Digital Object Identifier: 10.1109/ULTSYM.2008.0050

High Temperature Stability of Langasite Surface Acoustic Wave Devices

M. Pereira da Cunha[+,*], R. J. Lad[+,†], T. Moonlight[+], G. Bernhardt[+,†], D. J. Frankel[+]
Lab. for Surface Science and Technology[+], Dept. of Electrical and Computer Eng.[*], Dept. of Physics[†]
University of Maine, Orono, Maine, U.S.A.
mdacunha@eece.maine.edu

***Abstract*—High temperature acoustic wave (AW) devices capable of operating above 600°C and in hostile environments have opened potential applications for monitoring industrial processes, power plants, and aerospace systems. The authors have reported on the development of thin film electrodes and protective ceramic layers to allow surface acoustic wave (SAW) device operation up to 800°C on langasite (LGS) crystals. This success motivated further study of the electrode material and protective ceramic overlayer, as well as investigations of long term performance, temperature cycling and shock behavior, which are reported in this work. Among the results reported are: behavior of a co-deposited Pt/Rh/ZrO_2 composite electrode structure up to 1000°C; investigation of oxygen rich and nitrogen rich SiAlON protective ceramic layers; long term (4080 hours, or about 5½ months) operation of a two-port SAW resonator at 800°C; cyclical thermal tests between room temperature and 850°C; and thermal shock tests of crystals between 700°C and room temperature.**

Keywords - high temperature; thin film electrode; langasite; protective ceramic over-layer; harsh environment

I. INTRODUCTION

The possibility of operating components such as acoustic wave (AW) devices at high temperature opens up interesting and challenging harsh environment application opportunities for the fields of communication, frequency control, and sensing. Space exploration, harsh industrial environments, power plants, and the aerospace industry are prime areas for high temperature acoustic wave device use.

Recently, the authors reported on the development of stable thin film composite electrode structures, and successful demonstration of a langasite (LGS) SAW device operating for over 2½ months at 800°C [1]. Figure 1 shows pictures of the packaging used, part of a LGS interdigital transducer (IDT) exposed to 800°C, and an image of a 125 nm thick 24-layer Pt/ZrO_2 IDT electrode structure fabricated and tested. These encouraging results motivated further investigations into the formidable challenges of this enabling technology. Topics reported in this paper include: (i) fabrication and analysis of thin film co-deposited Pt/Rh/ZrO_2 electrodes; (ii) test of these thin films at temperatures up to 1000°C; (iii) investigation on the effects of varying the composition of ultra thin SiAlON protective ceramic over-layers; (iv) testing of two-port SAW resonators for extended periods at 800°C; (v) thermal cycling tests of SAW resonators between room temperature and 850°C; and (vi) initial testing of LGS crystal thermal shock resistance.

Section II discusses fabrication and testing techniques and equipment. Section III presents thin film electrode and ceramic protective layer results and analysis; long term and multiple cycled responses of two-port SAW resonators and test fixtures, with focus on the center frequency response, quality factor, and transmission loss. Finally, Section IV concludes the paper.

II. METHODOLOGY OF THIN FILM FABRICATION AND DEVICE TESTING

The co-deposited Pt-Rh/ZrO_2 thin film electrodes used in this paper were fabricated by simultaneously evaporating Pt/10%Rh and Zr from separate electron beam evaporation sources (Telemark, Fremont, CA) in a 10^{-5} mbar O_2 background [1]. The protective ceramic SiAlON coatings, when applied, were deposited on top of the entire surface by reactive RF magnetron co-sputtering of Al and Si targets in O_2/N_2/Ar gas mixtures [2]. Thin film analyses reported in this work employed several techniques, including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD),

