Chapter 8

Powder Process with Photoresist for Ceramic Electronic Components

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Additional information is available at the end of the chapter

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Abstract

This chapter proposed a patterning process for ceramic electronic components. The proposed process uses a photoresist, and it is combined with the photolithography process and the printing process. By using both technologies, a high-aspect-ratio and fine conductive pattern is achieved because the patterned photoresist hold the filling paste during the dry process. Moreover, a different material pattern in a ceramic sheet can be formed simultaneously when the photoresist covers on the ceramic sheet with a through-hole pattern. The examples of the patterning process and the fabricated pattern are shown. The fine conductive pattern was formed by using a liquid photoresist, and the line width and the thickness were 10.3 and 1.85 μm, respectively. In the ceramic pattern, the conductive paste and low-temperature co-fired ceramic (LTCC) slurry were filled to the ferrite sheet. As a result, the ceramic sheet that had three different materials was achieved. It realizes the miniature ceramic inductor suppressing the minor loop. However, the photoresist process showed some problems with the fine pattern and the different material pattern. These problems are solved by adjusting the viscosity and the composite ratio of the slurry. The optimization of the type and thickness of the photoresist is required.

Keywords: photoresist, multilayer ceramic technology, fine conductive pattern, different material sheet

1. Introduction

Powder technology has been used as an industrial fabrication technology. For example, a metal powder combine with the binder or solvent, a conductive paste is achieved. Moreover, the conductive paste using the nanometer order metal powder realizes the low temperature fired. On the other hand, not only the metal material but also a ceramic material uses the powder technology. The ceramic material is used for various fields. The most general product is a dinnerware. In addition, examples of being used as vehicle parts have also been reported because it is a high-temperature-tolerant material and it has a chemical resistance [1, 2]. Particularly, the ceramic material is paid attention as electronic components.

In the electronic components field, a miniaturization technology is an important factor. Communication devices such as a PC or smartphone have desired the miniaturization and a high functionalization. To miniaturize a device body, the miniature integrated components and the miniature control circuit are required. By realizing the miniature control system, many components and the large battery can set in the miniature communication devices. Moreover, the miniaturization of the control systems possible a low-loss system because circuits wire that connects to each electronic components become short length.

To achieve the miniature control system, the ceramic material is used for the integrated circuit (IC) packaging [3] and the miniature electronic components. The fine ceramic has some electronic characteristics. Ferrite ceramic shows magnetic characteristic, $BaTiO_3$ is ferroelectric ceramic, and Pb (ZrTi) O_3 is used as the piezoelectric ceramic. These ceramic materials support the miniaturization of passive components [4–8].

The conventional fabrication process of the ceramic passive components is the sheet process of the multi-layer ceramic technology [9]. The ceramic components are formed through a firing process. However, the fired ceramic is hard material and it is difficult for any processing. Therefore, it forms the ceramic sheet that is the mixture of the ceramic powder, a binder, and organic solvents, in the first step. The circuit wire patterns are printed on these sheets. After that, the printed sheets are stacked and laminated. In this process, the circuit patterns require a connection between an upper layer and a lower layer. The connection pattern is achieved by forming a through-hole pattern and filling the conductive paste at the printing process. The laminated ceramic sheets are dicing to the designed size, and then, the miniature multi-layer ceramic components are achieved by the firing process. The advantages of this technology are that the three-dimensional (3D) circuit pattern is realized inside the ceramic material, and the electronic characteristics can use for the components.

However, the conventional fabrication process has some problem for further miniaturization. The circuit pattern is formed by a screen printing process in general. This technology shows high productivity, it is suitable for the electronic components. The conductive pattern is made from a conductive paste and it is printed through a mesh pattern. The printed paste requires the leveling time for removing the mesh mark. It is the cause of a deformation of the conductive pattern. In the fine pattern, the adjacent conductors are connected and shorted. And then, to form a fine and high-aspect-ratio pattern is difficult.

Moreover, a high-functional device will be required, and a complex component that has various characteristics will be desired for the miniaturization. To achieve the complex component, the various materials are introduced. However, the conventional research of the different ceramic material pattern is inserting the ceramic sheet [10]. Therefore, it is difficult to form the one point different material pattern.

In this chapter, the photoresist process is proposed. It is possible to form the fine and high-aspect-ratio conductive pattern. The proposed process uses a photolithography process for the

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patterning process, and printing process for the filling process is combined. The exposed and developed photoresist serves as a mask holding the paste. Moreover, this process is applied for forming the different material pattern. The example of the patterning process of the fine conductive pattern and the different ceramic material are shown with the fabricated pattern.

2. Photoresist process

In this chapter, the fabrication process for the ceramic electronic components is proposed. The multilayer ceramic technology is usually used for the fabrication process of the ceramic components, but it has some problems. Therefore, the photoresist process is proposed for the production process. The concept, base process and applications of the photoresist process as is following.

