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Laser writing of 2D data matrices in glass

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Abstract

The labeling of glass is an important processing step for the pharmaceutical industry that allows tracing and controlling of their products. The current techniques, i.e. color bar codes or labels, have several disadvantages, e.g. lack of permanency and susceptibility for tampering, limited adhesion and problems during sterilization. Direct laser engraving on the surface is a very flexible method that allows permanent marking of vials with 2D data matrix codes. The feasibility of this technique for an industrial environment was proven by determining the influence of key parameters such as laser fluence, pulse number and laser wavelength. The visual appearance of the data matrix can be controlled by varying the pulse number, laser fluence and marking precision.

Keywords: Laser marking; Pharmaceutical glass vials; 2D data matrix

1. Introduction

Glass vials for pharmaceutical purposes have to be labeled to allow tracing and controlling along the distribution line by the producing company. This is currently performed by colored lines, bar codes or by printed labels. These techniques, however, have several disadvantages, e.g. the ink and/or the glue of the label have limited or no adhesion on many surfaces such as silicone and they are not resistant to sterilization. By directly engraving the data matrix on the surface, it is possible to mark almost any material using the appropriate laser parameters such as wavelength and laser energy.

A 2D data matrix offers the possibility to store a clearly defined amount of product information on a relatively small area. As an example, the applied 10×10 matrix corresponds to 6 digits, while a 16×16 matrix contains already 24 digits. The matrix can be read by a commercial optical read-out device.

There are basically three ways to write the matrix on the glass. The first method uses more than one laser marking (e.g. a 3×3 array) to create one pixel of the whole matrix, as shown in Fig. 1. The second method utilizes only one laser marking for each pixel of the matrix, as shown in Fig. 2. The samples were moved relative to the laser beam for both methods during the initial proof of principle experiments. The third possibility applies a mask to mark the complete matrix with one or several laser pulses without moving the sample.

Each method has its own advantages and disadvantages. The multi-spot marking is less susceptible to errors by processing, e.g. the matrix is still readable with missing pixels. The disadvantage of this technique is the high number of necessary laser marks (e.g. 4860 pulses for the 10×10 matrix shown in Fig. 1), which can be overcome by the application of high repetition rate lasers (e.g. kHz). The single-mark method needs much less time since the number of marks is smaller (486 vs. 54 markings for the examples seen in Figs. 1 and 2), but higher laser fluences are necessary, which may not be obtained for high repetition rate lasers. The last method would be the fastest and is less depending on a high repetition rate lasers, but is less flexible for online changes of the matrix and for each change the mask has to be changed too. Another encountered problem is the necessity to apply very high laser energies and a quite large beam profiles to illuminate the complete mask (e.g. 1.5×3.5 cm^2 beam profile of the ArF laser for a 1×1 cm^2 mask) since the complete beam energy cannot be utilized.

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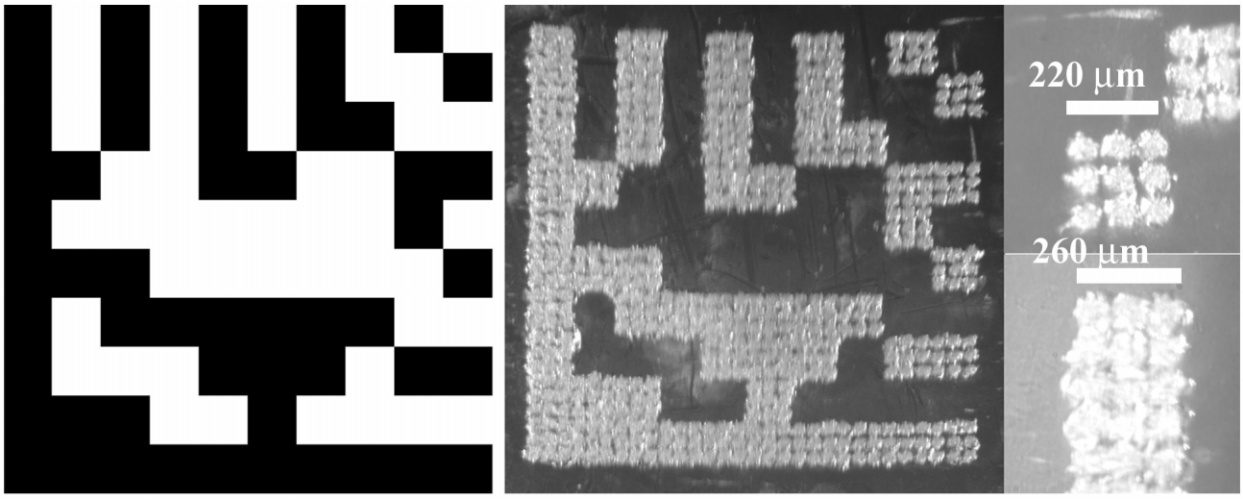

