Orolia Switzerland SA
Rue du Vauseyon 29
CH - 2000 Neuchâtel
tél.: +41 32 732 16 66
fax: +41 32 732 16 67
space@spectratime.com
www.spectratime.com

Advanced Glass Cell Technology for Extended GNSS Atomic Clocks Lifetime

AGAL

Executive Summary Report

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AUTHOR	Project Manager	Qinghua Wang	Qinghua Wang	Qinghua Wang cn=Qinghua Wang, o=Orolia Switzerland SA, email=qinghua.wang@orolia.com, c=CH 2021.07.05 13:53:50 +02'00'
CONTRBUTED	R&D engineer, CSEM	Ivan Marozau	[signature]	05.07.2021
APPROVED	Mechanical Engineer	Vito Genna	Vito Genna	Digitally signed by Vito Genna DN: cn=Vito Genna, o=Orolia Switzerland SA, email=vito.genna@orolia.com, c=CH Date: 2021.07.05 14:13:02 +02'00'
APPROVED	Maser Product Manager	Jacques Pittet	[signature]	05.07.2021
RELEASED	Technical Director	Pascal Rochat	Pascal-André ROCHAT	Signature numérique de Pascal-André ROCHAT DN : cn=Pascal-André ROCHAT, o=T4Science Inc., ou, email=rochat@t4science.com, c=CH Date : 2021.07.05 19:38:25 +02'00'

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COMPANY	NAME	QUANTITY
ESA	Marco Belloni	
Orolia Switzerland SA	Documentalist	

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1 Scope

This document is dedicated to the Executive Summary Report for Advanced glass cell technology for extended GNSS atomic clocks lifetime (AGAL) project in the frame of ESA's Basic Technology Research Programme (TRP). After a short introduction which summarizes the scope of the project, the main achievements and results of the project are presented.

2 Applicable Documents

Doc. Id.	Document Nr.	Document Title	Issue
[AD01]	E8A Contract No. 4000126202/18/NL/HK	ESA Contract No. 4000126202/18/NL/HK «Advanced glass cell technology for extended GNSS atomic clocks lifetime»	
[AD02]	ESA-TRP-TEC-SOW-010280	Statement of Work ESA Express Procurement Plus - EXPRO+ Advanced glass cell technology for extended GNSS atomic clocks lifetime	Issue 1, revision 0, 29/06/2018

3 Introduction

In the Passive Hydrogen Maser (PHM), a glass cell is used as the hydrogen dissociator, a key part serving as the plasma confiner where hydrogen molecules are dissociated into atoms. In this application, chemical etching and other mechanisms related to interaction between the hydrogen plasma and vessel inner walls, may change the boundary conditions and then affect the discharge sustainability. Solutions for limiting such phenomena and then to extend the atomic clock lifetime are demanded.

The main objective of the activity is the identification of proper coating materials and processes to reduce wear-out effects in PHM hydrogen dissociators, with the following high-level objectives:

1. to understand the mechanisms responsible of glass properties modification over time as effect of interaction with plasma in Hydrogen dissociators.
2. to identify materials and coating processes able to counteract the identified wear-out mechanisms without affecting the hydrogen dissociator functionality.
3. to demonstrate by means of samples integrated in a representative test bench, the effectiveness of the identified solution.

Under this contract, we undertook the identification and verification of coating material and process aiming to reduce wear-out effects in PHM hydrogen dissociator bulb, and to deliver documents, as well as virgin and aged bulbs with coating.

4 Work Performed and Main Results Achieved

4.1 Task 1 Define Preliminary Requirement

Task 1 was dedicated for Requirement analysis, including the definition of the bulb geometry, the full understanding of the Hydrogen dissociator functionality, and the understanding of wear-out effects.

The current design of the dissociator bulb, made of fused quartz SiO_2, for the Galileo space PHM is retained as the baseline of the AGAL. The technical requirements for the hydrogen dissociator bulb were detailed.

The identified wear-out mechanism involves:

1. Etching of the SiO_2 material from the bulb bottom by the H plasma. The bulb bottom region where the etching is observed is located close to the RF electrode. The resulting SiO_2 surface exhibits conical and/or pyramidal structures which are characteristic for the differential etching

2. The removed SiOx material is then re-deposited at the side walls, where the optical darkening is observed. The formed layer(s) constitutes of the reduced SiO_{2-x} or a mixture of SiO_{2-x} and microcrystalline Si.

