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(54) **A METHOD AND A SYSTEM FOR APPLYING A LIQUID TO AN OBJECT IN A VACUUM SYSTEM**

(57) A vacuum system for applying a liquid to an object, the vacuum system comprising: a first module (A) for generating a vacuum; a second module (B) with a user chamber (8) and an injection chamber (9) for applying the liquid to the object under vacuum conditions; and a third module (C) comprising a set of components for preparing the liquid and supplying the liquid to an injection needle (11). The first module (A) is tightly connected to the second module (B) and the second module (B) is tightly connected to the third module (C). The second module (B) is connected to the third module (C) via a sealed linear movement system (13). The injection needle (11) passes through the sealed linear movement system (13) to inject the liquid prepared in the third module (C), so that the injection needle (11) protrudes from the linear movement system (13) into the interior of the injection chamber (9) in the second module (B) and is movable in the horizontal axis relative to the object (10) located in the second module (B) onto which the liquid from the injection needle (11) is to be sprayed.

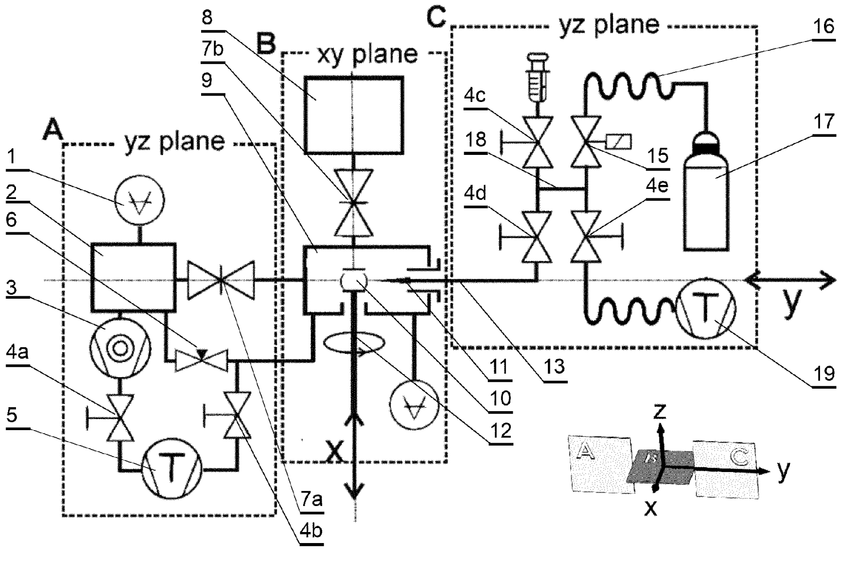

Fig. 1

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Description

TECHNICAL FIELD

[0001] The present invention relates in general to the field of applying a liquid to a surface of an object located in a vacuum environment.

BACKGROUND

[0002] In industry and science, there is a need to modify surfaces of objects by applying a specific material to the surface. This may aim to obtain unique surface properties of the object, to protect the surface, to prepare the surface for a further processing stage, etc. Modification of the surface by coating it with a material can be performed using gases, liquids and solid matter.

[0003] There are known vacuum systems that provide high purity of the application process. These systems allow removal of air and contaminants contained in the air from the surroundings of the object, so that the surface of the object can be properly modified. So far, modification of the surface of an object located in a vacuum by exposing it to gases or by applying materials in a solid state to the surface has been well mastered. However, effective methods for applying materials in a liquid form to an object, particularly in a high vacuum environment, have not been satisfactorily developed yet.

[0004] There is a particular need for systems that would enable solutions of organic molecules and their complexes, ionic liquids and other similar compositions to be effectively applied to objects. Applying liquids to an object in a high vacuum environment is problematic because liquids introduced into the vacuum begin to boil, i.e. evaporate dynamically throughout their volume.

[0005] The systems for applying liquids to an object in a vacuum environment that have been developed so far have some disadvantages.

[0006] A common feature of most of the known systems is that they use a needle positioned above the object to apply the liquid to the object. For example, such solutions are described in the publications "Real Space Observation of Double-Helix DNA Structure Using a Low Temperature Scanning Tunnelling Microscopy" (by Takashi KANNO et al., in Jpn. J. Appl. Phys. Vol. 38 (1999) pp. L 606-L 607), "Controlled injection of a liquid into ultra-high vacuum: Submonolayers of adenosine triphosphate deposited on Cu (110)" (by Sobrado, J. M. et al., in Journal of Applied Physics 120.14 (2016): 145307), "Microcontroller design for solution-phase molecular deposition in vacuum via a pulsed solenoid valve" (by Margaret Wolf et al., in J. Vac. Sci. Technol. A 38, 022413 (2020)), "The direct injection of liquid droplets into low pressure plasmas" (by Ogawa, D. et al., in Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 27.2 (2009): 342-351). The disadvantage of this type of solutions is that a droplet of liquid may form on the tip of the needle from which the liquid is injected, wherein this droplet may fall onto the object in an undispersed form, which makes it necessary to resume the process all over again.

