Journal of Optoelectronics and Advanced Materials Vol. 7, No. 3, June 2005, p. 1359 - 1364

LASER ASSISTED SURFACE MICROSTRUCTURING OF METAL/CERAMIC BILAYERED THIN FILM SYSTEMS

E. Krumov, J. Pirov, N. Starbov*

Central Laboratory of Photoprocesses "Acad. Jordan Malinowski" –Bulgarian Academy of Sciences Acad. Georgy Bonchev str., bl.109, 1113 Sofia, Bulgaria

A novel method for microstructuring of metal/ceramic bilayered thin film systems based on a combination of pulsed laser irradiation and electroless metal plating is developed. The ceramic thin films of ZrO_2 or Al_2O_3 are deposited on clean glass substrate by electron beam evaporation under high vacuum conditions. Thick alumina films are also prepared on Al plates by electrochemical anodizing. Conventional thermal evaporation technique is applied for vacuum deposition of very thin Bi, Sb or Ag films (d<10 nm) on the free ZrO_2 and Al_2O_3 surface. The samples thus prepared are irradiated via excimer (λ=193 nm) or Nd:YAG (λ=1064 nm) laser through suitable metal mask in order to remove the top metal film in the exposed areas. Further, the metal/ceramic bilayered systems are processed in electroless chemical bath for selective deposition of Cu or Ni on the rest metal micropattern. All processing steps are studied under SEM and by energy dispersive X-ray microanalysis (EDS). Possibilities for photochemical microstructuring of metal/ceramic bilayered thin film systems in order to obtain electroconductive Cu or electroresistive Ni microcirciuts are shown. The method developed is simple, versatile and it could be applied for rapid fabrication of circuits on any metal/ceramic system.

(Received May 5, 2005; accepted May 26, 2005)

Keywords: Thin ceramic films, Microstructuring, Photochemical processing, Electroconductive pattern

1. Introduction

The fabrication of conductive microcircuits is one of the key design problems in micro-, opto-electronics and sensor techniques. Several ideas for solution of this problem are published and methods used could be classified in two fields – photolithography and laser machining. Using classical optical or electron-beam lithography combined with dry ion etching is possible to obtain micron and submicron scaled metal interconnections in microelectronic devices as VLSI chips [1, 2]. Nowadays this approach is applied for microstructuring of polysilicon or metals like Pt, Au, etc. coated on different substrates for manufacturing either micromechanical devices [3], microheaters [4] and conductive electrodes [5] respectively. Recently, a more cheep laser radiation methods are developed for fabrication of conductive microschemes. Direct writing by either mask projection or contact printing of passive electronic components is usually made via laser ablation of metal coatings [6]. Most sophisticated methods as laser induced transfer (LIFT process) [7] and matrix evaporation (MAPLE process) or their combination (MAPLE-DW process) [8] are applied for production of electrodes, microheaters, resistors, capacitors and other electronic circuit elements. However, the most of the laser assisted methods are subtractive, i.e. parts of the thick metal coating, sometimes in substantial amount are removed and wasted.

This paper aims to present a new additive method for metal circuits printing based on laser assisted photochemical processing of ceramic materials.