4.2 Task 2 Identify low bulb aging technology

Task 2 was dedicated to identify the solution to counteract the identified wear-out effects.

The proposed mitigation approach was based on the initial wear-out hypothesis of the reduction of SiO_2 material from the side walls. To prevent the reduction of SiO_2, a thin conformal layer of Al_2O_3 (20-30 nm) was deposited at the inner bulb surface. The layer shall serve as a barrier against reduction since the thermodynamic stability of Al_2O_3 in atmosphere with low p(O2) is considerably higher as compared to SiO_2.

The test plan and test procedure for technology/design evaluation and bulb acceptance at the Beginning of Life (BOL) was determined with a threefold objective:

- to demonstrate repeatability and full control of the coating process
- to verify the compliance status to bulb technical requirements, including validation of functionality when integrated in the long term test bench
- to assure compliance to space environment (vacuum) and radiation in particular

The test benches, which would be used in Task 3 and Task 4 to validate the effectiveness of the identified solution, was defined. Three DTBs (Dissociator Test Benches) in the frame of PHM industrialization program were made available for AGAL for the adaption, added with HDO vacuum assembly, external HDO driver, vacuum station and acquisition system, to be representative of working conditions of the actual PHM dissociator and HDO under vacuum.

4.3 Task 3 Manufacture samples with low bulb aging technology

Task 3 was dedicated to manufacture and test the samples in order to prove coating process control and compatibility with Hydrogen dissociator technical requirements.

During this task 9 dissociator bulb samples, replica of the current flight PHM design (i.e. same material, same geometry, same treatment), were manufactured from the same manufacturing batch:

- DTB02: standard bulbs, 1 mounted (SN160), 1 backup (SN161, not used)
- DTB03: coated bulbs: 1 mounted (SN162), 1 backup (SN163, not used)
- DTB04: coated and irradiated bulbs: 1 mounted (SN168, replacing the previously SN167 broken during the integration)
- Virgin coated bulbs: 2 deliverables sent to ESA (SN164, 166), 1 as verification bulb (SN165) at CSEM

7 bulbs (SN162 to 168) were submitted to CSEM for coating.

Deposition of Al_2O_3 layers was performed by Molecular Vapor Deposition (MVD) technique. The process is carried by successive deposition of water and TMA (Trimethylaluminum) precursors in the chamber. The quality and thickness homogeneity of the Al_2O_3 layers was confirmed using the X-ray reflectivity and AFM measurements. The adhesion and thermal stability of the layers was proved by performing rapid temperature cycling tests from 5°C to 100°C.

Two coated bulbs SN167&168 were then subjected to the irradiation testing at ESTEC Co60 facility during 24.09 – 07.10.2019 (12.8 days), applying TIDL of 124.5 krad and dose rate of 406 rad/h.

The testing of three bulbs under the test benches (Figure 4-1) demonstrated the compliance to dissociator bulb technical requirements at BOL, although the degradation was indicated on the bulb SN168 during the accelerated test.

Figure 4-1 Pictures of AGAL Test Benches

4.4 Task 4 Test and assess low bulb aging technology

Task 4 was dedicated to test the sample in a representative test bench and to analyze the aged bulbs in order to assess the effectiveness of the identified solution against wear-out and ageing effects.

The long term testing were performed continuously under nominal operational condition according to the test plan during 9 months from 25.02.2020 to 26.11.2020.

Table 4-1 compares the key performances of bulbs at BOL and EOL and verification of the compliance to the requirement.

Parameters	Requirement	Measurements				C / NC (Remark)
		Condition	Standard Bulb SN160	Coated Bulb SN162	Coated & Irradiated Bulb SN168	
Dissociation Light	0 – 1.2 V	BOL, nominal	0.656 V	0.549 V	0.600 V	C
		BOL, accelerated	0.485 V	0.424 V	0.251 V	C
		EOL, nominal	0.485 V	0.426 V	0.387 V	C
Atomic signal amplitude	≥ 2 dB	BOL, nominal	2.69 dB	3.85 dB	3.19 dB	C
		BOL, accelerated	2.80 dB	3.83 dB	2.52 dB	C
		EOL, nominal	2.97 dB	4.11 dB	1.65 dB	C / NC (SN168)
Operational atomic linewidth	≤ 3.5 Hz	BOL, nominal	3.21 Hz	2.56 Hz	2.67 Hz	C
		BOL, accelerated	3.14 Hz	2.61 Hz	2.58 Hz	C
		EOL, nominal	3.19 Hz	2.77 Hz	4.52 Hz	C / NC (SN168)
Dissociation efficiency	≥ 40 %	BOL, nominal	76,4%	66,1%	64,6%	C
		BOL, accelerated	67.9 %	53.6 %	14.9 %	C / NC (SN168)
		EOL, nominal	58,0%	55,3%	38,6%	C / NC (SN168)

