Colour marking of transparent materials by laser-induced plasma-assisted ablation (LIPAA)

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Abstract. We demonstrate colour marking of a transparent material using laser-induced plasma-assisted ablation (LIPAA) system. After the LIPAA process, metal thin film is deposited on the surface of the ablated groove. This feature is applied to RGB (red, green and blue) colour marking by using specific metal targets. The metal targets, for instance, are Pb3O4 for red, Cr2O3 for green and [Cu(C32H15ClN8)] for blue colour marking. Additionally, adhesion of the metal thin film deposited on the processed groove by various experimental conditions is investigated.

1. Introduction
Laser visible marking technology has been widely applied in a variety of commercial and personal products such as glass, aerospace and electronics. Although this technique meets demands of various industries, it is often characterized by low contrast between the mark and the background. Also, a very limited colour-marking palette is available: most often black and shades of gray, and more recently, limited shades of colour.

On the other hand, the laser-induced plasma-assisted ablation (LIPAA) process, in which a single conventional pulsed laser is used, defines an alternative process for high-quality, high-speed and high-visibility marking of transparent materials like glass and polymer [1-5]. The high visibility results from the metal deposition on the ablated groove. In this process, the substrate must be transparent to the wavelength of the laser beam, so that the laser beam, which is transmitted through the substrate, irradiates a metal target placed behind the substrate at a distance from 0 to a few hundred µm as shown in Fig. 1. For laser fluence above the ablation threshold for the target and below the damage threshold for the substrate, the plasma generated from the target surface propagates forwards to the rear side of the substrate at high speed. Then, the absorption of the laser beam is generated, resulting in high-quality ablation at the rear surface of the glass substrate by the incident laser beam [8]. In addition to etching of the substrate, the metal thin film is deposited on the ablated region. This process can be performed in a single pulse irradiation when an adequate pulse width laser (~ several tens ns) and an adequate distance between the target and the substrate (less than several hundreds µm) are used. Colours can be varied by changing the metal target. In this paper, we report on RGB (red, green and
blue) and other colour marking by the LIPAA using various metal targets. In addition, adhesion of the metal thin film deposited on the abated groove is investigated.

2. Experimental

2.1. Colour marking

Standard silicate glass (MATSUNAMI GLASS IND, thickness, 1.0 mm) was used as the transparent material in this experiment. Before irradiation, the substrate was ultrasonically cleaned with ethanol and then rinsed with deionized (DI) water for 5 min. For the colour marking experiment, metallic compounds such as Pb3O4, Cr2O3, and [Cu(C32H15ClN8)] and elemental metals such as Al and Cu plates were used as the target. The target-to-substrate distance, the laser fluence and the scanning speed were set at 0 µm, 6.8 J/cm2 and 30 mm/min, respectively.

2.2. Adhesion of the metal thin film

Adhesion of the metal thin film deposited on the ablated groove by the LIPAA process was investigated by the Scotch tape test. For adhesion evaluation, three different light sources of a near-IR femtosecond laser (775 nm, 180 fs, 1 kHz), a Q-switched Nd:YAG laser (532 nm, 500 ps, 1 kHz) and a Q-switched Nd:YVO4 laser (532 nm, 9 ns, 10 kHz) were used. In this experiment, the ablation rate was held constant at 2 nm/pulse for each laser type and a Cu plate was used as the target. After exposure, the processed glass substrates were ultrasonically cleaned with ethanol to remove metallic residue around the ablated groove. Finally, the Scotch tape test was carried out for adhesion evaluation of the substrate prepared by different pulse width lasers and the target-to-substrate distances.

3. Result and discussion

3.1. Colour marking

It has been well known that metal thin film deposits on grooves formed by the LIPAA process [1-5]. As one of applications of the metal deposition, colour marking by the LIPAA has been proposed by Hong et al [5]. However, variation of colour marking such as RGB colours has not yet been achieved. For industrial applications, RGB and some other colour marking by the LIPAA process is attractive.