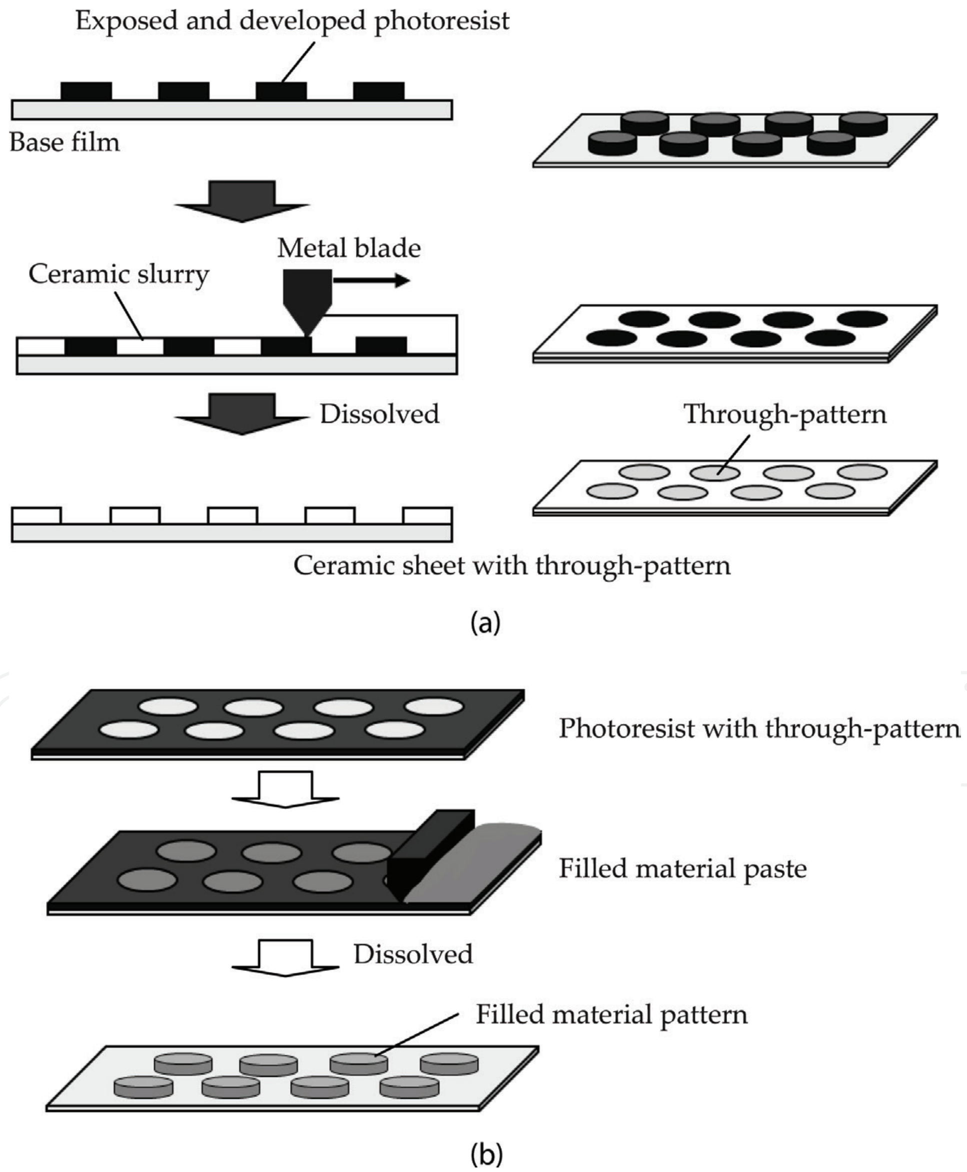

Figure 1. Schematic illustration of photoresist process (a) patterned ceramic sheet process, (b) patterning process.

2.1. Concept and base process of photoresist process

The proposed process uses the photoresist pattern. The first step, the photoresist is exposed for forming the designed pattern. The sacrifice patterns of the photoresist are obtained after development. In a case of a ceramic sheet with a through-pattern, the green sheet of the base material is formed using the doctor blade. At the time, the gap between the blade and the surface of the resist film is adjusted to zero. Therefore, the slurry fills surrounding the sacrifice pattern. Then, the specimens are dried. After the sacrifice pattern is dissolved, the green sheet of the base material with the through-pattern is achieved. To form the pattern, the through-pattern is exposed and developed on the photoresist. The ceramic slurry or conductive paste is filled into the through-pattern, after the dissolving process, the ceramic pattern, or conductive pattern is achieved. **Figure 1** shows the schematic illustration of the process for producing the patterned different material into the green sheet.

A liquid type photoresist and a film type photoresist are chosen for the achieved pattern. For a fine pattern, the liquid type photoresist is used. And then, the film type photoresist is employed for forming the sheet pattern because it realizes the uniform thickness. In this chapter, the different pattern process uses the film type photoresist, and the fine conductive pattern uses the liquid type.

The advantage of this process is that it uses a photolithography process. The photolithography process is used for the IC or microelectromechanical systems (MEMS) sensor fabrication process. Both products have a fine conductive pattern and miniature structure. Therefore, the proposed process that uses the photolithography process is suitable to miniaturize. Moreover, the flexible pattern designing is possible. In addition, the sacrifice resist pattern forms the through-hole pattern. On the other hand, it is a mask pattern that covered on the ceramic sheet. The photoresist mask pattern holds the filling paste as the ceramic slurry or conductive paste. It is possible to form the high-aspect-ratio pattern. These characteristics are used for the production process of the miniature ceramic components.

3. Fine conductive patterning process

The fine conductive pattern is desired for miniature electronic elements, a packaging ceramic, an interposer, and the furthermore. In the conventional process for forming the fine pattern, a vacuum process is used. However, this process has the issue that required the high fabrication cost and the extensive system. Therefore, the researcher focuses on the printed electronics. The screen printing process has been used for the ceramic electronic components already, and then, the gravure printing and ink-jet printing are introduced. However, it is difficult to realize the fine pattern and the low fabrication cost simultaneously only the printing technology. Therefore, the references the line widths of the fine pattern in the production and in the research field are 50 and 10–30 μm, respectively.

The proposed photoresist process can form the fine pattern by the simplified process that combined the photolithography process with the printing process. The fabrication process was base photoresist process (**Figure 1**), and a specific process is shown in **Figure 2**. For the fine pattern, liquid type photoresist was coated on a glass substrate. The designed line and