Table 4-1 Verification to Performance Requirement at BOL and EOL

The three bulbs were visually inspected at the end of the test campaign. Ageing effects are obvious as observed on three bulbs, whitening centered in the bottom and browning in the side wall. We observed similar discoloration on standard bulb SN160 and coated SN162. The browning coloration appears more severe on the irradiation SN168.

Table 4-2 summarizes the Statement of Compliance (SOC) of the proposed coating solution for the hydrogen dissociator bulb, verified by the long term tests comparing with a standard Galileo PHM dissociator bulb.

Reference to requirement [AD02]	Requirements	Compliance	Coated bulb under verification
RQ-007_1	Functional requirements	C	SN162, SN168
	Performance requirements		
-	Dissociation efficiency	C	SN162
-	Dissociation light	C	SN162
-	Atomic signal amplitude	C	SN162
	Operational atomic linewidth	C	SN162
	Operational requirements		
RQ-002	Thermal operational environment	C	SN162
RQ-003	Hydrogen pressure	C	SN162
-	HDO operational parameters	C	SN162
RQ-006_2	Lifetime *	C	SN162
	Environmental requirements		
-	Barometric pressure environment	C	SN162
-	Radiation environment	NC	SN168

* Similar parameter evolution trend as standard bulb SN162, based on the current long term test.

Table 4-2 Compliance Matrix to Specification

The coated bulb SN162 has demonstrated comparable performance with respect to current bulb design SN160, and technical requirements following the long term testing at representative nominal condition are satisfied with SN162. The coated bulb SN168 subjected to prior radiation exposure is not compliant to performance requirements.

The following investigations were performed: Visual optical inspection, SEM/EDX analysis, TEM/EDX analysis, XRD analysis, Raman spectroscopy analysis. The main conclusions of the performed bulbs' investigations are (please refer to Figure 4-2 for the schematic representation of the layers and features discussed below):

- At the side walls, AlOx coating and the SiO_2 wall bulk under it are intact and are not affected neither by gamma irradiation nor by the H-plasma aging test
- The observed visual darkening of the bottom side wall is due to the additional layer(s) that are grown on top of the AlOx layer. This layer is composed of reduced SiOx and Si
- The re-deposited SiOx layer(s) originates from the etching of the SiO_2 material from the bulb flat bottom part, where the optical roughening is observed. The roughness is caused by the formation of conical structures as a result of differential etching
- The origin of the two layers in the bulb 162 is probably linked to the forced plasma interruption during the H-plasma aging tests.