[0007] A European patent application EP3034182A1 discloses a coating system comprising a coating chamber having arranged therein a coating apparatus for providing a substrate with an organic coating layer. The substrate has a form of a tape that is moved on rollers near a horizontally positioned needle that sprays a liquid substance in a vacuum chamber onto the moving tape. This poses a risk of contamination of the tape being coated with the drop of liquid that could form on the tip of the needle and fall therefrom onto the tape. A system for adjusting the distance between the needle and the object being coated is also used, wherein the system is installed in the same vacuum chamber wherein the coating is carried out, which introduces a risk of carrying contamination from the adjustment system mechanisms into the operating chamber where the coating is carried out, and exposes the mechanical components of the adjustment system to harmful fumes of the substance being sprayed, which can be detrimental to the adjustment system mechanisms.

SUMMARY

[0008] There is a need to improve vacuum systems for applying liquids to an object, to at least reduce the drawbacks of the state-of-the-art systems described above.

[0009] In one aspect, the invention relates to a vacuum system for applying a liquid to an object, the vacuum system comprising a first module for generating a vacuum; a second module with a user chamber and an injection chamber for applying the liquid to the object under vacuum conditions; and a third module comprising a set of components for preparing the liquid and supplying the liquid to an injection needle. The first module is tightly connected to the second module and the second module is tightly connected to the third module. The second module is connected to the third module via a sealed linear movement system. The injection needle passes through the sealed linear movement system to inject the liquid prepared in the third module, so that the injection needle protrudes from the linear movement system into the interior of the injection chamber in the second module and is movable in the horizontal axis relative to the object located in the second module onto which the liquid from the injection needle is to be sprayed.

[0010] The system according to the invention ensures that objects can be coated by very thin layers, of the order of even a few nanometers, by maintaining conditions of controlled needle-to-object distance under conditions of high vacuum. In the injection chamber, there are no unnecessary components; it basically contains only the object to be processed and the injection needle, while the components for preparing the liquid and for moving the injection needle are located outside the injection chamber.

[0011] The sealed linear movement system can be a linear bellows manipulator. This is a particularly preferable solution with regard to ensuring high vacuum conditions. Moreover, it allows the needle-to-object distance to be adjusted.

[0012] The injection chamber may comprise a manipulator to rotate the object. This allows the object to be coated from different sides. When the surface of the object is uneven, the uniformity of the coated layer can be achieved by adjusting the needle-to-object distance.

[0013] The second module may further comprise a user chamber separated from the injection chamber by a vacuum-tight gate valve. This allows a clean object to be prepared in the user chamber, moved to the injection chamber in a tight manner and, after the coating has been applied, moved again in a tight manner to the user chamber, where it can be further tested under tight conditions with regard to the applied coating.

[0014] The system may comprise an externally controlled manipulator to move the object between the user chamber and the injection chamber. Controlling the manipulator from the outside ensures tightness between the chambers.

[0015] The injection chamber may be separated from the user chamber by a high-tightness gate valve mounted on a ConFlat class fitting. The injection chamber can be separated from a pumping chamber in the first module by a high-tightness gate valve mounted on a ConFlat class fitting. Preferably, the linear movement system ensures tightness through mounting on a ConFlat class fitting. The use of components mounted on the ConFlat class fittings allows high vacuum conditions to be maintained in the injection chamber.

[0016] In another aspect, the invention relates to a method for applying a liquid to an object in the vacuum system as described herein. The method comprises: in the injection chamber in the second module, generating vacuum conditions with a pressure of $p < 9E-9$ mbar; moving the object from the user chamber, with pre-generated pressure of $p < 9E-9$ mbar, to the injection chamber; closing the valve that separates the injection chamber from the user chamber; preparing the liquid to be injected in the third module; equalizing the pressure between the injection chamber and a reservoir with the liquid to a value between 1E-1 and 1E1 mbar; spraying the object with the liquid using the injection needle, and adjusting the spraying parameters while spraying, by adjusting a distance of the injection needle from the object and parameters of a pulsed operation of a valve supplying a gaseous medium to the reservoir with the liquid; after the spraying is finished, sealing the injection chamber against the reservoir with the liquid, reducing the pressure in the injection chamber to below 9E-9 mbar and opening the valve that separates the injection chamber from the user chamber; and moving the object from the injection chamber to the user chamber.

