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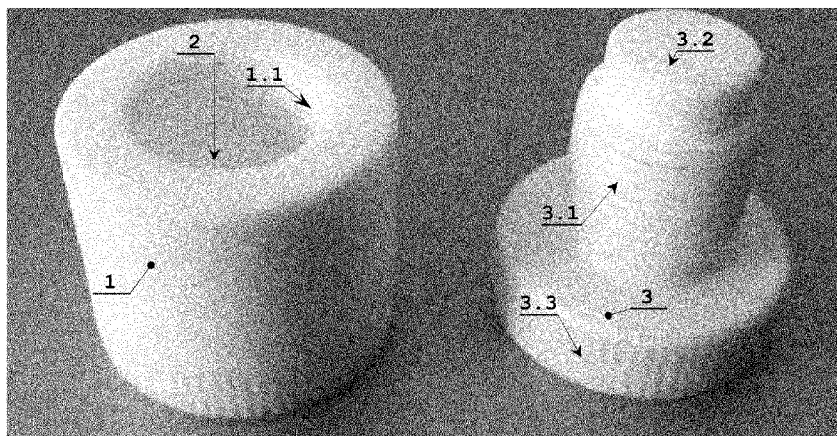


Figure 1A

(57) Abstract: -23- ABSTRACT The present invention discloses a process for forming ready-to-use quartz crystal microbalance sensors (QCMS) with atomically flat surface suitable as sample support for scanning tunneling microscopy (STM) measurements. The process consists of the following steps: A. deposition of the gold or another metal on atomically flat Si or similar wafer; B. pairing of the said wafer with already deposited gold or another metal surface with the quartz microbalance sensor also having surface of the same metal; and C. performing thermal compression bonding (TCB) to bond the metal surfaces together. The pressure exerted in step C. is applied by mechanically pressing the said structure where the pressure remains applied even after TCB in step C. is finished. The obtained ready-to-use quartz microbalance sensor remains confined within the said press used in step C. and until it is ready to use. The said mechanical press is used also as a transporting and storing means for the said sensor.



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**PROCESS FOR FORMING READY-TO-USE QCM SENSORS WITH ATOMICALLY FLAT
SURFACE SUITABLE FOR STM MEASUREMENTS**

DESCRIPTION

Technical Field

The present invention relates to the technical field of quartz crystal-microbalance (QCM) sensors; more particularly, to details or improvements of such quartz crystal-microbalance sensors (QCMS) with gold or another metal surfaces (GS). The improvements of the said QCMS allow other measurements, such as scanning tunneling microscopy (STM) or atomic-force microscopy (AFM), to be performed in conjunction (in parallel or separately) with the QCM measurements on the same substrate.

Technical Problem

Two techniques for investigating surfaces became a standard in the surface science; the scanning tunnelling microscopy (STM) and the high resolution, molecular and sub-molecular resolution, atomic-force microscopy (AFM). It is well known in the art that the STM is used for imaging surfaces at the atomic level. For the STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm (10 pm) depth resolution. With this resolution, individual atoms within materials are routinely imaged and manipulated. The STM can be used not only in ultra-high vacuum but also in air, water, and various other liquid or gas environments, and at temperatures ranging from near 0°K to over 1000°C. The AFM is another type of scanning probe microscopy, with demonstrated resolution on the order of a nanometer, 1000 times better than the optical diffraction limit. The information is gathered by "feeling" or "touching" the surface with a mechanical probe. Piezoelectric elements that generate tiny but

accurate and precise, electronically controlled movements enable such a detailed scanning of the surface.

On the other hand, QCM measures a mass variation per unit area by measuring the change in frequency of a piezoelectric quartz crystal resonator. The resonance is disturbed by the addition or removal of a small mass due to a thin layer or a film deposition or decay at the surface of the piezoelectric resonator. Frequency measurements with a resolution of $1:10^{-10}$ in a one second interval are easily made, thus deposited mass can be measured even below 1 ng/cm^2 - that is, the deposition of less than a monolayer of molecules or particles may be detected. The QCM can be used under vacuum, in gas phase and in liquid environments. It is routinely used for monitoring the deposition rate in thin film deposition systems under vacuum. In liquid, it is highly effective at determining the affinity of (bio)molecules; ligands or proteins, in particular - to surfaces functionalized with recognition sites. Larger entities, such as viruses or polymers, are investigated, as well.

The standard QCM sensors are not suitable for the above cited STM and AFM techniques due to rather high root mean squared (RMS) surface roughness of approx. 2-4 nm. In general, an RMS value translates to a peak-to-peak value which may be 6 to 8-fold larger than the RMS value for the studied region or section of the signal. Consequently, if the sensor's surface roughness amplitude is greater than the characteristic size of molecules or particles deposited on the surface for study then the said molecules or particles will be hidden by the features, the valleys or troughs, of the sensor's surface. Thus, the excessive roughness prevents usage of the cited techniques.

Therefore, the first technical problem is to form the atomically flat surface with the RMS smaller than 0.4 nm, preferably about 0.2 nm, suitable for AFM and STM measurements in conjunction with the QCM measurements, more particularly to the STM measurements and

having in mind that the sensor surface should be electrically conductive for STM; preferably the QCMS with the gold surface (GS).

Next, it is observed that *in situ* manipulation of the QCMS are quite complicated regarding the contamination issue; the QCMS should be properly cleaned and treated before its actual use, to allow the deposition of the new material layer. So, the second technical problem is how to produce *in situ* ready-to-use QCMS that does not require cleaning and/or pretreatment before use.

The above mentioned technical problems were solved with the mechanical press used in process of adjusting / forming the QCMS with the atomically flat surface that is used further as the transporting and storing means for the said sensors. Also, it is possible to re-use the said mechanical press practically endlessly.

