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Soldering mask laser removal from printed circuit boards aiming copper recycling

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ABSTRACT

Management of waste of electric and electronic equipment (WEEE) is a key issue for modern societies; furthermore, it contains valuable materials that can be recycled, especially in printed circuit boards (PCB), which have approximately one-third of their weight in copper. In this study we demonstrated the use of laser to strip the covering soldering mask on PCB's, thus exposing the copper underneath so that extraction techniques may take place. Using a Q-Switched Nd:YAG laser operating at 1064 nm and 532 nm we tested the procedure under different energy conditions. The laser stripping of the soldering mask was achieved with satisfactory results by irradiation with 225 mJ at 1064 nm. However, when using similar parameters at 532 nm the process of the coating ejection was not promoted properly, leading to a faulty detachment. Infrared laser PCB stripping presents itself to be technically viable and environmental friendly, since it uses no chemicals inputs, offering one more option to WEEE treatment and recycling.

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1. Introduction

One of the most challenging issues for society in the near future is handling and processing the waste of electric and electronic equipment (WEEE). Technology advances drive the production of new electronics while making them more accessible to the final customer, an increase in WEEE in recent years comes as no surprise. Studies suggest that between 20 and 50 million metric tons of WEEE are produced per year, with an annual increase of 3–5 percent (Luda, 2011; Neto et al., 2016; Yamane et al., 2011). However, awareness of this subject is also growing (Akcil, 2016), prompting the search for new ways to reutilize these components. To illustrate this scenario, entries related to the keywords "printed circuit board recycling" in scientific databases[1] indicate an increase of the number of publications at a rate of 35% per year on average over the last decade.

WEEE disposal presents a broad spectrum of materials in its composition, leading to a complex processing for its reuse. However, motivations for recycling do exist. For instance, it helps to reduce environmental impact due to mining, appeasing the growing demand for electronic inputs (metals and precious metal). Also, it promotes appropriate handling of hazardous materials that exist in such equipment, which pose an environmental threat.

A common item found in almost every piece of electronic system is a copper-based printed circuit board (PCB) (Kasper et al., 2011; Luda, 2011). It is reported that 23%–30% of the PCB weight in Cu are recoverable using chemical methods (Imre-Lucaci et al., 2012). An estimate shows that the fraction of PCB in the overall WEEE ranges from 3 to 8 percent (Luda, 2011), which translates to, at least, 3% of 20 million metric tons of WEEE produced, resulting in 600 thousand tons of PCB. Recovering 23% of such material would yield 138 thousands of tons of copper, worth a little over 1.2 trillion dollars each year - values that may increase as a consequence of the growing trend of WEEE produced.

The mainstream methodology to recover metals from PCB (Luda, 2011) consists in size reduction as dismantling and grinding, followed by material separation by physical properties such as magnetic and density, among others (Chagnes et al., 2016). In a further step, the metal extraction/separation is achieved using a leaching process to dissolve metals in an acid/alkali solution (Castro and Martins, 2009; Kiddee et al., 2013). This technology is easily scalable, but it ends up shuffling all kinds of materials together in the first step, requiring the segregation afterwards. There are interesting efforts pushing this approach ahead, as an example the cryogenic milling study (Tiwary et al., 2017) demonstrated an environmentally friendly route, but energetically costly.

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Some other studies approached the problem without the crushing process, using either: anodic dissolution to recover the copper (Imre-Lucaci et al., 2012); or cathodic electrodeposition (IMRE-LUCACI, 2011). Having the advantage of being energetically less demanding, these methods require the removal of the Soldering Mask (SM) - an epoxy coating which protects the copper layer - so the electrical contact may be established. Usually, a solution of sulfuric acid (H_2SO_4) is applied to expose the copper (Imre-Lucaci et al., 2012) for the recovery by electrical means to take place. Another study has shown that it may take up to 24 h with a 10 M sodium hydroxide solution to perform a faulty SM removal (Jadhav and Hocheng, 2015), posing a time consuming task.

