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METAL OXIDE COATINGS FOR PIEZOELECTRIC EXHAUST GAS SENSORS
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Abstract

We have deposited ZrO_2, TiO_2, and SnO_2 films on ST-cut quartz surface acoustic wave (SAW) devices via sol-gel techniques. The films range from 100 to 300 nm thick and have porosities after calcination at 300 °C that range from 82-88% for ZrO_2, 77-81% for TiO_2, and 57-66% for SnO_2. In all cases, we have varied the synthesis and processing parameters over a wide range to optimize film properties: metal ion concentration (0.05-1.0 M), the H_2O:metal ratio (0.3-5.3), the acid concentration in the sol (0.02-0.7 M), the modifier ligand:metal ratio (r = 0.0-1.0), the processing conditions (100-900 °C). The modifer ligand, triethanolamine (TEA), is added to each solution to allow multilayer films to be made crack free. The multilayer films are studied by optical microscopy, ellipsometry, X-ray diffraction, and N_2 sorption. Preliminary high temperature frequency response measurements to target gases, such as, H_2, NO, NO_2, and propylene indicate limited sensitivity for the configurations tested.

INTRODUCTION

Inexpensive exhaust gas sensors are needed to directly monitor the concentrations of CO, NOx, and hydrocarbons (HC) produced by internal combustion engines. Such sensors can be used for three important applications: (1) to document vehicle compliance with Government mandated maximum emission levels, (2) to monitor the effectiveness of catalytic converters, especially in the lean-burn regime, and signal an On Board Diagnostics (OBD) package when they have failed or corroded, and, (3) in the long term, to provide feedback to a closed-loop engine control system to optimize engine performance.

The challenge is to devise a chemically and thermally robust, specific sensing system capable of operating at temperatures of 100-500 °C in high water content environments. Surface acoustic wave (SAW) devices provide an inexpensive sensor substrate capable of operation in this temperature range and under harsh conditions. Beyond the packaging concerns, the primary challenge is to develop sensitive coatings capable of operating at these temperatures. Organic coatings, although well known for their chemical specificity, are not viable at these temperatures. An attractive alternative is metal oxide thin films.

The goal is to develop several semispecific coatings that can be used in an array of sensors. In this paper we report investigations of the transition-metal and main-group-metal oxides ZrO_2, TiO_2, and SnO_2. These metal-oxide based sensors have relatively low lying d-orbitals and thus display an affinity for electron-donating species, such as CO and NO, and NO_2.

METAL OXIDE COATINGS

Coating Solutions

Coatings for SAW devices must be crack free (to prevent scattering the acoustic wave), and have a high enough accessible volume (surface area and thickness) to provide desired sensitivity. Sol-gel techniques provide porous coatings in which the physics and chemistry of the films can be tailored by changing the chemistry of the sol (e.g.

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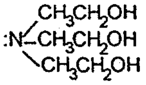
alkoxide ligands, chelating agents, solvent, water:metal ratio). Metal oxide films made by these techniques tend to be a few hundred nanometers thick at most, so it is advantageous to make multilayer films. To make multilayer, porous coatings it is necessary to initially deposit high surface area films and then minimize the shrinkage during consolidation and densification. To maximize surface area and prevent shrinkage requires films with a high modulus. The modulus is maximized by creating small open fractal structures in the sol and extensively crosslinking them in the gel.

Our strategy was thus to employ metal precursors with rapidly hydrolyzable, sterically small alkoxide ligands and use high water to metal ratios (*h*) to promote hydrolysis and condensation of the alkoxides [1]. These conditions favor rapid cluster formation and aggregation into open structures that contain a high concentration of hydroxyl groups. When the clusters percolate and gel they should form a stiff gel owing to the large extent of crosslinking. A stiff gel should experience less shrinkage during consolidation than a weak gel formed from partially hydrolyzed species (as formed when low concentrations of water or sterically bulky alkoxide ligands are employed) and should lead to a more porous network. However, if the precursors are hydrolyzed and condensed too quickly, very large fractal aggregates can form. This leads to a low modulus and the film is subject to cracking during densification. We surmised that a relatively low concentration of a ligand capable of multidentate bonding could help regulate the growth of the precursor species and lead to a higher modulus film. The film could then withstand a greater tensile stress during desification. We used the multidentate ligand triethanolamine



