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PHOTO-CHEMICAL PROCESSING OF VACUUM DEPOSITED ALUMINA THIN FILMS

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Amorphous Al_2O_3 thin films electron-beam deposited onto glass and chemically roughened stainless steel substrates were irradiated using ArF* excimer laser pulses (λ=193 nm, τ=20 ns) at different energy density and pulse number. Chemical electroless plating bath was used for Ni deposition on laser processed samples. Optical spectrophotometry, scanning electron microscopy (SEM), EDS and X-ray analysis were applied in order to characterize the virgin as well as the photo-chemically treated alumina films. An evolution of γ-Al_2O_3 was observed as a result of laser irradiation of the films studied. It was established that electroless Ni plating of the alumina thin films occurs selectively on laser modified areas, thus demonstrating the catalytic activity of alumina γ-phase. Further, at an optimal laser energy density of 0.25 J/cm^2, and proper electroless plating conditions a growth of individual Ni clusters is observed, which are uniformly distributed over the irradiated film surface. On the basis of elemental X-ray mapping the number of Ni clusters per unite area is evaluated. The results obtained reveal a possibility for deposition of catalytic active metal on Al_2O_3 surface and could be used for development of novel method for heterogeneous catalyst design.

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1. Introduction

The ceramic thin films are modern functional materials that find a wide scope of applications in catalysis, sensor technique and microelectronics. As known, the active part of the contemporary catalysts represents highly dispersed nanostructured metal clusters on proper catalyst supports. Therefore, the metallization process is of great importance for development of advanced materials on the base of ceramics. However, reliable and reproducible deposition of metals on thin ceramic films still remains a key problem that need to be optimized since the experience on the metallization of bulk ceramics can not be directly applied to thin film materials.

Variety of methods and techniques for modification of ceramic thin films and their properties are described in the literature [1-3]. In that respect, the excimer lasers are between the most powerful and efficient tools. Recent investigations show that laser irradiation of sintered alumina induces extremely fast melting/quenching processes resulting in the evolution of γ-Al_2O_3 [4]. The latter is known to be responsible for the catalytic activity of alumina ceramics towards electroless metal plating. On the other hand, microstructure modification and separation of metal phase in ceramic thin films under excimer laser exposure is also found to take place [5,6]. On this

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basis it seems reasonably to combine the potential of the excimer laser radiation and proper electroless metal plating for metallization of alumina thin films.

It is the aim of the present work to check the possibility for electroless Ni plating of excimer laser processed Al_2O_3 as an alternative method for design of catalysts.

2. Experimental

The experiments were carried out with 1.0 μm thick alumina films vapour deposited on glass or chemically roughened stainless steel substrates. The samples were prepared by e-beam evaporation of high purity (99.99%) Al_2O_3 tablets under background pressure of the order of 1.10^{-3} Pa and mean deposition rate of 0.3 nm/s. The substrates were kept at room temperature during the film deposition. The irradiation was performed in air by means of pulsed ArF* excimer laser (λ=193 nm, τ = 20 ns) with single shots or in repetitive rate regime. The pulse energy density (E_d) at the sample surface was varied in the range 0.2 – 1.7 J/cm^2. Further, the laser modified samples were processed in electroless Ni bath "Elnic 101" - Mc Dermit at 90 °C and pH = 5. The samples were analyzed applying various imaging and spectroscopic techniques. The optical transmission or reflection spectra of the films studied were recorded by means of Cary 5E UV-VIS-IR spectrophotometer in the wavelength range 250 – 800 nm. The recorded X-ray diffraction spectra (XRD) revealed the crystalline structure and phase composition of as deposited and laser modified films. Scanning electron microscopy (SEM) and elemental X-ray mapping (EDS) were applied to study the sample surface morphology and Al as well as Ni distribution, correspondingly.

3. Results

The alumina thin films studied are optically transparent in the visible wavelength range with amorphous structure as evidenced by X-ray diffraction spectra.