* Corresponding author: nstar@clf.bas.bg

2. Experimental

The samples studied have metal/ceramic bilayered structure coated on different substrates of either Na-Ca-silica glass or aluminium plates. ZrO_2 or Al_2O_3 films with thickness d of about 1 μm are deposited onto glass substrates via e-gun evaporation in high vacuum better than 4×10^{-4} Pa. Substantially thicker alumina films (d>20 μm) are obtained by anodizing of Al plates in electrochemical bath of diluted H_2SO_4, the current density being about $1A/dm^2$. Further, very thin metal film of antimony or silver is vacuum deposited onto ceramic free surface by thermal evaporation technique. The thickness of Sb or Ag film (d = 8 - 10 nm) is carefully selected as compromise between the minimal metal quantity for efficient laser absorption and the maximal amount of Sb or Ag in order to produce electroless plated Cu or Ni circuits with good adhesion to the ceramic substrate. The samples thus obtained are exposed trough a metal mask with single shot or multipulse Nd:YAG (λ=1064 nm, τ=200 μs) or ArF^+ excimer (λ=193 nm, τ=20 ns) laser radiation. A contact printing is applied, using chromium or rigid stainless steel masks with micrometer- and milimeter-sized linear paths respectively. The exposure conditions are carefully selected in order to remove the top metal film in irradiated areas via laser evaporation. As a result, a negative metal image of the copied mask is obtained which could be amplified in electroless metal plating bath until electroconductive pattern is produced. The electroless metal deposition is carried out in alkaline copper (pH=12,6) or base nickel electrolyte (pH=5,0) which are electroless active at 50 °C and 85 °C respectively. The mean metal deposition rate is 2 – 5 μm/h. In both cases the bath composition could be varied so that thick electroconductive coating with good adhesion to ZrO_2 and Al_2O_3 to be obtained. In addition, the electroless Cu or Ni metalization is preceded by short activation of the metal pattern. For copper plating this procedure is made in hydrochloric acid solution of Pd^{2+}, whereas the Ni plating is made after pretreatment in the same nickel bath adjusted at pH=8. The duration of this sample pretreatment is short – 5-10 s, but it increases very effective the activity of the rest metal for starting the electroless copper or nickel plating. Fig. 1 demonstrates the general steps of the invented new photochemical method for microstructuring and metalization of the bilayered metal/ceramic systems.

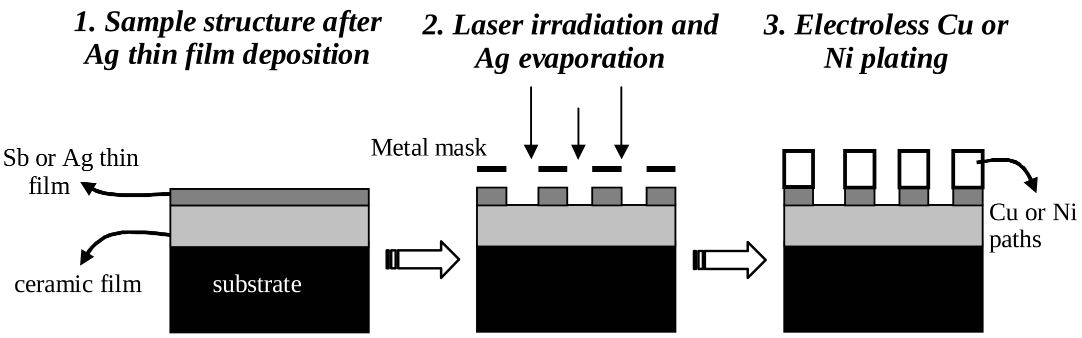
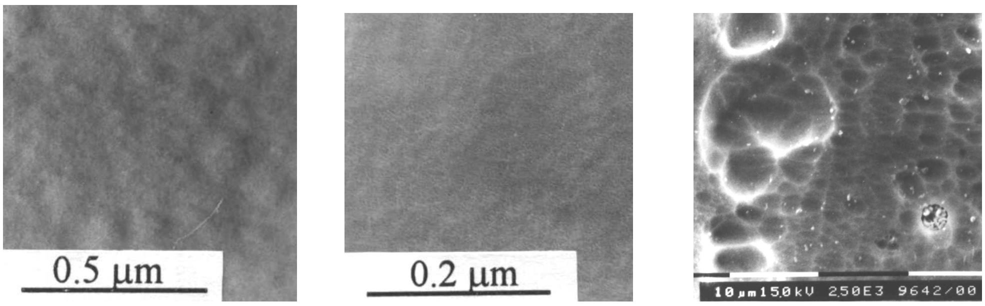


Fig. 1. Sequential steps of the laser assisted fabrication of conductive metal circuits.

