Femtosecond Laser Direct Joining of Copper with Polyethylene Terephthalate

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We succeeded in directly joining Cu with polyethylene terephthalate (PET) using femtosecond laser pulses, which were focused through PET onto the Cu surface which was thermally adhered to PET prior to the laser irradiation. A maximum tensile strength of 5.5 MPa was obtained. X-ray photoelectron spectroscopic spectra of the fractured surface suggested the chemical bonding of Cu with PET. TEM images of the sample showed no voids or no cracks. They also showed the mechanical mixture of Cu with PET around the interface of the joint. We suggest that the ultrashort pulse width of the laser enables the direct joining of these dissimilar materials, thereby avoiding graphitization of the polymeric material. [doi:10.2320/matertrans.MD201229]

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1. Introduction

Nano-/microjoining of dissimilar materials is becoming one of the most important technologies for the assembly of nano/micro electro mechanical systems (NEMS/MEMS).^{1,2)} NEMS/MEMS comprise various kinds of materials such as metals, ceramics, glasses, polymers, which have quite different physical properties. The direct-joining method, which produces only a small heat-affected zone in the materials, is essential for achieving highly precise assemblies of these dissimilar materials without using glues and with no strain.

Femtosecond laser pulse is one of the most promising tools for realizing nano-/microjoining.³⁾ The intensity of the femtosecond laser pulse, which is equivalent to energy per unit time and unit area and is proportional to the square of the electric field intensity, is extremely high even with low energy because the pulse width is extremely short. Therefore, the laser pulse can melt the material and create only a small heat-affected zone.⁴⁾ The femtosecond laser pulse can also melt and vaporize the transparent materials owing to nonlinear phenomena such as multiphoton absorption.^{5,6)} These unique features of the femtosecond laser pulse play a key role to realize the direct microwelding of similar/dissimilar glass substrates,^{7–11)} glass with semiconductor,¹²⁾ and glass with metal.¹³⁾

Despite the fact that both the polymers and metals are important electronic materials in microelectronics field,¹⁴⁾ there are no reports on their direct microjoining. Although their macrojoining has been reported, this method seems hardly applicable to NEMS/MEMS because bubbles with tens of micrometers are formed in the polymer after the processing.¹⁵⁾ Here we report the direct joining of a metal with a polymer using femtosecond laser pulse, aiming to apply this method in microelectronics. We chose Cu as the metal and polyethylene terephthalate (PET) as the polymer, both of which are important in microelectronics. PET becomes graphitized during conventional thermal processing because the thermal decomposition point of PET is much

lower than the melting point of Cu, which prevents these materials from joining. However, we succeeded in joining these materials using an ultrashort pulsed laser, thus avoiding the graphitization of PET. We investigated the influence of the laser conditions on the state of the joint, such as the strength, the graphitization of PET, and the microstructure, and we propose a process for the joining.

2. Experimental Method

The mirror-finished surface of pure copper (99.99%) was heated to 100°C on a hot plate and then adhered to PET, which had a thickness of 1 mm and was softened by the heat from Cu. The oxide layer on Cu was removed by hydrochloric acid just before the adhesion. Table 1 shows the thermal properties of Cu and PET. Femtosecond laser pulses (Spectra-Physics Spitfire) with a wavelength of 800 nm, a pulse width of 130 fs and a pulse energy of 10 μJ were focused using a plano-convex lens with a focal length of 70 mm through PET onto the Cu surface, as shown in Fig. 1. We defocused 600 μm from the focal point, resulting in the diameter of the ablated region of around 34 μm. We here define the distance between pulses in the *x*-direction as the pulse-to-pulse distance d_x and those in the *y*-direction as the line-to-line distance d_y . We varied d_x by changing the laser scanning speed from 1 to 10 mm/s. Both d_x and d_y were taken as 1, 30, 50, 100 and 150 μm.

After the laser irradiation, we performed tensile test of the joint with the strain rate of 1 mm/min. The joint strength σ was estimated by dividing the tensile force measured by laser scanning area of 25 mm². After the tensile test, the C content in the fractured surface and the chemical bonding

Table 1 Thermal properties of Cu and PET.

Sample	Glass transition point $T_g/^\circ\text{C}$	Melting point $T_m/^\circ\text{C}$	Thermal decomposition point $T_d/^\circ\text{C}$	Boiling point $T_b/^\circ\text{C}$	Coefficient of thermal expansion $\alpha/^\circ\text{C}^{-1}$
Cu	—	1083	—	2570	1.7×10^{-5}
PET	76	255	408	—	1.5×10^{-5}

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Fig. 1 Schematic illustration of setup for the femtosecond laser joining of Cu with PET.

Fig. 2 Tensile strength of the Cu-PET joints fabricated by varying the pulse-to-pulse distance (d_x) and line-to-line distances (d_y) of the femtosecond laser pulses.

Fig. 3 (a) SEM image and (b) EPMA mapping result of C on Cu irradiated with the pulse-to-pulse distance (d_x) of 1 μm and the line-to-line distance (d_y) of 50 μm . (c) SEM image and (d) EPMA mapping result of C on Cu irradiated with the d_x of 100 μm and the d_y of 100 μm .

state of the residual material on the Cu surface were analyzed using an electron probe micro-analyzer (EPMA, JEOL JXA-8700) and X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-850M), respectively. The microstructure of the joined interface was observed using transmission electron microscopy (TEM, JEOL JEM-2100F) after being thinned by an Ar-ion beam (JEOL Ion Slicer EM-09100IS).