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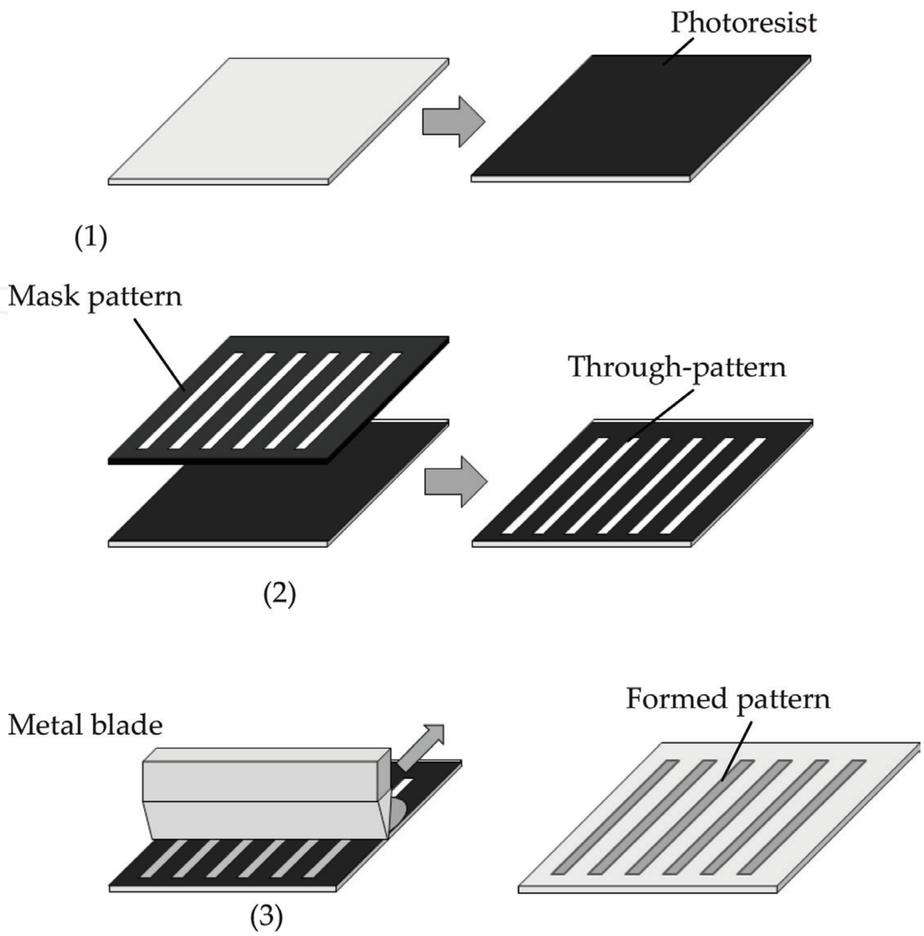

Figure 2. Fabrication process of fine conductive pattern. (1) glass substrate is coated with liquid type photoresist. (2) exposed and developed. (3) filled paste and dissolved.

space were 10 μm, respectively. The conductive paste that combined with microparticle metal powder (under 0.1 μm) was used. The filled conductive paste was dried on the hot plate keeping 60°. After that, the photoresist pattern was removed by remover.

The low viscosity paste was required for form the fine pattern, the photoresist pattern held the paste at the drying process. It can form the high-aspect-ratio pattern. The developed photoresist pattern and the conductive pattern on the glass substrate are shown in **Figures 3** and **4**.

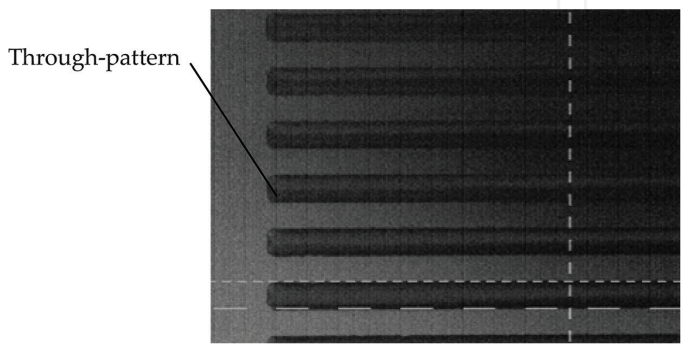

Figure 3. Patterned liquid type photoresist for fine conductive pattern.

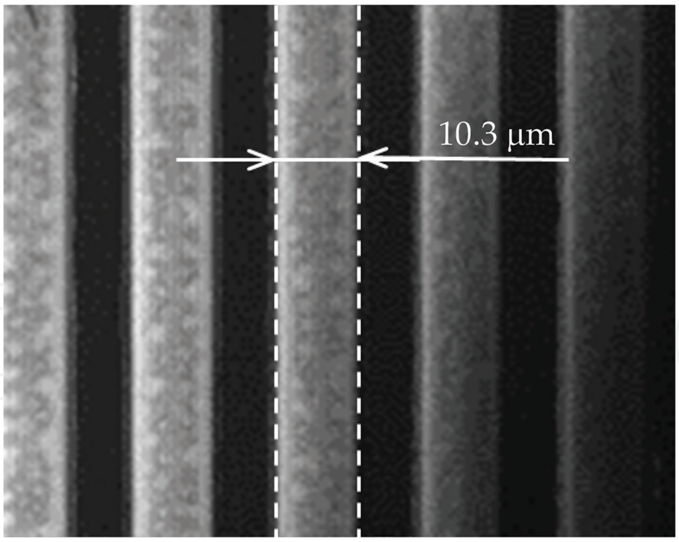

Figure 4. Formed fine conductive pattern.

These images were observed by the confocal microscope. The filling process was metal blade method. A pore and a crack were not shown on the surface of the conductive pattern, and the paste was filled completely. The width and height of the pattern were 10.3 and 1.85°μm, respectively. The fine and high-aspect-ratio pattern was achieved. However, a thin-film conductor around the line pattern was observed. It is a residual conductive paste that was coated on the resist pattern. When the conductive paste was filled, the gap between the metal blade and the resist pattern was occurred. And then, the dried paste on the resist remained with the side of the pattern. The schematic illustration of the mechanism of the residual pattern is shown in **Figure 5**. 3D measuring result of the conductive pattern using same fabrication process is shown in **Figure 6**. The side of the conductor formed the thin pattern. It is solved by adjusting the gap between the blade and the resist surface.

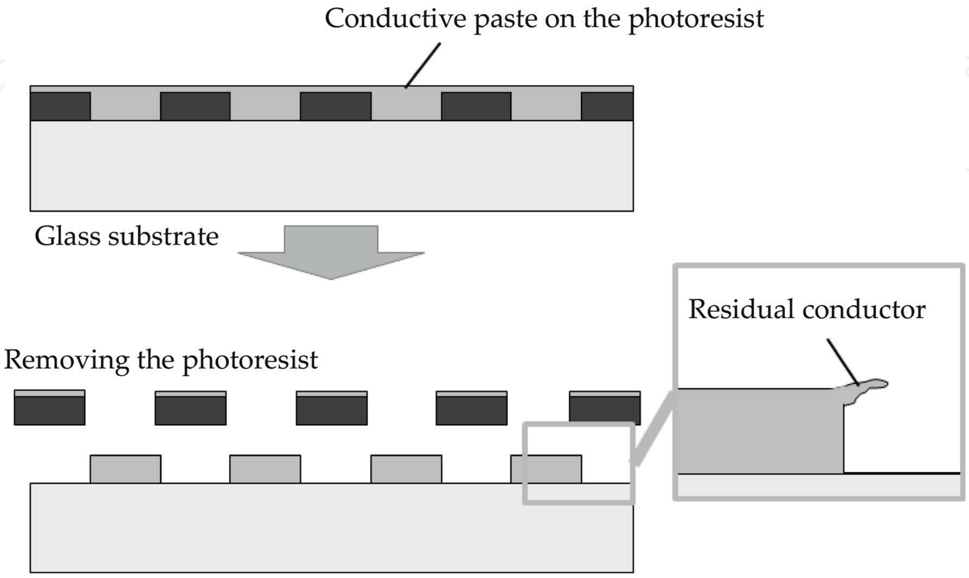

Figure 5. Schematic illustration of mechanism of residual pattern.

