# 폴리머의 레이저 어블레이션 시 발생하는 Surface Debris의 제거공정 개발

## Elimination of Surface Debris On Laser Ablation of Polymer

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### I. 서 론

The laser fabrication technique is a clean, safe, and convenient process for the manufacturing of microelectromechanical systems (MEMS) devices, especially in contrast to other technologies such as chemical etching, the deposition process, and lithography [1]. In particular, the advantage of applying an excimer laser is that its nonthermal effects make it suitable for machining polymer [2, 3]. The use of a pulsed excimer laser for the ablation of polymers, in general, and of polyimide, in particular, has attracted considerable attention in recent years because polyimide film is widely used as a substrate for flexible printed circuits, motor slot liners, transformer and capacitor insulators, dielectric layers in multi-chip modules, micro-and nanoelectromechanical systems [4].

In order to explain the reaction mechanism between an excimer laser beam and polymer, the photochemical bond-breaking theory and the thermal reaction theory have been introduced [5]. In any polymeric system, the decomposition and ablation is predominantly photochemical, being caused by the excitation of chemical bonds to energy levels that are above the dissociation energy. The fragmented debris is finally ejected explosively by the scission of bonds [6]. In the case ofthe ablation of polyimide, the debris is composed of a soot-like graphite network on the surface of the organic polymer, whereas the gas products are carbon oxides, benzene, HCN, and elemental carbon [6, 7, 8].

The debris problem is a serious defect because carbon particles function not only conductor in microelectronic components but also dust in mechanical systems. That is, surface debris reduces the chemical, mechanical, and electronic precision of products. Thus, the process of eliminating the surface debris has typically done by ablating polyimide in a helium, oxygen [9], and vacuum [7] environment. However, there is no perfect process for removing surface debris.

#### Ⅱ. 실험방법

Figure 1 shows the geometry and dimensions of the workpiece that we used for inducing the surface debris with a KrF excimer laser (LightDeck OPTEC S.A.). The laser was used under the following conditions: the power was 3.1 J/cm², the repetition ratio was 200 and number of pulses per hole was 700. The mask projected rectangular beam (50x300 µm) in the image plane was irradiated in zigzags as illustrated in Fig. 1. In our experimental approach, we subjected polyimide films (Kapton<sup>TM</sup>, 75 µm thick) to an ambient atmosphere under normal conditions of temperature and pressure for excimer laser ablation.

Figure 2 shows SEM photos of the distributed surface debris after the laser ablation of the polyimide. From Fig. 2a, we can see that the surface debris is broadly distributed around the ablated patterns. The surface debris between the ablated patterns has a multilayer because the rectangular pattern was ablated consecutively and a shockwave peel-off previously formed a debris layer, as shown in Fig. 2b. In contrast, the surface debris below the rectangular pattern has a single layer, as shown in Fig. 2c.

Figure 3 shows the surface debris after ultrasonic cleaning (Elma TRANSSONIC 890/H) in an acetone bath and an alcohol bath. Ultrasonic cleaning for one hour failed to completely remove the surface debris of the ablated polyimide, as shown in Fig. 2. We therefore conclude that the adhesive force between the surface debris and the polyimide too strong to allow its removal by wet cleaning with an ultrasonic device and with acetone and alcohol. To remove the surface debris, we consequently used the black ink found in whiteboard markers (STAEDTLER 488 51-9).

Figure 4 shows the debris-free process of laser ablation with black ink. The five-step process, which is briefly illustrated in Fig. 4, makes a microstructure without surface debris. From Fig. 4b, we can seen that polyimide is pasted with the black ink, which, in general, comprises a solvent (propyl-alcohol), a pigment (carbon-black), a dispersing agent, and a release agent. The ink layer, which is shown in Fig. 4c, can endure the plasma and shockwave of the ablation mechanism. In this process, the numerous pieces of carbon debris are ejected from the polyimide by a scission of the bonds. Figure 4d shows that the ejected carbon debris is distributed around an ablated rectangular pattern and combined with the black ink because of the adhesive force of the dispersing agent. Consequently, as shown in Fig. 4e, the combination of surface debris and black ink can be stripped by adhesive tape (3M Scotch Magic<sup>TM</sup> Tape). On the other hand, the ultrasonic cleaning in an alcohol bath can detach the combination of surface debris and black ink from the polyimide because the solvent in the black ink is propyl-alcohol.