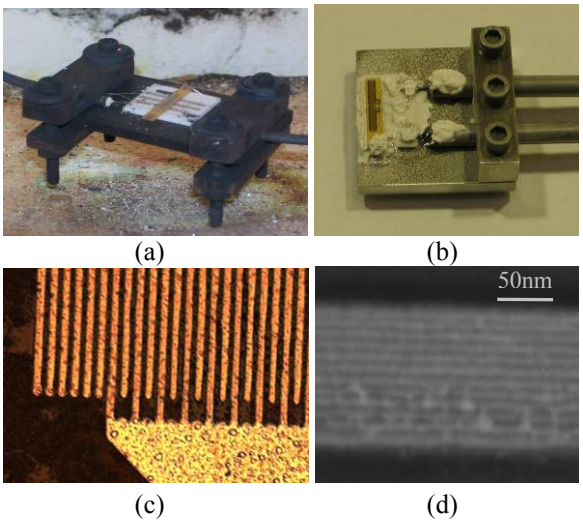

Figure 1. (a) and (b): high temperature packaging fixtures used up to 1000°C; (c) Pt/Rh/ZrO_2 co-deposited SAW transducer (4µm wide electrodes) after exposure to 800°C; (d) Scanning electron microscopy cross sectional image of a 24 layer Pt/ZrO_2 electrode film (125nm thick).

scanning electron microscopy (SEM), and X-ray Energy Dispersive Spectroscopy (EDS).

Two-port SAW resonators were fabricated using lift-off techniques and consisted of 80 fingers per IDT, 4 μm finger width, 1:1 mark to space ratio, 50 wavelength aperture, and 500 electrode short circuit reflectors. On-wafer tests were performed with the aid of a Cascade™ Microtech probe station (Cascade Technologies, Inc., Beaverton, OR.). When packaging was performed, a Unitek parallel gap welder (Miyachi Unitek, Monrovia, CA) with 1 and 4 mil Pt wire was employed. The SAW device responses were monitored with an Agilent 8753ES network analyzer (Agilent Technologies, Santa Clara, CA) and the reported high temperature tests were performed at atmospheric pressure in laboratory air using a Thermolyne furnace (Thermolyne, Dubuque, IA).

III. Experimental Results and Analysis

Long term, 4080 hours (over 5½ months), 800°C stable operation of a langasite SAW resonator device has been demonstrated [3]. Figure 2 shows optical and SEM images of a typical IDT before exposure to high temperature (a and b) and after testing at 800°C for 5½ months (c and d). Recrystallization and severe dewetting of metallic electrodes, which results in loss of electrical continuity and device failure, as happens with pure Pt films [1], were significantly retarded through the use of the co-deposited $Pt/Rh/ZrO_2$ electrodes allowing stable operation at 800°C. However, Figs. 2c and 2d indicate that these electrodes still suffer some morphological changes after heating.

Both XRD and EDS analyses [4] of co-deposited $Pt/Rh/ZrO_2$ films heated to 1000°C for 16 hours suggest that the bright spots in Figs. 2c and 2d are crystallites formed during the film recrystallization. The EDS analysis of the darker regions within the electrode film shown in Fig. 2c show the presence of Zr but not Pt or Rh, indicating the Zr is likely from the initial adhesion layer and that these dark areas are small holes in the metal electrode film. The brighter spots in Figs. 2c and 2d show the presence of Zr, Pt, and Rh indicating they are agglomerations of recrystallized metal from the electrode film. The XRD measurements indicate that high temperature heating promotes the growth of (111) oriented Pt or Pt-Rh grains and conversion of at least some of the ZrO_2 present in the films from an amorphous to crystalline phase.

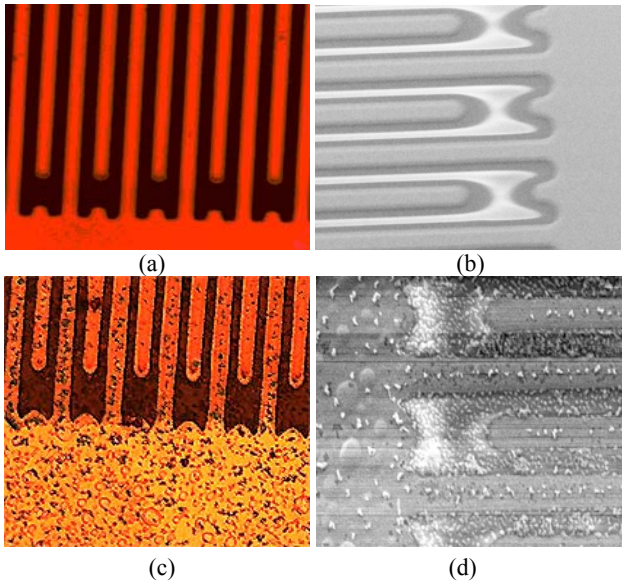

Figure 2. (a) Optical and (b) SEM images of a section of a co-deposited $Pt/Rh/ZrO_2$ IDT electrode prior to heating; (c) optical and (d) SEM images of a co-deposited $Pt/Rh/ZrO_2$ IDT electrode after operation for 5½ months at 800°C. Electrodes are 4μm wide.

