Hybrid Laser Scribing and Chemical Etching Technique using Pulsed Nd^{3+}:YAG Laser to Fabricate Controlled Micro Channel Profile

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Laser scribing is carried out using a Q-switched (Brilliant B, Quantel) Nd^{3+}:YAG laser system to scribe micro channels on copper coated on polyimide film, where copper thickness is approximately 35 microns and polyimide film thickness is 50 microns. Chemical etching is performed using $FeCl_3$ solution for the laser scribed micro channels and from the experimental results it is observed that depth of the channel after etching is increasing with a reduction in the recast height. It is observed that with the increase in concentration of $FeCl_3$ and the etch time, the material removed from the copper target increased. The height of recast for the 50 μm wide micro channel scribed using 20 mJ of energy and a laser wavelength of 532 nm reduced from 10 μm to 5 μm in case of 10% $FeCl_3$ etched for 1 min. However the overall thickness of the copper thin film is observed to reduce from 35 μm to 30 μm. Hence a hybrid technique using NaCl as the scribing medium is developed, so that $CuCl_2$ formed in the process of scribing helped in achieving a localized etching inside the channel without affecting the total target thickness.

DOI: 10.2961/jlmn.2018.03.0002

Keywords: nano second laser scribing, laser assisted chemical etching, copper thin films, micro channels, recast layer

1. Introduction

There is a growing interest in applying pulsed lasers for micromachining of a large variety of materials including plastics, metals, semiconductors, ceramics, and other materials that are difficult to process, such as diamond, graphite and glass. In most metals and glasses/crystals the removal is by vaporization of the material due to heat. Laser material interaction and the micro machining process depend on the laser parameters as well as the medium in which the ablation takes place [1]. It is well known that with high intensity the metal target melts as well as vaporizes. The melt pool formed is ejected out due to the recoil pressure produced due to high velocity vapor expanding away from the target material [2]. In many cases the ejected melt is recast around the ablated crater/channel. This recast layer is highly undesirable in case of precision manufacturing and research is in line for developing different techniques to avoid the recast of the ablated metal. One such method is to incorporate chemical etching.

Chemical etching is the manufacturing process where temperature regulated etching chemical is used to remove material in order to create an object with the desired shape. It is a process of removing select layers of a metal surface through chemical erosion. The process involves immersing the part to be etched in a corrosive chemical known as an etchant. The etchant reacts with the material and dissolves the solid material thus producing the required cut. This technique is commonly used in electronics, aerospace and precision engineering industries. Acids, bases and even neutral salt solutions [3] have been used as etchants. The common etchants for copper include cupric chloride, ferric chloride, ammonium per sulfate, ammonia, 25-50% nitric acid, hydrochloric acid and hydrogen peroxide. The ideal etchant solution should have low undercut, stable and controlled etching process and environmentally acceptable. Usually Cupric chloride and Ferric chloride are commonly used etchants for removing selective layers of copper [4] due to lower cost and faster etching rate. However, to perform localized etching this technique is not favorable as it requires masking and protective coatings [5]. Localized chemical reactions can be stimulated and small structures with a micrometer precision can be produced through the use of laser-assisted chemical etching [6-9]. Laser etching of materials could be obtained both by direct laser ablation and by activation of chemical reactions at the solid - etchant interface. The thermal load on the workpiece is low due to the localized etch reaction. The reaction rate can be enhanced by applying external electric field due to the ionic nature of reactants. Fast etching of aluminum in a chlorine atmosphere with an excimer laser is presented [10]. The process involves ablation of aluminum chloride which is produced in the absence of laser irradiation due to the reaction between the chlorine ambience and the aluminum sample. A similar mechanism is used to etch copper, and the effect of gas pressure and substrate temperature on the etch rate is studied at different laser fluences [11].

In the current study initially the etch rate of $FeCl_3$ and $CuCl_2$ for etching copper cladded on polyimide is analyzed. The concentration of the etchant and the etch time are optimized with respect to the thickness of copper etched. Subsequently, laser scribed micro channels are etched using $FeCl_3$ etchant and the effect on the depth and the recast layer height is studied. Finally, a hybrid laser etching technique is proposed and demonstrated using NaCl neutral solution for localized etching inside the micro channel. A chemical liquid or its dissociation products react chemically with materials resulting in a simultaneous etching via electrochemical route. Surface reaction between ablated copper and the chlorine ions present in the NaCl solution is expected to result in localized etching. Due to the molten pool flushing and selective etching effect of NaCl, recast or redeposition above the copper surface is expected to reduce.