The surface morphology as well as the composition of the laser and electroless bath processed samples is investigated under transmission (JEM 100B) or scanning electron microscope (SEM 515 Philips). Elemental analysis of the microstructured and metallized area is made by means of energy dispersive spectroscopy (EDS) and X-ray mapping (Philips SEM 505/EDAX 9100). The sample thickness is controlled via stylus profilometry (Talistep, Rank Teylor Hobson Ltd.) and DC conductivity measurement is used in order to estimate resistivity of the individual copper or nickel circuit paths.

3. Results and discussion

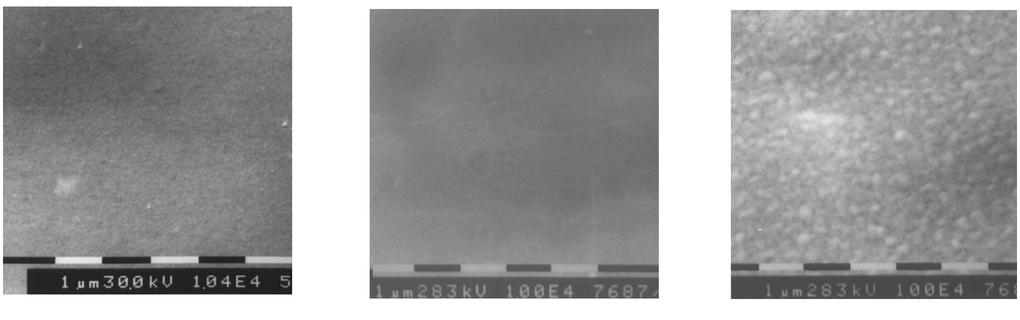
TEM investigations show that the ceramic films obtained via vacuum deposition are amorphous while the anodized alumina is polycrystalline. The visualized under TEM and SEM surface micromorphology of vacuum deposited ZrO_2 or Al_2O_3 films is granular. However, the individual grains with mean size of about 50 - 100 nm are build up from substructural units with one order of magnitude lower dimension. The Al_2O_3 film obtained during the anodizing is also smooth in microscale, but it copies the initial surface structure of the Al plates. Fig. 2 demonstrate the revealed microstructure of the virgin zirconia or alumina films obtained. This surface micromorphology is not substantially changed during the vacuum deposition of Sb or Ag on samples top surface. At the selected small thickness of 8 – 10 nm the antimony film is amorphous and has a smoothing effect on the initial ceramic microstructure. The silver coating with the same thickness is polycrystalline with uniform grain size of about 250 nm [9]. These morphology features of Sb and Ag films are presented on Fig. 3 when both metals are deposited onto zirconia top surface. However, there is no substantial difference in the film microstructure of antimony or silver coated onto alumina obtained either by e-gun vacuum deposition or by anodizing of aluminium plate.



a) b) c)

Fig. 2 Surface microstructure of: e-gun deposited onto glass substrate ZrO_2 – a), and b) - Al_2O_3, as well as of alumina film obtained after anodizing of Al plate – c). Visualization mode: a) and b) – TEM of Pt/C replica and c) – SEM. SEI - tilt angle 0°.

The laser microstructuring of metal/ceramic samples needs different energy density E_d depending on the laser radiation used. To remove the Sb or Ag thin film from the irradiated area a single shot excimer laser exposure at E_d = 250 – 300 mJ/cm^2 is necessary. If Nd:YAG radiation is applied the metal evaporation requires multipulse exposure (20 - 50 pulses at repetition rate of 1 Hz) at two times higher energy density.