$$:N\begin{cases} CH_3CH_2OH \\ CH_3CH_2OH \\ CH_3CH_2OH \end{cases}$$

as a modifier ligand that is capable of interacting with zirconium or titanium alkoxides through both the nitrogen or oxygen atoms in both bridging and nonbridging linkages to form alcoxyaminates [2].

For ZrO_2, TiO_2, and SnO_2 we studied the H_2O:metal ratio ($h = 0.3$-5.3), time the solution is aged before deposition (15 min to 12 d), acid concentration ($[H^+] = 0.02$-3.6 M), TEA:metal ratio ($r = 0.0$-1.0), and the metal ion concentration ($[M] = 0.05$-1.0) by systematically varying each parameter. Each coating solution was spun onto a polished silicon wafer and the optical and physical properties of the resulting film were analyzed. We found that crack free films with the highest porosity generally resulted when $[M] < 0.5$ M and the coating solutions had been aged one day or less; there is a wide range of h, r, and $[H^+]$ that gives films with similar porosities, although r must be greater than zero to make films more than two layers thick without cracking. The following optimized procedures were then followed to make solutions suitable for coating SAW devices.

ZrO_2 - 70% zirconium (IV) propoxide in 1-propanol solution (Aldrich), 200 proof ethanol (Aaper Alcohol and Chemical Co.), HNO_3 (JT Baker, A.C.S. Reagent Grade, 69.0-71.0%), and, to form a second solution, triethanolamine (JT Baker, Reagent Grade) were mixed in a H_2O:Zr:HNO_3:(TEA) molar ratio of 5.3:1:3.55:0 and 5.3:1:3.60:0.14 (15.62 mmol Zr). The vigorously stirred solution was heated at 60 °C for 45 min. The solution without TEA was diluted with 2 eq. ethanol for coating, and the solution with TEA was diluted with 4 eq. of ethanol for coating. The solutions were pale yellow and clear. The final concentrations of Zr were 0.30 M and 0.17 M, respectively. The solutions were used immediately for coating.

TiO_2 - Titanium (IV) ethoxide in excess ethanol (Ti ~20%, Aldrich), 200 proof ethanol, conc. HNO_3, and triethanolamine were mixed in a H_2O:Ti:HNO_3:TEA molar ratios of 1.5:1:0.28:0.79 (9.54 mmol Ti). The vigorously stirred solution was heated at ~50 °C for 55 min. The Ti concentration was 0.4 M in the clear yellow solution. The sol was aged 2.5 h at room temperature prior to coating.

SnO_2 - Tin (IV) *t*-butoxide (Gelest, 95%), isopropanol (EM Science), conc. HCl (JT Baker, A.C.S. Reagent Grade, 36.5-38.0%), and triethanolamine were mixed in a H_2O:Ti:HCl:TEA molar ratio of 1.7:1:0.54:1 (~12 mmol Sn). The solution was stirred and heated at ~40 °C for 85 min and then at 60 °C for 50 min. The solution was pale yellow and slightly turbid; the concentration of [Sn] was 0.11 M. The solution was aged 17 h and diluted with one equivalent of isopropanol before coating.

Deposition and Processing

Polished silicon substrates and quartz ST-cut SAW devices are prepared for deposition by washing with ethanol and masking the electrodes and transducers with Scotch Brand™ cellophane tape. Immediately before the substrates are coated they are flooded with ethanol, spun for 30 seconds, and allowed to completely dry. The coating solutions are transferred into a 5 mL syringe fitted with a 0.2 μm PTFE filter to remove dust. The ~1 cm x ~1/2 cm substrates are flooded with coating solution and then spun off at 4000 rpm for 30 seconds. Films that do not contain a modifier dry within a few seconds. Films that contain a modifier exhibit diffuse scattering after 30 seconds. All coated substrates are then examined with optical microscopy (100x to 400x magnification) to check for large defects and cracks.