2. Laser Scribing using Nd^{3+}:YAG laser

2.1 Experimental Setup

Q-switched (Brilliant B, Quantel) Nd^{3+}:YAG laser system with a fundamental wavelength of 1064 nm was used for scribing copper thin film cladded on a polyimide substrate. The fundamental wavelength of 1064 nm was frequency transformed to the second harmonic (532 nm) and third harmonic (355 nm) using nonlinear optical crystals. Maximum average powers of 8, 5 and 3 W are available at 1064, 532 and 355 nm, respectively. The repetition rate of the laser is 10 Hz. The laser beam was directed on to the workpiece using beam alignment optics, such as dichroic mirrors and a quartz lens with a focal length of 250 mm as shown in Fig.1. The focused spot size was considered as ~ 300 µm (taken on burnt paper). The workpiece consists of copper thin film cladded on a polyimide substrate. The thickness of copper is 35 µm and the thickness of polyimide is 50 µm. Experiments in air medium were performed by mounting the workpiece on a motorized X-Y stage with a resolution of 2 µm/s. The velocity of the XY stage is chosen for a laser spot diameter overlap of 95 % i.e 150 µm/s. 20 number of shots were applied per location Surface characterization after the scribing process was carried out using a non-contact optical profilometer (Contour GT-I, Bruker). All experiments are performed at room temperature.

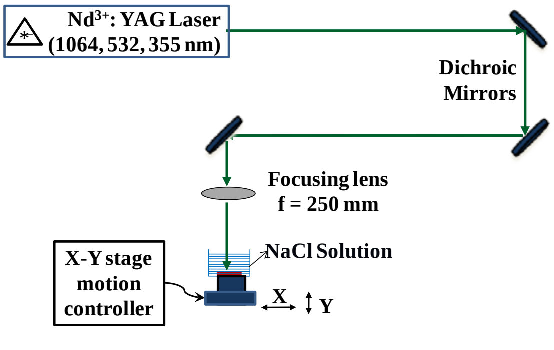


Fig.1 Schematic of experimental setup used for laser scribing

2.2 Experimental Results

Copper work pieces were scribed with laser wavelength of 532 nm and pulse width at full width at half maximum of 6 ns. The energy was varied from 10 mJ to 40 mJ (fluence 25-100 J/cm^2) to achieve micro channels of 50 µm width. The depth of the micro channel increases with energy. A depth of ~ 30 µm was obtained using laser energy of 40 mJ. The height of the recast layer increased with increase in energy but not matching with the rate of channel depth. The depth variation in the laser scribed micro channel measured at different positions along the channel was found to be around 1 µm. When the laser energy was increased from 20 mJ to 40 mJ, the recast height was not increased as the recoil pressure generated was not sufficient to thrust the melt pool completely out of the channel. As a result, the melt pool was redeposited on the side walls and the edges of the channel. Fig. 3 shows a typical micro channel image captured using a non-contact optical profilometer where the melt recast is seen in red colour along the edges of the channel. The thickness of the melt pool is ≈9 µm for laser wavelength of 532 nm and energy of 20 mJ when scribed in air.