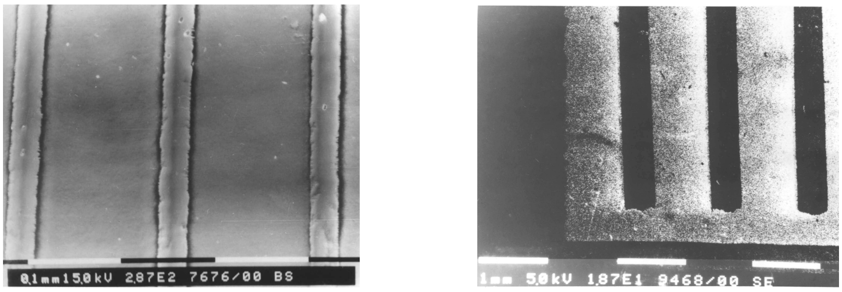


a) b) c)

Fig. 3. Micromorphology of ZrO_2 thin film obtained by e-gun evaporation – a), and of vacuum deposited onto zirconia free surface 10 nm thick film of Sb – b), or Ag - c).

After irradiation the exposed areas are free of Sb or Ag and the rest metal shaded from the mask could be used as promoter for selective electroless metal deposition. It should be mentioned here that the bilayered samples studied have different stability in the alkaline electrolytes used for copper or nickel metalization. One micrometer thick ZrO_2 films are very stable in electroless baths even at pH=12 and good quality circuits from thick Cu or Ni could be printed easily onto microstructured metal/zirconia surface. However, the alumina films are not resistive against base electrolytes. Either amorphous or crystalline alumina dissolves quickly even at pH =7.5 – 8.0. At this drastic etching activity of the electroless bath against Al_2O_3 the discontinuous metal film is easily sub-etched and removed from the sample surface. Therefore, in the case of vacuum deposited alumina films one can easily observe parts of the laser microstructured Ni or Cu image floating in the electrolyte used. Therefore, the method developed in the present study is applied on very thick Al_2O_3 coatings only [10]. The thickness of fabricated Cu or Ni coatings depends on the treatment duration in the electroless plating bath.

Using the method described a good quality 0.5 μm thick paths of bright copper or nickel are coated their resistivity being 5 –7 μΩcm. This value is comparable to the resistivity of the massive high purity Ni and about 3 - 4 time higher than that of bulk pure Cu. Fragments of two typical printed circuits with different path dimensions are illustrated on Fig. 4. As seen on Fig. 4a, 30 μm broad copper interconnections could be fabricated without any problems. However, the resolution achieved by the laser assisted photochemical microstructuring depends on sample microstructure – the substrate smoothness and the micromorphology of the ceramic film, as well as of the vacuum deposited metal. Besides, the printing accuracy is determined by both the mask quality and the laser exposure conditions.



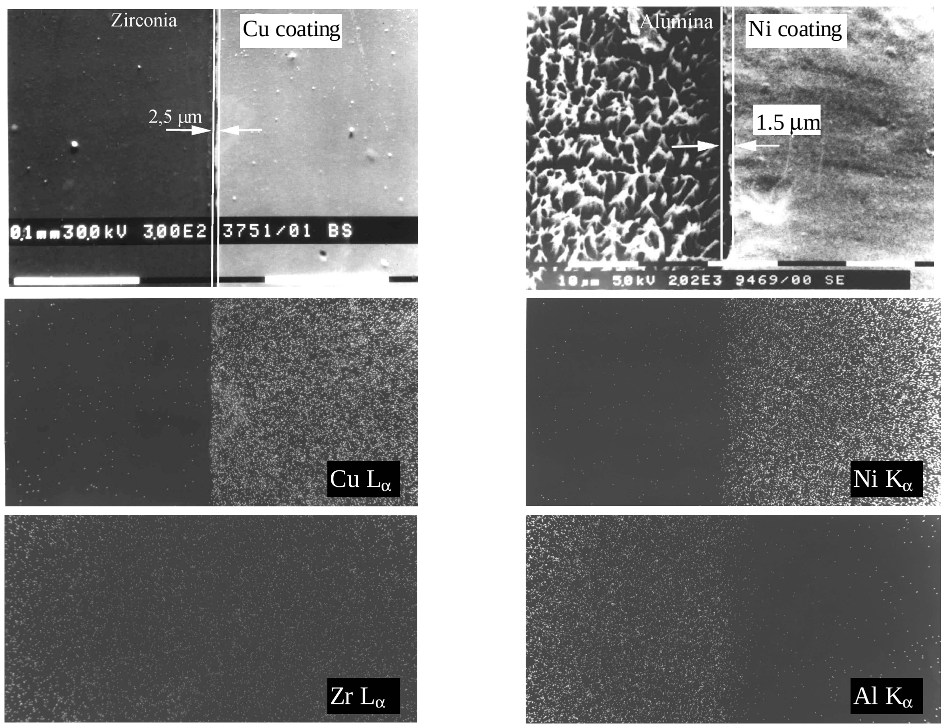
a) b)