Multilayer films of ZrO_2 and TiO_2 are made by a coat-fire-coat-fire $(cf)^n$ or coat-coat-fire (c^nf) process. As the two processes produce calcined films with very similar thicknesses and refractive indexes, it is generally preferable to use the $(cf)^n$ method as it leads to uniform films that are not washed off in multiple-coat procedures. Once the desired number of coats have been applied, the films are calcined. SAW devices are calcined to 500 °C or less to avoid crossing the phase boundary at T_c = 573 °C and to avoid severe oxidation and peeling of the gold interdigital finger pairs and electrodes. For ZrO_2, TiO_2, and SnO_2 the changes in film thickness, index of refraction, and porosity are studied as a function of calcination temperature with ellipsometric techniques as shown in Figures 1-4.

SAW devices coated with ZrO_2 and TiO_2

SAW devices are coated with ZrO_2 solutions made by the process described above. The solutions are spin-coated at 4000 rpm for 30 seconds. A cfcfcf process is used. The intermediate firings are done at 100 °C for 5 minutes. A film made from a solution with $r = 0$ cracked after two coats; a film made with $r = 0.14$ did not crack after three coats and calcination at 450 °C for 18 h. The three-layer TEA derived film has a thickness of 357 nm and a refractive index of 1.535, indicating a volume fraction solids (V_s) of 57%; a thickness of 298 nm and a refractive index of 1.945, indicating V_s = 88%(an identical previous preparation gave V_s = 82%), after heating 2 °C/min to 300 °C and holding for 30 minutes; and a thickness of 263 nm and a refractive index of 2.023, indicating V_s = 93%, after heating at 450 °C for 18 h. Isothermal N_2 sorption measurements are analyzed with the BET method [3] and indicate a specific surface area of ~2.94 cm²/cm² for the sample heated at 300 °C. X-ray diffraction indicates the sample shown in Figure 1 crystallizes at 500 °C. The films appear smooth and featureless when imaged with SEM.

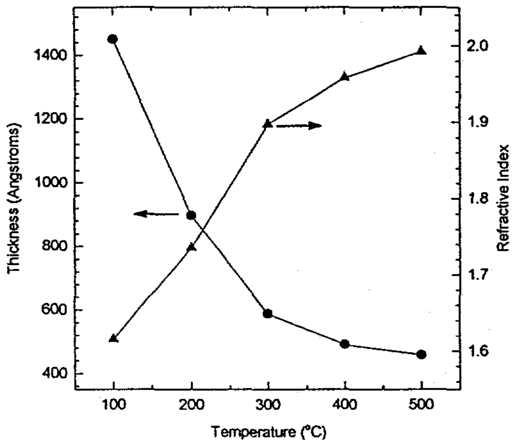


Figure 1. Evolution of thickness and refractive inde with calcination temperature for a single layer ZrO film. The film was deposited from a [Zr] = 0.35 M [H⁺] = 0.45 M, h = 2.03 solution that was aged 2 at room temperature and spin coated on a Si wafer a 4000 rpm for 30 s. The film was heated for 15 min.

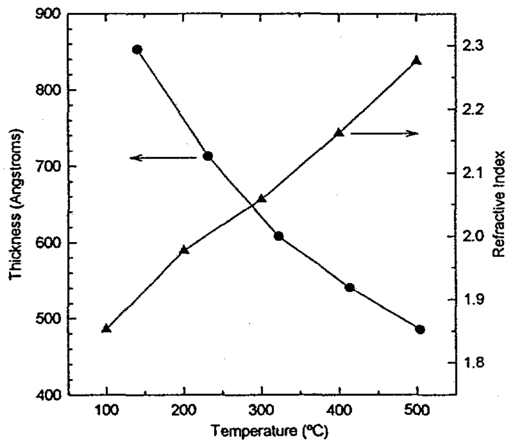


Figure 2. Evolution of thickness and refractive index with calcination temperature for a single layer TiO_2 film. The film was deposited from a [Ti] = 0.30 M, [H⁺] = 0.16 M, h = 1.83 solution that was aged 5 d at room temperature and spin coated on a Si wafer at 4000 rpm for 30 s. The film was heated for 15 min.