Concentrations by weight of ZrO_2 in the Pt-Rh film deposition were varied from 6 to 24 atomic % [3], [5], and it was found that optimum concentrations in retarding grain growth lie around 10 to 12%. Extensive high temperature testing has shown that the ZrO_2 present in the co-deposited film is critical for retarding (111) Pt-Rh grain growth and thus extending the maximum operating temperature of the SAW devices.

The ultra-thin (25 nm) protective SiAlON ceramic layer can exist over a range of stoichiometries, $Si_xAl_yO_zN_{1-x-y-z}$. Nitrogen and oxygen rich coatings with 1:1 Si to Al ratio were deposited over both blanket electrode films and SAW devices. Figure 3 shows optical and SEM pictures of $Pt/Rh/ZrO_2$ codeposited films heated to 1000°C for 16 hours without any protective layer, and with nitrogen-rich (N-rich) and oxygen-rich (O-rich) SiAlON coatings. For the N-rich film, XPS analysis performed indicated a 60/40 N to O ratio, while for the O-rich film, a 10/90 N to O ratio was measured. It has been verified after the test period that the nitrogen decreases in the surface region as the SiAlON film oxidizes through high temperature heating. The SiAlON film provides a potential protective alternative for the surface and may also be used to retard dewetting and recrystallization of the electrode, as shown in Fig. 3.

Figure 4 plots normalized film resistance of a deposited film versus time for the indicated temperature profile (Fig. 4a) up to 1000°C. The performance of the pure Pt film over a Zr adhesion layer, Fig. 4b, is included for reference. Figs. 4c, 4d, and 4e show the normalized resistance for a bare codeposited

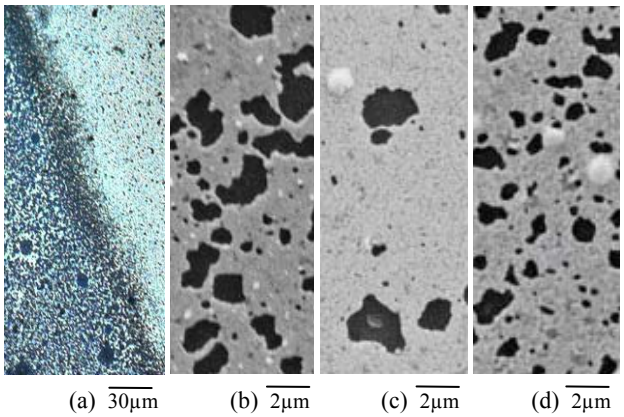

Figure 3. Optical (a) and SEM (b,c,d) pictures taken of co-deposited $Pt/10\%Rh/ZrO_2$ films heated to 1000ºC for 16hrs. (a) Boundary between bare film (left) and O rich SiAlON layer (right); (b) a bare co-deposited film; (c) a co-deposited film with a 25nm nitrogen-rich SiAlON cap, (d) a co-deposited film with a 25nm oxygen-rich SiAlON cap. All films had a total thickness of about 120nm.