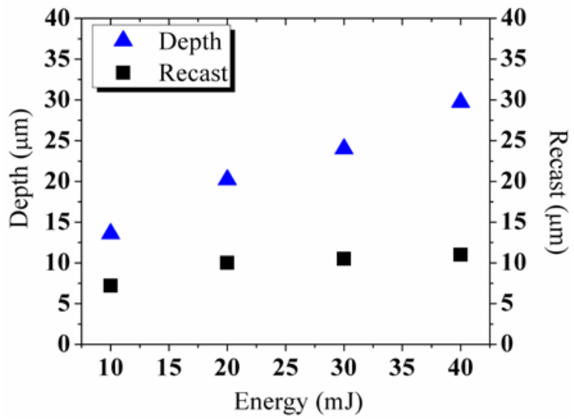


Fig. 2 Depth and recast for increasing energy using laser wavelength of 532 nm

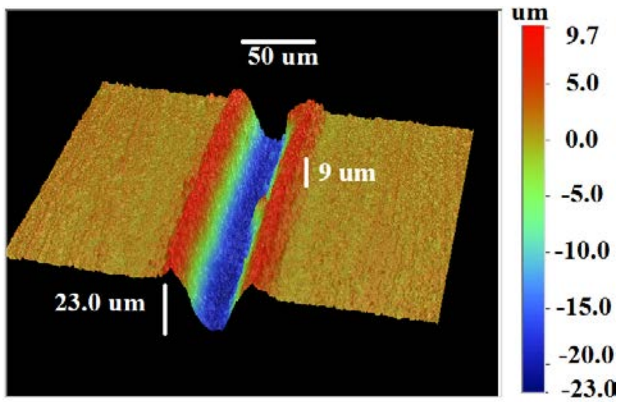


Fig. 3 A typical 3D optical profilometer image of micro channel scribed using 20 mJ energy

3. Chemical Etching using $FeCl_3$ and $CuCl_2$

To study the etch rate for different etchant concentrations thin copper films cladded over polyimide substrate are considered. The thickness of these films is measured for before and after etching conditions to estimate the thickness of copper etched. The measurements are taken using a digital micrometer having a least count of 1 µm. The etching solution was prepared by mixing anhydrous $FeCl_3$/$CuCl_2$ powder in deionized water. The etchant was mixed in deionized water in weight/volume (g/ml) ratio. The concentration of the etching solution was estimated based on the weight of etchant (W in grams) in 100 ml (V) of deionized water and expressed as W/V%. The etching process was carried out in ultrasonic cleaner which generates vibration at a high frequency to initiate and accelerate chemical reactions during etching process. The copper work pieces are immersed in the etching solution for a specific period of time, referred as etching time in ultrasonic cleaner. The copper work pieces were cleaned with acetone to remove any impurities before etching process. Etching of the scribed samples was done by immersing half of the work piece inside etching solution and other half outside to compare the profile of the same micro channel before and after etching.

3.1 Etching rate of copper in $FeCl_3$ Solution

Etching rate of copper in $FeCl_3$ solution of different W/V % concentration and the influence of etching time on material removal at a particular concentration were investigated. In the study, 10 mm × 10 mm copper cladded polyimide films were used as work pieces. Total thickness before and after etching were measured using digital screw gauge and difference in thickness was used to determine the thickness of copper etched. Etching was done with 5%, 10%, 20% and 30% (W/V) $FeCl_3$ solution for 1-5 minutes. During chemical etching every etchant reacts differently with the solid material. The chemical reaction of copper with $FeCl_3$ is as given in equations 1 and 2.

$$FeCl_3 + Cu \rightarrow FeCl_2 + CuCl \quad (1)$$
$$FeCl_3 + CuCl \rightarrow FeCl_2 + CuCl_2 \quad (2)$$

The ferric ions oxidize the copper forming cuprous chloride (CuCl) and ferrous chloride ($FeCl_2$). CuCl is oxidized further in the etchant solution to produce $CuCl_2$. The copper thickness removed is plotted against etching time for all concentrations and is presented in Fig. 4. As shown in Fig. 4, the etch rate was increased with concentration and time. The etched thickness of copper for 10% $FeCl_3$ and etch time of 2 minutes was 12 μm and for the same concentration and for etch time of 4 minutes the etched thickness increased to 16 μm. But for 20% concentation the increase in etched thickness of copper with etch time of 1 minute was ≈15 μm. This shows that the rate of copper dissolved by the etchant increased with increase in the concentration. For low concentration (10%) it is easy to control the etch thickness as the rate of etching is slower than high concentration (20 %). For 5 % concentration the etch rate was quite low and the time required for etching was increased.

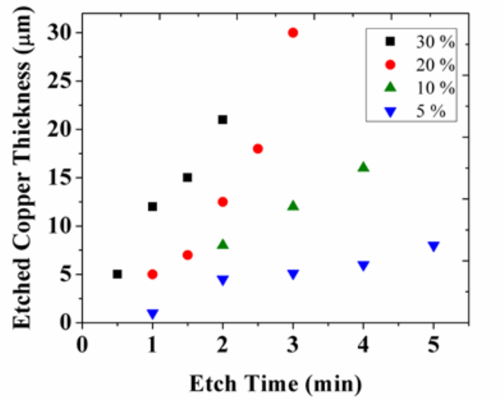


Fig. 4 Etching of copper at different concentrations of $FeCl_3$

3.2 Etching rate of copper in $CuCl_2$

The influence of etching time on material removal at a particular concentration was studied for $CuCl_2$ solution, similar procedure was followed for solution preparation as discussed in section 3.1. The etching of copper using $CuCl_2$ can be expressed using the following equations.