An innovative approach to remove coatings such as paintings or varnishes is via laser irradiation with a technique known as Laser Stripping or Laser Coating Removal. Several applications have been reported, ranging from radioactive waste management (Potiens et al., 2014) to painted artwork cleaning (Georgiou et al., 1998) and varnish removal from brass (Mateo et al., 2009). This method presents several advantages over the conventional approaches, e.g.: no need for chemical substances, high cleaning speed and easy automation. However, in a thorough review (Luda, 2011) no mention of attempts at applying laser as a WEEE recycling tool was found.

Laser Stripping has already been reported and explained (Roberts, 2004) as a process in which the laser is partially transmitted by the paint/varnish and absorbed by the underneath metal, which sublimates, ejecting the coating above. This sublimation is a process known as laser ablation (Phipps, 2007) in which the material is heated quickly and locally by a pulsed laser, passing from solid to a plasma state, which generates pressure, stripping away the coating. There are a great variety of lasers with different irradiation conditions, each one producing ablation with different features (Chichkov et al., 1996). For Laser Stripping, in general, the laser applied has pulse duration of a few nanoseconds and tens of milijoules, resulting in a megawatt peak power. As the process is achieved using pulsed lasers the amount of energy transferred is on average low, ideally leading to small overall temperature increases of the material under treatment. In this way, it is possible to use this phenomenon to remove the Soldering Mask without chemicals. Fig. 1 illustrates the laser beam interacting with a PCB, resulting in the varnish ejection.

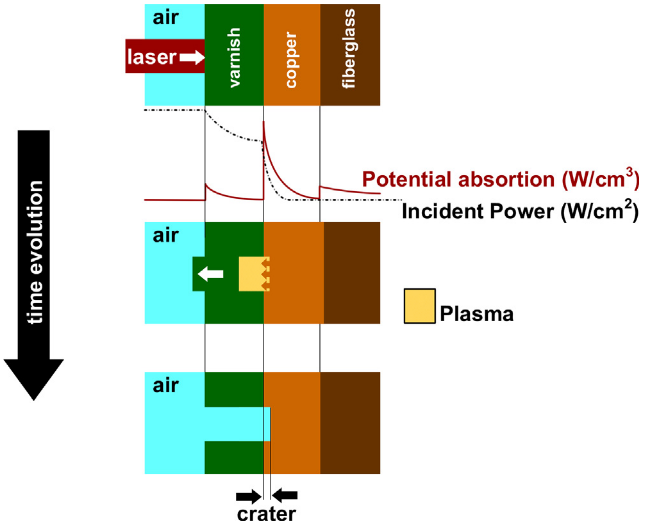

Fig. 1. Laser coating ejection process schematic figure (out of scale). The laser is transmitted by the varnish and is absorbed by the metal, causing an explosion leading to coating removal.

Thus, supposedly, running the laser beam over the PCB area without any previous treatment should remove all the SM when using the correct laser irradiation parameters to expose the copper allowing it to be recovered by an anodic dissolution approach.

Thus, the objective of this work was to study the laser stripping as an approach to Soldering Mask removal from used Printed Circuit Boards, enabling the recovery of the exposed copper using methods such as electrochemical or leaching processes.

2. Experimental

The laser source used was a pulsed Nd:YAG laser (Brilliant, Quantel Laser, Les Ulis Cedex, France) operating at 1064 nm or at 532 nm through the use of Second Harmonic Generator (SHG) with nominal maximum energy per pulse of 350 mJ@1064 nm and 160 mJ@532 nm, repetition rate of 20 Hz and both with 5 ns of pulse duration. The optical setup was restricted to a pair of dielectric mirrors for directing the laser beam, which was used without focusing optics, i.e., collimated for the infrared laser (1064 nm) and a using 1000 mm converging lens for the green laser (532 nm) at 300 mm from the sample to compensate the divergence introduced by the SHG module. To move the sample, a pair of motorized translation stages (LTS300/m, Thorlabs Inc., New Jersey, USA) were mounted with 300 mm of travel range, 50 mm/s maximum speed.

The laser path over the surface to process an area is done using a pattern known as “raster”. Considering that a pulsed laser is used, it is necessary to ensure overlapping so all the surface can be irradiated by the laser shots, as shown in Fig. 2. For this purpose, a program was developed to control the translation stages in a LabVIEW (National Instruments, Texas, USA) environment.