Fig. 1. 10×10 pixel 2D data matrix on clear glass using a 3×3 array for one pixel: computer-generated pattern (left), laser marking (middle), magnification (right). The matrix (1180×1180 mm^2) was created with an irradiation wavelength of 266 nm, with a fluence of 7 J cm^{-2} and 10 pulses.

2. Experimental

The third and fourth harmonics (266 and 355 nm) of an Nd:YAG laser (Quantel Brilliant B) were applied as irradiation wavelengths for the pulse by pulse experiments. An ArF (193 nm) excimer laser (Lambda Physik LPX 300) was utilized for the experiments with the complete mask. The samples were mounted on a computer-controlled XYZ stage and the ablation spots were characterized with a profilometer (Dektak 8000). The samples were cleaned in an ultrasonic bath with methanol, hexane and isopropanol for several minutes prior to the experiments. Experiments were performed with two types of glass (FIOLAX-amber® and FIOLAX-clear® from Schott labeled 'brown' and 'clear') at two different irradiation wavelengths (266 and 355 nm) with different pulse numbers and fluences.

3. Results and discussion

The 'brown' glass samples reveal a high absorption to both irradiation wavelengths and can be marked at both wavelengths. The 'clear' samples, however, are highly transparent at 355 nm (90% for 1.0-mm wall thickness) and rear-side ablation can be observed at fluences below the threshold fluence of the glass. This phenomenon cannot be described as 'normal' ablation, i.e. as a consequence of homogeneous volume absorption of energy and evaporation of heated or decomposed material. Ablation of highly transparent materials can be

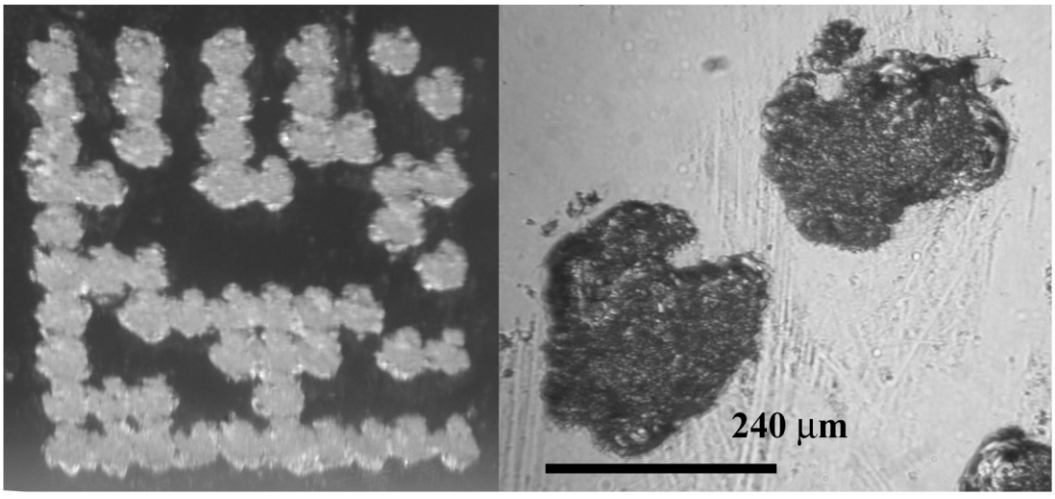

Fig. 2. Two-dimensional data matrix on clear glass using large pixels: complete matrix (left), magnification (right). The matrix was created with an irradiation wavelength of 266 nm, with a fluence of 7 J cm^{-2} and 10 pulses.