#### Ⅲ. 실험 결과 및 고찰

Figure 5 shows SEM photos of the distributed surface debris after laser ablation of the ink-pasted polyimideunder the same laser conditions as shown in Fig. 2. In the case of the

ink-pasted polyimide, the surface debris has a small distribution in comparison with the ablated surface of the bare polyimide film, as shown in Fig. 2a. We found no multilayer between the ablated patterns in Fig. 5b. However, we easily found a multilayer in the case of the ablation of the bare polyimide, as shown in Fig. 2b. The reason for these phenomenons is as follows: the dispersing agent of the black ink enabled the surface debris and solid pigment to be uniformly immersed in the ink layer. Moreover, the adhesive force of the dispersing agent against solid particles and the thermal stability of the carbon black both protected the ink layer from the shockwave and the heat of the plasma. Figure 5c shows evidence of the combined reaction between the dispersing agent and the surface debris.

Figure 6 shows SEM photos after the cleaning process of the ablated polyimide. In the tape cleaning process, we can detach the surface debris or the black ink or both after attaching adhesive tape to the ablated product. As shown in Fig. 6a and Fig. 6b, the surface debris of the ablated film without the black ink pasting remained on the substrate; however, the surface debris of ablated film after the black ink pasting was eliminated perfectly by the adhesive tape due to the function of release agent.

On the other hand, by using alcohol for the wet cleaning, we effectively removed the combination of debris and black ink because the ink was alcohol-based. As shown in Fig. 6c, the wet cleaning could remove the surface debris and the black ink with the aid of an ultrasonic cleaning in a solvent bath that was an alcohol environment. Thus, the wet cleaning process is beneficial in the case of manufacturing fragile products or complex three-dimensional patterns.

#### Ⅳ. 결 론

The purpose of this research was to develop a process for eliminating the surface debris generated by the laser ablation of polyimide. After black ink is pasted to the polyimide, the surface debris caused by the laser ablation immerses into the ink layer because of the function of the dispersing agent. Furthermore, the function of the release agents helps to divide into the ink layer and the polyimide because pigments cannot be attached to dry polyimide film. We can then use adhesive tape or an alcohol-based solvent to eliminate the surface debris on the ablated polyimide with the ink layer.

Aside from being found in polyimide, surface debris by laser ablation can be found in other polymers such as metal and glass. Therefore, the debris-free process with black ink is useful for the micro-fabrication of various items such as electronic devices, bio-devices, and micro-optic devices that use laser ablation.

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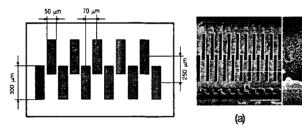


Figure 1. Geometry and dimensions of the workpiece

Figure 2. SEM photos of the distributed surface debris after laser ablation of polyimide: (a) laser ablated pattern of polyimide, (b) the surface debris between the rectangular pattern, and (c) the surface debris below the rectangular pattern

(b)

(c)

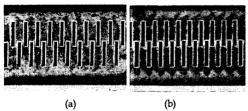


Figure 3. SEM photos of the distributed surface debris after ultrasonic cleaning for one hour (a) in an acetone bath and (b) in an alcohol bath

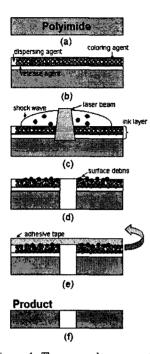


Figure 4. The removal process of the surface debris: (a) polyimide film, (b) black ink pasting process, (c) laser ablation process of ink-pasted film, (d) the combined surface debris, and (e) the stripping of the surface debris with black ink

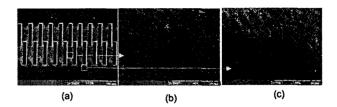


Figure 5. SEM photos after laser ablation of ink-pasted polyimide: (a) a laser ablated pattern of ink-pasted polyimide, (b) surface debris between patterned holes, and (c) surface debris below patterned holes

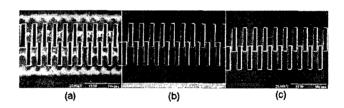


Figure 6. SEM photos after the cleaning process of the ablated polyimide: (a) adhesive tape cleaning of the ablated polyimide without the ink pasting process, (b) adhesive tape cleaning of the ablated polyimide after the ink pasting process, and (c) wet cleaning of the ablated polyimide after the ink pasting process