of the substrate species into the films. The developed novel process can be utilized for integration of electronic ceramic films with ULSI technology in designing new generation semiconductor devices.

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Epitaxial metal oxide thin film heterostructures for tunable chemical sensors

X.Q. Pan[a,*], J.E. Dominguez[a], W.W. Kim[a], A. Allenic[a], S.J. Wang[b]
[a]*Department of Materials Science & Engineering, University of Michigan, Ann Arbor, MI 48109, USA*
[b] *Institute for Materials Science and Engineering, Singapore 119260, Singapore*
* Corresponding author.

Thin film sensors based on oxide heterostructures have an advantage over conventional chemical sensors in terms of lower cost, lower power consumption, lower weight, and faster response. In this paper, we present our recent studies on the epitaxial SnO_2/TiO_2 and SnO_2/Cr_2O_3 heterostructures deposited on the sapphire and TiO_2 substrates by a femtosecond pulsed laser deposition. We have successfully synthesized epitaxial oxide heterostructures consisting of p–n junctions. It was found that the electrical properties and gas sensitivities of the epitaxial heterostructures can be tuned by chemical doping in oxide and by electrical bias across the p–n junctions. We also found that the electrical transport properties of semiconductive oxide multilayers strongly depend on the layer thickness and the structure of the hetero-junctions. This study suggests that epitaxial metal oxide heterostructures with p–n junctions could make a new avenue for the development of selective, tunable chemical sensors.

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Control of microporous structure for semiconductor gas sensor

N. Yamazoe
Faculty of Engineering Sciences, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan
Tel.: +81-92-583-7538; fax: +81-92-583-7537.
E-mail address: yamazoe@mm.kyushu-u.ac.jp
(N. Yamazoe).

Oxide semiconductor gas sensors detect a target gas (analyte) from a change in electrical resistance. Thanks to extensive R&D effort to data, this type of sensor has grown to be produced in a massive scale for various applications such as gas leakage alarms, CO detectors, breath checkers, auto dampers, alcohol checkers and so on. Yet, there are many kinds of gases else, which are desired to be targeted for sensor detection, including volatile organic compounds (VOCs), endocrine disrupting chemicals (EDCs), and bio- or food-related various gases. Most of these gases are present at small concentrations, so that the relevant sensors are required to have very high sensitivity. High-sensitivity design seems to be one of the most urgent research subjects for semiconductor gas sensors.

From a basic viewpoint, it has been recognized that the receptor function of this type of sensor is provided by the surface of oxide grains or a foreign substance (sensitizer) dispersed on them, while the transducer function is by the grain boundaries. However, this scheme ignores microstructure of polycrystalline devices except that it predicts that unusual situation arises when the grain size becomes smaller than twice the thickness of the surface space charge layer of grains. The importance of microstructure or microporous structure is made evident when one considers that gaseous molecules diffuse in the polycrystalline device, while if inflammable, they are consumed by the reaction with the surface oxygen of the grains. Based on a simple diffusion–reaction equation, sensor response (sensitivity) at steady state for a thin film device can be formulated under simplifying assumptions to be linear to $(1/m)\tanh m$, where $m = L(k/D_k)^{1/2}$ and L is the film thickness, k the first order reaction rate constant and D_k Knudsen diffusion constant. Thus, S becomes larger when m is small (<1), or, in other words, when the device has open structure (large D_k and small L). The control of microporous structure is therefore decisively important for designing a high sensitivity sensor, beside exploration for sensitizers. Some examples of recent studies will be introduced to demonstrate the importance of microporous structure control.

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Bio-inspired processing of electroceramic thin films and micropatterning

K. Koumoto*, Y. Masuda, Yanfeng Gao
Department of Applied Chemistry, Nagoya University, Nagoya 464-8603, Japan
* Corresponding author. Tel.: +81-52-789-3327;
fax: +81-52-789-3201.
E-mail address: g44233a@nucc.cc.nagoya-u.ac.jp
(K. Koumoto).

There has been a growing interest recently in “bio-inspired” or “bio-mimetic” approaches to prepare ceramic thin films at ambient temperatures in solutions, as they are expected to enable us to develop novel processing methods and manufacturing processes that are low cost and environment-friendly. Conventional lithography technology is facing many problems, and alternative novel technology is intensely required to overcome the present issues and to better match the future nanotechnology. Bio-inspired processing

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 TiO_2, ZrO_2, and $SrTiO_3$.

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

E. Comini, G. Faglia, G. Sberveglieri*
GSL, INFM, Brescia University, Brescia, Italy
* Corresponding author. Tel.: +39-030-371-57-71;
fax: +39-030-209-12-71.
E-mail address: sbervegl@tflab.ing.unibs.it
(G. Sberveglieri).

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 WO_3/TiO_2 and MoO_3/TiO_2 thin films. Due to the relatively low sublimation temperature of MoO_3 with respect to the melting temperature of WO_3 and 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

E. Di Bartolomeo, M.L. Grilli, E. Traversa*
Department of Chemical Science and Technology, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, 00133 Rome, Italy
* Corresponding author. Tel.: +39-06-7259-4492;
fax: +39-06-7259-4328.
E-mail address: traversa@uniroma2.it (E. Traversa).

The environmental concerns oblige to face the problems of pollutant emissions from vehicles. According to EU studies, the primary sources of CO and 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 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.