

is regarded as one of the promising methods to meet such a requirement.

We have attempted to develop new methodology based upon bio-inspired processing to easily fabricate ceramic micropatterns of high quality. Our method employs organic self-assembled monolayers (SAM) formed on solid substrates. They are used as templates to control site-selective deposition processes in solutions through various interactions at organic/inorganic interfaces.

The first approach is principally based on heterogeneous nucleation and growth on SAM surfaces. By utilizing the chemisorption properties of the organic functional groups, it is possible to modify the nucleation process, thereby facilitating the site-selective deposition of thin films leading to high-resolution micropatterns. This approach achieved very nice high-resolution micropatterns of  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{SrTiO}_3$ .

The second approach is based on the electrostatic interactions between homogeneously nucleated particles and the substrate. Surface charges, either negative or positive, would determine the deposition process in this case. A micropattern of hydroxyapatite was successfully fabricated.

The third approach is a little different from the above two. We succeeded in low-temperature fabrication of ZnO micropatterns through site-selectively catalyzed deposition in an aqueous solution. SAM with phenyl/OH-surface functional groups was used as a template. Prior to the deposition of ZnO, the phenyl-group regions of the substrate were selectively catalyzed with Pd colloid particles. ZnO was then electroless deposited on the Pd catalyst attached to the phenyl-surfaces giving rise to a high-resolution micropattern of ZnO particulate thin films.

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### Latest results regarding binary metal oxide semiconductor deposited by sputtering for gas sensing applications

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Nanostructured materials exhibit unique properties for many fields of application, there are remarkable improvements or at least deviations from the properties of the coarser grained material. The explanation for these particularities is attributed to the significant increase in grain boundary area due to the smaller grain sizes.

In the gas-sensing field the applications of nanostructured materials are manifold, it has been proved experimentally and theoretically that decreasing of grain size leads to an enhancement of the sensing performances. The main problem is that the annealing process necessary for the stabilization

of the sensing layer causes grain-coalescence, in pure titania for example the grain size, for an annealing at 800 °C, becomes higher than 100 nm.

There is a great effort in reducing the grain dimension and increasing the surface area exposed to the interaction with gaseous species. One of the strategies used is the addition of a second element, which can inhibit the grain growth. Such a possibility was exploited in the past over  $\text{WO}_3/\text{TiO}_2$  and  $\text{MoO}_3/\text{TiO}_2$  thin films. Due to the relatively low sublimation temperature of  $\text{MoO}_3$  with respect to the melting temperature of  $\text{WO}_3$  and  $\text{TiO}_2$ , such systems exhibit a very interesting and complex evolution during thermal treatment.

This methodology of preparation of thin films is referred to as selective sublimation processing (SSP). This technique can prevent grain-coalescence. Furthermore, the relative proportion of the oxides can be varied when sublimation starts being effective. Finally, an effect on film porosity is also expected, depending on the extent of oxide segregation from the nanosized film.

In such a way, there is the possibility to tailor the properties of a nanosized thin film. We have demonstrated that simply through annealing we can control the material properties in term of composition, structure and in turn sensing properties.

Thin films of Mo–W, Ti–Mo, Sn–Fe, Ti–Nb, Ti–Ta mixed oxides were achieved by reactive sputtering, assisted by the selective sublimation processing technique. The layer were characterized by standard volt–amperometric technique in the range of temperatures between 200 and 500 °C towards CO, ethanol and possible interfering gases.

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### Gas sensing mechanism of high-temperature electrochemical sensors based on YSZ with oxide electrodes

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The environmental concerns oblige to face the problems of pollutant emissions from vehicles. According to EU studies, the primary sources of CO and  $\text{NO}_x$  emissions are automotive vehicles. To control and reduce these emissions, standards introduced in the majority of the countries world-wide foresee the use of On-Board Diagnostic (OBD) systems. At present, given the lack of reliable CO/hydrocarbons and  $\text{NO}_x$  sensors, OBD is performed using two oxygen sensors. The development of sensors for the direct measurements of pollutants is of paramount importance for improving the OBD system performance.

This paper reports the efforts made in our laboratory to develop electrochemical sensors that might detect  $\text{NO}_x$  at high temperatures for OBD application. The non-Nernstian behaviour of zirconia-based electrochemical  $\text{NO}_x$  sensors with various oxides as sensing electrodes was studied in the temperature range 500–700 °C. Both pellets and tape-casted layers (150  $\mu\text{m}$  of thickness) of yttria-stabilized zirconia (YSZ) were used for fabrication of the sensors. One of the electrodes was made of a thick-film of oxide. Various oxides were tested as sensing electrodes, either p- or n-type semiconductors, including  $\text{WO}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{LaFeO}_3$ , and  $\text{La}_2\text{CuO}_4$ . The role of ionic conductivity of the oxide electrodes was investigated using Sr-doped perovskite-type oxides, such as  $\text{La}_x\text{Sr}_{1-x}\text{FeO}_3$ , a mixed electronic-ionic conductor. All the oxides were chosen for their catalytic activities in  $\text{NO}_x$  reduction or their good performance as conductometric  $\text{NO}_x$  sensors. The sensors were tested in potentiometric devices. Amperometric and electrochemical impedance spectroscopy measurements were performed to understand the sensing mechanism. Long-term measurements were carried out to investigate the stability of the sensors. The performance of these devices was promising: fast (about 15 s for  $\text{WO}_3$ -based sensors) and stable responses to different  $\text{NO}_2$  concentrations (20–1000 ppm in synthetic air) were observed at high temperatures. Good reproducibility was observed, even though a CO cross-sensitivity was measured. The role of the metallic electrodes was also studied. Particular attention will be given to the sensing mechanism of the sensors, which in some cases cannot be ascribed to mixed potential [E.D. Bartolomeo, M.L. Grilli, E. Traversa, Sensing mechanism of potentiometric gas sensors based on stabilized zirconia with oxide electrodes: is it always mixed potential?, *Journal of the Electrochemical Society* 151 (2004) H133–H139]. For practical application in OBD systems, field tests were performed testing the sensors on an engine, and the results will be presented.

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### Relaxor-based piezoelectric single crystals: recent development and present understanding

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Single crystals of the solid solutions between relaxor  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  [PMN] or  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  [PZN], and ferroelectric  $\text{PbTiO}_3$  [PT], exhibit outstanding piezoelectric properties that have pointed to the next generation of electromechanical transducer applications. On the other hand, the mechanism of relaxor ferroelectricity remains a fascinating puzzle. It is believed that the excellent properties of the relaxor-based single crystals are closely related

to the morphotropic phase boundary (MPB) effects, the symmetry of the MPB phases and the formation of meso- and macrodomain structures. Studies of the MPB-related properties, especially the symmetry of the MPB phases (with the presence of a monoclinic phase), the polarization rotation paths, and the domain structures, have helped us understand the fundamental of the enhanced piezoelectricity in these systems.

This talk will give an overview of recent developments in relaxor-based piezoelectric single crystals and the present understanding of the molecular mechanism of the outstanding properties in terms of polar nanostructure, crystal symmetry, morphotropic phase boundary, crystal growth, dielectric relaxation, domain structures and anisotropic properties.

### Further reading

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### Electrical properties of highly ionic conductive oxide thin films: applications in solid state fuel devices

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The highly ionic conductive oxide thin films, such as  $(\text{La,Sr})\text{CoO}_3$ ,  $\text{Gd:CeO}_2$ , and others, have been synthesized by pulsed laser ablation. Microstructural characterizations with X-ray diffraction and electron microscopy indicated