Laser etching of glass substrates by 1064 nm laser irradiation

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Abstract Glass substrates are transparent to 1064 nm laser irradiation and cannot be etched directly by 1064 nm pulsed laser. By placing the glass substrate in contact with copper sulphate (CuSO₄) solution and irradiating 1064 nm laser light through the glass, etching of the glass is observed on the downside of the glass, the contact side with the copper sulphate solution. The etching mechanism is proposed to be a two-step process. The first step is the deposition of copper from copper sulphate solution upon 1064 nm irradiation. It is followed by the absorption of the 1064 nm laser irradiation by the deposited copper, resulting in the etching of the glass. Using this technique, 1 mm thick soda lime glass slides can be cut through. Furthermore, various arbitrary shapes can be diced out from glass substrates. The formation of copper deposits is observed and characterized.

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1 Introduction

Glass has various useful properties, such as transparency to light of a wide spectrum of frequencies, and being durable and inert to many chemicals. These properties make glass an excellent candidate for a wide range of applications, from display panels to biomedical detection. However, glass is a fragile material which cracks under excessive thermal and mechanical stresses. Various glass processing techniques [1–9] have been developed and investigated. For direct laser ablation of glass, the glass has to absorb the laser energy. However, glass is transparent to 1064 nm irradiation and it is therefore difficult to process glass using a laser at 1064 nm. However, such lasers have a much higher and stable power output at 1064 nm wavelength compared to other lasers at higher harmonics and excimer UV lasers, and yet they are more affordable. Thus much lower cost can be achieved by using lasers at 1064 nm to process the glass.

In this work, aqueous copper (II) sulphate solution is used as the absorbing layer to absorb the irradiating 1064 nm laser light. This approach eliminates the need for toxic chemicals in processing the glass [4–7]. Copper salt solution has been used in various works [10–13] for the deposition of copper by laser irradiation. Various mechanisms for the deposition of copper have been proposed, including heat assisted reduction of copper due to photothermal effects [10–12]. In our work, upon continuous irradiation of the laser light, we managed to cut through glass of 1 mm thickness. The etching mechanism is proposed to be a two-step process. Copper is first deposited upon laser irradiation owing to the absorption of the laser light by the copper sulphate solution. The copper deposited on the glass surface subsequently absorbs the irradiating 1064 nm laser radiation and results in the etching of the glass. Using this technique, various arbitrary shapes can be diced out from the glass substrates.

2 Experimental

A Nd:YVO₄ laser at 1064 nm wavelength was used as an irradiating source. The output power used was ~ 12 W at a repetition rate of 20 kHz. A galvanometer with a Ftheta lens was used to control the scanning direction of the laser through Scanlab software. The scanning speed used is 400 mm/s. The calculated fluence is estimated to be ~ 2 J/cm² with a spot size $\sim 200 \ \mu m$. The glass substrates used is soda lime microscope glass slides. Copper (II) sulphate (VWR International) solution was prepared by dissolving the powders in de-ionized water to saturation, which is about 30 g/100 ml. The solution was placed in contact with the downside of the glass substrates. Light was irradiated from the front side of the glass and was focused onto the glass-liquid interface, which was then absorbed by the copper sulphate solution at the downside of the glass. Figure 1 shows the schematic experimental setup. Glasses A and B were placed in contact with each other. The glass to be etched is glass B. Glass A acts as a cover layer to prevent outflow of copper sulphate solution once the glass B was etched through. The desired shape or pattern was controlled and scanned repeatedly across the glass using the software and the galvonometer. The chemical composition of the deposited materials on the glass after the laser processing was analyzed by X-ray photoelectron spectroscopy (XPS), Quantera SXM from PHI. The absorption spectrum of the copper sulphate solution was measured by a UV-Vis system UVPC spectrophotometer.

3 Results and discussion

The absorption spectrum of the copper sulphate solution was measured and it was found that the copper sulphate solution absorbs strongly at 1064 nm wavelength. Light irradiating from glass A goes through almost unabsorbed but gets strongly absorbed by the copper sulphate solution at the focused point under glass B. The absorption of the laser light by the solution causes localized heating at the regions of laser irradiation, initiating the deposition of copper [10-12]onto the glass B surface in contact with the solution. Copper is expected to be deposited onto the downside of the glass by photothermal reduction of the copper sulphate solution. To verify this, XPS analyses were carried out at those specific surfaces to detect whether copper was deposited. Prior to the analysis by XPS, the samples have been washed in deionized water in an ultrasonic bath for 30 minutes to dissolve and remove any copper sulphate crystal residue. Figure 2 shows the wide and narrow band scan XPS results of the surfaces. There are significant copper signals picked up during the XPS scan. The XPS spectrum does not show any sulphur peaks. To determine the electronic state of the copper as well as the other detected elements, narrow band XPS analyses were carried out. From the narrow band XPS analyses (bottom picture), the silicon and oxygen peaks detected are from the composition of quartz. Some of the oxygen detected can also be deduced to be bonded to the carbon detected, which is probably due to environmental organic compounds. The narrow band XPS analysis of copper, which is the element of interest, is shown in the bottom picture of Fig. 2. The binding energy of the $2p_{1/2}$ electrons is at 932.61 eV, and the $2p_{3/2}$ peak is separated from the $2p_{1/2}$ peak by 19.80 eV. This relates to the element copper in the metallic state. From