Previous State of the Art

Considering the stated first technical problem, it is natural to look at the already published parallel AFM + QCM or STM + QCM studies; such as the ref. 1.:

- 1.) R. P. Richter and A. Brisson: „QCM-D on Mica for Parallel QCM-D - AFM Studies“ *Langmuir*, 2004, 20 (11), pp 4609-4613, DOI: 10.1021/la049827n;

<http://pubs.acs.org/doi/abs/10.1021/la049827n>

The present document teaches about the parallel quartz crystal microbalance with dissipation monitoring (QCM-D) and AFM study performed in liquid. The authors studied adsorption processes in liquid, such as the formation of supported lipid bilayers and protein adsorption. The authors noted in the abstract that the large intrinsic roughness of currently used gold-coated or SiO₂-coated QCM-D sensors limits the structural characterization by atomic force microscopy (AFM). The observed technical problem was solved by a

method for coating QCM-D sensors with thin mica sheets where mica inherently provides atomically flat surface. The authors demonstrate that the mica-coated sensors can be used to follow the formation of supported lipid membranes and subsequent protein adsorption. They concluded that the said method allows combining QCM-D and AFM investigations on identical supports, providing detailed physicochemical and structural characterization of model membranes. However, their method to attach the mica support by a layer of epoxy-glue reduces the Q-factor of the quartz sensor and suppresses higher harmonics, which beyond the 5th harmonic may not be detected.

Importantly, the used mica support, as it is nonconductive is not suitable for the STM measurements, so the stated technical problem was not solved with the teaching presented in the reference 1. Few other references disclosed similar techniques:

- 2.) J.-M. Friedt, K. H. Choi, F. Frederix, and A. Campitelli: „Simultaneous AFM and QCM Measurements; Methodology Validation Using Electrodeposition“, Journal of The Electrochemical Society, 150 (10) H229-H234 (2003);

<https://www.researchgate.net/publication/234991366>

- 3.) M. Westwood, A. R. Kirby, R. Parker, V. J. Morris: „Combined QCMD and AFM studies of lysozyme and poly-L-lysine-poly-galacturonic acid multilayers“; Carbohydrate Polymers 89 (2012) 1222- 1231:

http://bioforcenano.com/wp-content/uploads/ProCleaner-Papers/Combined_QCMD_and_AFM_studies_of_lysozyme_and_poly-L-lysine-poly-galacturonic_acid_multilayers.pdf

- 4.) J. M. Friedt, K. H. Choi, L. Francis and A. Campitelli: „Simultaneous Atomic Force Microscope and Quartz Crystal Microbalance Measurements: Interactions and Displacement Field

of a Quartz Crystal Microbalance"; Japanese Journal of Applied Physics, Volume 41, Part 1, Number 6A, (2002);

<http://iopscience.iop.org/article/10.1143/JJAP.41.3974>

The reference 5. describes the simultaneous use of the QCM and the STM technique and associated problems with the said use:

5.) M. Abdelmaksoud, S. M. Lee, C. W. Padgett, D. L. Irving, D. W. Brenner, and J. Krim: "STM, QCM, and the Windshield Wiper Effect: A Joint Theoretical-Experimental Study of Adsorbate Mobility and Lubrication at High Sliding Rates"; Langmuir, 2006, 22 (23), 9606-9609, DOI: 10.1021/la061797w

<https://www.physics.ncsu.edu/nanotribology/publications/ref103.pdf>

The careful reader will certainly note the section devoted to the STM imaging of a clean QCM Electrode which reveal the difficulties in proceedings with parallel STM + QCM technique.

The above cited documents form a general state of the art revealing the possibility for carrying on the STM/AFM + QCM technique in conjunction, i.e. on the same sample holder for minimizing the experimental errors. In addition, all documents teach about the pretreatment of the active, measuring sensor surface before the actual use, which is, by the hereby disclosed invention - unnecessary.

Reference 6. discloses a way of forming atomically flat surface for the scanning probe microscopy applications:

6.) M. Hegner and P. Wagner: „Procedures in Scanning Probe Microscopy"; section 2:2:4 - „Ultraflat Au surfaces";

<https://www.tcd.ie/Physics/research/groups/nanobionanomechanics/>

pdf/Hegner_Procedures_98.pdf

The mentioned technique uses epoxy-glue (EPO-TEK ® 377) to bond the gold with the Si wafer. Use of the epoxy-glue affects significantly the resonant modes of quartz oscillations used in QCM or QCM-D measurements. Therefore, the used technique cannot be straightforwardly applied to QCMS due to the side-effects of the epoxy-glue that is applied to the quartz crystal substrate.

Finally, the present invention uses in its process a part of the process described in the reference 7.:

7.) D. W. Mosley, B. Y. Chow, and J. M. Jacobson „Solid-State Bonding Technique for Template-Stripped Ultraflat Gold Substrates“; Langmuir 2006, 22, 2437-2440;

http://chowlab.seas.upenn.edu/files/Mosley%20et%20al_Langmuir_2006.pdf

The authors of ref. 7 disclosed the procedure of using gold diffusion bonding for the preparation of template-stripped gold (TSG). TSG surfaces are useful for surface studies because a very consistent flat gold surface with few defects can be easily prepared. The authors developed a method of producing TSG surfaces that relies only on gold diffusion bonding - thermal compression bonding (TCB) rather than epoxies, which has clear advantages over the method disclosed in the ref. 6. The resulting substrates are free from concerns of solvent compatibility, heat stability, and impurities. Bonding of centimeter-sized substrates is performed at 300°C for 2h using a vise, i.e. the press tool and aluminum foil as a buffer between the substrates and the press. The result is TSG surface on titanium and glass substrate.

This technique, i.e. TSG by TCB is used hereby to obtain the same technical result where, instead of the titanium and glass substrate, the substrate is a QCM sensor. Also, the Si or a similar highly

polished wafer is used for forming atomically flat gold surface, instead of the mica used in ref. 7. Except the use of the QCM sensor with the gold surface and Si wafer, the main difference between the teaching of the ref. 7. and the present invention is that pressure exerted to the wafer and QCMS during the TCB remains applied even after the TCB procedure. Furthermore, the tool used hereby for producing the necessary pressure for the TCB step of the procedure is used also as the transporting and storing means for the said QCM sensors; that renders this invention non-trivial. The closest prior art document, ref. 7. also discussed the removal of the mica in the section Results and Discussion. The same procedure can be applied for removing the Si wafer from the modified QCM sensor in the said invention.

The metal-metal diffusion rates, where metal films were deposited on wafers with Si or SiO₂ surfaces are disclosed elsewhere, for instance in the ref. 8.:

8.) T. Shimatsua and M. Uomoto: "Atomic diffusion bonding of wafers with thin nanocrystalline metal films"; Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena 28, 706 (2010);

<http://dx.doi.org/10.1116/1.3437515>

The ref. 8. shows that the two films' bonded structure was related closely to the self-diffusion coefficients of the metals used for bonding. A high atomic diffusion coefficient at the grain boundaries and film surfaces is likely to enable bonding even at the room temperature.