$$CuCl_2 + Cu \rightarrow 2\,CuCl \quad (3)$$
$$Cu^{2+} + Cu^{o} \rightarrow 2Cu^{+} \quad (4)$$

The copper thickness removed was plotted against etching time as shown in Fig. 5. The etching rate of $Cucl_2$ was low as compared to the etching rate of $FeCl_3$. The maximum etch rate was obtained using $CuCl_2$ with 30% concentration. The etch rate was reduced considerably with 50% concentration. Also the etching depth as seen from the Fig. 5 was increased at a slow rate as the concentration increased. The decrease in the etching rate with increase in concentration and time was attributed to CuCl passivation film formed above the target [2]. This film formed a barrier for diffusion between the etchant and the copper surface. From the above study it is understood that rough etching can be performed using $FeCl_3$ and for smooth etching where copper thickness of 2-3 μm is required to be etched, $CuCl_2$ can be used.

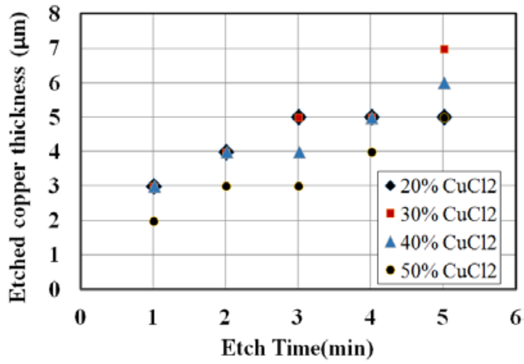


Fig. 5 Etching thickness of copper for different concentrations of $CuCl_2$ for increasing etch time

4. Influence of $FeCl_3$ etching on the scribed micro channel profile

The depth and recast height before and after 10%, 1 min $FeCl_3$ etching for 10mJ, 20mJ, 30mJ and 40mJ scribed channels is shown in Fig. 6. During etching of the micro channel, material was removed from the channel and from the top surface of the channel. As a result, the depth of the channel after etching was increased and recast height was reduced. Based on Fig. 6, after 1 min, 10% $FeCl_3$ etching, material removal inside the channel was more than material removal outside the channel. As shown in Fig. 7, the recast height of the micro channel was reduced after etching.

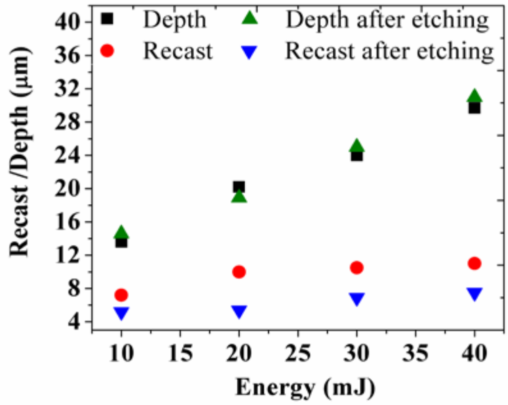


Fig. 6 Micro channel depth and recast layer thickness before etching and after etching

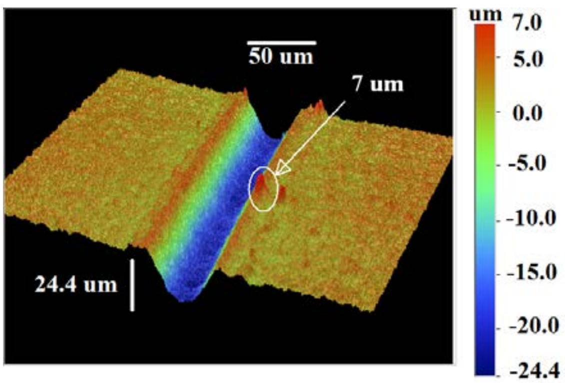


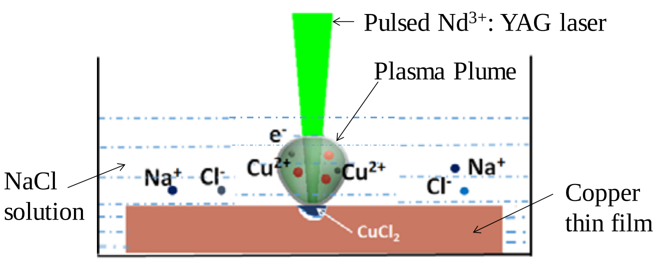
Fig 7. A typical 3D optical profilometer image of micro channel scribed using 20 mJ energy after etching with FeCl3

Based on the study, the overall thickness of copper was reduced with etching after laser scribing, which was undesirable. A localized etching technique was essential to avert reduction in the film thickness of the workpiece due to the dissolution of the entire workpiece by the etchant. Removal of material at the required location was needed and a hybrid technique of using laser along with NaCl solution was propose and demonstrated for this purpose.

