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Laser modification and chemical metalization of sol-gel zirconia thin films as potential material for catalytic applications

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The possibilities for modification of sol-gel ZrO_2 thin films by excimer laser radiation with respect to their potential application in heterogeneous catalysis are studied. It is established that as a result of laser irradiation, the film microstructure is strongly modified and a higher specific surface area is obtained. It is observed also that amorphous to crystalline phase transition occurs in the exposed film areas. The excimer laser modified surface is found to be active in promoting of electroless metallization with Ni and Cu. The results obtained are very encouraging for further catalytic applications of the thin sol-gel zirconia films.

Keywords: ZrO_2 thin films, sol-gel, excimer laser processing, electroless plating

INTRODUCTION

Thin films of ZrO_2 (zirconia) have beneficial ceramic properties [1] which offer various possibilities for technological applications as, for example, optical coatings, thermal barrier as well as catalysts or catalytic supports [2]. 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 needs 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 [3-5]. In that respect, the excimer lasers are among 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 [6]. 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 [7, 8]. Both types of phase transitions are known to be responsible for the catalytic activity of some oxide ceramics towards electroless metal plating. That approach could be applied for functionalization of zirconia films with respect to their application in heterogeneous catalysis.

Since the construction of three way catalysts for exhaust gases conversion, attempts for substituting ceramic supported noble metal catalysts by inexpensive transient ones or theirs oxides have been made. In this respect copper (Cu) and nickel (Ni) as well as their oxides are among the most intensively studied systems. The other way to produce a cheaper catalyst is to decrease the price of the catalyst support. A promising low cost technique for preparation of thin zirconia films is the sol-gel method, which has the advantage of being able to form homogeneous thin ceramic films at low temperatures onto complex shapes [9].

In the present paper the possibilities for surface modification of sol-gel ZrO_2 thin films by excimer laser processing are studied. Besides, the catalytic activity of exposed samples toward Ni and Cu electroless plating is investigated. The results obtained are discussed in the view point of potential application of the sol-gel ZrO_2 films in heterogeneous catalysis.

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EXPERIMENTAL

The experiments were carried out on sol-gel ZrO_2 thin films with thicknesses between 400 and 1000 nm. The samples were prepared via multiple spin coating from zirconium propoxide solution, stabilized by acetyl-acetone, at room temperature. The substrates used were preliminary cleaned Ca-Na silicate glass plates or sheets of chemically roughened stainless steel. The preparation procedure consisted in consecutive spin coating of a single layer followed by thermal treatment at 350 ^oC. Thus, multilayered ZrO_2 films with different thickness were obtained. These samples were exposed to excimer laser radiation and after that chemically treated in electroless baths for metal deposition. The irradiation was carried out by a KrF^+ (λ=248 nm) or ArF^+ (λ =193 nm) excimer lasers applying single shots or multiple pulses in repetitive rate of 1 Hz. During the exposures the pulse energy density was in the range between 0.4 and 1.7 J/cm^2 and was always kept below the ablation threshold of the material. For metallization of the exposed layers two commercial baths were chosen – one for Ni- and the other for Cu-plating. The surface morphology of the samples was imaged under Philips 515 scanning electron microscope after each stage of experimental process. The phase composition of irradiated and non-irradiated ZrO_2 films were followed under SEM and by means of XRD analysis.

RESULTS AND DISCUSSION

Fig. 1 presents SEM micrographs of the surface of non-irradiated (a) and irradiated by ArF^+ laser with 10 pulses at pulse energy density of 0.88 J/cm^2 (b) 400 nm thick ZrO_2 sol-gel film as well as the corresponding Zr X-ray mapping (Fig. 1c, d). As seen, due to the laser absorption, the microstructure of the films is strongly modified and is distinctly different from that of the non-illuminated sample. Besides, an appearance of fine morphological details like bubbles and pores in the exposed ceramic films is detected. Obviously, these changes are due to the occurrence of fast melting/re-solidification processes in the samples thus increasing their specific surface area. Moreover, the Zr X-ray maps evident that the ceramic film is uniformly distributed on the substrate and after laser irradiation remain unchanged. Therefore, the laser energy density is below the ablation threshold of the material and the radiation used do not causes films damages.