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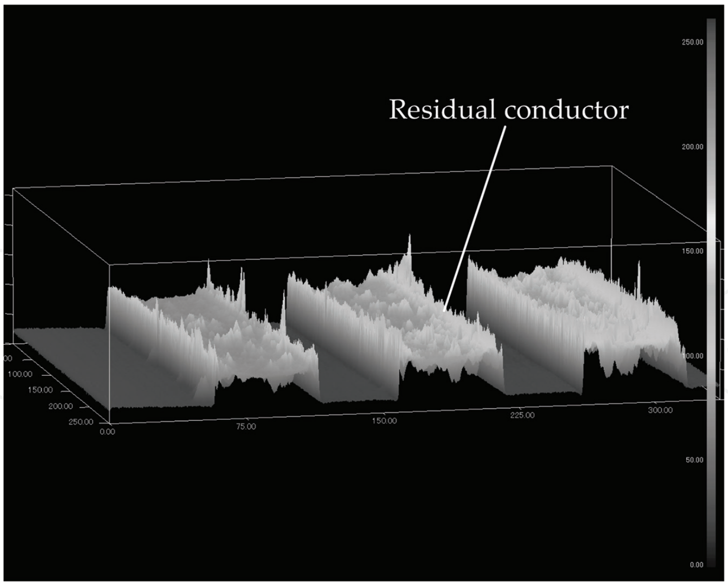

Figure 6. 3D measuring result of conductive pattern by photoresist process.

4. Different material patterning process

The different material patterning process can form some material patterns in one ceramic sheet without bump structure. The ceramic material is often used for the module circuit [11]. When the different ceramic materials are used, the module circuit with some electronic characteristics is realized. When the ceramic material and the conductive material are used, the conductive circuit pattern with high-aspect-ratio pattern and the flat surface pattern. **Figure 7** shows the patterning

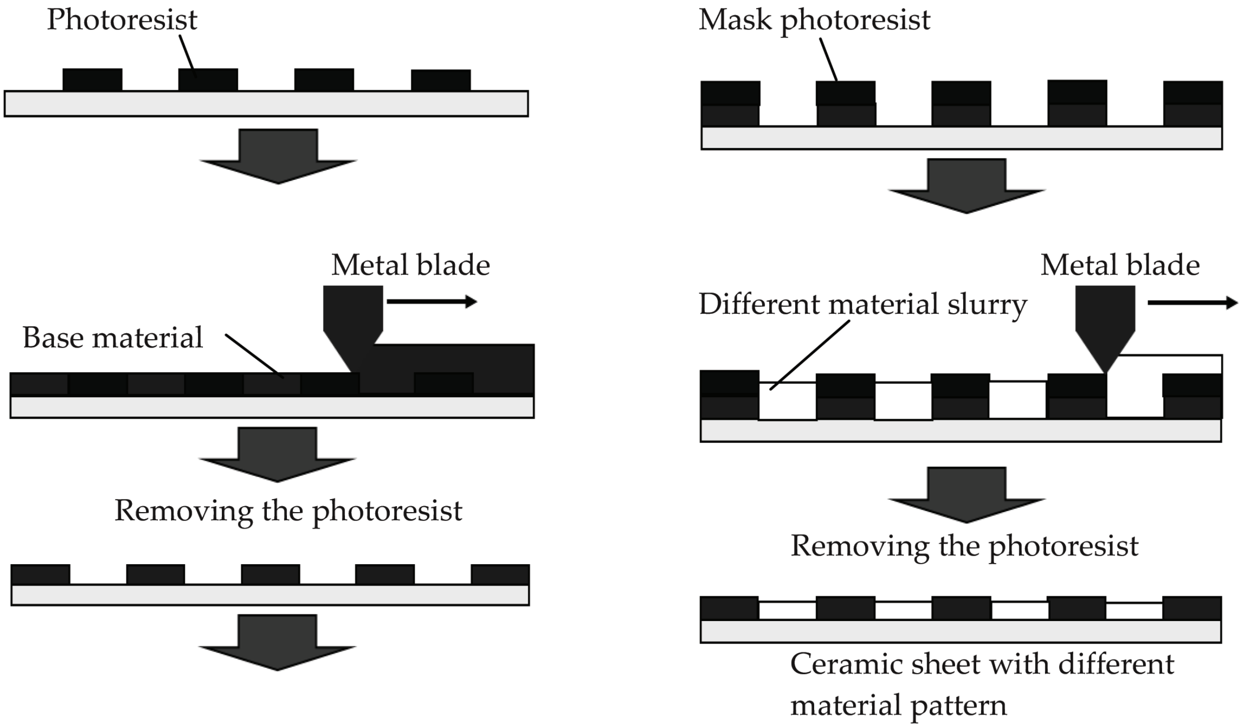

Figure 7. Schematic illustration of photoresist process for different material pattern.

process of the different material pattern. The first material sheet is formed by the base photoresist process. The ceramic sheet with the through-pattern is achieved. Another photoresist is prepared for covering the patterned ceramic sheet. In this time, the film type photoresist is used. The reversal pattern is exposed on the film type photoresist film, and then, the developed film is used for the mask film. The formed mask photoresist is laminated on the ceramic sheet with an alignment pattern. The different ceramic material slurry is filled in the only through-pattern because the first ceramic sheet is covered. After drying the sheet and removing the mask photoresist, the ceramic sheet with the patterned different material is achieved.

In the conventional patterning process for the different material, the pattern forms on the ceramic base sheet. **Figure 8** shows the schematic illustration of the conventional different pattern processing. Each material sheet is stacked, and it is difficult to form the different ceramic material pattern in the same ceramic sheet.