Finally, the technical problem of transporting and storing the modified QCMS is not the trivial one as it might appear at the first sight. There are many dedicated, highly technically involved solutions for the mentioned problem of keeping an atomically flat

surface away from contamination by the ambient atmosphere; e.g., the ref. 9. - the Ferrovac GmbH UHV suitcases:

9.) <http://www.ferrovac.com/?tool=ProductList&category=UHV+Suitcase>

This ultra-high vacuum suitcases enable transporting and storing the samples or probes before the actual use.

For the QCMS modified according to the present invention, it is necessary to keep the coated and atomically flat surface clean before the use - which is, indeed, achieved with the said invention.

Summary of the invention

The present invention discloses a process for forming ready-to-use quartz crystal microbalance sensors (QCMS) with atomically flat surface suitable for scanning tunneling microscopy (STM) measurements. The process consists of the following steps:

- A. deposition of the gold on a highly-polished, locally atomically flat Si wafer with the wafer's root mean squared surface roughness smaller than 0.2 nm;
- B. pairing of the said Si wafer (SiW) with already deposited gold surface (DG) in step A. with the quartz microbalance sensor having gold surface, where the previously deposited gold surface is sandwiched between the Si wafer and the gold surface of the said quartz crystal microbalance sensor (GSQCMS); and
- C. applying a pressure P_{TCB} to the structure obtained in step B. GSQCMS - DG - SiW with simultaneous heating with a temperature T_{TCB} to produce thermal compression bonding (TCB) of the said gold surfaces, GSQCMS and DG, in the desired atmosphere.

The pressure exerted in the step C. is performed by mechanically pressing the structure GSQCMS - DG - SiW where the pressure remains applied even after TCB process performed in the step C. is over. The obtained ready-to-use QCMS with atomically flat surface suitable for

scanning tunneling microscopy (STM) measurements remains confined within the said press used in step C. until its use.

The used process parameters for step C.; in case of Au-Au surfaces bonding are:

- T_{TCB} is selected to be between 100°C and 450°C;
- P_{TCB} is above 1.0 MPa; and
- the duration of the step C. is longer than 5 minutes;

wherein the step C. is carried out in ambient atmosphere such as $O_2 + N_2$, or in a non-reactive, such as Ar atmosphere. The applied pressure is monitored by the pressure sensor embedded in the used mechanical press. The deposition of the gold on atomically flat Si wafer, used in step A., is previously obtained by thermal evaporation, sputtering, or electroplating.

A mechanical press, used in the process above, consists of a casing, with an interior for nesting the GSQCMS - DG - SiW structure, a closure of the said press and one or more buffers (thin, flat disks of a material like aluminum, lead, indium, mica, PTFE or other polymers, softer than QCMS or SiW materials). The closure is designed to exert the pressure to the said GSQCMS - DG - SiW structure by pressing it to the bottom of the interior of the casing. The buffers are situated between the bottom of the casing and the said GSQCMS - DG - SiW system and between the GSQCMS - DG - SiW system and the closure.

The said mechanical press is used as transporting and storing means for the said sensor when the forming process is finished - until its use; and possible re-use in the new process for forming ready-to-use QCM sensor with atomically flat surface.

In one variant, the mechanical press is equipped with the pressure sensor; preferably electrical pressure sensor situated at the bottom of the casing interior.

In another variant of the invention, the screw-type closure is used. Said closure has the thread compatible with the thread formed on the inner side of the casing and the pressure is exerted by screwing the said closure towards the bottom of the press that act to the GSQCMS - DG - SiW structure. In that variant, one of the used buffers inserted under the rotating closure is formed to prevent the rotation of the GSQCMS - DG - SiW structure while the pressure, via screwing, is applied. The screwing can be applied by hand, or by a preset outer mechanical force to the said closure head.

The used buffers are preferably made as thin, flat disks of a material like aluminum, lead, indium, mica, PTFE or other polymers, softer than QCMS or SiW materials, while in yet another variant the casing and the closure of the said press are made of the polytetrafluoroethylene.

The user has to perform the following additional steps before the use of such prepared sensor for in situ measurement:

- removing the pressure by opening the press immediately before the use of said modified QCM sensor to release GSQCMS - DG - SiW structure; and
- removing the Si wafer from the deposited gold surface (DG) revealing the clean and atomically flat golden quartz crystal microbalance sensor with the surface roughness defined by the surface roughness of the used Si wafer.

Brief Description of the Drawings

The Fig. 1A shows the simplest press used to carry out the procedure according to the invention having the casing and the closure.

The Fig. 1B shows the same press from the Fig 1A. when ready to exert the pressure on the GSQCMS - DG - SiW structure situated within the said press.

The Fig. 2A shows the quartz crystal microbalance sensor with gold surface situated at the bottom of its casing. The Fig. 2B shows the Si wafer where the previously deposited gold surface is oriented towards the bottom of the casing, i.e. towards the gold surface of the QCMS from the Fig. 2A.

The Fig. 3A shows the quartz crystal microbalance sensor with the gold surface (left) and the squared Si wafer wherein the gold is previously deposited (right); before the TCB process is performed. The Fig. 3B shows the quartz crystal microbalance sensor with the gold surface and atomically flat gold surface thereon after the TCB process (right), and the Si wafer from which the flat gold surface is removed (left).

The Fig. 4 shows schematically inner cross section of the used press for carrying out the invention, together with other elements used, such as the pressure sensor and buffers.

Detailed Description

The present invention reveals a new process for forming ready-to-use QCM sensors with atomically flat surface suitable for investigating surfaces via AFM or STM measurements in conjunction with the standard QCM measurements.

The disclosed technique is very suitable for studying 2D materials, with STM and QCM techniques in conjunction. Namely, it is known that the 2D materials, such as MoS₂, WS₂ and graphene, are obtained via exfoliation from bulk, or, growing via chemical vapor deposition on diverse supports. Once the desired 2D materials are formed on the respective support, the said material is routinely transferred to the metal substrates such as monocrystalline Ir(111) or Au(111) surfaces via polydimethylsiloxane (PDMS) stamping process known from the soft lithography or via attachment to a layer of glue (a curing polymer). Once the 2D material flake is transferred to the

appropriate metal substrates and the stamp or glues are removed, the STM investigation can be performed. The usual problems are the price of used monocrystalline Ir(111) or Au(111) substrates and inability to perform further studies, such as the QCM measurements.

