In situ electrical characterization of $Y_xTi_y$ getter thin films during thermal activation

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Abstract. Transition metals alloys are the most studied getter films for wafer-level vacuum packaging of MEMS. In this work we investigated yttrium and $Y_xTi_y$ alloys films that could possibly overcome the limitations of usual getter materials, i.e. reversible sorption of hydrogen and low sorption ability for hydrocarbon gases. As a preliminary step towards this objective, properties of (co-)evaporated yttrium and $Y_xTi_y$ films were analyzed by SEM, EDS, XPS and in-situ sheet resistance measurements before, after and/or during annealing in vacuum. As deposited and annealed films have a small grain size and a columnar structure. It is shown that yttrium and $Y_xTi_y$ films can be activated after 1 hour of annealing in vacuum at 250 °C if the Y-content is larger than ~9 %. These results are promising for the use of Y-based films as low temperature getters for vacuum packaging.

1. Introduction

Vacuum packaging is required for various kinds of microelectromechanical systems such as resonant sensors, bolometers, RF switches and scanners. In most of cases, an internal pressure lower than $10^{-3}$ mbar for more than 10 years is mandatory to get and keep high performances. To comply with the general trend towards 3D integration of miniaturized systems and reduce its cost and size, vacuum packaging tends to be performed by batch processing at the wafer level. When low temperature is required, getter films must be integrated in the package microcavity to pump and trap gazes released during outgassing and bonding steps, then to compensate leaks through the bond during the device lifetime. Getter films are typically multilayers or alloys of highly reactive transition metals (Ti, Zr, V, Co, Hf …) eventually coated with a very thin passivating layer and/or doped with a rare earth additive. A first challenge is the lowering of the getter activation temperature while keeping efficient sorption properties. The next challenge is the pumping of hydrogen because of its reversible sorption in transition metals, and the pumping of hydrocarbon gases. This becomes critical because $H_2$ and $CH_x$ are at this moment the main remaining gases in packaged cavities.

Yttrium, because it can form stable hydrides [1] and is able to crack hydrocarbon gases [2], is a good getter film candidate to address these issues but it has received little attention. In this work thermal activation of evaporated yttrium and $Y_xTi_y$ films is investigated, mainly by in-situ sheet
resistance measurements under vacuum as a function of the temperature. Previous works have shown that this technique provides useful and reliable information on getter films activation [3].

2. Experimental details
Pure 200 nm thick Y and YₓTiᵧ films have been deposited by using UHV co-evaporation under a background pressure lower than 10⁻⁸ mbar to avoid contamination. The deposition rate was 0.5 nm/s. Hydrogen partial pressure has been checked during deposition using residual gas analysis (RGA). By varying relative deposition rates of yttrium and titanium, YₓTiᵧ alloys with x = {0, 9, 31, 65, 100} have been obtained. The films microstructure has been determined by high resolution Scanning Electron Microscopy (SEM) and the composition was measured by Energy Dispersive Spectrometry (EDS). X-ray Photoelectron Spectroscopy (XPS) analyses have been performed to quantify the diffusion of the native oxide before and after thermal treatment under UHV (< 10⁻⁹ mbar). An aluminum source has been used at 15 keV.

The sheet resistance has been measured by the 4-probes method after each deposition and as a function of temperature under partial vacuum, following the temperature cycle given in figure 1.

![Figure 1. Example of temperature and pressure variations during in-situ 4-probes measurement.](image)

The annealing starts with a 40 °C heating during 2 minutes. This step induces the desorption of gases and water adsorbed after venting the set-up for sample introduction. Then the temperature increases at a rate of 50 °C/min up to 200 °C then 10 °C/min up to 250 °C. The Temperature Coefficient of sheet Resistance (TCR) of the material is extracted from the resistance increase during the first heating stage. The annealing temperature is maintained for 75 min with or without controlled N₂ leak, under a pressure of 10⁻³ or 10⁻⁶ mbar respectively. Then the sample is naturally cooled under vacuum down to 30 °C and finally an entry of N₂ is operated.