The proposed process for the different material pattern will be applied to a multilayer ferrite inductor. In the conventional multilayer ferrite inductor, the minor magnetic loop causes the degradation of the inductance and the Q factor because the ferrite magnetic ceramic covered around the internal conductor. When the nonmagnetic ceramic is inserted between the conductors of each layer, it is possible to suppress the minor magnetic loop. The mechanism of the minor loop and suppressing pattern is shown in **Figure 9**. The image of the minor loop suppressing multilayer inductor is shown in **Figure 10**.

Examples of the designed different material pattern with the photoresist process are shown in **Figure 11**. This design includes the different ceramic material pattern. The base material was the magnetic material and the patterned material was nonmagnetic material. The film type photoresist was used to form a thick pattern. The thickness of the photoresist film for the through-pattern was 90 μm and the mask film was 35 μm, respectively. The photoresist films were attached to the poly ethylene terephthalate (PET) carrier film.

The co-fired NiCuZn ferrite was used for the magnetic material. The start materials of the ferrite powder were NiO, ZnO, CuO, and Fe_2O_3 and the molecular ratio was 8.8–32–10–49.2, respectively. The particle diameter of ferrite powder was about 300 nm. low-temperature co-fired

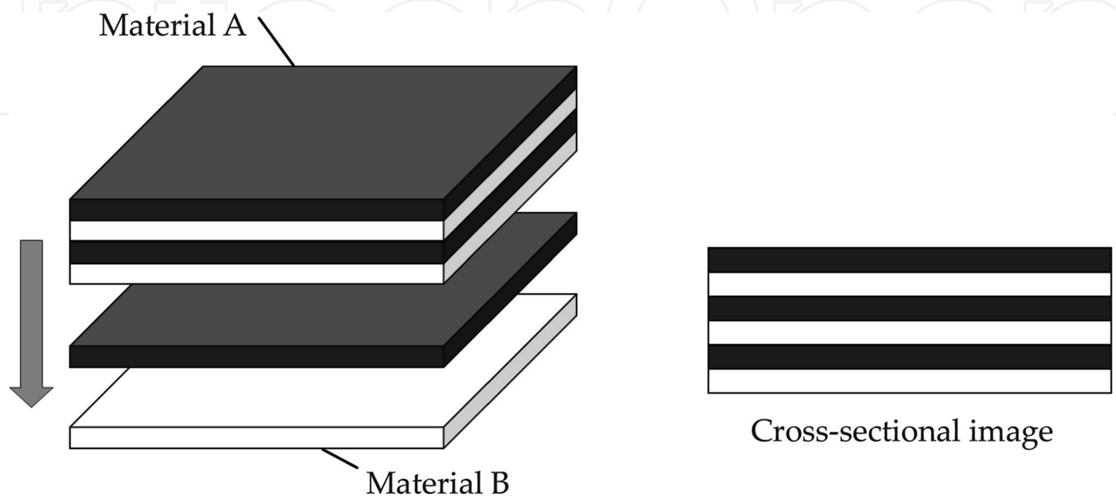

Figure 8. Conventional process to introduce a different ceramic material.

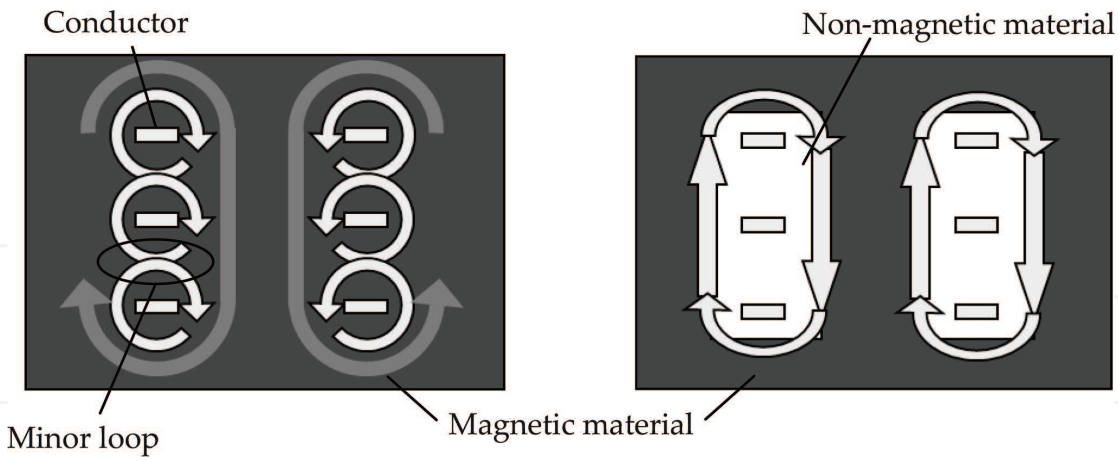

Figure 9. Mechanism of minor loop and suppressing pattern.

ceramic (LTCC) is mixed powder of a glass and an alumina ceramic, and it was used for the nonmagnetic pattern. The composite weight ratio of the glass powder and the alumina powder in the glass alumina composite material was 63 and 37. The glass powder was composed of $SrO-B_2O_3-Al_2O_3-SiO_2$. The particle diameter of LTCC powder 1 μm. The ceramic slurry of ferrite and LTCC was the mixture of the organic solvents and some additives. The composite material and composite weight ratio of each ceramic are shown in **Table 1**.

The microscope image of the fabricated LTCC pattern is shown in **Figure 12**. The complex pattern was shaped, and the different material slurry filled completely.