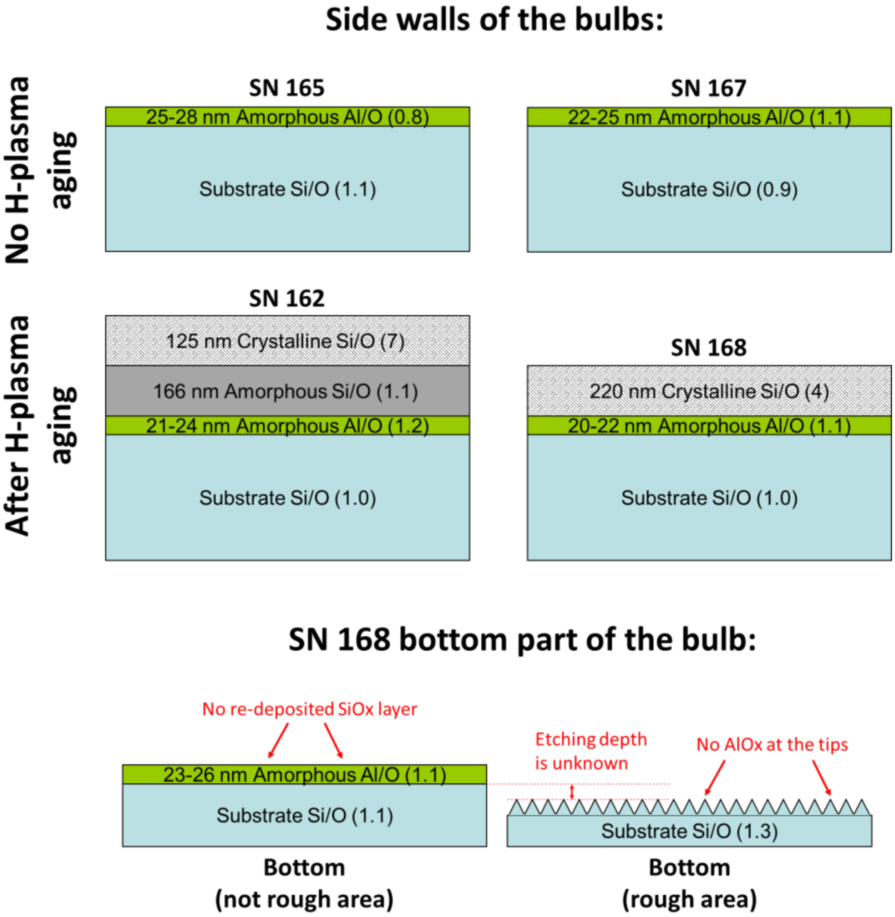

Figure 4-2 Schematic representation of the observed layers at the inner surface of the side walls of the investigated bulbs, and at the inner surface of the bottom flat part of the aged bulb SN 168. The value in the brackets indicates the EDX intensity ratio between the metals (Si or Al) and O. Please note that this is not the absolute stoichiometry coefficient. It shall only be used of the samples' comparison

5 Conclusion and recommendations

The Aluminum oxide coating solution, aiming for the wear-out effect mitigation in the hydrogen dissociator bulb, was identified, implemented and evaluated within the AGAL project.

The applied mitigation solution was an AlOx coating (20-30 nm thick) deposited at the inner side walls by MVD. The technique allows to deposit a continuous conformal AlOx layer at the entire curved inner surface of the bulbs. The primary objective of this coating was to protect the underlaying SiO_2 from the reduction by active atomic hydrogen species from the plasma. Results of the microstructural investigation of the AlOx-coated bulbs subjected to the accelerated H-plasma aging reveal that indeed the SiO_2 side wall material beneath the coating as well as the AlOx coating itself remain intact at the inner side walls. However, the coating could not stop etching of the bulb material in the bottom part close to the RF electrode. As described above, this has led to re-deposition of SiOx/Si at the side walls.

The solution is proved compliant to the functional, performance, operational and space vacuum environmental requirements for the dissociator bulb of the Hydrogen Maser. However, test results obtained during the 9-month period of the long-term test were not sufficient to provide adequate evidence that the ageing effect on the coated bulb is reduced comparing to the standard bulb, and the compatibility with the radiation could not be assured according to the testing.

The similar radiation test was not planned on a standard Galileo space PHM dissociator bulb and is out of the scope of the AGAL project, therefore no straightforward comparison can be provided between the coated bulb and the standard bulb testing in same radiation environment. However, it is noteworthy to mention that Galileo PHMs have years of in-flight experience. A complete PHM was endured radiation test by LND to mimic a solar flare although the cumulated total dose was low (1.2krad). The unit was also submitted to gamma burst. No specific problems with regard to the dissociation were noticed. Nevertheless it is still recommended to perform a similar radiation test on a standard dissociator bulb in the future PHM development activities.

Apart from the materials and coating of the dissociate bulb, the optimization of the plasma operation of the RF oscillator (HDO) matching with the bulb is another important solution in order to counteract the aging effect. The RF power, frequency and antenna coupling shall be optimized in order to minimize the interaction of the plasma on bulb surfaces, among others, concentrating as much as possible the plasma in the center of the bulb. For example, minimizing the interactions with bulb surfaces leading to much lower bulb aging has been successfully demonstrated within Rb plasma lamps.

The standard bulb SN160 has accumulated valuable data during the long-term test. It will be interesting to continue the testing in the frame of H2020, to gather more information of the aging behavior, and to demonstrate hopefully the plasma sustainability of the HDO design. For the time being the test has been continued with the same configuration as in AGAL.