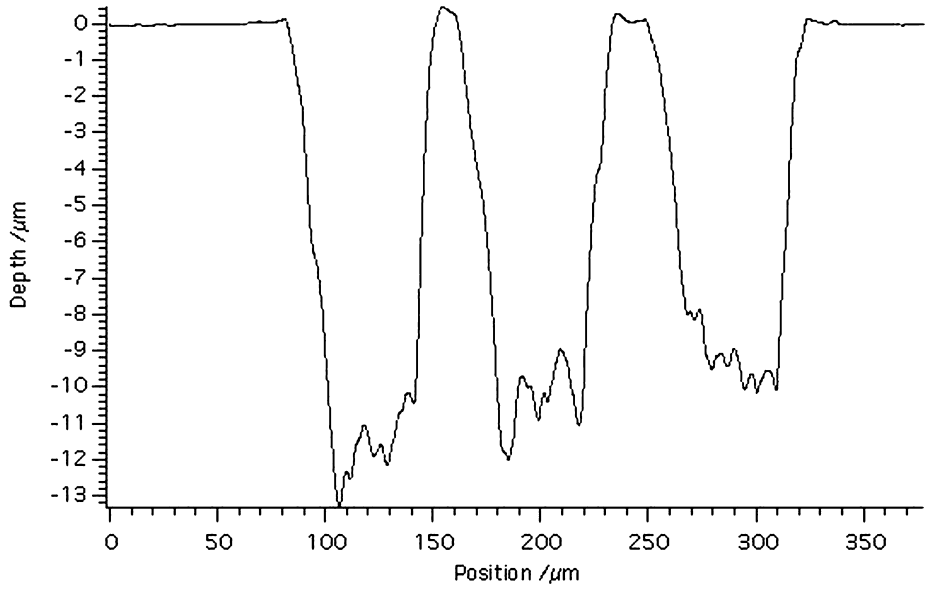

Fig. 3. Depth profile of three distinct markings on clear glass using an irradiation wavelength of 266 nm, a fluence of 5 J cm^{-2} and 5 pulses.

explained by scattering or absorption of radiation at singularities (impurities or other irregularities), which are mainly concentrated at the surface. The threshold fluences for rear-side ablation are much lower than that for front-side ablation, which can be explained by the Fresnel theory [1]. The theory describes that a wave is reflected at the front side with a phase shift of 180°, which results in a destructive interference with the original wave. At the rear side no phase shift occurs, leading to a constructive interference. This phenomenon can be useful for some applications but is clearly not desirable for marking of closed vials, which may contain photosensitive compounds. The possible reaction and the contamination from the glass ablation are absolutely a 'killer' criterion for marking of pharmaceutical products.

Rear-side ablation does not occur for any applied fluence at the irradiation wavelength of 266 nm. The transmission at this wavelength, according to Schott, is almost 0%, resulting exclusively in front-side ablation. The transmission of the glass vials during marking was measured by photometric measurements [2] and is in the range of 0.043%. This proves that the observed rear-side ablation is due to constructive interference.

The threshold for laser marking is much lower for the dark than that for the clear glass samples, due to the much higher absorption coefficients at both wavelengths. Experiments on flat samples revealed threshold fluences between 0.9 and 1.2 J cm^{-2} for dark samples and between 2.1 and 2.6 J cm^{-2} for clear samples. Measurements for clear glass vials showed a threshold fluence between 4.7 and 5.0 J cm^{-2} and no visible cracks were detected for fluences up to 20 J cm^{-2}. The flat glass samples were prepared from a cylindrical tubing by melting and stretching and were much thicker than the glass vials (1.0–1.5 mm vs. 0.5 mm for the vials). The lower transmission and large number of imperfections (e.g. air bubbles and waviness) are probably causing the lower threshold for the flat glass samples. Very rough surfaces were detected on the bottom of the ablation crater, as shown in Fig. 3. The uneven crater bottom is, however, beneficial for our application since the optical detection of the resulting matrix depends on the amount of light scattered by the marked surface. Incubation pulses were necessary for marking both glass types within the applied fluence range (4–15 J cm^{-2}) at the irradiation wavelength of 266 nm. A similar observation has already been reported for XeCl excimer (308 nm) and CO_2 (10.6 μm) laser irradiation of various optical and technical glasses (e.g. vitreous silica, borosilicate glass, float glass, lead glass) [3].