To achieve the suppressing inductor, the conductive pattern was formed by the photoresist process on the LTCC as the nonmagnetic material pattern. The fabrication process is shown

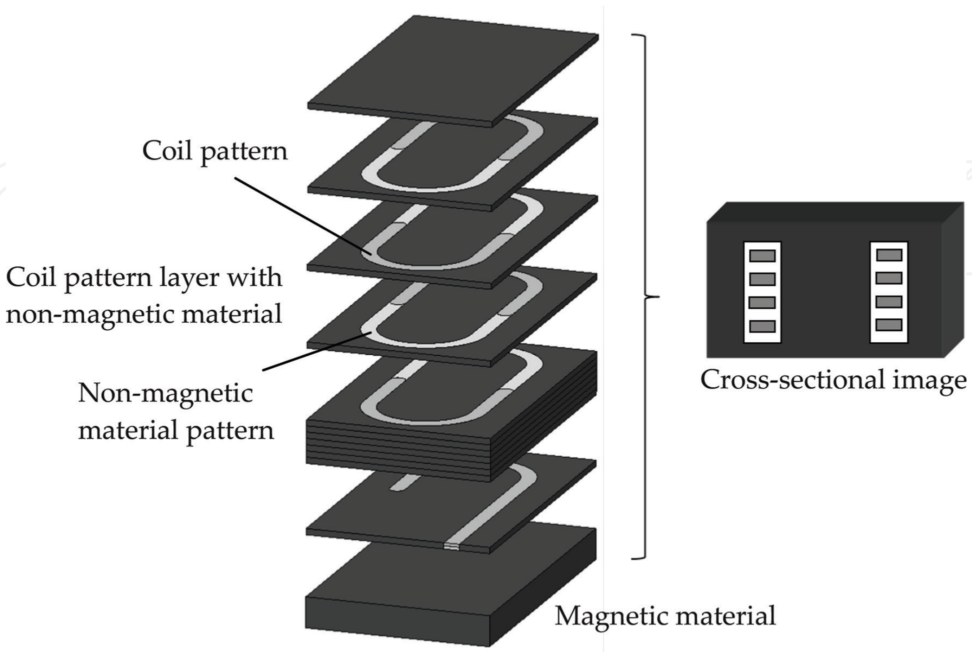

Figure 10. Image of minor loop suppressing multilayer ceramic inductor.

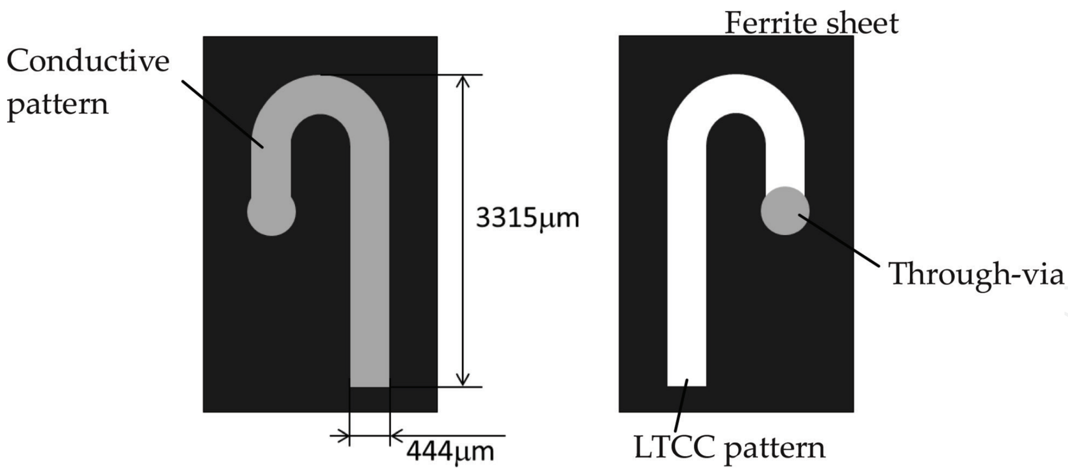

Figure 11. Designed different material patterns.

Material	Ferrite	LTCC
Ceramic powder	100	100
Binder	7	5
Dispersing agent	5	2.9
Plasticizer	1	1.3
Toluene	23	23
Xylene	23	23
Isopropyl alcohol	23	23

Table 1. Composition weight ratio of ceramic slurry.

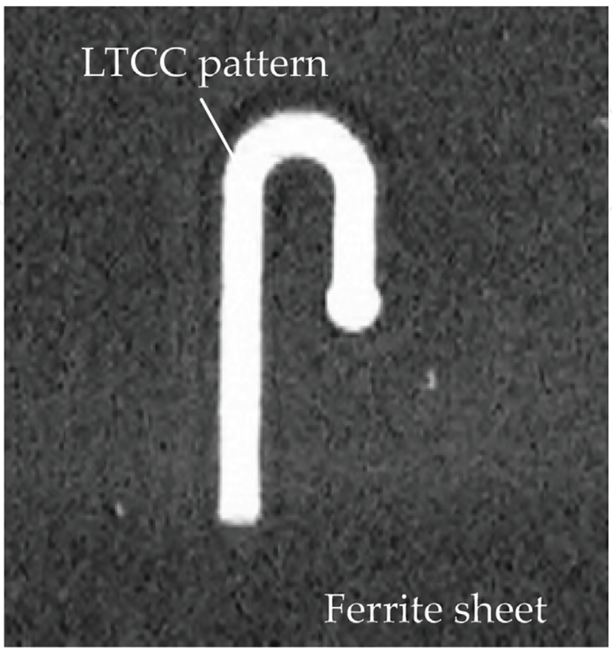

Figure 12. Microscope image of fabricated LTCC patterns on ferrite ceramic sheet.

in **Figure 13**. In this process, the through-hole to connect the circuit pattern on each layer was formed mechanically. The microscope image of the formed ceramic sheet is shown in **Figure 14**. The conductive pattern was formed on the LTCC pattern, and the through-hole was achieved by filling the conductive paste. By this result, the two different material patterns were formed on the ferrite sheet. However, the LTCC pattern is observed around the conductive pattern.

For the different material patterning process, the viscosity of the material slurry and the shrinking process are an important factor. **Figure 15** shows the cross-sectional image of the ferrite sheet by the microscope, and the round bump is observed around the edge of through-pattern. It is because of the surface tensions of the slurry. The proposed process requires the drying process the filled slurry was shrunk during the drying and peeling off the photoresist film. In this time, the edge part formed the round bump shape. It is easy to peel the resist pattern, but the thickness of the dried sheet or patterns become a nonflat pattern. By this reason, the LTCC pattern between the conductor and the ferrite pattern was formed. It is required that the viscosity is adjusted for form a clear pattern. **Figure 16** shows a schematic illustration of the shrinking process.

Moreover, the thickness of the mask photoresist influences the surface of the fabricated pattern. In this case, a thin film resist was 15 μm, and a thick film resist was 35 μm. The cross-sectional image of the fabricated patterns by the scanning electron microscope is shown in **Figure 17(a)** and **(b)**.