Height - adjustable Stage



Fig. 2 (*Top*) Wide band XPS analysis of the processed surface. Significant copper signals were picked up, showing the presence of copper on the processed surfaces. (*Bottom*) Narrow band XPS analysis on the ele-

ment copper. The binding energy of the $2p_{1/2}$ electrons is at 932.61 eV, showing the presence of copper. The $2p_{3/2}$ peak is separated from the $2p_{1/2}$ peak by 19.80 eV

the above analyses, it is concluded that after copper sulphate solution has been irradiated with the 1064 nm laser, copper is deposited on the surface of the glass substrate in contact with the solution at the areas processed by the laser.

Figure 3 shows the microscopic view of the glass surfaces processed by 1064 nm laser irradiation. The glass has been scanned in circular paths for 10 times. There is observable material deposition along the line edges, which is attributed to copper from the XPS analyses. In addition, the shiny appearance on the top right corner of the path, with a tint of light brown, is due to the reflection from the deposited copper. The scanned path has a width of ~60 μ m and in the middle of the path, etched crater can be observed. This illustrates that there is interaction between the laser and

the glass to cause the removal of the glass materials. Under normal circumstances, the irradiation of the glass substrates with 1064 nm laser light does not cause the removal of the glass materials. However, in this case, by placing the glass substrates in contact with copper sulphate solution and irradiating the substrates from the front with 1064 nm laser light, copper deposition and glass etching were observed. It clearly demonstrates that the copper sulphate solution plays an important role in the removal of the glass material.

Figure 4 illustrates the proposed mechanism of glass etching by the laser irradiation of 1064 nm light to the copper sulphate solution. During the first pulse, laser light passes through the glass substrate, irradiates it and heats up the CuSO₄ liquid. During the first few nanoseconds of the pulse, the temperature increases by a few hundreds of degrees Celsius. As the pulse ceases, the temperature starts to decrease on a millisecond time scale (Fig. 4a). The initial high temperature causes the $CuSO_4$ to decompose and initiate copper deposition (Fig. 4b). Upon the arrival of the second pulse, one part of the laser energy is absorbed



Fig. 3 Microscopic view of glass B surface in contact with copper sulphate solution after laser irradiation. There is observable material deposition along the line edges

by the CuSO₄ liquid, causing the liquid to heat up again, while the other part of the energy is absorbed by the deposited copper. Upon continuous irradiation, the copper absorbs more energy and heats up (Fig. 4c). At a high laser fluence, the deposited copper can be boiled off, producing a recoil force [9], which then attacks and removes the molten glass material (Fig. 4d), thus producing the etched craters as shown in Fig. 3. Hence, we have a continuous two-step process of copper deposition and subsequent removal of the glass with the assistance of the deposited copper film. This process has the advantage of a continuous supply of copper from the copper sulphate solution, which, in principle, enables the etching process to continue until the whole depth of the glass is etched through.

Using the galvanometer to control the laser scan paths offers greater flexibility to control the path of the laser beam. Various shapes can be designed on the Scanlab software and exact shapes can be scanned out by the laser beam. Employing this capability, various intricate shapes and designs are drawn out in the Scanlab software and used to control the path of the laser. Figure 5 shows various arbitrary shapes diced out from a 1 mm thick glass slide by this method. The top and bottom left pictures show a star and a circle shape that have been diced out from the glass slides. It is observed that the glass slides have remained intact and have





Fig. 5 (*Top* and *bottom left*) Glass substrates with a star and a circle diced out. The glass substrates have remained intact after processing. (*Top right*) Circles having diameters of 2 mm, 5 mm, and 1.5 mm, from *left* to *right*, diced out from the glass substrates. (*Bottom right*) Shapes have been cut out from the glass substrate, showing the star shapes and the alphabet's 'C' and 'G'

not suffered any significant cracking. The top right picture of Fig. 5 shows circles at different diameters diced out from the glass slides. The circles (from left to right) have diameters of 2 mm, 5 mm and 1.5 mm, respectively. The bottom right picture shows some of the shapes diced out from glass slides, the star shape and the alphabet's 'C' and 'G'. Other delicate shapes can also be processed and cut out using this technique as well.

4 Conclusions

Copper sulphate solution is used as the absorbing layer for the etching of the glass substrate. 1064 nm light is irradiated onto the sample from the top and etching occurs on the surface in contact with the copper sulphate solution. It is proposed that the etching process is a continuous twostep process: deposition of copper from the copper sulphate solution on 1064 nm light irradiation, and then subsequent absorption of the laser light by the deposited copper. This causes the melting and removal of the glass materials. XPS analyses confirm the copper deposition after 1064 nm laser irradiation. Using this technique, 1 mm thick glass substrates can be cut through, leaving the bulk glass intact. This technique has the ability to dice out various arbitrarily shaped glass structures.

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