To ensure operator and environmental safety all the tests were carried in a fume box with filters. A schematic view of the experimental setup is presented in Fig. 3.

To evaluate the efficacy of the laser stripping of the Soldering Mask from the Printed Circuit Board a scanning electron microscope (SEM, TM3000, Hitachi, Tokyo, Japan) was used along with an Energy Dispersive X-ray detector (EDS, Quantax 50, Bruker, Germany) and in order to measure the diffuse reflectance of the Cu and SM a spectrophotometer (Cary 5000, Agilent, California, USA) was employed.

3. Results and discussion

The first experiment aimed to check the feasibility of ejecting the varnish layer from a PCB by applying laser radiation. Thus, a study was conducted using a scrap PCB, fully mounted with all the original components. The laser energy was gradually increased

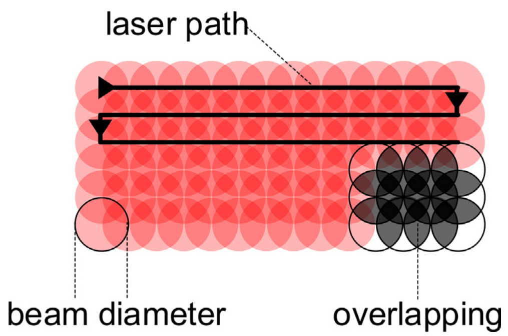

Fig. 2. Illustration of the laser rastering process used to remove the soldering mask from the Printed Circuit Board. At the bottom right, in black and white, the superposition of processed areas by the laser pulses are highlighted, in this example with of 50% of overlap was used.

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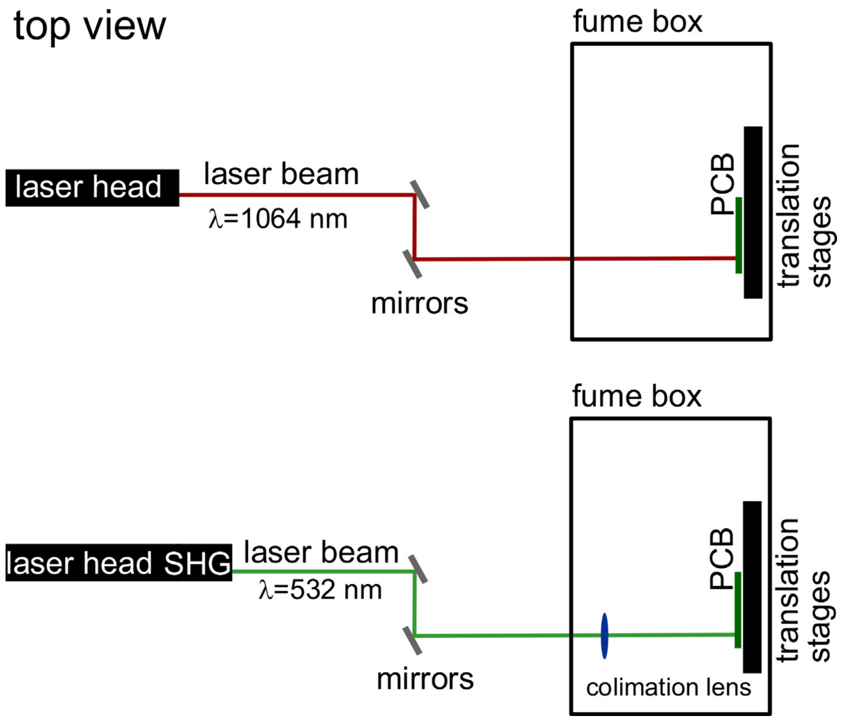
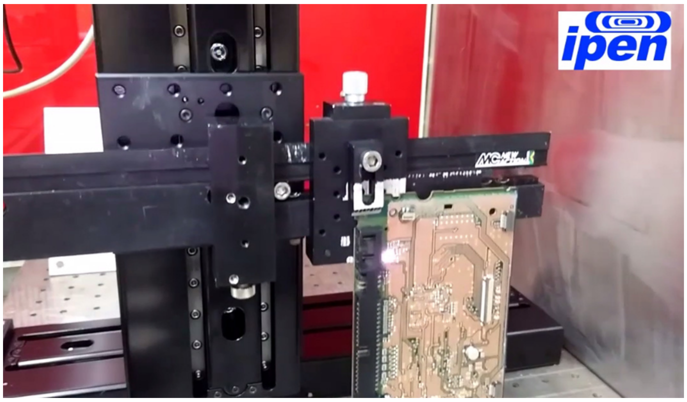


