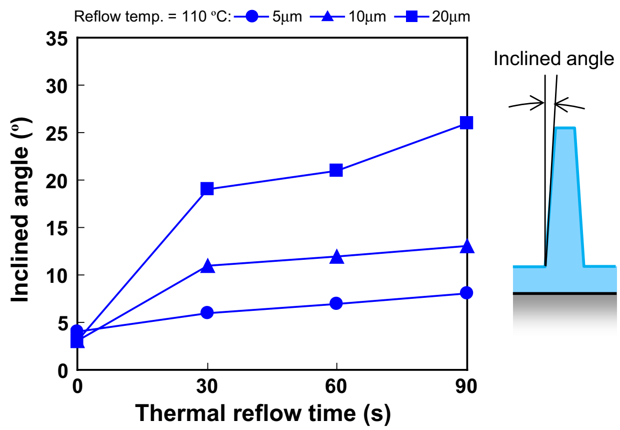


Fig. 9 Relationships between thermal reflow time and inclined angle in the case of presence of AZP493 photoresist's residual layer

width tended to spread. And this phenomenon led to the inclination of the sidewalls of the photoresist structures. Moreover, in the thermal reflow treatment at a comparatively high temperature, it became clear that photoresist structures got buried into the residual layer and disappeared for a brief period of time. These results mean that the cross-sectional shape of photoresist structures is controllable simply by the existence of the residual layer.

Acknowledgments Before the author used the laser lithography system, the author received technical advices from Dr. Kenta Suzuki and Dr. Hiroshi Hiroshima of the National Institute of Advanced Industrial Science and Technology (AIST).

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