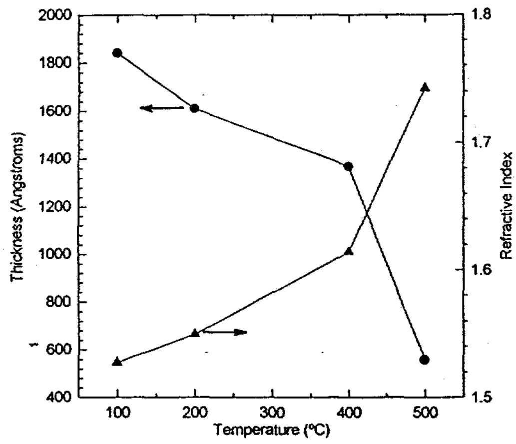


Figure 3. Evolution of thickness and refractive index with calcination temperature for a single layer SnO_2 film. The film was deposited from a [Sn] = 0.21 M, $[H^+]$ = 0.11 M, h = 1.75 solution that was aged 1 d at room temperature and spin coated on a Si wafer at 4000 rpm for 30 s. The film was heated for 5 min at each temperature.

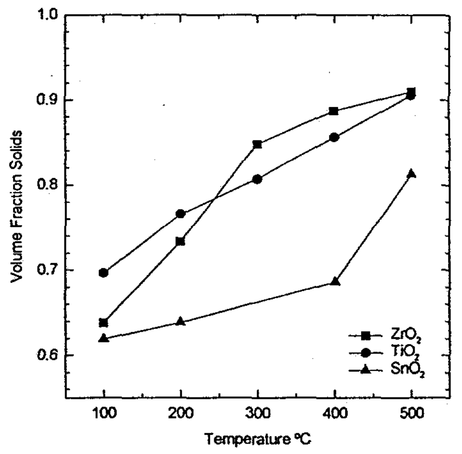


Figure 4. Volume fraction solids calculated from the Lorentz-Lorenz relationship [7] by assuming N_{ZrO2} (cubic) = 2.15, N_{TiO2} (anatase) = 2.53, and N_{SnO2} (cassiterite) = 1.98. The plot shows the porosity for the three films.

SAW devices are coated with TiO_2 solutions that are made by the process described above. The solutions are spin-coated at 4000 rpm for 30 seconds. A ccf process is used. The film does not crack after two coats are applied and the film is calcined at 300 °C for 30 min. The film has a thickness of ~130 nm and a refractive index of 1.62, indicating V_s = 56%, after one coat, and a thickness of only ~122 nm and a refractive index of 1.645 after two coats. The small negative change in thickness is confirmed by ellipsometry at 70° and 50° and indicates that the initial film was washed off by the second coat. After heating at 5 °C/min to 300 °C and holding for 30 minutes the thickness is ~109 nm and the refractive index is 1.99, which indicates V_s = 77% (4% lower than for films with r = 0). N_2 sorption measurements are analyzed with the BET method [3] and indicate a specific surface area of ~1.72 cm^2/cm^2 for the sample heated at 300 °C. X-ray diffraction indicates the sample shown in Figure 2 crystallizes at 400 °C. The films appear smooth and featureless when imaged with SEM.

HIGH TEMPERATURE RESPONSE OF COATED DEVICES

Several SAW devices coated with the metal oxide thin films have been characterized as gas sensors. Each device was exposed to one or more of the target gases H_2, propylene, CO, NO and NO_2 at a controlled elevated temperature. Preliminary results indicate limited sensitivity for the configurations tested.