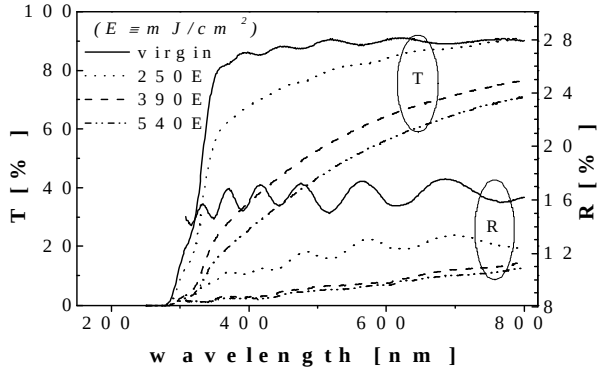
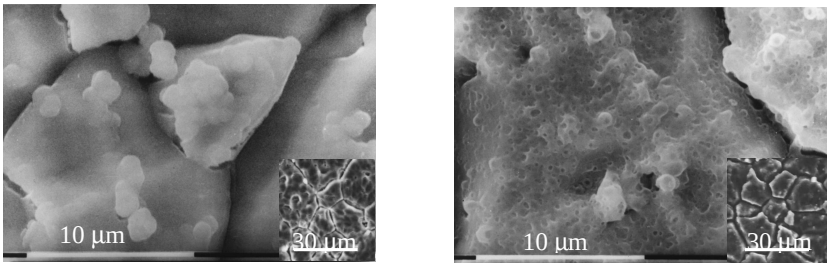


Fig. 1. Optical transmittance (T) and reflectance (R) spectra of 1.0 μm thick Al_2O_3 films, virgin and single – shot irradiated with a pulse energy density increase from 0.25 to 0.54 J/cm^2.

In our previous work it was found that the ArF* excimer laser radiation successfully modify the microstructure of the Al_2O_3 thin films. Fig. 1 shows the optical transmittance (T) and reflectance (R) spectra of the virgin and single shot irradiated alumina thin films on glass substrate varying the pulse energy density in the range of 0.25 – 0.54 J/cm^2. As seen, absorption edge shift to higher wavelengths is observed with increasing the pulse energy density. The higher the laser energy density the greater the absorption edge shift to lower energies. Besides, it is clearly seen a reflectance decrease in all irradiated areas as compared to non-irradiated ones. It should be noted that in principle reflectance measurements of Al_2O_3 films on stainless steel substrates as dependent

on laser parameters are possible. Nevertheless, the initially high surface roughness of these substrates would be considerable obstruction for obtaining of unambiguous results. However, applying the secondary electron imaging information for morphology changes as a result of laser light absorption within the Al_2O_3 films could be obtained. The low magnification image on Fig. 2a reveals a large grain-like and deep groove surface that is typical for uncoated stainless steel substrate. Also, it is seen that the grain size slightly increases due to the laser irradiation (Fig. 1b). Since, as deposited alumina films are structureless [7] under the present imaging conditions it could be concluded that they follow the substrate relief of unirradiated sample (Fig. 2a). As seen on Fig. 2b, two basic morphological features could be distinguished after pulse laser irradiation. These are an increase of the stainless steel mean grain size and appearance of fine morphological details like bubbles and pores in the ceramic thin film. These changes are obviously due to the occurrence of fast melting/resolidification processes in Al_2O_3 films.



a) b)

Fig. 2. Scanning electron micrographs of virgin (a) and single shot irradiated alumina thin films at E_d=0.25 J/cm^2.

As seen from the XRD spectrum on Fig. 3, multiple laser processing of Al_2O_3 thin films (E_d=0.8 J/cm^2) results in the evolution of γ-Al_2O_3 that is known as the most catalytically active alumina phase. Therefore, an amorphous to crystalline phase transition takes place in that case.