Fig. 3. Schematic drawing of the experimental setup (top for 1064 nm, bottom for 532 nm laser).

until the varnish began to be removed (around 150 mJ@1064 nm). The PCB was, then, translated laterally in order to remove a whole line of SM. Side effects, like damages in the labels and lettering of the PCB'S components were observed. Nevertheless, the energy was further increased to 225 mJ and 350 mJ (the maximum energy of the laser system), to check for the occurrence of unwanted damages to the copper, but none were observed, as shown in Fig. 4. Furthermore, there were no noticeable differences in the SM removal between the tested energies other than the removal line thickness.

The diameters obtained were 3.10 mm for 150 mJ; 2.80 mm for 225 mJ; and 3.40 mm for 325 mJ. Although 325 mJ presents the larger diameter, it also ends up removing more material from the superficial layers of copper, which can be noted by brighter copper color in the zoomed region in Fig. 4. Such a whiter color results from exposing deeper unoxidized copper. This effect can also be observed, albeit less pronounced, for 225 mJ, when compared to 150 mJ laser pulses.

The second experiment was designed to irradiate the whole PCB for a more thorough evaluation of the process. The laser energy studied was 250 mJ per pulse as it produced a good SM removal diameter allied with little ejection of copper material observed in the previous tests. The removal area using a single laser shot measured about the beam diameter. Aiming for 50% overlap between pulses and having a fixed repetition rate of 20 Hz implied a scan velocity of 40 mm/s for the translation stages. The PCB measured 90 × 130 mm, resulting in 12,000 mm^2 (120 cm^2) area for laser processing. The whole procedure was five minutes long, see complementary material - Video 1. The result is presented in Fig. 5.



Video 1.

Only small (negligible) stripping failures were observed, mainly in locations that exhibit thin and parallel copper tracks (Fig. 6-a), i.e., low copper density per area. The absence of copper underneath

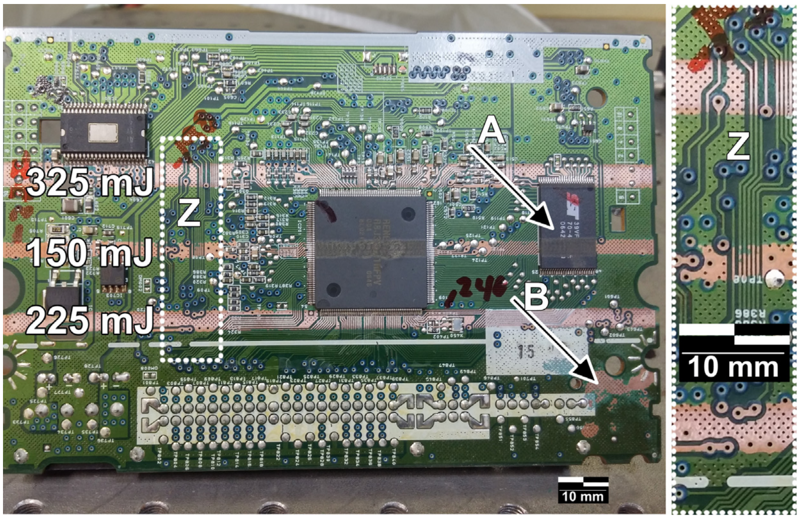


Fig. 4. Laser removal of the soldering masks for three different energies: Top line 325 mJ, middle 150 mJ and bottom 225 mJ. (A) shows the lettering removal; (B) first tests area; (Z) zoomed region.

