Structural and chemical analysis of laser marked microelectronic packaging modules

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Laser marking is an attractive technique allowing high-speed and high spatial resolution identification of materials, mechanical parts, tools or packaging modules for traceability, advertising, security or trademark protection reasons. The laser marking process, however, is very sensitive to the chemical composition, physical properties and texture of processed surfaces. We have investigated the role of surface chemistry and morphology of nickel-plated copper lids in achieving high optical contrast marking with a Q-switch Nd:YAG laser. Profilometry, scanning electron microscopy and x-ray photoelectron spectroscopy measurements have been carried out to characterize investigated samples. The results indicate that a low contrast marking results from poor absorption of the laser by the of $Ni(OH)_2$–rich surface. The primary mechanism of marking is related to laser-induced smoothing of the surface and not to the modification of the chemical composition of the irradiated material. Thermal processing of the lids in air or N_2 environments in the 300-350 °C range, before laser irradiation, has a pronounced effect on the chemical composition as well as on the color of the nickel-plated lids. Laser marking of such color-modified lids leads to both drastically improved resolution and contrast of the process.

Keywords: Laser marking, nickel plating, IC packaging, X-ray photoelectron spectroscopy, nickel oxide

1. Introduction

The marking of metal-based packaging modules designed for holding microelectronic circuits is an important step in the device fabrication processes and in providing valuable information both to the manufacturers and their clients. Conventional methods of marking, such as those based on ink-jet printing, suffer from the drawbacks related to the cost of consumables, durability of marking and flexibility of the process [1]. With the introduction of lasers in 1960s, many investigations into the laser ability to mark engineering materials have been carried out. Laser marking of microelectronic modules and packages is a technique used in the microelectronics industry to identify production lots and, e.g., manufacturing dates. The aim of the laser marking is to perform a permanent trace on the surface of the material in order to make it readable and recognizable. Laser marking has been used for more than 30 years, replacing inject marking in many cases due to its high speed and inherent flexibility [2]. In that context, marking of nickel plated packages of integrated circuits (IC) continues to grow and is clearly one of the most diverse market segments. Magnetic properties, corrosion resistance and solder ability of nickel plating are properties that have contributed the most to this success [3]. Among various parameters affecting the appearance of laser marked surfaces, the uncontrollable surface morphology and chemistry modification of different substrates could be the source of a reduced contrast marking. The related studies have investigated laser parameters, such as laser beam scanning speed, line width, frequency and power [5]. Fewer works have focused on investigation of the influence of surface morphology and surface chemical composition on the quality of laser marking [4].

We have investigated a series of nickel-plated Cu lids of IC packaging modules with the goal to determine the origin of a variable quality of laser marking produced with a Q-switch Nd:YAG laser. The focus of our study was surface morphology and surface chemistry of the investigated lids before and after laser irradiation.

2. Experiments

A total of 24 Ni-plated (2.5-7.6 μm) Cu lids of IC packaging modules were investigated in this work. The laser marking was obtained with a Q-switch Nd:YAG laser operating at 26 A and 7 kHz. The marking was achieved by X-Y computer controlled scanning at 200 mm/s.

The average brightness intensity (gray level) of the marked and unmarked regions was obtained from the analysis of microscopic images of the laser marked samples. The optical contrast was calculated from the ratio of gray level levels of marked and unmarked regions [5].

A stylus surface profilometer (Dektak 150, Veeco Instruments, Inc.) was used to measure surface roughness of the samples. The measurements were taken using a 2.5 μm radius stylus with a 3.0 mg contact force at 3.3 μm/s scan speed. Low-resolution 3D maps were obtained by scanning

a length of 100 µm in X direction with a 4 µm stepping in Y direction. These 3D maps provided a clear picture of surface morphology of 100 µm x 100 µm regions characterized by the root-mean-square (RMS) roughness, Rq. More detailed analysis of surface morphology was obtained by collecting scanning electron microcopy (SEM) images with a Supra 55 SEM microscope operating at 15 keV.

