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Comparison between Ir, $Ir_{0.85}Rh_{0.15}$ and $Ir_{0.7}Rh_{0.3}$ thin films as electrodes for surface acoustic waves applications above 800 °C in air atmosphere

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ABSTRACT

In this paper, we investigate the suitability of Ir, $Ir_{0.85}Rh_{0.15}$ and $Ir_{0.7}Rh_{0.3}$ thin films as electrodes for surface acoustic waves (SAW devices) applications taking place above 800 °C in air atmosphere. As expected, all films oxidize from 800 °C in IrO_2 or $Ir_xRh_{1-x}O_2$ phase. The electrical properties of the latter remain compatible with the design of SAW devices, with a specific electrical resistance of 151 and 100 μΩ·cm for x = 0.7 and x = 0.85 respectively. Moreover, we observe that the $Ir_xRh_{1-x}O_2$ phase is much more stable regarding sublimation effect than the IrO_2 phase, highlighting the interest of alloying Ir with Rh for high-temperature applications. SAW devices based on langasite substrate and $Ir_{0.85}Rh_{0.15}$ electrodes show a very good stability for at least several days at 800 °C in air. In the case of $Ir_{0.7}Rh_{0.3}$ electrodes, this stability is extended to temperatures up to 900 °C.

1. Introduction

Surface acoustic wave (SAW) sensors have a high innovation potential for use in high-temperature environments, owing to their large sensitivity to environmental conditions (temperature, pressure, strain or gas concentration), small size, and above all, the possibility to be wirelessly requested without battery or embedded electronics [1–4]. To develop such sensors, one of the main challenges to overcome is to grow highly conductive thin film electrodes, typically some hundred nanometers thick, able to withstand these harsh conditions and avoid any degradation related to agglomeration or oxidation phenomena.

In this context, various metallization structures have been previously considered and characterized. First studies were naturally made on platinum electrodes as this material shows an exceptional noble character, preventing oxidation phenomena. Moreover, the melting temperature of Pt, being equal to 1773 °C, seems high enough for SAW applications taking place below 1000 °C. However, 100 nm-thick Pt thin films undergo agglomeration phenomena from 700 °C, resulting in a final state consisting in a collection of separate Pt beads [5]. Agglomeration phenomena are specific of thin films and are driven by atomic diffusion. Therefore, the smaller are the diffusion coefficients, the slower are agglomeration phenomena. Consequently, one relevant strategy, developed by Pereira da Cunha et al. consisted in using Pt-10%Rh alloys instead of pure Pt thin films, and then Pt-10%Rh/ZrO_2 nanocomposites. A spectacular increase in stability was observed. Thus, an LGS-based SAW device with Pt-10%Rh/ZrO_2 nanocomposites electrodes was operated for more than 5 months at 800 °C in air atmosphere [6]. In order to reach higher temperatures, Frankel et al. have developed new nanocomposite films based on Pt [7]. The best performances were obtained by the Pt-Al_2O_3 and Pt-Ni/Pt-Zr compositions which show a specific electrical resistance in the order of 200 μΩ·cm after annealing in air for 4 h in the temperature range from 1050 to 1150 °C. However, the long-term stability of these films was not studied. Another relevant work concerns Al-Ru alloys thin films [8]. The Al-Ru films were annealed between 600 °C and 900 °C under high vacuum conditions or under air atmosphere. The authors show that heat treatment under high vacuum conditions results in a strong reduction in the specific electrical resistance, which is in agreement with the films recrystallization observed by XRD measurements. The situation is different for the samples annealed in air. Indeed, except for the samples annealed at 600 °C for which a

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reduction in the specific resistance was noticed as well, the samples annealed at higher temperatures are not conductive at all anymore.

Another strategy that can be employed to thwart agglomeration phenomena consists in replacing Pt by another noble metal with a higher melting point, and thus lower diffusion coefficients. In this context, iridium, whose melting point is as high as 2440 °C, is an appropriate candidate. Indeed, pure Ir electrodes show a far better resistance to agglomeration phenomena than Pt electrodes under vacuum conditions [5,9]. The use of Ir electrodes is more problematic under air atmosphere as Ir oxidizes in IrO_2 in the vicinity of 800 °C. Nonetheless, IrO_2 remains yet a good electrical conductor, with a specific electrical resistance of 47 μΩ.cm [10], i.e. only one order of magnitude above that of conventional conductors such as Al or Cu, and still significantly lower than those of some Pt-based alloys or nanocomposite thin films. A more serious issue consists in the transformation of IrO_2 into volatile IrO_3 at higher temperatures. This phenomenon occurs between 800 and 900 °C [11]. However, Osamura et al. demonstrated that Ir-Rh alloys, used to make spark plugs with superior performance, show a far better resistance to sublimation caused by oxidation phenomena than pure Ir spark plug electrodes [12]. Consequently, Ir-Rh thin film electrodes could have a great potential for SAW applications taking place above 800 °C in oxidizing atmosphere. To check this assumption, we have conducted first investigations on Ir_xRh_{1-x} thin films ($x \leq 0.5$) at high temperatures [13]. This study reveals that after an annealing of four days at 800 °C under air atmosphere, these films oxidize to form $Ir_xRh_{1-x}O_2$ films. However, this phase exhibits a reasonable resistivity suitable for the targeted application, especially as the Ir rate is high ($\rho \simeq 180$ μΩ·cm for $x = 0.5$).

In this context, the goal of the present study is to examine the behavior of the most promising Ir-rich compositions ($0.7 \leq x \leq 1$) above 800 °C in air atmosphere. In particular, we inspect carefully the interest of alloying Ir with Rh regarding the sublimation effect described hereinabove. In a second time, we investigate the reliability of SAW devices based on $Ir_{0.7}Rh_{0.3}$ or $Ir_{0.85}Rh_{0.15}$ electrodes and langasite (LGS) substrate during a 20 days-annealing period between 800 and 950 °C in air.