The formation of γ-Al_2O_3 phase is a substantial prerequisite with respect to the catalytic activity towards the electroless metal plating. As mentioned in the experimental part, the laser-modified samples were further subjected to short high temperature electroless Ni plating. In order to check the efficiency of the latter the samples were Ni (K_α) X-ray mapped. It is established that the X-ray images display nickel traces in all samples irradiated within the whole range of pulse energy density bellow the ablation threshold. It was also found that the amount of deposited Ni is related to the pulse energy density. The higher is the latter the greater is the number of X-ray nickel counts.

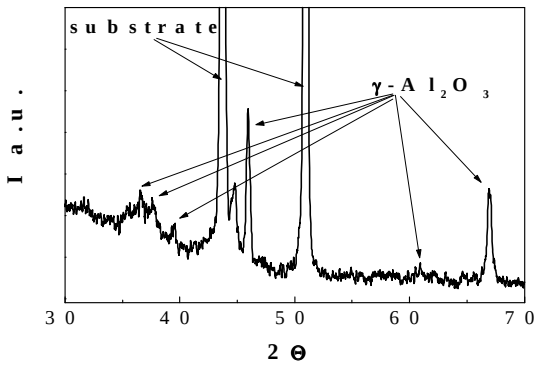


Fig. 3. X-ray diffraction spectra of excimer laser irradiated 1.0 μm thick Al_2O_3 films with 4 pulses and E_d= 0.8 J/cm^2.

Fig. 4 presents scanning electron micrographs and corresponding X-ray elemental mapping of Al (K_α) and Ni (K_α) of electroless Ni bath processed virgin (a) and irradiated (b) alumina films

(single shot, E_d = 0.25 J/cm^2). As seen, the aluminum distribution of both virgin and laser processed samples (Fig. 4c,d) is uniform. This means that the alumina films are chemically stable under Ni electroless plating conditions studied. Further EDS studies evidenced that Ni is above the detection limit in both irradiated and nonirradiated films and similarly to aluminum it is uniformly distributed within alumina thin film subsurface region (Fig. 4e,f). It should be noted that since Ni is an inherent component of stainless steel substrate used the detected.Ni counts on the virgin sample have to be considered as a background signal. It is clearly seen from X-ray maps on Fig. 4 that the concentration of Ni counts in laser-processed area is larger as compared to that of non-irradiated ones. The evaluation of nickel counts showed that the background EDS signal is of the order of 6.45×10^7 counts/cm^2 versus 1.45×10^7 counts/cm^2 for the irradiated area. On this basis it could be concluded that on laser modified regions of alumina thin films Ni has been effectively electroless plated.