3. Results and Discussion

3.1 Joint strength

Figure 2 shows the results of the tensile tests of the femtosecond laser-joined samples. A d_x of 100 μm and a d_y of 100 μm resulted in a maximum joint strength of 5.5 MPa. Samples fabricated under conditions that are not described in

Fig. 4 XPS spectra of (a) and (d) C1s, (b) and (e) O1s and (c) and (f) Cu2p_{3/2} for the samples which was failed to join (a)–(c) and with the maximum strength (d)–(f).

this figure were failed to join. When either d_x or d_y is more than 100 μm , the number of pulses was not enough to create a strong joint. On the other hand, when either of them is less than 100 μm , excess number of pulses reduced the joint strength because of the graphitization of PET, as described later in this paper.

3.2 C Content in the fractured surface

We analyzed the C content in the fractured surface of the joints that showed the maximum strength fabricated with a d_x of 100 μm and a d_y of 100 μm . We also analyzed samples which were fabricated with a d_x of 1 μm and a d_y of 50 μm and failed to join. Figure 3 shows the SEM images and EPMA mapping data of C on Cu. In the case of the sample which was failed to join, the trajectory of the laser pulses, as shown in Fig. 3(a), corresponds to the region in

which the C content is higher, as shown in Fig. 3(b). On the other hand, in the case of the joint with maximum strength, no trajectory of the laser pulses and no localized higher C content in the SEM image [Fig. 3(c)] and the EPMA mapping [Fig. 3(d)], respectively, are observed. C is distributed uniformly on the Cu surface for the maximum-strength joint.

3.3 Chemical bonding state of the residual material on Cu

The chemical bonding state of the residual material on Cu after the tensile test was analyzed using XPS. Figure 4 shows the XPS spectra of C1s, O1s and Cu2p_{3/2} for the sample which was failed to join (a)–(c) and for those with the maximum strength (d)–(f), all of which were fabricated under the same conditions described in Section 3.2. In

addition, we compared the spectra after etching by using an Ar-ion beam with exposure times of 1 and 24 s.

For the sample that failed to join, the spectra of C1s and O1s with no ion etching (shown in Figs. 4(a) and 4(b)), exhibited the fine structure usually exhibited by PET.¹⁶⁾ As shown in the figures, the heights of the peaks of both the C–O and C=O bonds decreased after Ar-ion etching of 1 and 24 s, which correspond to the etching depths of approximately 0.1 and 2.4 nm, respectively, whereas the C–H bond remains unchanged. The height of the Cu2p_{3/2} peak increased after Ar-ion etching, as shown in Fig. 4(c). This indicates more graphitization in PET nearer the interface, while the fractured surface retains PET. Therefore, we suggest that an excess number of laser pulses may induce graphitization of PET, resulting in failure to join or poor strength.

For the sample that showed the maximum strength, both the C1s peak and the O1s peak almost disappeared after the Ar-ion etching of 1 s, whereas the fractured surface exhibited PET alone, as shown in Fig. 4(d). The Cu₂O peak,¹⁷⁾ which is not shown for the sample which was failed to join, was present before and after the Ar-ion etching of 1 s, as shown in Fig. 4(e), which indicates that Cu₂O coexisted with PET (Figs. 4(d) and 4(e)). This Cu₂O is not the original oxide layer that existed before the joining because the Cu₂O peak does not appear for the sample which was failed to join. Therefore, we suggest that Cu reacted with O in PET, indicating at the chemical bonding of Cu with PET.

3.4 Microstructure in the joint

Figure 5(a) shows the TEM image of the joint with the maximum strength. There were no voids or cracks in PET, which indicates that PET was not graphitized. The Cu surface became rough, indicating that mechanical bonding was achieved in this region. Figure 5(b) shows the diffraction pattern of nanoparticles within the area enclosed by the solid circle. These nanoparticles, identified as Cu particles, are scattered throughout PET. The roughened surface of Cu and existence of Cu nanoparticles in PET indicate that the Cu was ablated and melted within this region where the temperature was much higher than the normal thermal decomposition point of PET.

3.5 Process of the joining

Based on the experimental results, we propose a joining process as follows. A femtosecond laser pulse passes through PET and is absorbed on the Cu surface that is adhered to PET. Local heating of Cu occurs because of the short-pulse width of the laser, causing melting and moderate ablation of Cu within the restricted region. This melting roughens the Cu surface, whereas the ablation ejects the Cu nanoparticles into PET. Thermal decomposition of the material is prevented because of the extremely short temporal duration of the higher temperature state in PET, which might be shorter than the temporal duration needed to complete the thermal decomposition. Mechanical joining is eventually achieved between Cu and PET, thus avoiding the graphitization of PET.

XPS spectra show the coexistence of Cu₂O with PET, which suggests the chemical bonding of Cu with O in PET. *In-situ* analysis of the dynamics of this reaction using

Fig. 5 (a) TEM image of the joint showing the maximum strength. (b) Diffraction pattern of the nanoparticles (identified as Cu) within the area enclosed by the solid circle.

electron^{18–20)} or X-ray^{21–23)} pulses with both of the femtosecond temporal resolution and nano/micrometer spatial resolution will make clear the detailed mechanism of this process.

4. Conclusion

In summary, we succeeded in directly joining Cu and PET materials with quite different thermal properties, using femtosecond laser pulses, thus avoiding the graphitization of PET, despite the fact that Cu would be melted and ablated. The ultrashort pulse width of the laser plays a key role in achieving the joining. Thus, femtosecond laser direct joining of dissimilar materials will open up a new way for the assembly of NEMS/MEMS in the field of nano-/microjoining.

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