The disclosed process, according to the said invention, is much easier to perform than the process described above. Also, there are benefits, such as the obtained surfaces which are not necessarily cleaned before the actual use, which is a clear advantage in comparison to the technique disclosed in prior art documents.

Process of modifying the QCMS

(i) Preparing the QCM sensor

The disclosed process is related to the modification of the standard quartz crystal microbalance sensors (QCMS) to be used for scanning tunneling microscopy (STM) measurements. For that, any QCMS can be effectively used; such as Biolin Scientific Q-sense sensors with appropriate Au coating:

10.) http://www.biolinscientific.com/zafepress.php?url=/pdf/Q-Sense/Products/Sensor%20%26%20Modules/QS_P_Modules-and-Sensors%20Brochure.pdf

Such sensors are usually provided with a rather smooth metallic electrode that has a surface roughness of less than 3 nm (RMS). However, that value is at least one order of magnitude larger than the values for a support used for reliable STM measurements. The gold and other metallic electrodes have to be cleaned prior to use with the appropriate solvent, to be ready for further processing. Notably, harmful solvents, acids and bases, oxidants are used and demand trained staff and elaborate chemical laboratory facilities - as demonstrated in the ref. 11.

11.) L. Zhu, Y. Gao, H. Shen, Y. Yang, and L. Yuan; "A Quartz Crystal Microbalance (QCM) Study of Single-Strand DNA Hybridization and Hydrolytic Cleavage"; *Journal of Analytical Chemistry*, Vol. 60, No. 8, 2005, pp. 780-783. From *Zhurnal Analiticheskoi Khimii*, Vol. 60, No. 8, 2005, pp. 877-880.

(ii) Preparing the Si wafer

Highly-polished locally atomically flat Si or similar wafer is used as the substrate for the gold deposition. Such a wafer can be obtained in any convenient way known in the art, such as those described in the ref. 12.:

12.) Editors: G. Dhanaraj, K. Byrappa, K. V. Prasad, M. Dudley, M. "Springer Handbook of Crystal Growth"; ISBN 978-3-540-74761-1, Springer-Verlag Berlin Heidelberg, 2010

<http://www.springer.com/cn/book/9783540741824>

The RMS surface roughness of the used wafer should be smaller than 0.2 nm; The wafer should be cleaned prior to the following step, as described in the ref. 11.

(iii) Gold deposition

The gold deposition (GD) on the prepared Si wafer from the phase (ii) is performed via one of the techniques frequently used in the art, such as: thermal evaporation, sputtering, or electroplating. The gold deposited on the Si wafer has RMS surface roughness comparable with the used Si wafer, on the side faced to the said Si wafer. The deposited gold layer has the typical thickness of approx. 100 nm. Notably, one wafer may produce many chips that will be used for pairing with QCMS.

(iv) Pairing of the gold surfaces

Pairing of the Si wafer (SiW) with already deposited gold surface (DG) in step (iii) with the gold surface of the quartz crystal microbalance sensor (GSQCMS) from the step (i) is performed in a way that the gold surfaces are laid one over the other. The obtained structure has the form which sandwiches DG from the step (iii) between the original sensor's gold surface GSQCMS and the Si wafer; i.e. GSQCMS - DG - SiW.

(v) The thermal compression bonding

The obtained structure in the step (iv) is subjected to the thermal compression bonding (TCB) by applying pressure P_{TCB} and temperature T_{TCB} to the said structure. The good process parameters for the Au-Au TCB are:

- T_{TCB} is selected to be between 100°C and 450°C;
- P_{TCB} is above 1.0 MPa; and
- the duration of the TCB is longer than 5 minutes;

The TCB is carried out in ambient atmosphere such, as $O_2 + N_2$, or in a non-reactive Ar or similar atmosphere; preferably in the quartz tube with adequate monitoring and controlling of the applied temperature T_{TCB} .

The pressure T_{TCB} is regulated by a mechanical press which will be discussed separately in details. The TCB step is the last step in modifying the said QCMS.

Other steps are performed *in situ* before the use of modified sensor in practical measurements.

(vi) Storage, transporting, use of the modified sensor

The pressure applied via the mechanical press in step (v) remains applied even after the TCB phase is finished. The modified QCMS remains confined within the said press. Said press is therefore used as the storage and transporting means for the said modified QCMS.

Before actual use, the user has to

- remove the pressure by opening the press immediately before the use of said modified QCM sensor to release GSQCMS - DG - SiW structure; and
- remove the Si wafer (SiW) from the deposited gold surface (DG); as described in the ref. 6.

Last step reveals the clean and atomically flat quartz crystal microbalance sensor (QCMS) with the gold surface having roughness defined by the surface roughness of the used Si wafer - below 0.4 nm and preferably about 0.2 nm.

The Fig. 3A shows GSQCMS (6.1) and DG (5.1) before the TCB process, while the Fig. 3B shows SiW (5) from which the DG (5.1) is successfully transferred to the GSQCMS (6.1) surface; that is revealed in the last step before the actual use of the QCMS.

(vii) Re-use of the mechanical press

For the person skilled in the art, it is evident that the mechanical press can be used again for modifying a next QCM sensor.

Mechanical press used in the process of modifying the QCMS

The mechanical press used in the process of modifying the QCMS is depicted in the Fig 1A. The said press consists of a casing (1) and a closure (3). The closure (3) exerts the pressure via closure tip (3.2) to the structure GSQCMS - DG - SiW, mentioned in step (iv) before, when the closure is inserted into an interior (2) of the casing (1).

Many types of presses can be used to achieve said task. However, possibly the simplest and the most efficient one is the press where the closure is the screw-type closure (3), equipped with the thread (3.1), the closure head (3.3) and the flat closure tip (3.2). The used closure thread (3.1) is compatible with the casing thread

(1.1). Open press is depicted on the Fig. 1A, and assembled press is depicted on the Fig. 1B.