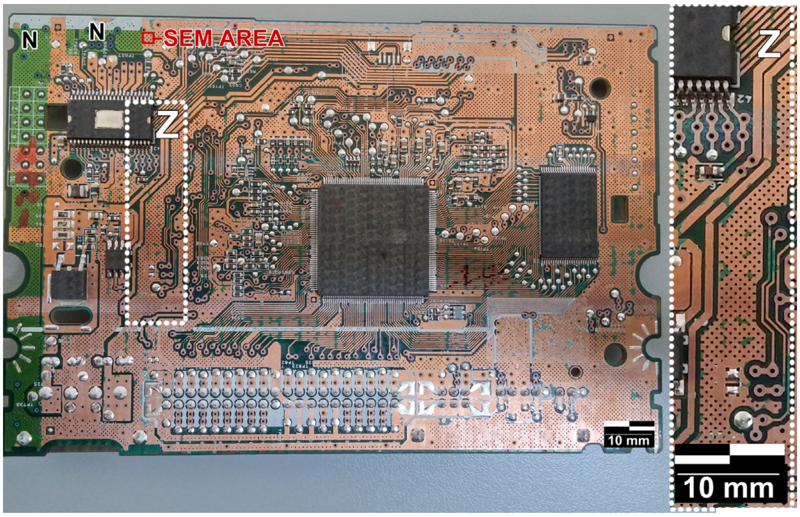


Fig. 5. Laser stripped PCB with 250 mJ. (N) regions not processed by the laser; (Z) zoomed area.

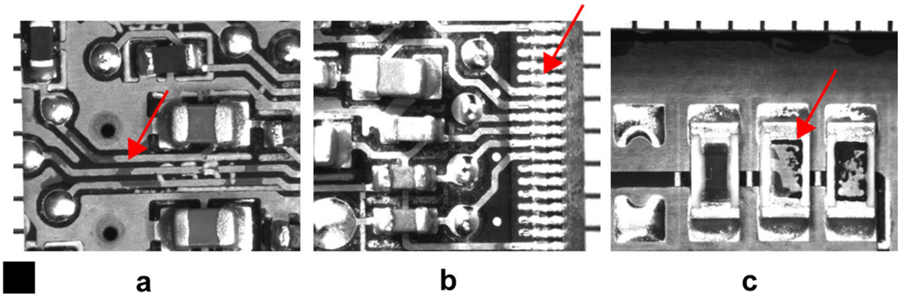


Fig. 6. Optical microscope images of the laser striped PCB, the black scaling square at the bottom left has 1 mm sides. Arrows indicate: a) Stripping failures on thin parallel tracks; B) Processor soldering terminals and the solder itself were visually unharmed; c) Some components presented casing damages.

such regions leads to weak coupling of the laser resulting in stripping fails, corroborating the explanation illustrated in Fig. 1. Other minor removal failures can be addressed to the raster pattern issues: the displacement between lines was larger than ideal, not allowing a proper overlapping to occur. That can easily be corrected with smaller raster intervals and better alignment of the PCB with the raster axis. The regular pattern of dark dots observed at the zoomed area (Z) is not due to stripping flaws, as they are holes on the copper substrate.

Overall, the laser action removed the majority of the SM from the PCB. The delicate soldering of the main processor seemed intact (Fig. 6-b). However, damages were observed in the electronic com-

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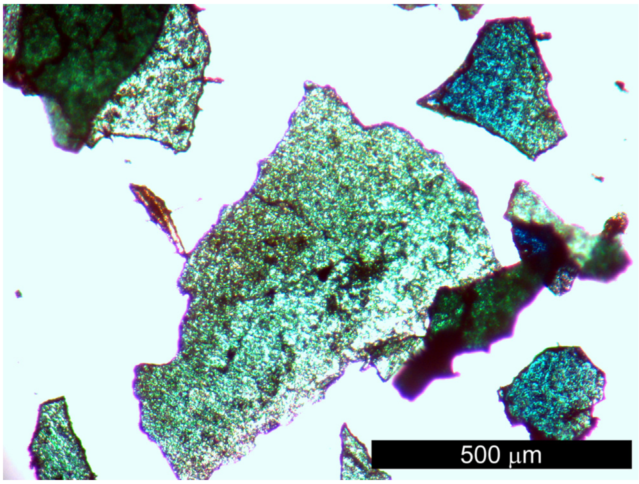

Fig. 7. Optical microscope image of varnish chips ejected in the laser stripping process.

ponent's casing (Fig. 6-c), suggesting possible functionality losses of these components. In fact, the functionality of the board was tested before and after the laser processing, confirming that the PCB was no longer functional.