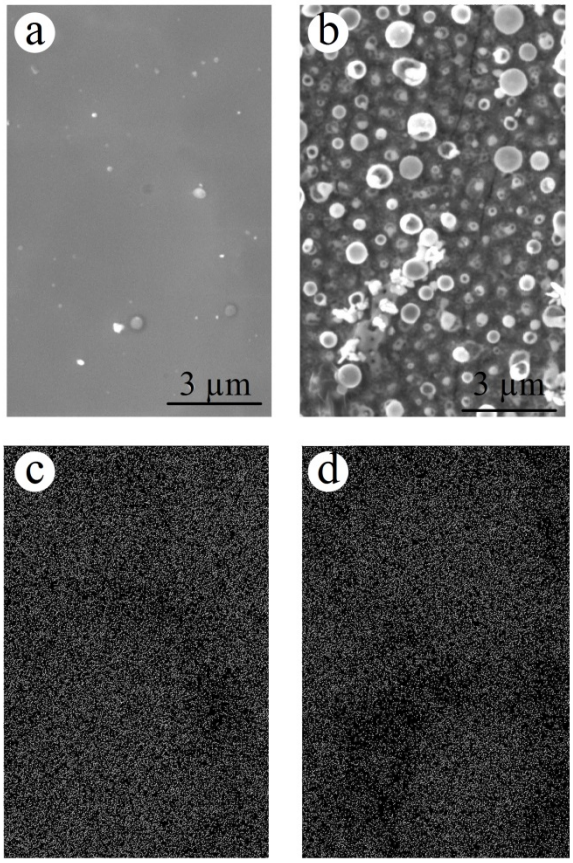

Fig. 1. Scanning electron micrographs (a, b) and corresponding Zr (K_α) (c, d) elemental X-ray maps of non-irradiated (a, c) and irradiated (b, d) 400 nm thick ZrO_2 sol-gel films deposited on stainless steel substrates.

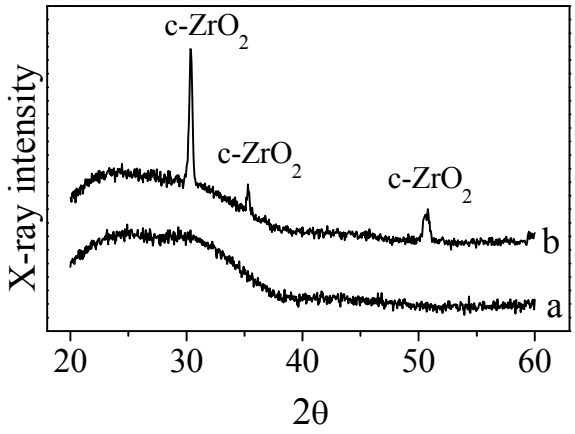

Fig. 2. X-ray diffraction spectra of 400 nm sol-gel ZrO_2 film deposited on glass substrate, before (a) and after irradiation (b).

Fig. 2 presents XRD spectra of 400 nm sol-gel ZrO_2 film, deposited on glass substrates, before (a) and after irradiation (b). Evidently, as a result of laser irradiation a phase transition from amorphous to crystalline state takes place. The crystalline phase was identified as high temperature cubic modification of zirconia, c-ZrO_2, known as a promising catalyst [2]. Unlike those deposited on

glass substrates, the sol-gel films coated on stainless steel plates comprise both amorphous and orthorhombic zirconia phase. Under conditions of single shot irradiation of 800 nm thick films, a complete amorphous to orthorombic zirconia phase transition takes place.

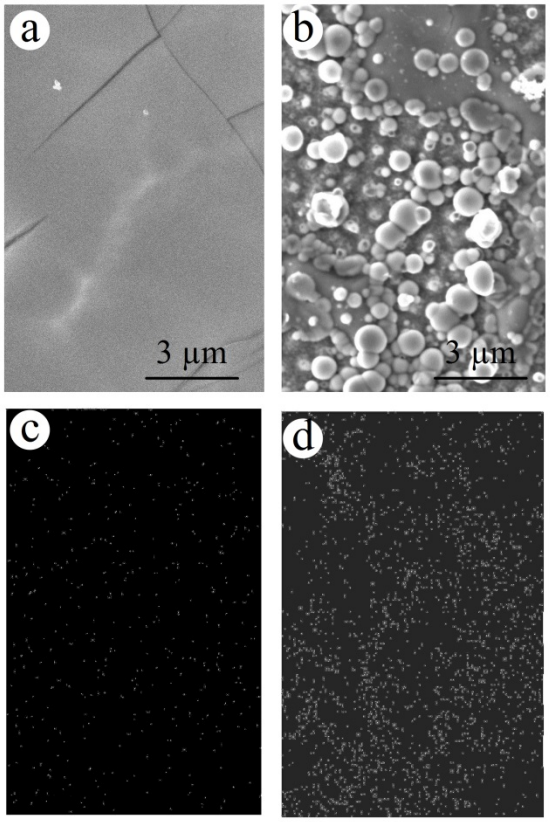

Fig. 3. SEM micrographs (a, b) and corresponding Ni (K_α) (c, d) elemental X-ray maps of non-irradiated (a, c) and irradiated (b, d) 400 nm thick ZrO_2 sol-gel films deposited on stainless steel substrates after electroless plating.