5. Laser induced chemical etching in NaCl Solution

A neutral salt solution was prepared by mixing NaCl to de-ionized (DI) water. 10 % concentration of NaCl was prepared by mixing 10 mg of NaCl in 100 ml of DI water. NaCl dissociates into Na^+ and Cl^- when dissolved in DI water. Localized etching by direct laser ablation was observed in case of NaCl solution due to the reaction of ablated Cu^+ ions with the Cl^- ions forming $CuCl_2$. Figure 8 presents a schematic of the laser ablation technique used to form the micro channels using hybrid laser etching. Initially laser ablation removes the copper from the surface then chemical etching is followed by appropriate etchants ($CuCl_2$) to remove remaining copper inside the channel. The depth of the channel increased with increase in the laser energy and hence the laser fluence as shown in Fig. 9. The channel width was approximately 200 µm. As the channel width was large as compared to the micro channel width of 50 µm in air, the laser fluence (J/cm^2) was estimated to be less resulting in lesser depth of micro channels as compared to that in air.

As seen from 3D optical profilometer image in Fig.10, there was no recast present when scribing was performed



Cu^{2+} + Cl^- ⟶ $CuCl_2$

Fig. 8 Schematic of selective laser etching of copper in NaCl Solution

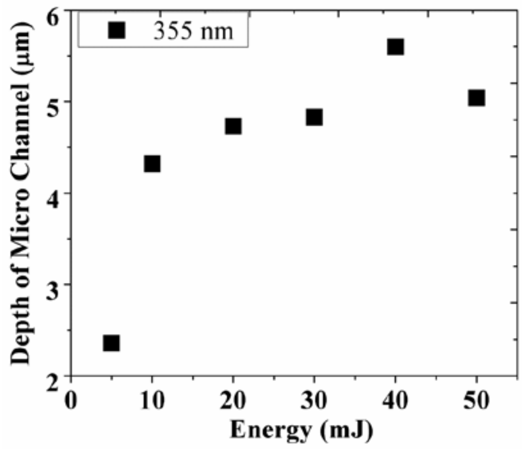


Fig. 9 Depth of micro channel produced using laser assisted chemical etching using a laser wavelength of 355 nm and 1mm layer of 10 % concentration NaCl

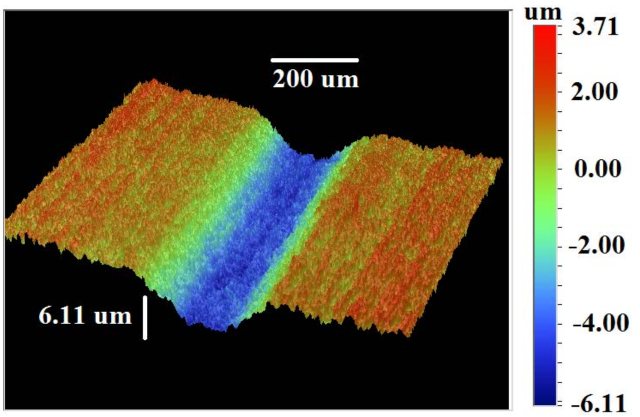


Fig. 10 Micro channel produced by laser assisted chemical etching in NaCl ambience for laser wavelength of 355 nm and laser energy of 40 mJ