2. Experimental

Pure Ir thin films, as well as $Ir_{0.85}Rh_{0.15}$ and $Ir_{0.7}Rh_{0.3}$ multilayers thin films were deposited on (0°, 140°, 25°) LGS substrates by sputtering method. LGS was chosen for this study, focusing on electrode composition, as this piezoelectric material is known for its stability under high-temperature air atmosphere [14]. Moreover, the knowledge of the high-temperature physical constants set of LGS is currently rather good, allowing the design of efficient SAW devices [15]. A 10-nm thick tantalum adhesion layer was firstly deposited on these substrates. Concerning the multilayers films, the respective thickness of the pure Ir and Rh nanolayers alternatively sputtered was calculated in order to control the overall stoichiometry of the films. The thickness of all considered films was fixed to 120 nm. Thus, to obtain $Ir_{0.85}Rh_{0.15}$ films, three 34 nm-thick Ir films were alternatively sputtered with three 6 nm-thick Rh layers. In the case of the $Ir_{0.7}Rh_{0.3}$ films, six 14 nm-thick Ir films were alternatively sputtered with six 6 nm-thick Rh layers. The resistivity of all the as-deposited samples measured using four points method is about 14 μΩ·cm, and is independent from their composition.

Some samples then underwent three successive annealing periods at 800 °C: the first one lasted for 4 days and the next ones 7 days each. Some other samples underwent a 7 days-annealing period at 900 °C after the first 4 days-annealing process at 800 °C. After each annealing period, the morphology, the microstructure, the chemical composition associated to the nanostructure, and the electrical properties of the thin films were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) in Bragg-Brentano geometry, scanning transmission electron microscopy-energy dispersive X-Ray spectroscopy (STEM-EDS) and 4-points probe resistance measurements respectively.

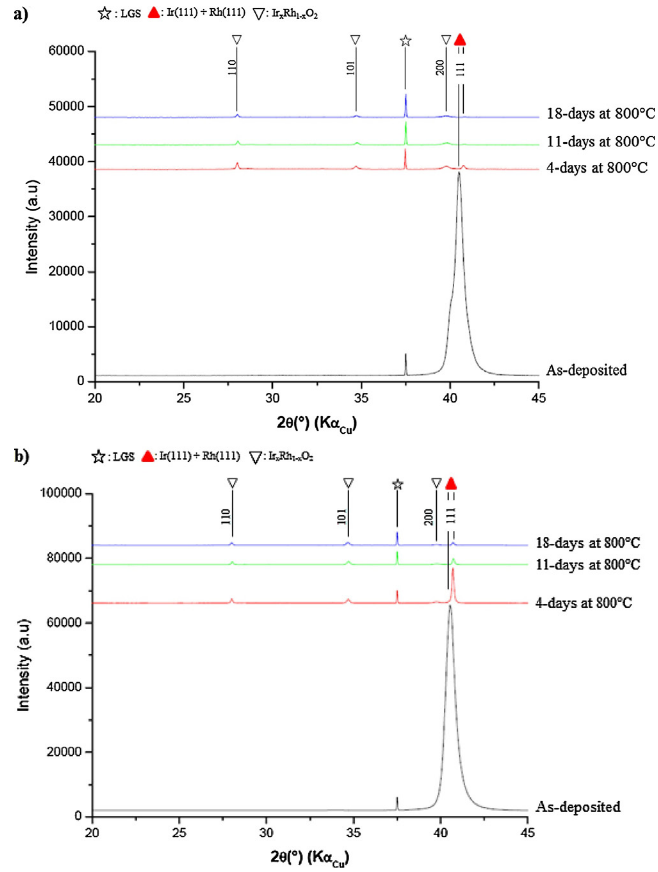

Fig. 1. XRD patterns of as-deposited and annealed $Ir_{0.7}Rh_{0.3}$ (a) and $Ir_{0.85}Rh_{0.15}$ (b) films.

Some other samples were processed using conventional photolithography and ion beam etching to carry out SAW delay lines with a wavelength of 24 μm. The devices underwent different annealing periods at temperatures ranging from 800 to 950 °C. The more severe annealing process consisted in twenty successive 24 h long annealing periods at four rising temperatures: 800 °C (day 1–5), 850 °C (day 6–10), 900 °C (day 11–15) and finally 950 °C (day 16–20). After each 1 day-annealing period, the morphology of the electrodes was observed by optical microscopy while the S_{21} frequency response of the SAW devices was measured at room temperature using a network analyzer (PNA 5230a, Agilent Technologies Inc., Santa Clara, CA) and an RF prober station (PM5 Suss-Microtech).

3. Results and discussion

3.1. Impact of annealing on $Ir_{0.7}Rh_{0.3}$ and $Ir_{0.85}Rh_{0.15}$ thin films

θ-2θ XRD patterns of the $Ir_{0.7}Rh_{0.3}$ and $Ir_{0.85}Rh_{0.15}$ multilayers thin films obtained before and after the successive annealing periods at 800 °C are visible on Fig. 1. As-deposited samples are constituted by (111)-oriented nanograins as indicated by the broad peak at $2\theta = 40.5°$. It is clearly visible in the case of the $Ir_{0.7}Rh_{0.3}$ multilayers films that this signal is actually the sum of two close peaks, namely (111) Ir and (111) Rh reflexes. One can assume that in the case of $Ir_{0.85}Rh_{0.15}$ multilayers thin films, the amount of Rh is so weak that the peak at 40.5° seems related to (111) Ir reflex