Further, the excimer laser modified surface was found to promote both the electroless plating of nickel and copper. Fig. 3 presents scanning electron micrographs of the surface of as deposited (a) and laser irradiated (b), processed in Ni-electroless bath as well as the corresponding nickel X-ray maps (c, d). As can be seen from the SEM micrograph in Fig. 3a, regularly distributed aggregates are formed on the surface of the laser-irradiated and chemically treated sample. In this case the X-ray map (Fig. 3d) evidences a high density of Ni (K_α) X-ray counts, which follow the distribution of the electroless deposited aggregates. It is thus clear that the laser-modified zirconia surface activates the process of the Ni-electroless plating. The micrograph in Fig. 3c displays Ni background signal that is consistent with the absence of metal aggregates on the surface of non-irradiated and chemically treated sample (Fig. 3a). It should be noted here that the EDS analysis performed reveals a uniform Zr distribution in both as-deposited and laser irradiated sol-gel films after the chemical treatment. This is an evidence for the relatively good chemical stability of laser-modified samples in the Ni bath used.

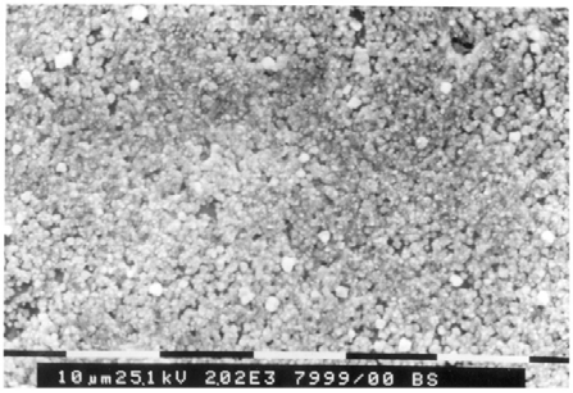

Fig. 4. SEM micrographs of irradiated by KrF* excimer laser 800 nm stainless supported ZrO_2 sol-gel film after Cu-electroless plating.

Similar experiments were performed in order to study the possibilities for electroless deposition of Cu on the surface of laser irradiated sol-gel ZrO_2 films. An example for the coatings obtained is demonstrated in Fig. 4, where a SEM micrograph of the surface of 800 nm stainless supported ZrO_2 film, irradiated by KrF^+ laser at pulse energy density 1.7 J/cm^2 is presented. It was also established that both irradiation and plating conditions can be efficiently optimized with respect to the size of deposited Cu clusters, which is an important prerequisite for practical application of the results obtained.

CONCLUSIONS

The results of the present study show that the excimer laser processing modifies significantly the structure of ZrO_2 thin films, obtained by the sol sol-gel method. The evolution of the specific surface area as a result of laser absorption combined with opportunity for electroless plating of catalytic active metals reveals possibilities for the development of both catalytic supports and catalysts, based on thin sol-gel zirconia films.

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ЛАЗЕРНА МОДИФИКАЦИЯ И ХИМИЧЕСКА МЕТАЛИЗАЦИЯ НА ЗОЛ-ГЕЛ ТЪНКИ ФИЛМИ ОТ ZRO_2 КАТО ПОТЕНЦИАЛЕН МАТЕРИАЛ ЗА КАТАЛИТИЧНИ ПРИЛОЖЕНИЯ

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(Резюме)

Изследвани са възможностите за модификация на зол-гел ZrO_2 тънки слоеве чрез ексимерно лазерно облъчване по отношение на потенциалните им приложения в хетерогенния катализ. Установено е, че в резултат на лазерното облъчване микроструктурата на слоевете се променя значително, което води до увеличаване на специфичната им повърхност. Също така е установено, че в експонираните области настъпва фазов преход от аморфно към кристално състояние. Намерено е, че лазерно модифицираните повърхности проявяват активност по отношение на отлагане на Ni и Cu при обработка в съответните химически бани. Получените резултати са многообещаващи с оглед на по-нататъшни каталитични приложения на тънки слоеве от циркониев оксид, получени по зол-гел метод.