Fig. 4. Printed Cu – a), and Ni – b), paths fabricated in different metal/ceramic systems: Sb/e-gun deposited ZrO_2 – a), and Ag/Al_2O_3 anodized film on Al – b). Visualization mode: a) – BEI and b) – SEI. Tilt angle 0°.

As shown earlier [9], excimer laser microstructuring is more precise since the metal is removed with single shot exposure, while the multipulse Nd:YAG laser irradiation leads to substantial local increase of the substrate temperature. Sometimes this sample overheating is accompanied with undesirable effects like photoexpansion, ablation and further damage of the ceramic film. Fig. 5 gives an idea about the good edge acuity of the printed Cu or Ni coatings as obtained at optimal laser exposure conditions via either excimer (Fig. 5a) or Nd:YAG (Fig. 5b) irradiation. It is clearly seen that using the method proposed an edge of the copied mask microstructures as good as ± 2 μm could be easily achieved. In addition, Fig. 5b demonstrates that the surface in the exposed area of the bilayered Al_2O_3/Al thin film system is strongly eroded, the etch pits being deep penetrating in the thick alumina coating. This means that the free surface of the alumina film is very intensively etched in the Ni electroless plating bath, while the rest silver catalyses the nickel deposition in the unexposed areas, thus preventing the erosion of the alumina underneath.

The results from EDS-elemental mapping of the same samples are also included in Fig.5. The distribution of the electroless plated metal Cu or Ni as well as of Zr and Al is presented on Fig. 5a and Fig. 5b respectively. Obviously, both copper and nickel are selectively deposited in non-irradiated areas only, which determines the good edge acuity of the printed paths. At the same time, the Zr-mapping gives a proof that the ceramic film in the irradiated through the mask areas is not removed from the substrate during the laser processing. The case of anodized Al_2O_3/Al sample is more complicated. From EDS results in Fig. 5b is not possible to establish whether the thick alumina film is fully dissolved during the pretreatment procedure in the alkaline Ni bath. However, the measured electrical resistivity in the nickel free parts of these samples is more than 1 GΩcm, i.e. although intensive etched the alumina coating is not fully dissolved and protects the fabricated conductive scheme from shortage through the aluminium substrate. In addition, the EDS-data on Fig. 5b show a very low aluminium content in the coated with Ni parts of Al_2O_3/Al samples. This result is due to the visualization conditions in scanning electron microscope. Obviously the accelerating voltage of 5 kV is not high enough for penetration of the electron beam through the 3 – 4 μm thick nickel film and for exciting of secondary X-ray radiation from the individual aluminium atoms in the alumina.

Finally, it should be mentioned that the obtained in this study electroless Cu or Ni coatings have very good adhesion to the ceramic film surface as it is proved with glue tape test of the laser microstructured and treated in electroless plating baths bilayered samples. This result is a prerequisite for applying of this method for fabrication of conductive circuits or heaters, which could be integrated in different devices in microelectronics or sensor techniques.



a) b)

Fig. 5. Edge acuity and EDX elemental mapping of Cu – a), and Ni – b), paths fabricated in different metal/ceramic systems: Ag/e-gun deposited zirconia – a) and Ag/alumina obtained via Al anodizing – b). SEM mode: a) – BEI and b) – SEI. Tilt angle 0°.