The SAW sensors are electrically configured as a delay-line feedback element in an oscillator loop [4]. As shown in Figure 5, an RF signal stimulates the interdigital transducer on the ST-cut quartz substrate, launching a surface acoustic wave that travels across the device. The second interdigital transducer converts the acoustic wave back to an electrical signal that is amplified and then fed back to the input of the sensor. When couplers or splitters are inserted into the loop, oscillation frequency (~ 97 MHz) and device insertion loss (RF power) can be monitored. Relative shifts in the frequency are related to velocity changes of the SAW. Gas interactions in the sensor coating perturb the wave velocity by altering the total mass, the film stiffness, the film conductivity, or the device temperature [5,6]. Any combinations of these interactions produces a potentially measurable shift in the frequency. SAW attenuation also can result from stiffness, conductivity, or temperature changes.

SAW devices are wire-bonded into flat pack containers and inserted into a specially-designed high temperature test fixture. Temperature is controlled to within 0.5 °C over the range 20 to 500 °C using resistive heater elements. A vapor test system delivers the target gases which flow across the sensor surface at < 1 liter/min. A reference thermocouple mounted in the test fixture measures the gas temperature just above the coating surface. The RF signals enter and exit the hot environment along transmission lines terminating in coax connectors mounted in a water-cooled block.

SAW transmission characteristics of the metal oxide coated devices are determined using network analysis prior to their use in the sensor test arrangement. By scanning the frequency range of the SAW passband (typically 97 ± 2 MHz) before and after coating deposition, mass loading and wave attenuation is evaluated. Typically, for acceptable coatings, operating frequency drops a few hundred kHz depending on film thickness and porosity, and loss increases from 2 to 6 dB due to wave scattering in the crystalline films. In one case, however, a dense TiO_2 coating produced a frequency increase (most often related to a mass loss) while attenuating the transmitted signal. This anomalous response is produced by a "fast" SAW in which the portion of the wave propagating in the film outruns that in the quartz substrate, creating power leakage into the substrate nondirectional to SAW propagation.

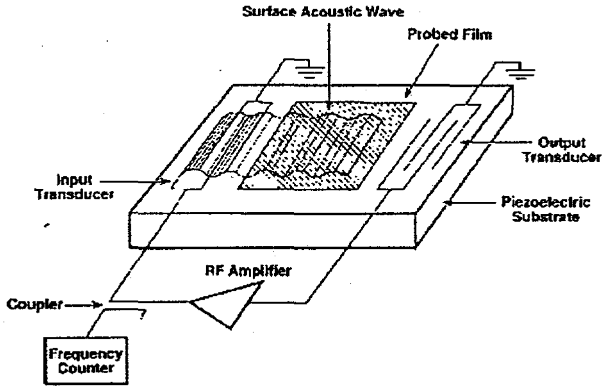


Figure 5. Schematic representation of a surface acoustic wave (SAW) device with interdigital transducers and a sensing film overlay.

One typical response for a SAW sensor is shown in Figure 6 for a 300 nm, ZrO_2-coated device at 400 °C exposed to pulses of hydrogen gas diluted in air. During the two minute intervals when the hydrogen concentration is 1.5%, both a frequency decrease and an attenuation increase occur. These shifts most probably result from the temperature increase produced by oxidation of the hydrogen at the hot device surface.

Figure 7 shows the measured frequency shift as a function of temperature for an uncoated ST-cut quartz SAW device and the ZrO_2-coated SAW sensor. The thin film coating has little affect on the response, which exhibits an approximately quadratic frequency dependence with a near-zero temperature coefficient at ambient [8]. (ST-cut quartz has a zero temperature coefficient at 20 °C, however, the deposition of metal electrodes and sensor coatings