3.1. Influence of marking parameters

There are several parameters that allow changing the general appearance (size, visibility, resolution) of the final marking. The laser fluence, pulse number, pixel spacing and resolution, i.e. the usage of one shot per pixel of the whole matrix vs. several shots per pixel (e.g. nine) have the most pronounced influence. The crater depth and size can be controlled by changing the laser fluence and the pulse number. Deeper and larger craters result generally in a higher surface roughness, which produces a better scattering of the light and thus a better visibility of the marking. The same is true for the pixel spacing, when several markings are used for one pixel. Overlapping pixels are better visible than clearly distinct pixels because they result in an increase

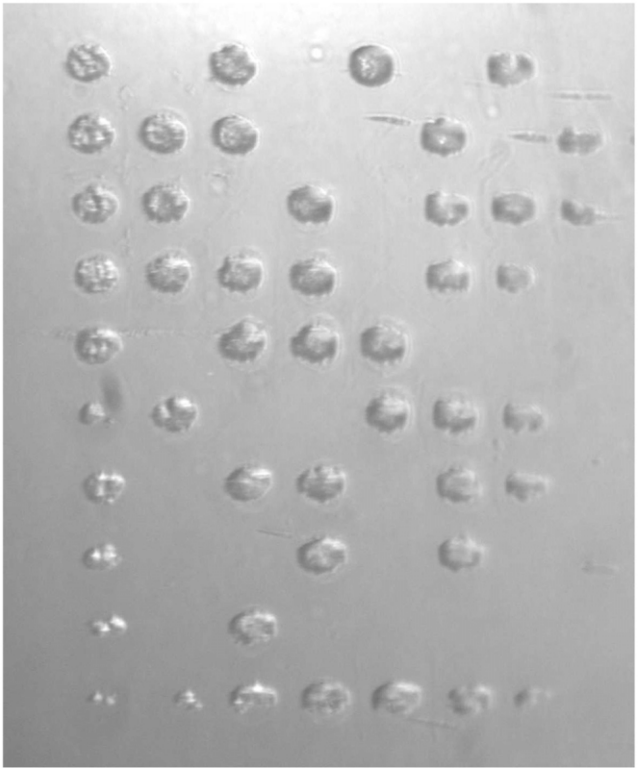

Fig. 4. Example of a matrix on clear glass marked with an irradiation wavelength of 193 nm using a complete mask. The fluence was 950 mJ cm^{-2}, and 200 pulses were needed.

of the light scattering surface of the matrix. Adjusting the degree of overlap allows to create markings that are only visible during illumination under a certain angle. The main differences between the first two techniques (single-mark per pixel vs. multi-mark) are the processing speed of the laser marking and the susceptibility to errors. The industrial requirements for speed make it necessary to apply a high repetition rate laser. The fabrication and filling velocity of pharmaceutical vials is in the range of 200 vials per minute. A laser with a repetition rate in the range of several kilohertz allows the marking of more than one vial per second, even for the marking method with multiple markings per pixel. The main disadvantage of utilizing a single-mark per pulse is the necessity for much higher laser energies at a constant matrix size. The necessary energy is at the moment not available from commercial lasers with a high repetition rate.

A totally different approach for marking is the application of a mask that contains the complete matrix instead of writing the matrix pixel by pixel. This technique could in principle result in a much shorter processing time, depending on the possible repetition rate and necessary pulse number. The disadvantage of this method is a decrease in flexibility as for every encoding a new mask has to be prepared before marking. Experiments were carried out with an ArF excimer laser (193 nm), which has a large beam profile (1.5×3.5 cm^2) and with a simple projection setup. The resulting matrix, however, revealed another disadvantage of this method. The mask does not allow the utilization of the high laser energy in the beam, resulting in the necessity to apply even higher laser energies than that for the previous method. A 1×1 cm^2 mask with 58 holes was applied which constitute only 26% of the mask surface. This results in a dramatic reduction of the applied laser energy as only 26% of the laser beam profile is applied. The laser pulse energy of 950 mJ cm^{-2} was therefore not high enough and an incomplete marking of the matrix was observed (Fig. 4). The incomplete etching results from the fact that the energy beam profile is not perfectly homogeneously 'flat top' and the applicable laser fluence is close to the marking threshold. Some areas of the mask were therefore illuminated with a lower laser power, which results in fluences below the threshold fluence. The maximum fluence that could be reached with the mask and the applied laser was 950 mJ cm^{-2}, and more than 50 pulses were necessary to create a visible marking.

4. Conclusion

The aim of the project was to determine the engineering parameters for a new laser marking setup for the pharmaceutical industry. Laser marking can be used to create a permanent marking for tracing products by adjusting various parameters such as laser wavelength, fluence and pulse numbers. Creating one pixel by several marking revealed a great flexibility to change the optical appearance of the resulting matrix, such as the encoded text and the visibility, a high reproducibility and low failure number. The results of this project were utilized to design a complete prototype laser marking setup for the pharmaceutical industry.

Acknowledgments

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