High temperatures eventually should cause the epoxy to release toxic gases (Kim et al., 2013), Fig. 7 shows the visual aspect of the ejected material collected on the fume box floor, in which no visual signs of heat damages such as burning, melting or color degradation were noticed. The overall PCB temperature maintained ambient values during and after the stripping since the majority of the laser energy was reflected or expended in the ablation process. The material was distributed mostly in a radius of 30 cm from the sample, but, smithereens were found as far as 80 cm, at the fume box ends. Collecting the ejected material is not a challenging task in an eventual real application, as the detached flakes are mainly macroscopic and, although the particle velocities have not been measured, it is not difficult to place a physical barrier to stop them or even design a suction system to perform the collection.

Images taken with the SEM are present in Fig. 8. They demonstrate that the exposed copper was not thoroughly clean even in areas that visually seemed so, as presented in the raw optical images in Fig. 5. Remains of SM were found all over the observed area. The EDS overlapped with SEM image confirms the exposure of the copper and the existence of elements present in the SM (carbon and silicon) sparsely distributed throughout the examined region of Cu substrate, displayed in false colors in Fig. 8-c. It is possible to see that, even though there is a large copper area (orange), there are C and Si spots (green) not only in the perforated regions of the copper plate underneath (large dark spots in the SEM images), but also scattered across the whole image, in lower concentrations. Higher magnification in the SEM (Fig. 8-b) confirms such results. Thus, despite the laser removing the SM almost completely, smaller portions remain adhered to the copper.

Using an optical profilometer (manufactured by ZYGO, model ZeGage) it was possible to access the relief of two regions, one treated by the laser using the optimal intensity regimen and other untreated (where the epoxy was peeled off). The height difference between the two measured 666.2 nm, Fig. 9. The thickness of the copper layer (taken with a micrometer) measured 50 μm, so the overall loss is about 1 percent.

Another experiment was conducted in order to get a better understanding of the process using the laser second harmonic at 532 nm (green). Other parameters were kept the same as used in the previous experiments, and a different scrap PCB was used as a sample. The SM could not be removed with this laser line even at the maximum energy available: 160 mJ. The measured spot diameter was, approximately 2.62 mm. The observed effect was a partial detachment of the SM along the raster lines. This partially detached varnish had a burnt appearance and made the surface irregular as presented in Fig. 10.

The observed effect could be due to poor laser coupling with the PCB at 532 nm, as well as the laser being more reflected by the varnish (due to the green coloring) than transmitted to the copper below. To test the hypothesis, the reflection spectra of the PCB was taken for the SM plus Cu (prior to SM removal with 1064 nm) and for the Cu only (after the removal).

Obtaining the reflection spectrum for both scenarios enables an analysis of the overall SM contribution. The spectra presented in Fig. 11 were measured using the spectrophotometer from 400 to 1300 nm, 1 nm sampling and results were normalized. The illustration at the bottom right exemplifies how the SM (green) affects the measured spectrum, as opposed to the case where only the copper (orange) is present.

Of special importance are the diffuse reflectance spectra at the used laser lines wavelengths (Fig. 11 vertical arrows). It is possible to see that for both spectra the region around 1064 nm is highly reflected, leading to weaker coupling when compared to the 532 nm region. At the latter wavelength, reflectance peak is observed for the SM + copper (black solid line). This peak is mainly due to the SM as it is not present for the copper-only reflectance (red dashed line), which is consistent with its green appearance. Still, even with this peak, the reflectance at around 532 nm is much smaller than the overall values for the infrared region and, thus, the coupling alone is not the cause for the obtained results.

Laser penetration depends on the optical absorption properties of the material. In this case, PCB varnish was optically transparent to the infrared wavelength used, reaching the copper. In metals, the energy absorption process is dominated by the free electrons, which transfers to the lattice phonons by collisions, resulting in heat. Ablation process occurs following phase transitions: melting, vaporization and plasma formation, leading to epoxy ejection.