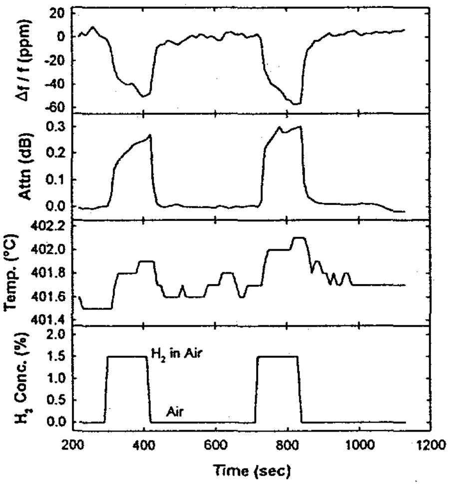


Figure 6. Response of a ZrO_2-coated SAW sensor to challenges of hydrogen gas. Shifts in SAW relative frequency response, SAW transmitted power attenuation, and gas temperature occur during the two minute intervals of gas exposure.

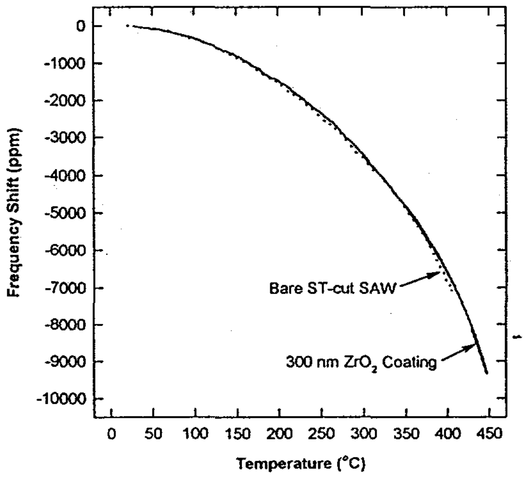


Figure 7. The frequency-dependent temperature response measured for two SAW devices: an uncoated ST-cut sensor (dotted line) and a ZrO_2-coated sensor (solid line).

shifts the zero point to lower temperatures.) At 400 °C the frequency-dependent temperature coefficient (FTC) is ~ 20 ppm/°C.

From the measured sensor response in Figure 6, the hydrogen gas interaction produces a frequency shift of ~ 60 ppm; the corresponding temperature shift would be 3 °C. A much smaller temperature shift is observed during the exposure period (see Figure 6), but the measured gas temperature is affected significantly by the test fixture temperature control system.

The frequency response of the ZrO_2-coated SAW sensor to hydrogen-air mixtures at other temperatures between 300 and 450 °C is consistent with the H_2-O_2 reaction-induced thermal fluctuations created at the metal oxide surface. The magnitudes of the measured responses for the ZrO_2-coated SAW sensor at 400 °C to hydrogen gas are $\leq 1.1 \times 10^{-2}$ (ppm Δf / ppm H_2) and $\leq 4 \times 10^{-5}$ (dB / ppm H_2). This same device shows a reduced response to propylene — an exhaust gas hydrocarbon simulant — but no measurable response, above the instrumentation noise level, for CO or NO gases. The potential exists for application as an exhaust hydrocarbon calorimeter. Based on these limited characterizations, however, improved sensor response will be necessary for demonstration of a viable, high temperature, piezoelectric gas sensor.

CONCLUSIONS

Alkoxide based coating solutions that contain the modifier ligand triethanolamine have been developed to provide crack-free, 100-300 nm films of the binary metal oxides ZrO_2, TiO_2, and SnO_2. In general the porosity at a given temperature varies over a fairly narrow range (<10 %) for each metal oxide system. Films with the highest porosity and best mechanical properties are formed when TEA is present. When TEA is present in concentrations greater than the concentration of the added acid, films with slightly greater porosity (4% for TiO_2) can be formed than when the TEA concentration is less than that of acid; however these films are more susceptible to washing off in mutiple-coat procedures. This is probably because the films are solutions are now basic rather than acidic and the amine exists in its free base form. Metal oxide films that contain d^0 or d^{10} valance configurations exhibit limited sensitivity to HC test gases at temperatures up to 450 °C.

Acknowledgments

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