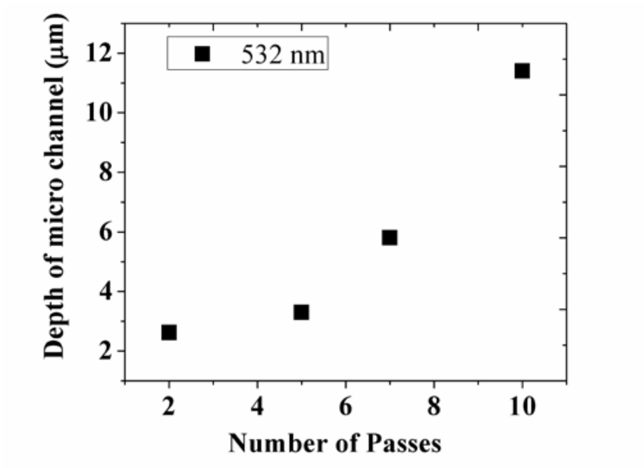


Fig. 11 Depth of micro channels for multi pass scribing using laser energy of 20 mJ and wavelength of 532 nm in NaCl solution

under NaCl ambience. The melt pool was flushed away as debris instead of getting redeposited on the channel edges. Further as shown in Fig. 8, Cl^- ions from NaCl solution were expected to interact with Cu^+ ions to form $CuCl_2$ which in turn would act as an etchant for improving the surface finish of the micro-channel. With increase in laser fluence the possibility of NaCl breakdown is high. The plasma plume formed at the air and NaCl solution interface due to the parasitic breakdown of NaCl solution creates a shielding effect, thus the scribing is performed at a lower energy. In order to improve the depth of the micro channels multi-pass scribing was performed. Figure 11 shows the increase in depth with increase in the number of passes for 20 mJ of energy and laser wavelength to 532 nm. Hence laser assisted chemical etching in NaCl ambience is an effective technique to produce micro channels with no recast layer.

6. Discussion

Combined laser scribing and chemical etching technique is used in order to control the depth of Cu micro channel profile without damaging the non-conductive substrate. In the initial study, the etch rate of $FeCl_3$ and $CuCl_2$ was investigated. The etched thickness of Cu film was measured to be ≈12 μm for 20 % concentration and 2 min etching time in $FeCl_3$ and the etched thickness of copper film was observed to be ≈4 μm for the same concentration and etching time of $CuCl_2$. The amount of material removed in case of $FeCl_3$ was large and it was used to etch laser scribed micro channels to improve the depth and remove the recast layer formed due to the redeposition of the melt layer. Also it was observed that a CuCl passivation film was formed above the target preventing the dissociation of copper when etched with $CuCl_2$ etchant. Hence, 10% etching concentration and 1 min time is considered appropriate for the etching of micro channels using $FeCl_3$. The disadvantage of using $FeCl_3$ is that due to etching of copper outside the channel, the effective copper thickness remaining after etching is less than 35 μm. Also the formations of etching defects and etch pits distorts the micro channel form which makes this technique ineffective. A hybrid technique of pulsed laser scribing of Cu in a neutral NaCl solution is proposed and demonstrated. The depth of the channel increased with increase in energy, but after 40 mJ of energy the depth starts to reduce, this could be due to the breakdown of the NaCl solution at the air water interface [11]. This breakdown of the ambience causes plasma which is combination of electrons, ions and neutral particles. This plasma tends to absorb the incident laser beam thus shielding it from the workpiece [12]. Hence the depth reduces after 40 mJ due to plasma shielding. However due to the liquid NaCl there is no recast or redeposition above the copper surface as seen from Fig. 9. Hence localized etching of copper using laser assisted chemical etching is a desirable technique compared to the two step technique of laser scribing followed by chemical etching as a post processing technique.

7. Conclusion

Laser scribing of micro channels using laser wavelength of 532 nm is performed on copper coated polyimide thin films. The recast layer formed at the edges of the micro channels increased with increasing depth. Chemical etching is performed to remove the recast layer using two different etchants, $FeCl_3$ and $CuCl_2$ respectively. The etching thickness of copper when etched with $FeCl_3$ etchant is observed to be 3 times higher compared to the etching thickness achieved when etched with $CuCl_2$. However the overall workpiece thickness is observed to reduce when etching is performed after laser scribing. A hybrid laser scribing technique is developed using a neutral NaCl solution. It is observed that there is no recast formed when laser scribing is performed in NaCl ambience. However the plasma shielding at higher energies due to the breakdown of the NaCl solution is limiting the depth of material removal.

Acknowledgments
This work was partly supported by the grant-in aid from the Indian Space Research Organization (EDD/1415/151/ISRO/NILE). The authors are grateful to micro electronics and MEMS lab, Department of electrical engineering IIT Madras for providing facilities for characterization.

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(Received: June 6, 2017, Accepted: October 7, 2018)