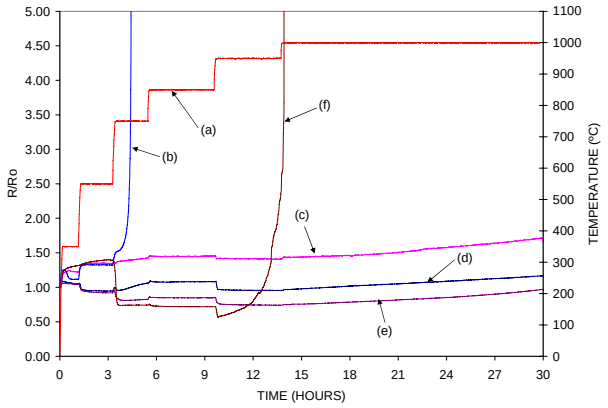

Figure 4. Normalized film resistance versus time measured up to 1000°C. All films are about 110nm thick unless stated otherwise; (a) Temperature profile: 350°C, 1h; 550°C, 2h; 750°C, 2h; 850°C, 4h; 950°C, 4h; and 1000°C, 16h; (b) pure Pt over Zr adhesion layer; (c) co-deposited Pt/10%Rh/ZrO_2 film; (d) co-deposited Pt/10%Rh/ZrO_2 film with a 25nm nitrogen rich SiAlON cap; (e) co-deposited Pt/10%Rh/ZrO_2 film with 25nm oxygen rich SiAlON cap; (f) co-deposited Pt/10%Rh/ZrO_2 film of 62.5nm total thickness.

Pt/10%Rh/ZrO_2 film; a codeposited Pt/10%Rh/ZrO_2 with 25 nm thick N-rich SiAlON overlay; and a codeposited Pt/10%Rh/ZrO_2 with 25 nm thick O-rich SiAlON overlay. The N-rich SiAlON covered film showed a marginally better performance with time over the test period, a result consistent with the SEM images in Fig. 3. The behavior of a 62.5 nm thick codeposited Pt/10%Rh/ZrO_2 film is shown in Fig. 4f. A 43% reduction in the film thickness results in rapid failure at 950°C, and poorer performance compared to the 110 nm thick films confirming that thinner films are prone to more rapid grain growth, recrystallization, and dewetting.

Figure 5a shows the center frequency response of a co-deposited Pt/10%Rh/ZrO_2 electrode two-port packaged SAW resonator cycled six times between room temperature and 850°C. With the exception of the first curve, where annealing of the high temperature electrode takes place, the remaining five curves fall on top of one another within measurement uncertainties. The major changes during the annealing takes place in the 550-850°C temperature range, as can be also noted in Fig 4. The equivalent response for a co-deposited Pt/10%Rh/ZrO_2 device capped with a 25nm thick N-rich SiAlON film is shown in Fig. 5b. As can be seen from Figs. 5a and 5b, the effect of the annealing for the SiAlON covered device is more pronounced when compared to the bare co-deposited electrode device.

Figure 6 shows the quality factor, Q, of packaged two-port SAW resonators with and without a SiAlON coating. After the first annealing cycle, the Q diminished 20% between the second and sixth cycle for the uncoated device and 48% for the coated device, when the devices were brought back to room temperature. In addition, after the first annealing cycle, the measured transmission loss ($|S_{21}|$) measured at room temperature increased from 13.6 dB to 16.2 dB for the uncoated packaged device, and from 21.7 dB to 27.7 dB for the SiAlON coated packaged device.