The literature suggests that, for copper, the threshold fluence, i.e., the minimum fluence necessary for ablation to occur is higher

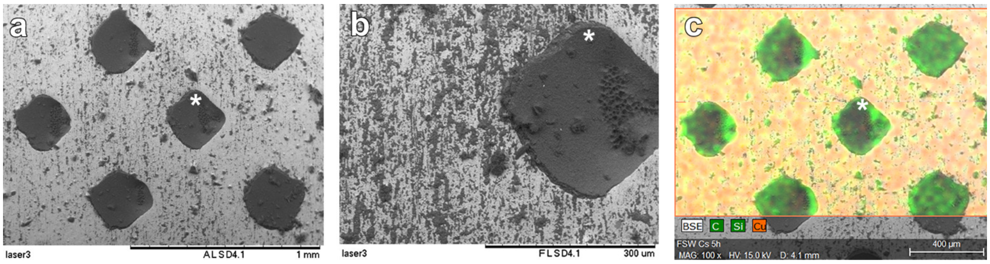

Fig. 8. SEM images in two different magnifications (a and b), and (c) the overlapped SEM image with EDS data in false colors: Orange for copper and green for carbon and silicon.

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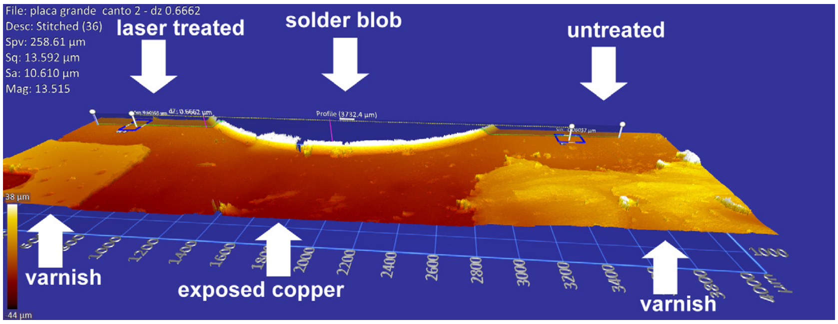

Fig. 9. White light profilometer image. Heights of two different regions of the copper layer were measured (laser treated and epoxy peeled).

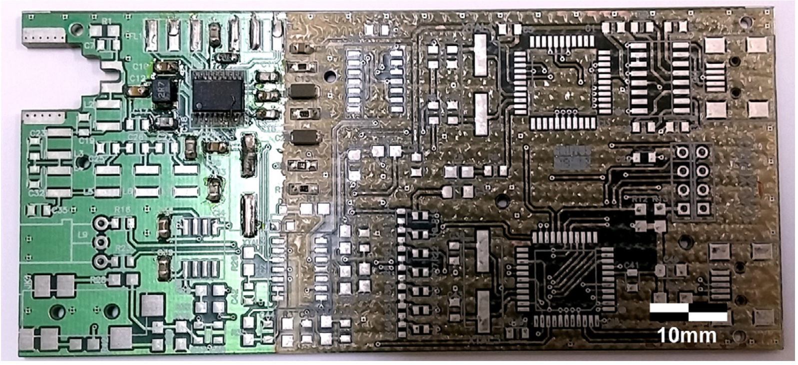

Fig. 10. PCB after an attempt of laser striping at 532 nm@160 mJ (right side). The varnish partially detaches from copper, forming a bubbly structure.

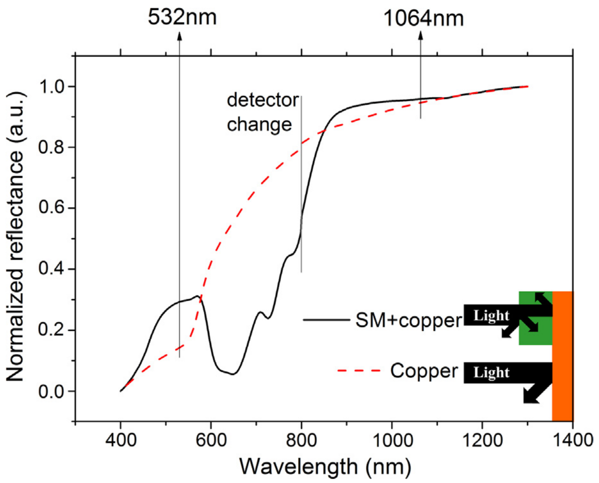

Fig. 11. Diffuse reflectance spectra of PCB with and without the soldering mask (SM).