The assembly of GSQCMS - DG - SiW, which has to be pressed and subjected to the TCB procedure, is depicted via Figs. 2A and 2B. The GSQCMS (6.1) is positioned within the interior (2) of the casing (1). Then, the DG-SiW part is inserted in a way that the DG part is faced toward the GSQCMS in a manner that SiW (5) back side is oriented towards the closure (3), i.e. closure tip (3.2). Having in mind that the closure tip (3.2) is rotating while exerting the pressure; the use of one or more buffers (4.1, 4.2) is desirable. The technical role of the said buffers is to prevent the rotation of the GSQCMS - DG - SiW structure while the pressure via screwing is applied, see the Fig. 4.

In one embodiment, the first buffer (4.1) is positioned between the closure tip (3.2) and the SiW (5); while the second buffer (4.2) is situated between the QCMS (6) and the bottom of the casing (1). The buffers (4.1) and/or (4.2) are preferably made of thin, flat softer disks made of materials like aluminum, lead, indium, mica, PTFE or other polymers that are softer than materials of QCMS or SiW.

In yet another embodiment, the load cell (7), e.g. the pressure sensor, is situated between the last buffer (4.1) and the bottom of the casing (1), as depicted in the Fig. 4. Any pressure sensor (7) is acceptable that is configured for the pressures above 1 MPa. This pressure sensor communicates via appropriate wirings (7.1) with the pressure monitoring device which is not shown here.

This pressure sensor may also serve as a control sensor informing that the assembly GSQCMS - DG - SiW was closed and gold surface was clean and intact in storing and transporting process.

In any case, the pressure exerted by the closure tip (3.2) can be applied by hand, or by a preset outer mechanical force to the said closure head (3.3), such as a torque wrench or pneumatic / electric

closing mechanism exerting predefining moment to the closure head (3.3). It is important that the press is correctly tightened with the pressure above the nominal pressure needed for the TCB.

The casing (1) and the closure (3) can be made of any suitable material, however, the polytetrafluoroethylene (Teflon®) seems to be the best choice having in mind low thermal expansion coefficient that ensure constant pressure exerted on the GSQCMS - DG - SiW during and after TCB. Teflon has a good thermal conductivity that is necessary to transport the heat energy during the TCB to the GSQCMS - DG - SiW system.

Industrial Applicability

The skilled person in the art will immediately recognize the potential of the said invention where, instead of the Si wafer, the SiO₂ or any polished dielectric wafer can be used equally for obtaining the same technical effect. Also, the coating surface of the used QCM sensor and the corresponding counterpart wafer surface that is deposited with the metallic material can be made of any material that allows coating / deposition and exhibits a good TCB properties. Such materials are: Al-Al, Ag-Ag, Au-Au, Cu-Cu, and Ti-Ti; as described in the ref. 8.) when the appropriate TCB process parameters are used.

The polytetrafluoroethylene press proves to be easy to manufacture and easy to work with it. Despite its simplicity at the first sight, this press proves to be extremely useful in the process of modifying the QCM sensors in order to enable them as sample supports for STM / AFM measurements and for storing and transporting of the modified QCMS. Therefore, the industrial applicability of the said invention is obvious.

References and abbreviations

1	casing
1.1	casing thread
2	interior
3	closure
3.1	closure thread
3.2	closure tip
3.3	closure head
4.1	upper buffer
4.2	lower buffer
5	Si wafer [SiW]
5.1	deposited gold surface [DG]
6	quartz crystal microbalance sensor [QCMS]
6.1	gold surface of the quartz crystal microbalance sensor [GSQCMS]
7	load cell / pressure sensor
7.1	load cell wirings, i.e. jack
QCM	quartz crystal microbalance
QCM-D	quartz crystal microbalance with dissipation monitoring
QCMS	quartz crystal microbalance sensor
GSQCMS	gold surface of the quartz crystal microbalance sensor
SiW	Si wafer
DG	deposited gold surface
GS	gold surface
STM	scanning tunneling microscopy
AFM	atomic-force microscopy
TCB	thermal compression bonding
RMS	root mean squared
TSG	template-stripped gold

CLAIMS

1. A process for forming ready-to-use quartz crystal microbalance sensors (QCMS) with atomically flat surface suitable for scanning tunneling microscopy (STM) measurements; wherein said process consists of the following steps:
 - A. deposition of the gold on a highly-polished, locally atomically flat Si wafer with the wafer's root mean squared surface roughness smaller than 0.2 nm;
 - B. pairing of the said Si wafer (SiW) with already deposited gold surface (DG) in step A. with the quartz microbalance sensor having gold surface, where the previously deposited gold surface is sandwiched between the Si wafer and the gold surface of the said quartz crystal microbalance sensor (GSQCMS);
 - C. applying a pressure P_{TCB} to the structure obtained in step B. GSQCMS - DG - SiW with simultaneous heating with a temperature T_{TCB} to produce thermal compression bonding (TCB) of the said gold surfaces, GSQCMS and DG, in the desired atmosphere;
characterized by that,
 - D. the pressure exerted in step C. is performed by mechanical pressing of the said structure GSQCMS - DG - SiW which remains applied even after TCB of step C. is finished; and
 - E. the obtained ready-to-use quartz crystal microbalance (QCM) sensor with atomically flat surface suitable for scanning tunneling microscopy (STM) measurements remains confined within the said press used in steps C. and D. until its use.
2. The process for forming ready-to-use quartz crystal microbalance sensors (QCMS) with atomically flat surface suitable for scanning tunneling microscopy (STM) measurements according to the claim 1, wherein the used process parameters for step C. for proper Au-Au TCB are:
 - T_{TCB} is selected to be between 100°C and 450°C;
 - P_{TCB} is above 1.0 MPa; and

- the duration of the step C. is longer than 5 minutes;
wherein the step C. is carried out in ambient atmosphere such,
as $O_2 + N_2$, or in a non-reactive Ar atmosphere.