Figure 2 (a) shows colour marking by the LIPAA process using the different targets. Line and space patterns were fabricated by the LIPAA process. The targets are Pb3O4 for red, [Cu(C32H15ClN8)] for blue, Cr2O3 for green, Al for white and Cu for brown. It is clear that well-defined colour marking was formed on the glass substrate. The printed colours almost correspond to those of the targets. The tone of colour marking can be adjusted by changing the target-to-substrate distance. Figure 2 (b) shows control of colour tone when using the Cu plate as the target. The target-to-substrate distance was increased in 5 µm steps from 5 µm to 250 µm with the line and space patterns written from left to
right side. The focal point was always set at the rear side of the substrate for each target-to-substrate distance. Therefore, the laser fluence at the metal target changed as the target-to-substrate distance changed. From Fig. 2 (b), colour marking turns pale as the target-to-substrate distance increases. The reason for pale tone in colour with increase of the target-to-substrate distance is the loss of kinetic energy of species in the plasma during the flight in air. Thus, fewer species with high energy in the plasma can reach the glass substrate, resulting in a decrease of the deposited film thickness, thereby, yielding the pale tone.

In the conventional method, a special treatment of the transparent material is necessary for the colour marking. In this method, laser marks are made directly on the material in a multi-step process [6,7]. On the other hand, the LIPAA can perform the colour marking by a single-step process; thereby great advantages are obvious for practical applications.

3.2. Adhesion of the metal thin film

Strong adhesion of the metal thin film deposited on the glass is important for practical applications. In order to clarify adhesion of the metal thin film and to optimize the process parameters, dependence of adhesion on the pulse width was investigated as shown in Fig. 3 (a). From Fig. 3 (a), adhesion of the Cu film becomes stronger as the pulse width increases. In cases of using the fs laser with the pulse width of 180 fs and the Nd:YAG laser with the pulse width of 500 ps, most of the Cu film was easily peeled off by the tape test. In particular, most of the film was removed for the 180 fs laser. The Cu film was remained attached only when 9-ns pulse duration was used for the Nd:YVO4 laser. The reason for the strong adhesion with 9-ns pulses is due to longer interaction time between the laser beam and the plasma.

The laser-induced plasma is generated from the metal target at several hundreds ps after the laser irradiation [8]. Therefore, the laser pulse is over long before the plasma generation for the 180 fs laser. In this case, no ablation can take place by a single pulse irradiation on the glass substrate due to the late arrival of the plasma long after the laser beam has passed. The metal thin film is only deposited on the substrate after the laser pulse irradiation. For the 500 ps laser, the interaction time between the laser beam and the plasma is very short, so that the most of the metal thin film is deposited after the laser pulse. On the other hand, the longer pulse width (e.g. 9 ns) laser irradiates the rear surface of the substrate for during a relatively long portion of the plasma attack. As a result, ablation at the rear side of the substrate takes place due to the interaction between the laser beam and the plasma. In addition to ablation, a molten region was found at the ablated surface suggesting that metal atoms should be incorporated here. Finally, a graded composite structure composed of metal thin film, metal atom doped glass and glass substrate is defined. Such a structure would be responsible for the high adhesion.

Figure 3 (b) shows the dependence of adhesion of the Cu film on the target-to-substrate distance. For this experiment, Nd:YVO4 laser with 9 ns pulse width was used as the light source. For the target-
to-substrate distance of 0 µm, the tape test revealed that adhesion of the Cu film is strong. However, for the target-to-substrate distance of 100 µm, most of the Cu film was peeled off by the tape test. The decrease of adhesion by increasing the target-to-substrate distance is also explained by the shorter interaction time between the laser beam and the plasma.

![Image]

Figure 3. (a) Dependence of adhesion on the pulse width. The ablation rate was set at 2 nm/pulse. Target-to-substrate distance was set at 30 µm. (b) Dependence of adhesion on the target-to-substrate distance. The laser fluence and the scanning speed are set at 6.8 J/cm² and 30 mm/min, respectively.

4. Conclusion

RGB colour marking of glass by the laser-induced plasma-assisted ablation (LIPAA) was achieved by using various metal-containing targets. Targets were Pb₃O₄ for red, Cr₂O₃ for green and [Cu(C₃₂H₁₅ClN₈)] for blue colour marking. The dependence of metal film adhesion on the pulse width and the target-to-substrate distance suggests that strong adhesion can be achieved by irradiation with ns duration laser pulses at a shorter target-to-substrate distance. At long interaction time between the laser beam and the plasma is necessary at the glass substrate for strong adhesion of the metal thin film. Thus, we conclude that colour marking by LIPAA using a conventional ns pulse width laser has great potential for high-quality and cost-effective marking in the laser-marking industry.

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