In addition, ex-situ electrical measurements have also been performed after sample annealing in an oven under a regular flux of argon at 1 bar. This allowed the extraction of an activation energy associated to the diffusion of surface oxides inside the volume.

3. Pure yttrium

3.1. Ex-situ annealing
The sheet resistance of yttrium films has been measured just after deposition. Samples have been then annealed during 1h15’ under argon pressure at 250 °C, 300 °C and 350 °C and the ex-situ sheet resistance values have been measured. Results are reported in figure 2.
After annealing at 250°C, the sheet resistance increases of around 5 % whereas it is multiplied by 100 for annealing temperatures of 300 °C and 350 °C. It is attributed to a surface oxidation of the film during annealing, thanks to residual oxidizing species contained in argon.

This hypothesis was confirmed by using RBS analysis (see figure 3) on annealed samples.

The yttrium peak (around channel 1500) allow to determine in a first approach the oxygen profile in depth. Oxygen is mainly present in the upper half part of the film for 250 °C annealing. Using the same method, it is determinate that the 300 °C and 350 °C annealed films are totally oxided.

3.2. XPS analysis

Figure 2. Sheet resistance of yttrium after annealing in argon at different temperatures.

Figure 3. RBS analyses of yttrium thin films annealed at 250 °C.

Figure 4. XPS spectra of yttrium before and after annealing at 250°C.
Table 1. Surface composition before and after annealing.

|                  | Before annealing | After annealing |
|------------------|------------------|-----------------|
| Y (at %)         | 4 %              | 46 %            |
| Y₂O₃ (at %)      | 96 %             | 54 %            |
| Y₂O₃/Y           | 22               | 1.2             |

XPS analyses have been performed before and after annealing at 250 °C in UHV (see figure 4). As shown in Table 1, the oxygen content in the surface layer (analysis depth is around 6 nm) decreases after annealing. Thus, the quantity of metallic atoms of yttrium increases from almost 0 to 1/3 of the total amount of yttrium in the analysed volume. This demonstrates that oxygen diffusion in the film bulk already occurred at 250 °C, but is not complete.

In conclusion, electrical measurement as well as composition analysis shows that activation of yttrium is effective between 250 °C and 300 °C. It also shows that sheet resistance measurement is a convenient method to determine the activation temperature.

4. YₓTiᵧ alloys

4.1. Y₃₁Ti₆₉ analysis

In-situ 4-probes sheet resistance of quite-rich Ti sample (69 %Ti) has been recorded under partial pressure of 10⁻⁶ and 10⁻³ mbar (figure 5).

![Figure 5](image)

Figure 5. In-situ sheet resistance of Y₃₁Ti₆₉ during an annealing at 250 °C under different pressures as function of time and temperature.

Results show that the TCR is negative (-3.0 x 10⁻⁴ °C⁻¹) below 200°C then it becomes positive (figure 5-right). The influence of the leak pressure is strong. During the annealing at 250 °C, the sheet resistance increases of about 67 % and 109 % for the samples annealed under a 10⁻⁶ mbar and 10⁻³ mbar air pressure respectively. Close to the end of the annealing step, the sheet resistance seems to saturate at 10⁻³ mbar (figure 5-left). During the cooling phase, the sheet resistance increases at the same rate than temperature. Sheet resistance is sensitive to many phenomena occurring in the material, such as phase or microstructure changes, oxidation and diffusion. Furthermore, the TCR is also dependent on temperature. So no clear explanation on the different contributions leading to the observed behavior could be drawn.

Nevertheless, the influence of a pressure can be studied and provides useful information on the getter alloy film. First, we extracted the sheet resistance before and after annealing which provides an indication of oxidation generated by annealing, and thus an effective gettering capability including both surface and bulk. TCR was also determined in the 60 – 100 °C range during heating and between 150 and 100 °C during cooling. By plotting the TCR before annealing as function of the resistivity, we also check the validity of the Mooij rule for the different film compositions.
For this sample, the sheet resistance increases more rapidly during the 75 minutes annealing stage, under a $10^{-3}$ mbar pressure. The leak is indeed composed of $N_2$ gas with traces of oxidizing species. We suppose this is the signal of the presence of oxides stocked in the thin film due to both absorption and diffusion.