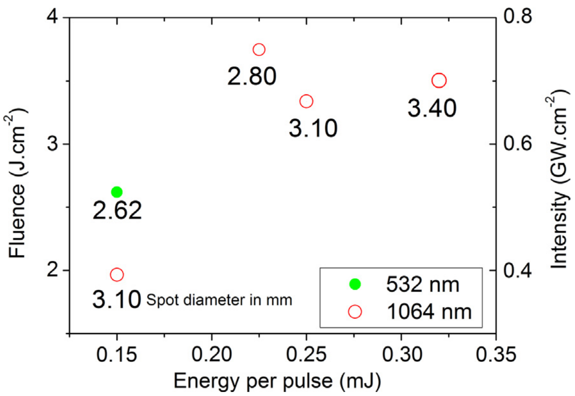

Fig. 12. Correspondence between energy and fluence. The spot size (laser beam diameter) is represented by the circles' sizes and the label shows its value in mm.

at the visible wavelengths than at the infrared region (Katavić et al., 2010). Indeed, studies indicate that the threshold fluence for the 1064 nm on copper is in the order of 0.3 J/cm^2 (Mottner et al., 2003) to 0.4 J/cm^2 (Siatou et al., 2006), while there are reports of calculated threshold fluences as high as 1.9 J/cm^2 for 532 nm (Tang et al., 2012), all values considering nanosecond pulses. As Indicated in Fig. 12, both of our experiments were above the ablation threshold. For the 1064 nm laser, despite the high reflectance, the fraction absorbed was enough to ablate the copper surface, ejecting the varnish almost completely. The 532 nm laser, although supplying enough energy for copper ablation, strongly interacted with the SM. That causes the observed degradation (photochemical) and attenuates the laser energy that reaches the underlying copper, impairing the ablation process, thus explaining why the SM was not ejected. Thus, in such situations, in which the wavelength is not optimal and the copper ablation is not achieved, the irradiation may promote high temperatures in the epoxy, and toxic gases are more likely to be released.

4. Conclusions

This study tested the viability of laser stripping of the varnish, also known as soldering mask (SM), applied in printed circuit boards (PCB) aiming to expose the copper underneath for subsequent recovery via electrochemical reactions.

PCBs were irradiated with two different wavelengths: 1064 nm and 532 nm, with a Nd:YAG Q-Switched laser. The infrared wavelength (1064 nm) was effective to promote the varnish detachment due to the high transmissivity of the varnish in this spectral region, which allowed the laser to be partially absorbed by the copper causing ablation and ejecting the varnish. The phenomenon was possible for energies as low as 150 mJ, however, presented more consistency for energies above 250 mJ.

For the 532 nm laser (green), it was not possible to remove the coating, as the laser interacted strongly with the SM, absorbing a significant part of the incident energy, causing thermal effects in the SM (degradation). That inhibited the copper ablation and, consequently, the epoxy ejection.

It is worth mentioning that different colors of SM (besides the green) such as red and blue are commonly found, which can be the object of further investigation. Another important aspect to be further studied is the characterization of harmful gases that may be released in this process.

Lasers emitting at 1064 nm are robust and widely available with energies that can achieve the soldering mask detachment with an accessible cost. This methodology naturally has pros and cons. As for drawbacks, we can cite the laser cost and the issues to scale this process up. On the other hand, the laser approach uses no chemicals. Although the laser repetition rate in this study is low (20 Hz), rates of tens of kHz are broadly available, shortening the processing. The residual material is easy to collect for further management and disposal. Printed circuit boards were processed with and without the electronics components, and it had no side effect on the soldering mask removal, showing one more facet of this technique.

When compared with chemical techniques (Jadhav and Hocheng, 2015), laser stripping promotes a more complete and faster coating removal if performed with the appropriate parameters. Although lasers have been used for WEEE characterization (Aguirre et al., 2013) in this work we demonstrated for the first time that laser ablation also can be used in recycling processes.

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