3. The process for forming ready-to-use quartz crystal microbalance sensors (QCMS) with atomically flat surface suitable for scanning tunneling microscopy (STM) measurements according to the claim 2, wherein the applied pressure is monitored by the pressure sensor embedded in the used mechanical press.
4. The process for forming ready-to-use quartz crystal microbalance sensors (QCMS) with atomically flat surface suitable for scanning tunneling microscopy (STM) measurements according to the claim 1 or 2, wherein the deposition of the gold on atomically flat Si wafer is obtained by thermal evaporation, sputtering, or electroplating.
5. A mechanical press used in the process for forming ready-to-use quartz crystal microbalance sensors (QCMS) with atomically flat surface suitable for scanning tunneling microscopy (STM) measurements according to any of the claims 1-4, which consists of a casing (1), an interior (2) for nesting the GSQCMS - DG - SiW structure, a closure (3) of the said press and one or more buffers (4.1, 4.2), **characterized by that:**
 - the said closure (3) exerts the pressure to the said GSQCMS - DG - SiW structure by pressing it to the bottom of the interior (2) of the casing (1);
 - the said buffers (4.1, 4.2), are situated between the bottom of the casing (1) and the said GSQCMS - DG - SiW system, and optionally, between the GSQCMS - DG - SiW system and the closure (3);wherein the said mechanical press is used as transporting and storing means for the said sensor when the forming process is finished - until its use; and possible re-use in the new process for forming ready-to-use quartz microbalance (QCM) sensor with atomically flat surface.

6. The mechanical press according to the claim 5, wherein the mechanical press is equipped with the pressure sensor (7); preferably electrical pressure sensor situated at the bottom of the casing interior (2).
7. The mechanical press according to the claims 5-6, wherein the closure (3) is screw-type closure with the thread compatible with the thread formed on the inner side of the casing (1) and wherein the pressure is exerted by screwing the said closure towards the bottom of the press that act to the GSQCMS - DG - SiW structure, with provision that one of the said buffers inserted under the rotating closure (3) is formed to prevent the rotation of the GSQCMS - DG - SiW structure while the pressure via screwing is applied.
8. The mechanical press according to the claim 7, wherein the screwing is performed by hand.
9. The mechanical press according to the claim 7, wherein the screwing is performed by applying a preset outer mechanical force to the said closure head (3.3).
10. The mechanical press according to the claims 5-9, wherein the used buffers (4.1, 4.2) are preferably made of thin, flat disks of material like aluminum, lead, indium, mica, polytetrafluoroethylene or other polymers that are softer than SiW or QCMS materials.
11. The mechanical press according to the claims 5-10, wherein the casing (1) and the closure (3) of the said press are made of the polytetrafluoroethylene.
12. Use of the ready-to-use quartz crystal microbalance sensors (QCMS) with atomically flat surface suitable for scanning tunneling microscopy (STM) measurements according to any of the

claims 1-3 wherein the user has to perform the following additional steps before the use of such prepared sensor for *in situ* measurement:

- F. removing the pressure by opening the press immediately before the use of said modified sensor QCM sensor to release GSQCMS - DG - SiW structure; and
- G. removing the Si wafer (SiW) from the deposited gold surface (DG) revealing the clean and atomically flat golden quartz crystal microbalance sensor (QCMS) with the surface roughness defined by the surface roughness of the used Si wafer.