4. Conclusions

The present study demonstrates the feasibility of novel method for rapid fabrication of conductive metal circuits in metal/ceramic thin film systems. The laser assisted photochemical printing consists of three step sample processing:

- vacuum deposition of very thin metal film onto top ceramic surface,
- imaging trough a suitable mask via laser evaporation and

  metal deposition of conductive coating in electroless plating bath.

In the method developed vacuum deposited Sb or Ag film, as thin as 8 –10 nm, is used as laser radiation absorbing medium and as precursor for electroless metal plating. Further, it is shown that pulsed laser exposure in very broad wavelength range (193 nm – 1064 nm) could be applied in order to evaporate the irradiated through a suitable mask thin metal film. It is demonstrated that at appropriate exposure conditions the metal is completely removed from the irradiated areas. The non-irradiated rest metal is effective enough to initiate the electroless deposition of several micrometer thick metal coating in either Cu or Ni electroless plating bath. Thus, a positive copy of the mask is obtained, the resistivity of the printed paths of bright Cu and Ni being comparable with that of bulk copper or nickel metal. The reproduction quality is determined mainly by both the laser exposure parameters as well as mask quality. In the present paper edge acuity as good as ± 2 μm is demonstrated without any special processing precautions to be taken. Better imaging resolution could be also achieved even in sub-micrometer region. In this case the microstructure of the vacuum deposited thin metal film could be a limiting factor. However, such problem could be easily solved with amorphous metal film as the antimony top layer used in the metal ceramic samples studied in the present paper.

It should be noted here that the method proposed is simple, versatile and not restricted to contact printing only. The laser assisted microstructuring could also be made via either mask projection or direct recording by focused laser beam. Besides, the method presented here could be applied not only for rapid fabrication of conductive circuits on zirconia or alumina ceramic surface, but also on other metal/ceramic bilayered systems.

Acknowledgements

The authors are highly obliged to M. Radoeva and D. Popov especially for the electrochemical processing of the samples studied. Many thanks to Dr. K. Starbova for TEM and SEM imaging as well as for the constant interest and very helpful discussions during the development of the method disclosed here.

References

[1] P. A. Flinn, A. S. Mack, P. R. Besser, T. N. Marieb, MRS Bull. **12**, 26 (1993).
[2] J. Strandberg, Connections **1**, 42 (2000).
[3] W. I. Jang, C. A. Choi, C. H. Jun, Y. T. Kim, M. Esashi, Sens. Actuators **A 115**, 151 (2004).
[4] M. Baronchini, P. Placidi, G. C. Cardinali, A. Scorzoni, Sens. Actuators **A 115**, 8 (2004).
[5] B. Mazzolai, V. Mattoli, V. Raffa, G. Tripoli, D. Accoto, A. Menciassi, P. Dario Sens. Actuators **A 113**, 282 (2004).
[6] T. Tong, J. Li, Q. Chen, J. P. Longtin, S. Tankiewicz, S. Sampath, Sens. Actuators **A 114**, 102 (2004).
[7] J. Bohandy, B. F. Kim, F. J. Adrian, A. N. Nette, J. Appl. Phys. **63**, 1558 (1988).
[8] A. Pique, D. B. Chirsey, R. C. Y. Auyeung, S. Lakeou, R. Chung, R. A. McGill, P. K. Wu, M. Duignan, J. Fitz-Gerald, H. D. Wu, SPIE Proc. **3618**, 330 (1999).
[9] K. Starbova, E. Krumov, M. Radoeva, N. Starbov, D. Popov, G. Schlaghecken, E. W. Kreutz, Appl. Surf. Sci. **217**, 118 (2003).
[10] E. Krumov, D. Popov, N. Starbov, accepted for publcation in Centr. Europ. J. Chem.