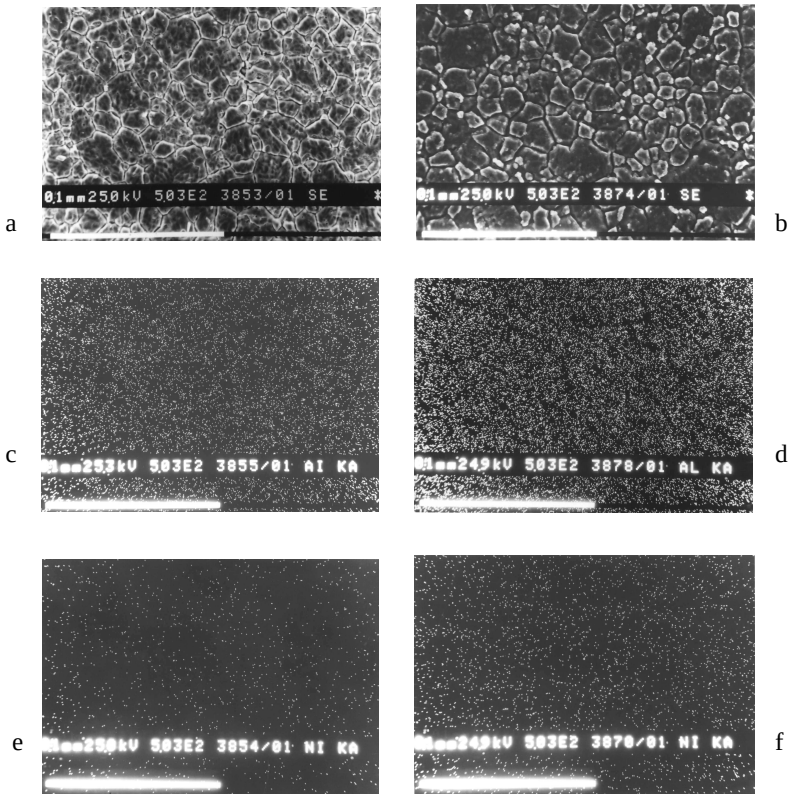


Fig. 4. Scanning electron micrographs and EDS X-ray maps (Al K_α and Ni K_α) of virgin (a,c,e) and single-shot irradiated at 0.25 J/cm^2 (b,d,f) 1,0 μm thick Al_2O_3 films on stainless steel substrate.

4. Discussion

The results from the present study showed that absorption of short UV pulses within the alumina films induces photodarkening effect that is accompanied by the evolution of γ-Al_2O_3. Since the photon energy of ArF* laser radiation used is far below the band gap of pure Al_2O_3 (10 eV) an occurrence of a multiphoton absorption during excimer laser irradiation could be assumed. On the other hand a separation of new nanosized aluminum phase within the alumina film and formation of thin film nanocomposite could be attracted for explanation of observed photodarkening efect. The present results on Al_2O_3 thin films are consistent with those obtained for other excimer laser processed thin film of refractory materials like ZrO_2 and TiO_2 [5,8]. In contrast to electroless plating of zirconia films, where Zr clusters provoke the film metallization [9], having in mind the possibility of γ-A_2O_3 and Al to activate electroless Ni deposition, it could be assumed that both phases

contribute to that deposition process that is. Additional experiments are necessary to be carried out in order to prove that suggestion.

On the other hand the successful electroless plating of laser modified alumina films under wide range laser parameters offer a possibility for finding optimal processing for different application purposes. Usually, the lowest pulse energy density would be the most advantageous. On this basis the lowest energy density value for modification of alumina thin films of 0.25 J/cm^2 is considered as optimal.

5. Conclusions

The present work demonstrates the evolution of catalytically most active γ–Al_2O_3 phase in excimer laser modified amorphous thin alumina films and the formation of nanocomposite material. The latter is shown to exhibit a great activity toward electroless metal plating. On this basis an opportunity for deposition of nanostructured Ni clusters on laser processed e-gun deposited alumina thin films is demonstrated thus revealing a new route for the designing of alumina supported catalysts.

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References

[1] J. Liu, C. J. Barbero, J. W. Corbett, K. Rajan, H. Leary, Mat. Res. Soc. Symp. **311,** 239 (1993).
[2] W. K. Choi, S. C. Choi, H. J. Jung, S. K.Koh, D. J. Byun, D. W. Kum, J. Vac. Sci. Technol. **A 16(6),** 3311 (1998).
[3] B. Stolz, G. Backes, A. Gilner, E. W. Kreutz, Appl. Surf. Sci. **109-110**, 242 (1997).
[4] L. D. Laude, K. Kolev, M. Brunel, P. Deleter, Appl. Surf. Sci. **86**, 368 (1995).
[5] K. Starbova, V. Mankov, N. Starbova, D. Popov, D. Nihtianova, K. Kolev, L. D. Laude, Appl. Surf. Sci **173**, 177 (2001).
[6] A. J. Pedraza, M. J. Godbole, M. J. DeSilva, D. H. Lowndes, MRS-Proc. **285**, 203 (1994)
[7] E. Krumov, V. Mankov, K. Starbova, Vacuum **76**, 211 (2004).
[8] V. Yourdanova, K. Starbova, K. Kolev, L. D. Laude, Nanoscience and Nanotechnology **4,** eds. E. Balabanova and I. Dragieva (Heron Press,Sofia, 2004) 297.
[9] E. Krumov, J. Dikova, K. Starbova, D. Popov, V. Blaskov, K. Kolev, L.-D. Laude, Journal of Materials Science – Materials in Electronics **14**, 759 (2003).