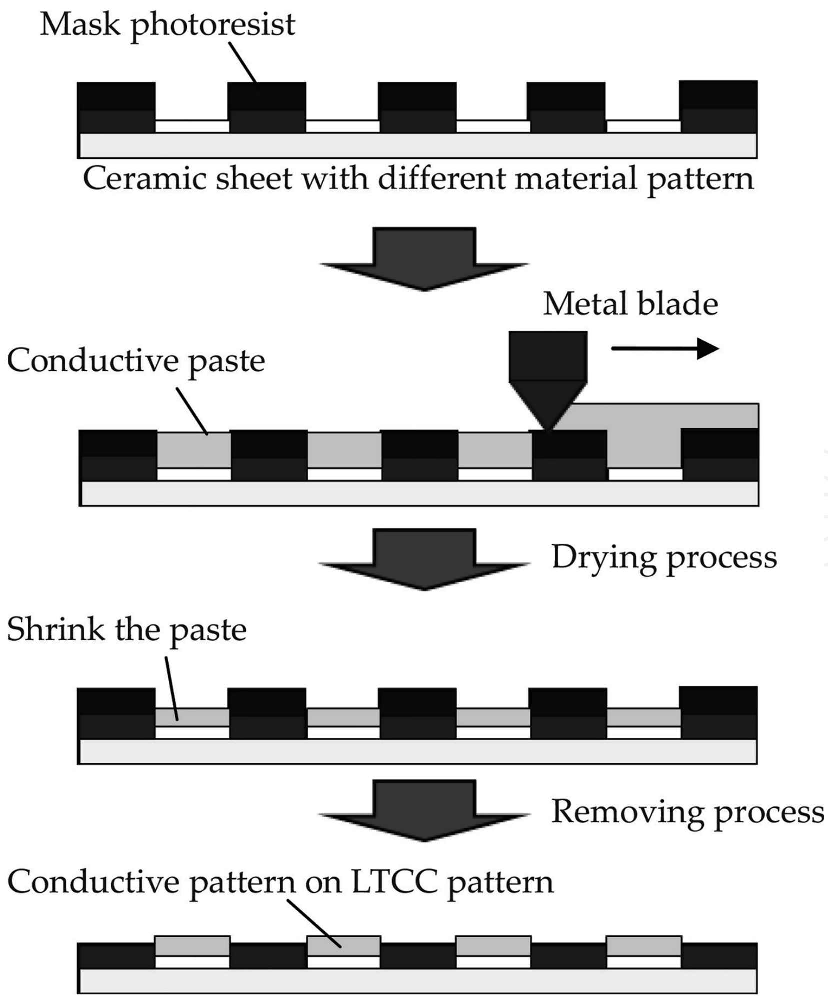

Figure 13. Fabrication process of filling conductive paste.

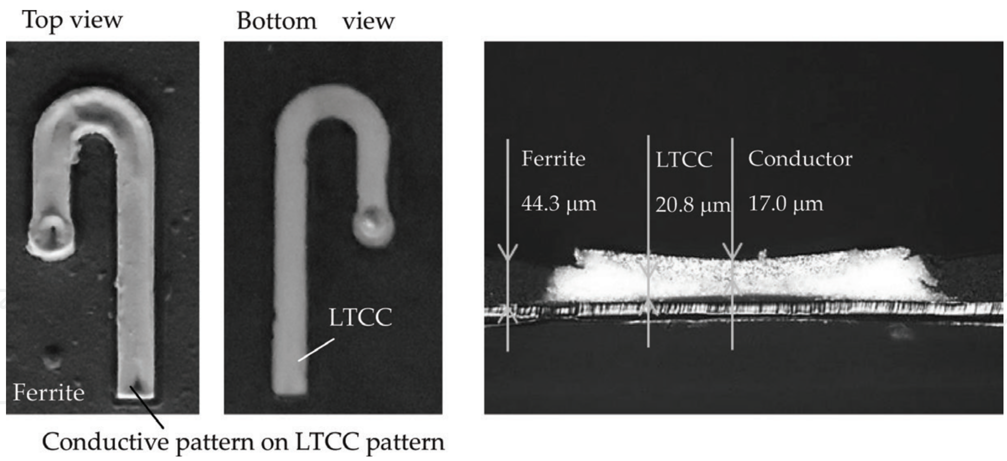

Figure 14. Microscope image of formed ferrite sheet with conductive pattern and LTCC pattern.

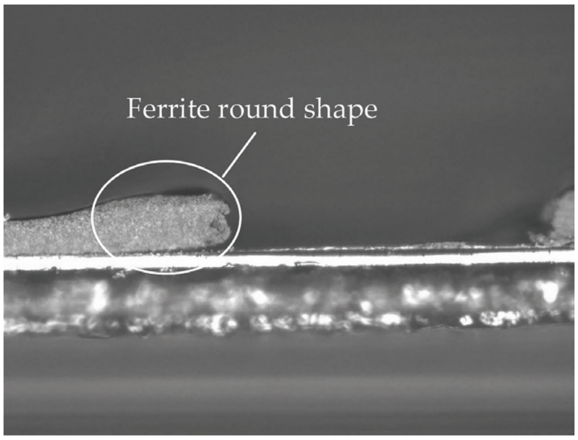

Figure 15. Cross-sectional image of fabricated ferrite sheet with through-pattern by microscope.

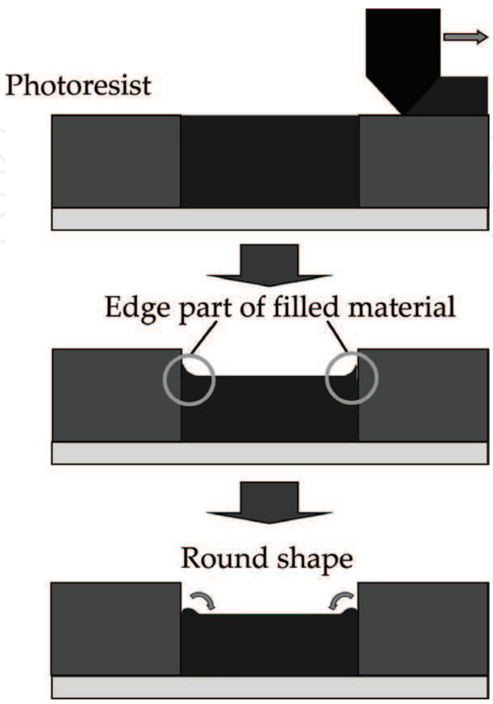

Figure 16. Schematic illustration of the shrinking process.