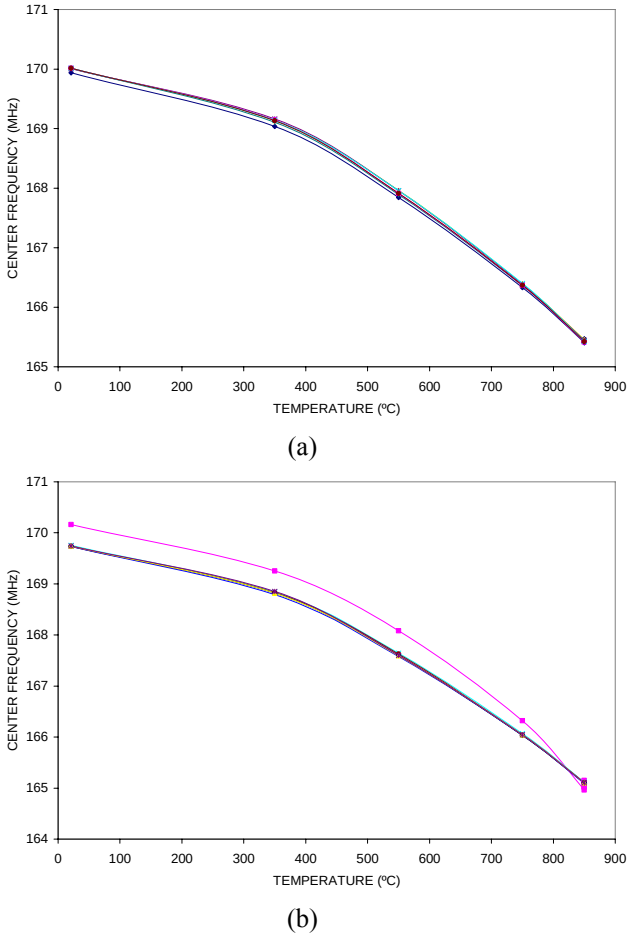

Figure 5. Measured center frequency for a two-port SAW resonators while being cycled from room temperature to 850ºC six times; (a) bare single layered co-deposited Pt/10%Rh/ZrO_2 device; (b) SiAlON coated single layered co-deposited Pt/10%Rh/ZrO_2 device.

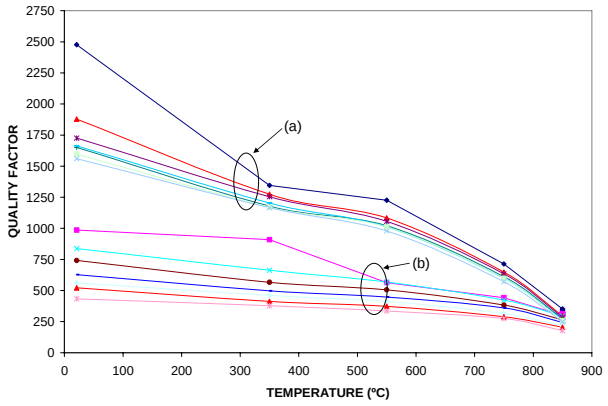

Figure 6. Two-port SAW resonator Q versus temperature for six consecutive cycles from room temperature to 850ºC; data points taken at 21ºC, 350ºC, 550ºC, 750ºC, and 850ºC; (a) co-deposited Pt/10%Rh/ZrO_2 film, (b) co-deposited Pt/10%Rh/ZrO2 film with a 25nm SiAlON cap, Both co-deposited films are about 110nm thick. The quality factor decreased after each consecutive cycle for both (a) and (b).

This higher degradation of the packaged SiAlON coated SAW resonator under cycling conditions prompted the question of whether the degradation was due to the device packaging or the device itself. To investigate this, the high temperature cables used in the test were independently cycled six times between room temperature and 850°C, and verified to perform repetitively and consistently, other than during a first annealing cycle. Next, unpackaged SiAlON coated and uncoated devices were cycled between room temperature and 850°C, and measured at room temperature in the probe station. Figure 7 shows Q as a function of cycling, and indicates a reduced degradation when compared to the packaged device, also corroborated by the measurement of $|S_{21}|$. These results show evidence that further investigation is needed regarding the packaging, including the wire bonding, and also regarding the interaction between SiAlON and the co-deposited film on the SAW device.

Finally, a thermal shock test was performed with the LGS crystal to simulate the rapidly changing conditions that may be encountered in harsh environments, such as those found in jet engine applications. An optically polished LGS sample approximately 10mm x 3mm x 0.5mm in size was rapidly introduced through the front door of a box furnace pre-heated to 700°C. The LGS was secured to a carrier coupon of Hastalloy HX using a section of 4mil Pt bonding wire without any high temperature epoxy to eliminate any effects due to an adhesive and mismatches in temperature coefficients of expansion. After inserting the sample into the pre-heated box furnace, the furnace was allowed to stabilize at 700ºC (for 3-5 minutes) and after that the crystal was left there for an additional five minutes. The LGS sample was then quickly withdrawn from the furnace and placed directly in front of a room temperature air gun until the device cooled to approximately 21°C (room temperature). The LGS sample was then optically examined for cracks or imperfections under the microscope (10x to 20x magnification), and no problems were found. This test was successfully repeated two additional times suggesting that the LGS material can survive repeated thermal shocks.