Surface chemistry has been investigated with the X-ray photoelectron spectroscopy (XPS) technique employing a Kratos Analytical, AXIS Ultra DLD spectrometer equipped with a 150 W Al Kα source and operating at a base pressure of $1x10^{-9}$ Torr. The surface survey and high resolution scans were observed in constant energy modes with 50 and 20 eV pass energy filters, respectively. The size of an analyzed area on the investigated samples was set at 220 µm x 220 µm. The XPS spectra were recorded for samples after laser irradiation and after the RTA step. The collected data were processed using Casa XPS 2.3.15 software. To compensate for the surface charging effect, all XPS data binding energies were referenced to the adventitious C (C_{adv}) 1s peak at the BE of 285.0 eV.

3. Results and Discussions

3.1 Laser marking contrast investigation

Fig. 1 shows microscopic image of sample No 2 with low contrast (a) and sample No 11 with high contrast (b) marking. It clearly shows that the gray (brightness intensity) difference between marked and unmarked regions on sample No 11 is quite obvious. However, on sample No 2, it is difficult to distinguish the laser marked region from that of the initial (non-marked) region.

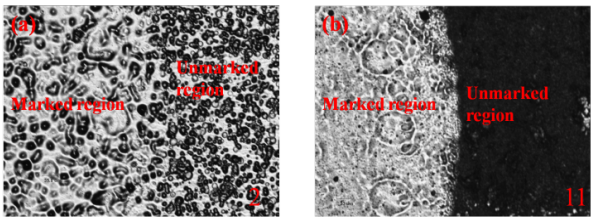

Fig. 1 Microscopic image of the sample No 2 with low contrast (a) and the sample No 11 with high contrast (b).

Table 1 demonstrates gray scale intensities of 5 samples selected from the group of investigated samples (No. 11, 18, 5, 17 and 2). It can be seen that sample No.11 exhibits the largest intensity ratio between the unmarked and laser marked regions, while sample No. 2 shows the weakest laser marking contrast.

Table 1 Intensity of marked and non-unmarked regions of 5 laser marked samples selected from the pool of 24 samples.

Sample No.	Intensity		Intensity ratio
	Marked	Unmarked	Mark. /unmark.
11	172	58	2.96
18	157	110	1.43
5	196	142	1.38
17	122	96	1.27
2	144	115	1.25

3.2 Surface morphology investigation

In order to investigate the effects of surface morphology on the achievable laser marking contrast, we compare in Table 2 the R_q values for the samples discussed in Table 1. Sample No 11, which exhibits the largest marking contrast, also shows the lowest roughness of the laser marked region. At the same time, sample No 2, which exhibits the poorest marking contrast, shows the highest roughness of the laser marker region. Generally, it can be seen that the increasing ratio of R_q^{Mrk}/R_q^{Unk} is associated with the decreasing contrast of laser marking. The likely reason of this behaviour is a decreasing reflectivity of the increasing roughness surface [6]. The laser energy is scattered more efficiently by a high roughness surface, which affects the micro/nano structures generated during laser irradiation. Also, an increased roughness surface will scatter more efficiently white light used for reading the laser marked symbols and, thus, it will result in a reduced contrast of laser marking [6].

Table 2 Root-mean-square (R_q) roughness of as-received (unmarked) and laser marked samples

Sample	R_q (nm)		R_q^{Mrk}/R_q^{Unk}
	Marked	Unmarked	
11	352	547	0.6
18	636	956	0.7
5	481	478	1.0
17	602	670	0.9
2	793	719	1.1

Fig. 2 shows SEM images of non-processed and laser marked surfaces of samples No 14, 5, and 17. Based on the contrast and surface morphology measurements, the marking quality decreases from sample No 14 and 5 to 17. Note the differences in the surface morphology of non-processed regions: the roughest initial surface characterizes the worst laser marking quality sample. On the processed regions of samples No 14 and 5, a series of laser fabricated spots can be seen quite clearly. The spots on the sample No 17, however, are almost invisible.

