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Laser assisted selective chemical metalization of Al_2O_3 films

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Abstract: Thick aluminum oxide films are prepared on Al plates by anodizing. On the ceramic surface thus obtained a very thin Ag film is deposited via vacuum thermal evaporation. The Ag/Al₂O₃/Al samples prepared are irradiated by Nd:YAG laser through a suitable metal mask in order to remove the top metal film in the exposed areas. Thus, a negative silver image of the copied mask is obtained. Further, the samples are processed in Ni electroless chemical bath activated by the rest of silver. All processing steps are studied by scanning electron microscopy (SEM). EDS X-ray mapping is applied to study the final distribution of Al and Ni in the processed areas. In addition, the DC conductivity of the fabricated Ni wires obtained is measured. The proposed new method for selective chemical deposition of electroconductive Ni onto laser microstructured Ag/Al₂O₃/Al samples is simple, versatile and not restricted to the metal/ceramic system studied as well as to the electroless deposited metal.

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1 Introduction

In the last decades, the integration and miniaturization degree of the microelectronic and sensor devices dramatically increases. This trend determines the current interest for the application of ceramic thin films with good insulating properties as a promising functional media in the contemporary advanced technologies. Alumina is widely used as

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a substrate in sensor technique, because of its suitable electrical and thermal properties [1,2]. In the sensor device the substrate should be integrated with a microheater as very important part for the sensor recovery. In addition, many sensors operate of accelerated temperatures in order to achieve better sensitivity, selectivity and response time. Usually, the microheaters are realized as polysilicon or electroresistive metal microstructures on bulk insolating substrate by various techniques [3–5]. However, the standard coating and fabrication procedures developed for sintered ceramics are not suitable for thin film materials. Therefore, many attempts are made to develop new methods for microstructuring of ceramic thin films.

As known, the Nd:YAG laser is a high-tech powerful tool for material processing, including micromachining of ceramics [6,7]. A high-energy laser radiation is often used for surface modification of metal oxide thin films in order to improve their microstructure and properties [8,9]. Besides, the laser assisted processing reveals a good possibility to develop a new approach for microstructuring of ceramic surface.

It is the aim of the present work to demonstrate the possibility for microcircuit printing of metals on alumina films by suitable combination of laser processing and electroless chemical plating.

2 Experimental

The experiments were carried out on thick alumina films prepared on Al substrates by anodizing. For that purpose 1 mm thick aluminum plates were used as anode in an electrolytic bath of diluted $\rm H_2SO_4$. A current density of about 1 A/dm² was applied in order to produce $\rm Al_2O_3$ films with thickness 20 – 30 μ m. Further, 10 nm thick Ag films were vacuum deposited on the free ceramic surface by thermal evaporation technique. The top metal film was prepared at 1×10^{-4} Pa background pressure and mean deposition rate of 0.1 nm/s. The Ag/Al₂O₃/Al system thus obtained was exposed trough a suitable metal mask by means Nd:YAG radiation (λ =1064nm, τ =200 μ s) (Fig. 1), the metal film being removed in the irradiated areas by laser evaporation. As a result, a negative silver image of the copied mask was obtained. A standard Ni electroless bath ELNIC 101 (MacDermit, pH 4.8) was applied for metalization of the rest Ag on the alumina surface.

The surface microstructure and the composition of the laser or/and electroless bath processed samples were investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) X-ray mapping. In addition, the electrical resistivity of the fabricated Ni wires was estimated by DC measurements.

3 Results and discussion

Fig. 2 presents SEM micrographs of surface microstructure of Al_2O_3 films prepared on the Al plates during the anodizing process. It is clearly seen that the alumina coating obtained has a grain like micromorphology the mean grain size being of about $2-3~\mu m$. It should be noted here, that the thickness of Ag film further deposited onto free alumina surface

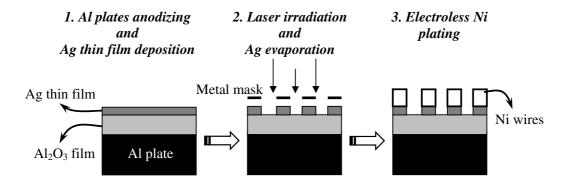


Fig. 1 The general steps scheme of Ag/Al₂O₃/Al system processing.