During the cooling phase, the leak is closed. Then after approximately 140 minutes of natural cooling, when the temperature is quite stable (~28 °C), the leak is activated again to put the chamber at room pressure. This insertion of $N_2$ induces an increase of the sheet resistance (figure 6).

![Figure 6. Sheet resistance of $Y_{31}Ti_{69}$ during venting with $N_2$ after annealing at $10^{-3}$ and $10^{-6}$ mbar.](image)

The evolution is similar for the two samples but the variation is smaller for the sample annealed at $10^{-3}$ mbar (0.39 % in 100 minutes) than for the sample annealed at $10^{-6}$ mbar (0.43 % in the same time). This variation can be understood by the fact that the getter surface is not saturated and that the higher the pressure during annealing, the lower the number of free sites for oxidation.

In conclusion, $Y_{31}Ti_{69}$ sheet resistance variation between before and after annealing is of 6.9 Ω and 11.1 Ω that to say 67 % and 109 % for $10^{-6}$ and $10^{-3}$ mbar annealing respectively. Resistivity is around 200 μΩ.cm and TCR strictly negative, that is in accordance with Mooij rule.

4.2. $Y_xTi_y$ comparisons

The same analysis has been done for the different alloys deposited. Figure 7 shows that the variation of sheet resistance after annealing depends on alloy composition. Minor variations are obtained for $Y_9Ti_{91}$ (-0.7 % and -0.9 % at $10^{-3}$ mbar and $10^{-6}$ mbar respectively). Conversely, composition with a high content in yttrium presents large variations, up to 100% for $Y_{31}Ti_{69}$.

![Figure 7. Relative variation of sheet resistance of $Y_xTi_y$ films after 1h of annealing at 250°C at $10^{-3}$ mbar and $10^{-6}$ mbar.](image)
Study of sheet resistance before annealing shows that the YₙTi₁₋ₙ alloys deposited present low TCR and high resistivity (figure 8). Pure yttrium as well as Y₉Ti₀₁ present a positive TCR and do not respect the Mooij rule that pretends that alloys with a resistivity larger than 150 μΩ.cm have a negative TCR [4]. This might be due to a particular microstructure or the content in hydrogen.

![Figure 8. TCR of YₓTi₁₋ₓ films as a function of composition (left) and resistivity (right).](image)

4.3. SEM
SEM analyses showed that Y-poor alloys are very porous (Figure 9-left) and that Y-rich alloys have a small grain size (figure 9-right). Grain size varies between 20 nm (Y) and 35 nm (Y₉Ti₀₁). Films have a columnar structure that is known to be a suitable structure for gettering properties.

![Figure 9. SEM surface images of Y₉Ti₀₁ (left), Y₃₁Ti₆₉ (middle) and Y₆₅Ti₃₅ (right).](image)

SEM analyses realized after an annealing at 250 °C on yttrium show that grain size doesn’t change in a consequent way. The very porous state of Y-poor alloys could explain some issues: low sheet resistance variation may be due to low length of diffusion (low absorption capacity) and high resistivity.

5. Conclusion
Sheet resistance and XPS measurements show that thermal activation of yttrium getter film starts at 250 °C but become significant above 300 °C. No grain size growth was observed by SEM after annealing. Sheet resistance measurement is a simple method to detect changes in YₓTi₁₋ₓ getter thin films during or after annealing but variations are complex and difficult to extract without additional physico-chemical measurements.
Acknowledgements
The authors gratefully acknowledge the C2N facilities clean room for processing. The authors also want to thank warmly the CEMHTI and especially Hélène Lecoq and Thierry Sauvage for the RBS analyses.

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