Ultrasensitive metal-oxide gas sensors obtained using colloidal templates

Il-Doo Kim,[1*] *Avner Rothschild,*[2] *Takeo Hyodo,*[3] *Harry L. Tuller*[2]

[1] Optoelectronic Materials Research Center, Korea Institute of Science and Technology, P.O.BOX 131, Chengyang, Seoul, Korea
[2]Department of Material Science and Engineering, Massachusetts Institute of Technnology, Cambridge, MA, 02139, USA
[3]Department of Mateiral Science and Engineering, Faculty of Engineering, Nagasaki University, Japan
idkim@kist.re.kr

Introduction

Physical vapor deposition (PVD) techniques such as sputtering or pulsed laser deposition (PLD) provide notable advantages for gas sensor fabrication, e.g., high reproducibility and compatibility with microfabrication processes, compared to chemical solution deposition processes such as screen printing or spraying. The resultant films, however, are typically dense and therefore the interaction with the gas phase is confined to the geometric surface of the film. As a result, the sensitivity of thin film gas sensors produced by PVD techniques often scales with the *L/H* ratio, where *H* is the film thickness and *L* is the width of the depletion layer adjacent to the surface. Given that *L* is on the order of 10 nm under typical conditions, the film thickness should be well below 100 nm to obtain high sensitivities. Unfortunately, interdiffusion and other irreversible interactions between the sensing film and the supporting substrate become increasingly important in such ultra-thin films, and the interfacial charge at the film/substrate interface adversely interferes with the surface gas sensing interactions at such critical film dimensions. These deleterious effects often counteract the beneficial effects of reducing the film thickness to nanoscale dimensions. In this paper we present a novel synthesis strategy that enhances the surface area of PVD deposited thin films and, at the same time, reduces the interfacial area between film and substrate, thus providing a unique solution to this dilemma. Organic microspheres are used as sacrificial colloidal templates onto which the inorganic metal-oxide sensing film is deposited. Upon subsequent removal of the organic template by thermal decomposition (calcination), the residual inorganic film exhibits a macroporous structure with large surface area and small interfacial area between film and substrate. Consequently, its gas sensitivity is markedly improved compared to similar films deposited on untreated substrates as demonstrated in the following.[1]

Experimental

$CaCu_3Ti_4O_{12}$ (CCTO) [2-3] or TiO_2 films were deposited by PLD onto the microsphere templated substrates, as well as onto untreated substrates for comparison purposes. Following the PLD deposition, the samples were calcined in air at 800°C for 2 h to remove the organic templates. X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) were used to examine the phase composition and microstructure of the films, respectively. The sensitivity of the macroporous films towards H_2, CO, CH_4 and NO_2 gases was tested at temperatures between 200 and 400°C, and compared with similar films deposited on untreated substrates.

Results and discussion

Figure 1 shows SEM micrographs of templated CCTO films after the calcination step. The resultant films consisted of a monolayer of hollow hemispheres with diameter commensurate with the diameter of the polymer microspheres. The wall thickness of the hemispheres was ~80-90 nm and the grain size varied between ~60 and 110 nm. These parameters can be controlled by adjusting the PLD deposition conditions and post-deposition calcination conditions. A network of voids between the film and substrate provides easy accesses of the gas phase to the internal surfaces of the hemispheres. Consequently, the effective surface area is much larger than in planar films deposited on untreated substrates. Figure 2 shows the resistance responses of templated and untemplated CCTO films upon exposure to increasing concentrations of H_2 in air (between 100 and 1000 ppm) at 300°C. The templated films were found to be quite sensitive to H_2, whereas the sensitivity of the control films deposited on untreated substrates was negligible. The remarkably enhanced sensitivity of the templated CCTO films is attributed to their macroporous structure with the high surface area promoting interactions with the gas and the relatively small interfacial area mitigating the deleterious effects between film and substrate. Further results on the sensitivity to different gases and a comparison between CCTO and TiO_2 films will be presented in the meeting.

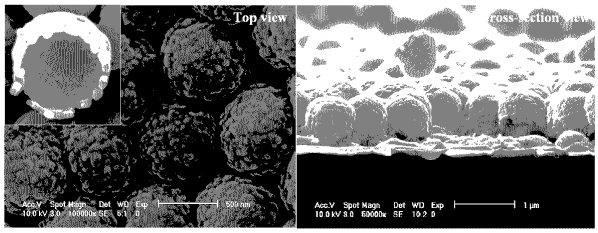

Figure 1. SEM micrographs of (**a**) the surface and (**b**) cross-sectional view of the macroporous CCTO films following calcination at 800°C. The inset in (**a**) emphasizes the grain structure of the hemispheres

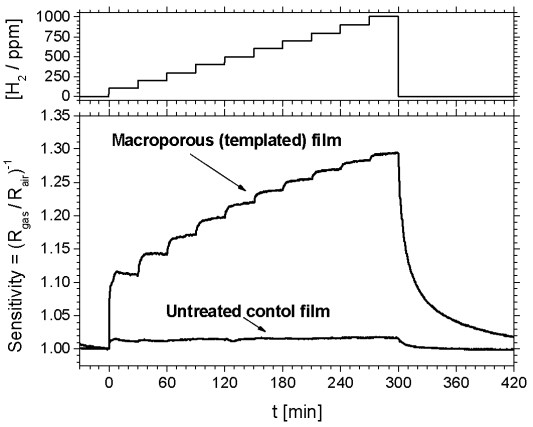

Figure 2: The resistance response of CCTO films deposited on templated (blue curve) and plain substrates (red curve) during exposure to increasing concentrations of H_2 at 300°C. From Ref. 1.

Conclusions.

Chemical and physical synthesis routes were combined to prepare macroporous thin films of semiconducting metal-oxides such as $CaCu_3Ti_4O_{12}$ and TiO_2 by pulsed laser deposition onto poly(methyl methacrylate) (PMMA) microsphere templated substrates. Subsequently, the colloidal templates were removed by thermal decomposition. The remaining inorganic films comprised a monolayer of hollow hemispheres with diameter commensurate with that of the microspheres. This unique morphology increases the surface area and reduces the interfacial area between film and substrate. Consequently, the surface activity is markedly enhanced while deleterious interfacial effects between film and substrate are significantly reduced. Both effects are highly advantageous for gas sensing applications. Indeed, microsphere templated films showed remarkably enhanced gas sensitivity compared with control films deposited onto untreated substrates.

References

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