IV. Conclusions

This paper presents recent research and development findings regarding high temperature co-deposited Pt/Rh/ZrO_2 thin films electrodes and protective ultra-thin SiAlON ceramic layers on LGS substrates for acoustic wave applications. Tests ranging from several hours to long-term (up to 5½ months) in the range of 800°C to 1000°C showed stable electrode resistance and SAW device responses. The Pt/Rh/ZrO_2 composite film and the SiAlON protective layer have been analyzed with respect to their composition, thicknesses, and integrity using several techniques, including XPS, XRD, SEM, EDS, AFM, and normalized resistance measurements up to 1000°C as a function of time.

The center frequency response of two-port SAW resonators monitored for six consecutive cycles between room temperature and 850°C showed consistent frequency responses after the first annealing cycle. For the packaged and SiAlON protected devices, variations in quality factor and transmission loss after each cycle indicated that further studies need to be performed to optimize the device response and repetitiveness. Preliminary thermal shock tests between room temperature and 700°C were repeated three times with the same sample and verified the capability of the LGS crystal to be exposed to extreme variations of temperature over short time periods.

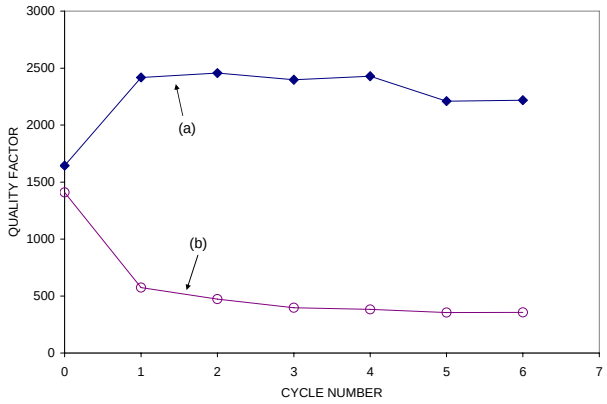

Figure 7. On-wafer measurements of two-port SAW resonator Q versus cycle number after six consecutive cycles from room temperature to 850ºC; data points taken at room temperature; (a) co-deposited Pt/10%Rh/ZrO_2 film, (b) co-deposited Pt/10%Rh/ZrO2 film with a 25nm oxygen rich SiAlON cap, Both co-deposited films are about 110nm thick

The results presented in this work indicate that this technology is extremely promising for a wide range of potential applications including health monitoring of turbine engine components, measurement of engine behavior for performance optimization, industrial and military communication components, frequency control devices, and sensors operating in high temperature harsh environments.

Acknowledgments

This research has been partially funded by the following agencies: Air Force Research Laboratory USAF Grants # FA8650-06-C-5209 and F33615-03-D-5204; Air Force Office of Scientific Research AFOSR Grant # FA9550-07-1-0519; The Petroleum Research Fund Grant ACS PRF# 42747-AC10; National Science Foundation NSF ECS 0134335

References

[1] M. Pereira da Cunha, T. Moonlight, R. Lad, G. Bernhardt, D. J. Frankel, "Enabling Very High Temperature Acoustic Wave Devices for Sensor & Frequency Control Applications" Proc. IEEE Ultrason. Symp., 2007, pp. 2107-2110.

[2] J.I. Krassikoff, G.P. Bernhardt, M. Call, T.A. Dunn, D.D. More, R.J. Lad, "Synthesis and characterization of SiAlON thin film coatings," Society of Vacuum Coaters Tech. Proceedings vol. 46, pp. 627, 2003.

[3] M. Pereira da Cunha, T. Moonlight, R. Lad, D. J. Frankel, G. Bernhardt, "High Temperature Sensing Technology for Applications Up to 1000°C," *7th IEEE Conference on Sensors Proceedings*, Lecce, Italy, October 2008 (in press).

[4] D.J. Frankel, G. Bernhardt, B. Sturtevant, T. Moonlight, M. Pereira da Cunha, R.J. Lad, "Stable Electrodes and Ultrathin Passivation Coatings for High Temperature Sensors in Harsh Environments," *7th IEEE Conference on Sensors Proceedings*, Lecce, Italy, October 2008 (in press).

[5] US Patent Application Serial No. 11/891,081 for "Ultra-Thin Film Electrodes and Protective Layer for High Temperature Device Applications", filed August 9, 2007.