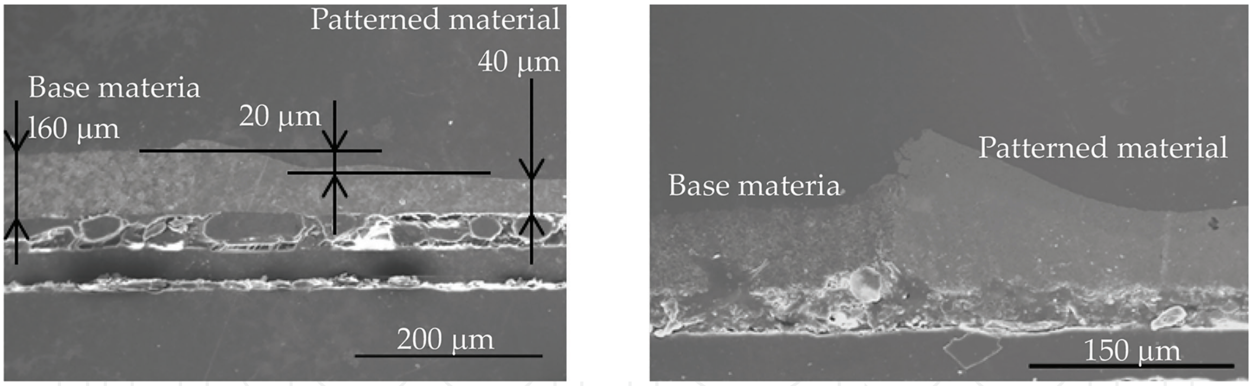

Figure 17. Cross-sectional image using each thickness mask photoresist film (a) 15 μm mask film, (b) 35 μm mask film.

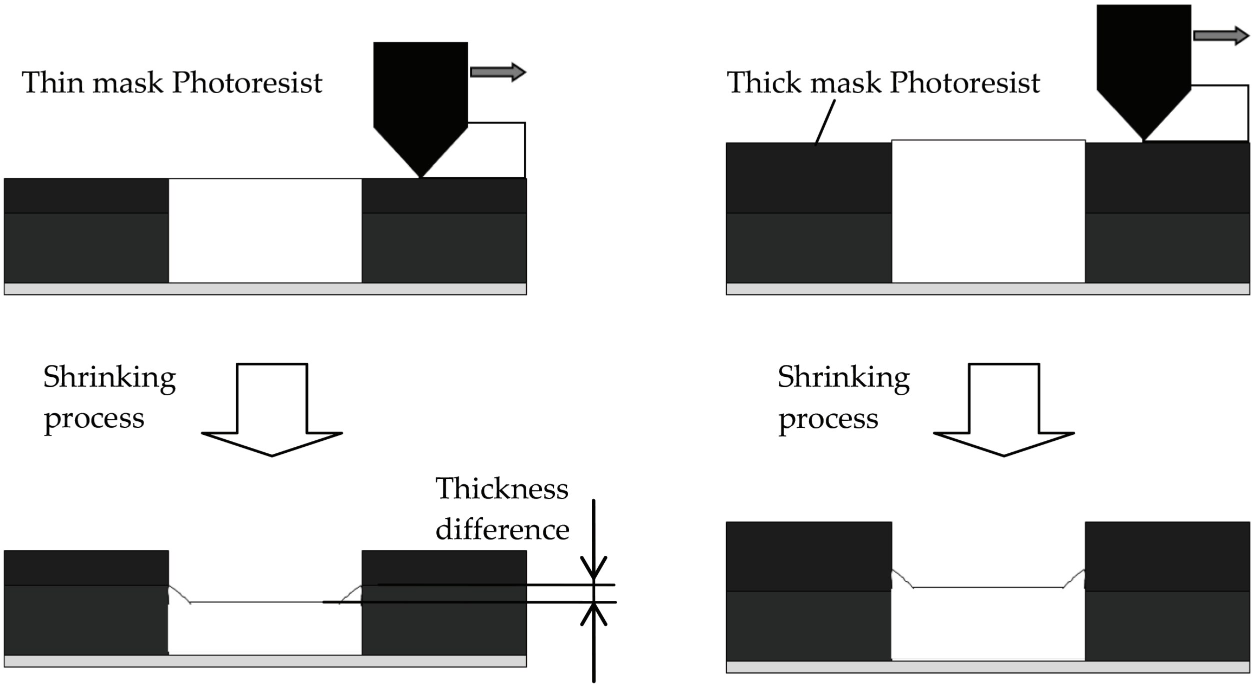

Figure 18. Schematic illustration of mechanism of the different thickness.

The result of using the thin mask resist showed the distance between the LTCC pattern surface and the ferrite pattern surface, and it was 20 μm. On the other hand, the flat surface of the different materials pattern was achieved by using the thick mask resist. The formed pattern showed the shrinking, the higher thickness than the base layer is required to hold the large volume of the filler material. The mechanism of the different thickness is shown in **Figure 18**.

5. Conclusions

In this chapter, the photoresist process was proposed. The proposed process is combined with the photolithography process and the printing process. The fine pattern for the conductor was formed by the photolithography process, because it is usually used for the production process of the IC. The printing process was used for the filling process as the conductive paste and the different material pattern.

The examples of the patterning process and the fabricated pattern were shown. In the conductor pattern, the fine pattern was formed, and the line width and thickness were 10.3 and 1.85 μm, respectively. The proposed process held the filled conductive pattern the high-aspect-ratio pattern was achieved. In the ceramic pattern, the ferrite ceramic sheet that had the LTCC pattern was achieved. It was realized by using the photoresist for the mask pattern. The fabricated pattern shaped complex pattern, and the LTCC was filled into the through-pattern on the ferrite sheet completely. Moreover, the conductive paste was filled with the LTCC pattern, and then, the ceramic sheet that had three different materials was achieved. By using the proposed process, it is possible to achieve the miniature multilayer ceramic inductor that suppresses the minor loop.

However, the patterning process combining the photoresist and material slurry showed some issues. The fabricated fine pattern was observed the thin-film conductor at the line edge. The fabricated different material pattern showed the round pattern. These problems can be solved by adjusting the viscosity and the composite ratio of the material slurry. In addition, the optimization of the type and thickness of the photoresist is required.

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