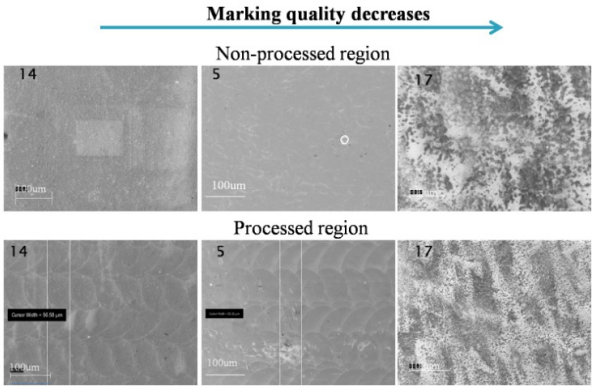

Fig. 2 SEM image of non-processed and processed regions of the samples No 14, 5 and 17.

3.3 Surface chemical investigation

Fig. 3 shows the Ni XPS spectra of non-processed and processed regions of the sample No 14, which belongs to the group of samples exhibiting a good quality laser marking. The spectra are fitted with the asymmetric line shape and plasmon loss peaks for Ni metal (red) and an empirical fit of the NiO (green) and $Ni(OH)_2$ (blue) line shapes [7]. The offset of the higher binding energy end of the background was used to improve the fit of the peak shapes. This background offset is determined using an iterative approach while monitoring a residual plot of the 2p 3/2 area [8]. Peak positions of these chemical compounds are presented in Table 3.

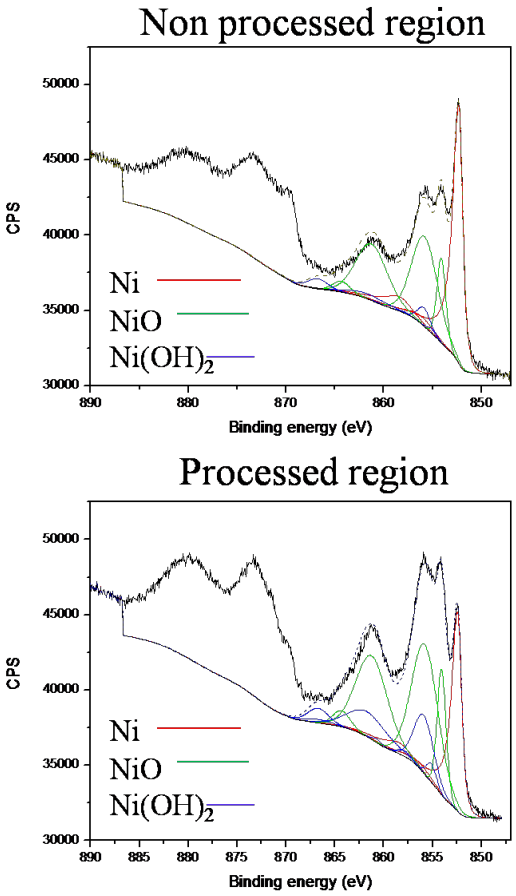

Fig. 3 Ni XPS spectra of non-processed and processed regions of sample 14 (good quality laser mark)

Table 3 Binding energy of chemical compounds used to fit the Ni 2p 3/2 spectrum.

	Peak 1 (eV)	Peak 2 (eV)	Peak 3 (eV)	Peak 4 (eV)	Peak 5 (eV)	Peak 6 (eV)
Ni	852.4	856.0	858.4			
NiO_x	854.1	855.8	861.2	864.3	866.7	
$Ni(OH)_2$	855.1	855.9	857.9	860.7	861.7	866.7

The atomic percentage of Ni, NiO_x and $Ni(OH)_2$ for non-processed and processed regions of the sample No 14 is shown in Table 4. These results indicate the increasing concentration of NiO_x and some decrease of $Ni(OH)_2$.