is very important parameter for successful microstructuring of the ${\rm Ag/Al_2O_3/Al}$ system. Two mutual competing requirements – high laser radiation absorptivity as well as good chemical stability of Ag in Ni bath, should be satisfied since the laser energy absorption rises with the Ag film thickness increase. However, the thicker the metal film the lower the adhesion of the Ag coating on the alumina surface. Preliminary experiments have shown that both requirements are satisfied at an optimal thickness of the Ag thin film of about 8-10 nm. At this film thickness the silver coating is continuous and polycrystalline with granular surface morphology with the mean grain size being of about 250 nm [10]. This means that the vacuum deposited silver film follows the surface microstructure of the sample, which is a prerequisite for homogeneous evaporation of Ag in spite of alumina granular morphology. For samples thus obtained a multipulse exposure (50 pulses at pulse energy density of 0.5 J/cm², repetition rate 1 Hz) is necessary for removing of the metal from the irradiated areas.

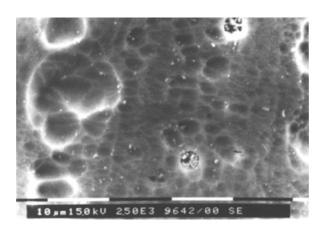


Fig. 2 SEM micromorphology of anodized Al plate surface.

The scanning electron micrographs of laser irradiated and electroless Ni plated Ag/Al₂O₃/Al system are shown on Fig. 3 together with corresponding images of EDS-elemental analysis. It is clearly seen (Fig. 3a), that the details of the mask are successfully copied by electroless deposited Ni coating. The micrographs from the X-ray mapping confirm the Ag removing from the irradiated area (Fig. 3b) as well as the Ni coating onto

unexposed rest of silver (Fig. 3c). In addition, the electroless bath processing provokes different morphology changes in the samples studied. It is clearly seen on Fig. 4, that the Ni coating has a smoothing effect on the initial surface morphology of the alumina film (for comparison see Fig. 2). Simultaneously, the irradiated areas have a very rough microstructure, which is a result of the free alumina surface etching during the bath processing. This surface roughness between the Ni wires could be very useful for good adhesion of any insulating and protective coating on which the sensor itself should be designed. Moreover, Fig. 4 demonstrates a very good edge acuity - about 1.5 μ m, of the Ni wires.

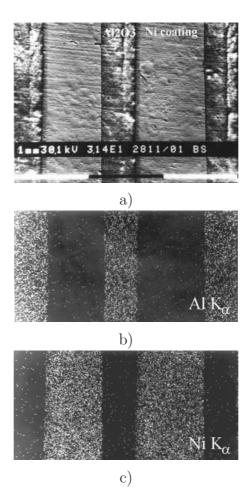


Fig. 3 SEM micrographs of microstructured under Nd:YAG laser exposure $Ag/Al_2O_3/Al$ system at energy density 0.5 J/cm^2 and 50 pulses (a), and corresponding X-ray maps for Al (b) and Ni (c).

Following the method proposed, a good conductive Ni coating is prepared at the experimental condition used in this study. As demonstrated by the DC conductivity measurements, the Ni wires resistivity - $\rho = 5 \times 10^{-6}~\Omega {\rm cm}$, is very close to that of high purity bulk nickel - $\rho = 7 \times 10^{-6}~\Omega {\rm cm}$. For microheaters preparation, much higher resistivity material is often used, for instance nichrom ($\rho = 1.1 \times 10^{-4}~\Omega {\rm cm}$). In order to increase this microheater parameter more complicated baths for simultaneous deposition of metal alloy or combination of metals could be applied.

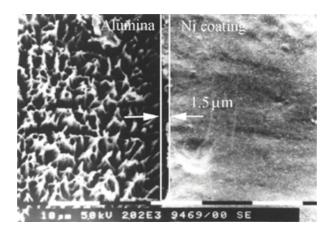


Fig. 4 SEM micrograph of the microstructured $Ni/Ag/Al_2O_3/Al$ system demonstrating the edge acuity.

Finally, it should be mentioned that the electroless Ni coatings obtained have very good adhesion to the Ag/alumina ceramic surface as it is proved with glue tape test of the circuits printed onto $Ag/Al_2O_3/Al$ system studied.

4 Conclusions

A new method for selective laser photochemical processing for fabrication of metal circuits onto alumina ceramic films is developed. The method proposed is simple, versatile and could be applied for rapid microstructuring of printed electrodes or microheater circuits with good edge acuity in the micron range. This laser assisted photochemical processing is suitable for microelectronics and sensor technique and its application is not restricted to the metal/ceramic systems used or electroless plating baths.

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