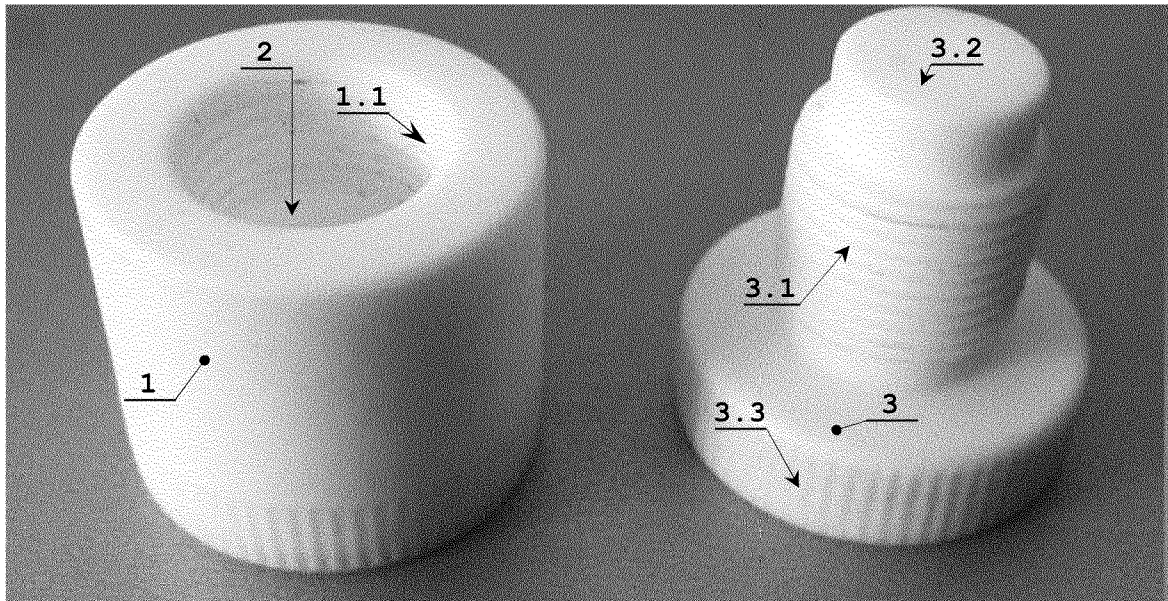


Figure 1A

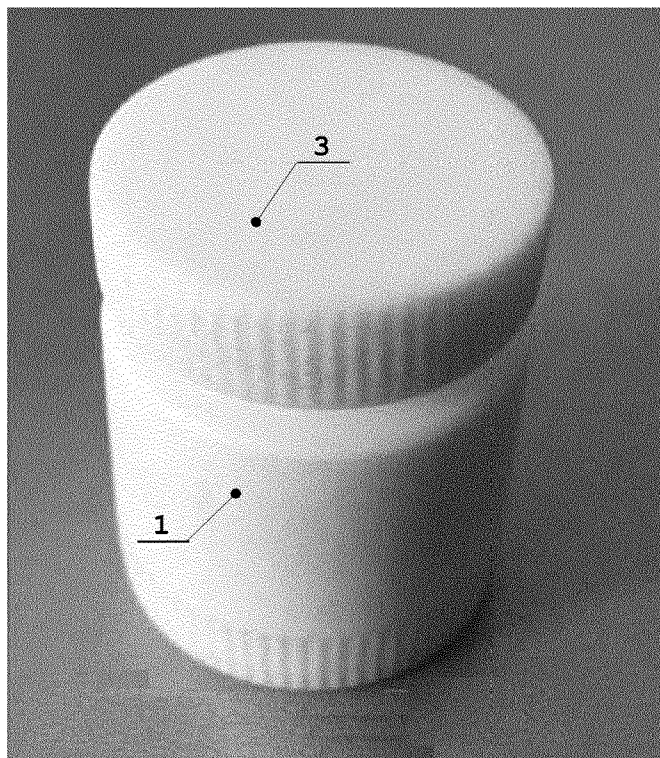


Figure 1B

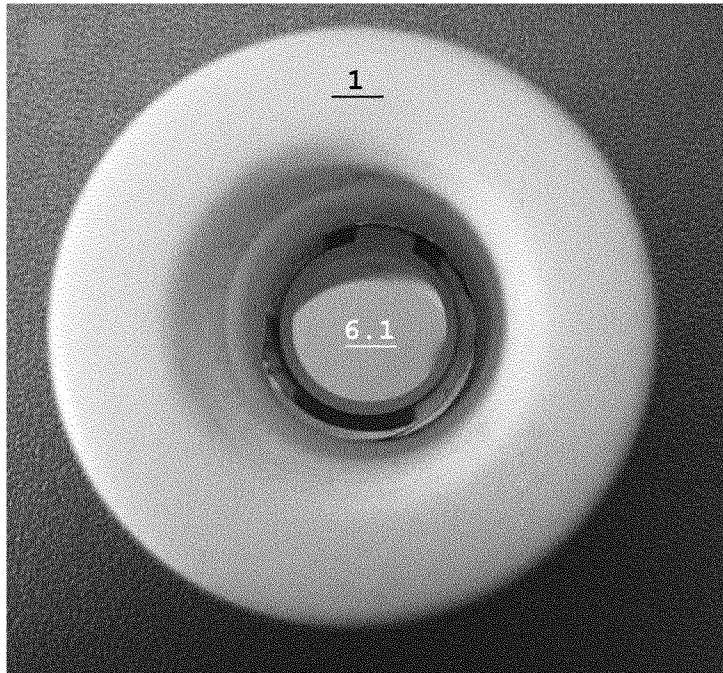


Figure 2A

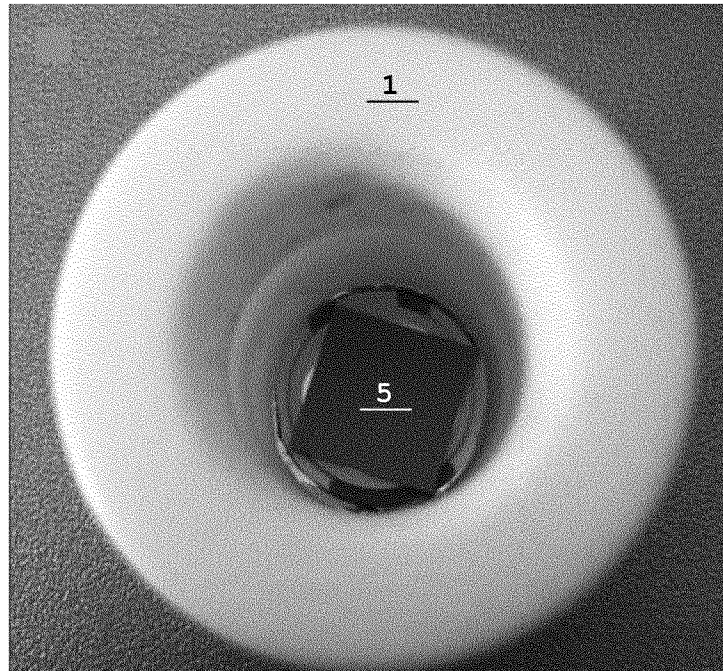


Figure 2B

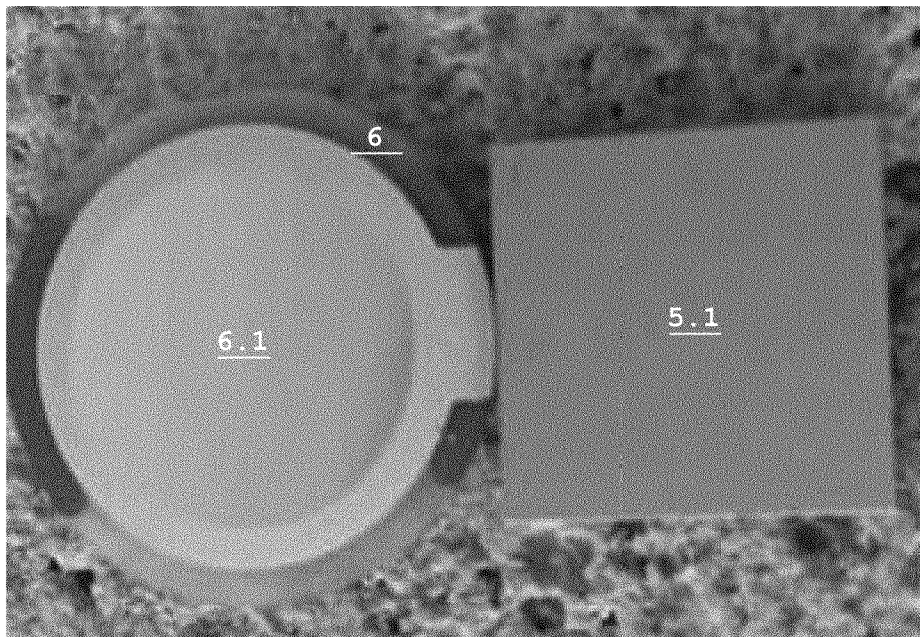


Figure 3A

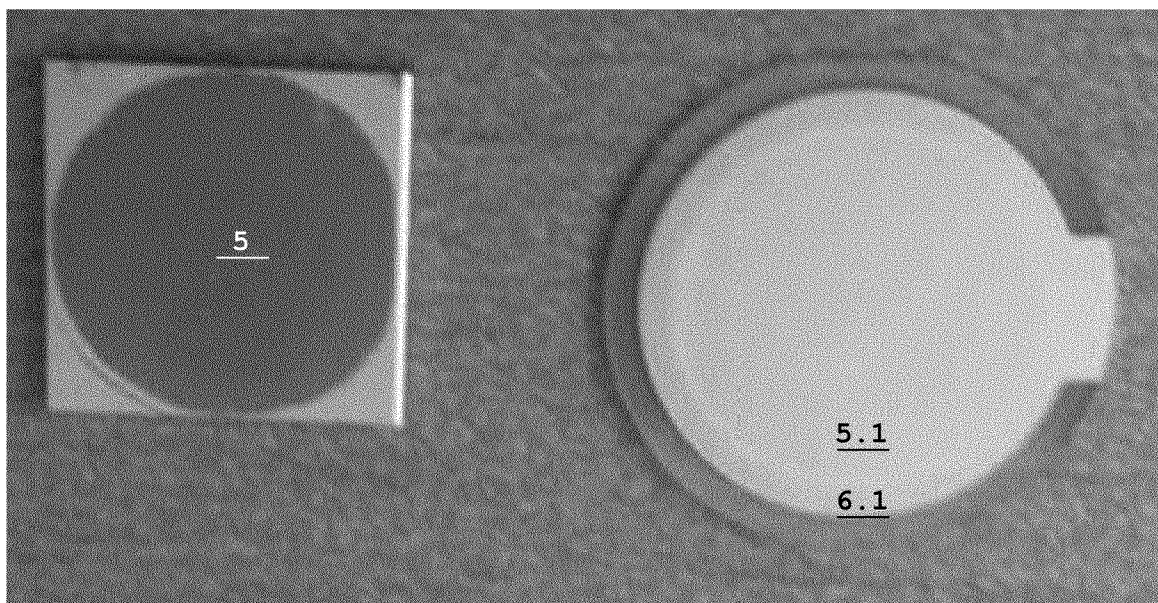


Figure 3B

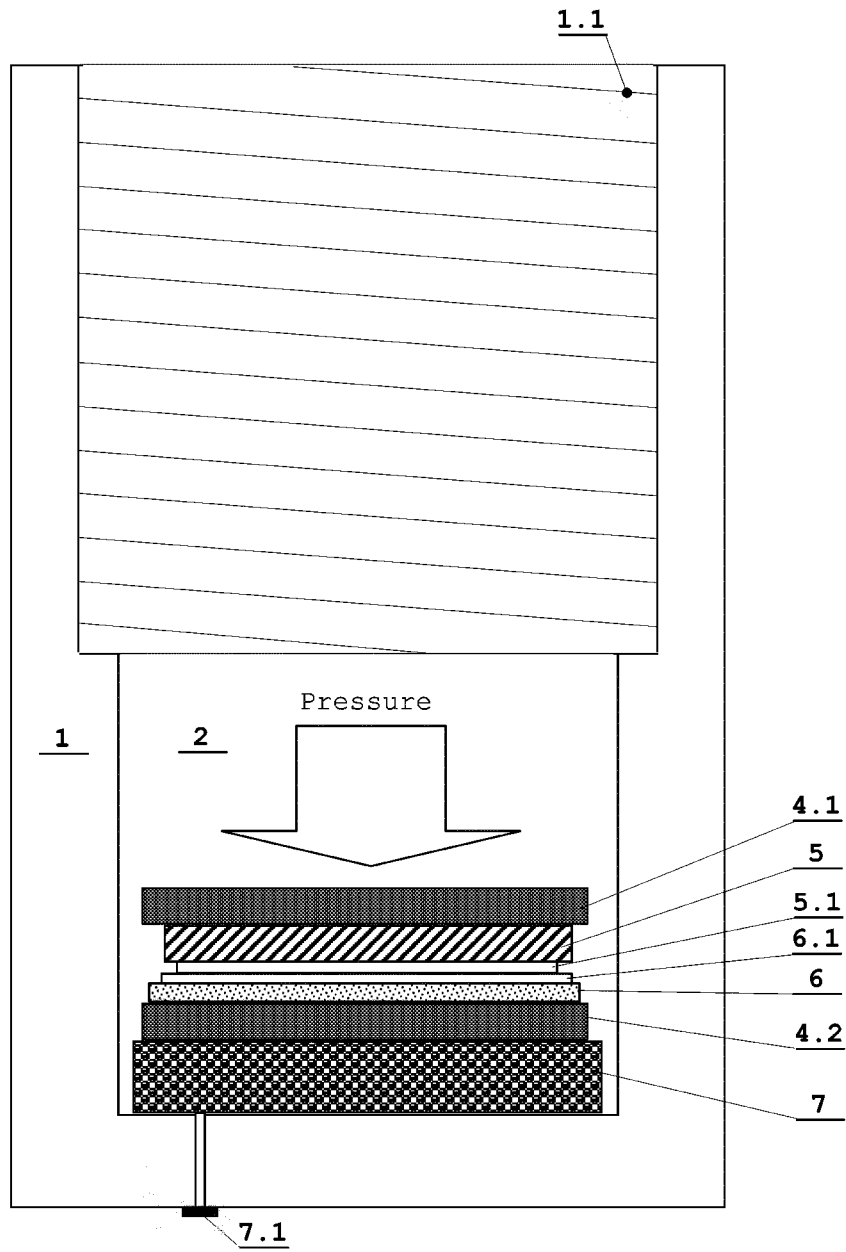


Figure 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/071817

A. CLASSIFICATION OF SUBJECT MATTER
 INV. G01Q30/02 G01N29/02 G01N29/24 G01N5/02
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 G01Q G01N B81C B06B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BERG STEFFEN ET AL: "Quartz crystal resonators with atomically smooth surfaces for use in contact mechanics", REVIEW OF SCIENTIFIC INSTRUMENTS, AIP, MELVILLE, NY, US, vol. 74, no. 8, 1 August 2003 (2003-08-01) , pages 3845-3852, XP012041007, ISSN: 0034-6748, DOI: 10.1063/1.1588751 figure 1 paragraph [0011]	1-12

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search 20 April 2018	Date of mailing of the international search report 02/05/2018
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Polesello, Paolo
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/071817

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>Martin Hegner ET AL: "Ultraflat Au surfaces" In: "Procedures in Scanning Probe Microscopy", 1 January 1998 (1998-01-01), John Wiley and Sons, XP055468799, pages 2:2;4 1-2:2:4 7, cited in the application figure 1 paragraph [Sample] -----</p>	1-12