Table 4 Atomic percentage of Ni, NiO and $Ni(OH)_2$ of non-processed and processed regions of the sample No 14

	Ni	NiO_x	$Ni(OH)_2$
Non-processed	25.52	54.80	19.68
Processed	18.96	58.24	22.81

In Table 5, we present concentration (at. %) of Ni, NiO_x and $Ni(OH)_2$ observed on non-processed regions of the samples No 14, 5, 9 and 17 that represent, respectively, the decreasing laser marking quality. It can be seen that the concentration of $Ni(OH)_2$ increases as the marking results become worse.

Table 5 Atomic percentage of Ni, NiO_x and $Ni(OH)_2$ on as-received series of selected samples. The intensity ratio was calculated based on gray scale of the as-received and laser marked materials.

Sample	Intensity ratio	Ni	NiO_x	$Ni(OH)_2$
14	2.93	25.52	54.80	19.68
5	1.38	27.06	38.86	36.83
9	1.29	15.71	35.16	48.56
17	1.22	20.98	28.57	48.18

For comparison, the concentration of Ni, NiO_x and $Ni(OH)_2$ on the surface of laser irradiated samples No 14, 5, 9 and 17 are shown in Table 6. It can be seen that the chemical composition of all the samples are similar and no trend could be observed that would correspond to the decreasing/increasing contrast of laser marking.

Table 6 Atomic percentage of Ni, NiO_x and $Ni(OH)_2$ on the laser processed surface of selected samples.

Sample	Intensity ratio	Ni	NiO_x	$Ni(OH)_2$
14	2.93	18.96	58.24	22.81
5	1.38	18.56	66.15	15.41
9	1.29	18.86	57.15	23.26
17	1.22	15.14	66.90	15.94

Therefore, it seems reasonable to assume that the marking contrast is not due to the differences in surface chemical composition between as-received and laser processed surfaces. The surface roughness differences appear to be the main reason of the observed laser marking contrast..

3.4 Results of preheating sample before laser marking

Since the excesive concentration of $Ni(OH)_2$ on the as-received surfaces of the investigated lids was found responsible for poor quality marking, we have also carried out laser marking of samples that were thermally treated to reduce $Ni(OH)_2$ known to decompose at temperatures exceeding 300°C [9]. Table 7 compares the XPS results ob-

tained for samples before and after heating at 300 and 350 °C in N_2 for 20 minutes. It shows that the annealing even at 300 °C completely removes $Ni(OH)_2$ from the surface of the lid. At the same time, a more than 3-fold increase of the NiO_x concentration has been observed.

Table 7 Atomic percentages of Ni, NiO_x and $Ni(OH)_2$ on substrates before and after heating at 300°C and 350°C for 20 minutes in N_2

	Ni	NiO_x	$Ni(OH)_2$
Before heating	20.98	28.57	48.18
Heating at 300°C	0.60	96.47	2.92
Heating at 350°C	0.07	97.36	2.56

In addition to significant changes of the chemical composition, the samples annealed at 350 °C exhibited gray-to-blue transformation of their color. This transformation is related to the changing stoichiometry of NiO_x [10,11], however the exact mechanism of this transformation is the subject of a current study. It has been determined that the 350 °C annealed lids offer excellent conditions for high-contrast and high-resolution laser marking with the Q-switch Nd :YAG laser.

4. Conclusion

The results of this study have indicated that non-uniformly Ni-plated Cu lids of microelectronic packaging modules could exhibit poor quality laser marking that is difficult to correct by varying laser parameters. However, thermal annealing at 350 °C of the as-fabricated lids produces color changed material that offers an excellent conditions for the high-contrast and high-resolution laser marking with the Q-switch Nd :YAG laser. The implementation of this approach for laser marking will require the development of a robust annealing method for the fabrication of surfaces with a durable background color of the lids.

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