[0017] Starting the process under conditions of high vacuum and maintaining tightness throughout the process ensures that a high degree of purity is maintained in the injection chamber, so that, through the operation of the valve and the needle-to-object distance, only a precisely defined amount of sprayed liquid is delivered to the object. This allows for very good control over the parameters of the applied layer. The object is not exposed at any stage to any liquid or gas other than that used intentionally during the application process; in particular, it is not exposed to air and contaminants contained therein.

BRIEF DESCRIPTION OF DRAWINGS

[0018] The object of the invention is presented by means of example embodiments in the drawing, wherein:

Fig. 1 shows schematically a structure of an embodiment of the system according to the invention in a cross-sectional view.

Fig. 2 shows a diagram of sealings between individual elements of the system according to the embodiment of Fig. 1.

Fig. 3A-3C, 4A-4C show test results related to a first embodiment.

Fig. 5A-5D, 6A-6B show test results related to a second embodiment.

DETAILED DESCRIPTION OF EMBODIMENTS

[0019] An example embodiment of the system according to the invention is shown in Fig. 1. The system comprises three modules: a first module (A), referred to as a vacuum generation module; a second module (B), referred to as a operating module; and a third module (C) referred to as a liquid dispensing module. The structure of the individual modules is schematically shown in a cross-section in two different planes in Fig. 1: the first module (A) is shown in a vertical cross section (in the yz plane), the second module (B) is shown in a horizontal cross section (in the xy plane) and the third module (C) is shown in a vertical cross section (in the yz plane). It is important to note that the third module (C) is positioned next to the second module (B) and is movable with respect to the second module (B) in a horizontal plane on the y-axis. The first module (A) can be positioned anywhere relative to the second module (B) - for example, next to, above or under the second module (B).

[0020] Individual components of the modules A, B and C should be made of vacuum-compatible materials, for example made of stainless steel. The sealing elements should be made of materials that are resistant to solvents used in the process.

[0021] The first module (A) comprises components for vacuum generation. The detailed structure of this module is not essential for the invention and different types of vacuum generation modules that will be capable of ensuring high vacuum conditions, in particular capable of providing a pressure $p < 9E-9$ mbar in the second module

(B), can be used. In the embodiment shown here, the first module (A) comprises a pumping chamber 2 connected by a gate valve 7a to the second module (B). A wide-range vacuum gauge 1 (which allows accurate measurement of high vacuum) and a turbomolecular pump 3 are connected to the pumping chamber 2, the turbomolecular pump 3 being connected by a manual isolation valve 4a, 4b to a dry pump 5 that, in turn, is connected to the pumping chamber via an infiltration valve 6.

[0022] The second module (B) is the operating module comprising a user chamber 8 into which the user can introduce the object onto which the liquid layer is to be applied. In the user chamber 8, tests may be carried out on an object with a layer applied thereon. The user chamber 8 is connected by a gate valve 7b to an injection chamber 9, where the liquid is sprayed onto an object 10 from a needle 11, also known as an injection needle. The object can be moved between the user chamber 8 and the injection chamber 9 using a manipulator 12, allowing movement along the x-axis and rotation of the object around the x-axis.

[0023] The third module (C) is a module for preparing liquid to be injected through the needle 11. The detailed specification of its components is irrelevant to the essence of the invention, and various types of liquid preparation components well known in prior solutions for applying liquids to an object under vacuum conditions, including those in which the needle is positioned vertically above the object, can be used. For example, the components for preparing liquid to be injected include a container 14 (for example, a syringe) with liquid, connected to isolation valves 4c, 4d, 4e and a solenoid valve 15, between which a reservoir 18 with liquid to be injected is formed. The amount of liquid being injected is adjusted by the solenoid valve 15 with a pulse length controller, also connected to a reservoir 17 with a gaseous medium. The gaseous medium can be noble gases (for example, argon) or other gases, such as those that do not react with a given object and liquid (for example, nitrogen).

[0024] It is important that between the second module (B) and the third module (C), a linear movement system 13 is mounted and it allows the third module (C) to be moved relative to the second module (B) in a horizontal plane along the y-axis. For example, it could be a bellows-based system that can be precisely stretched and compressed. For example, a linear bellows manipulator can be used that comprises vacuum-tight metal bellows that can be accurately compressed and stretched, causing a change in the distance between the connection points located at the ends of the bellows. Thus, the bellows may comprise the injection needle 11, one end of which extends above the first end of the bellows in the injection chamber 9, and the other end of which extends above the second end of the bellows in the third module (C) for preparing liquid and is connected there to liquid preparation components which, in turn, are connected by flexible hoses 16 to the reservoir 17 with gaseous medium and a pump 19. Thus, the entire third module (C) or an assembly of components for preparing liquid to be injected (in particular, the assembly of valves 4c, 4d, 4e and 15, between which the reservoir 18 with liquid to be injected, preferably also the container 14 with liquid, is formed) connected by the flexible tubes 16 to the reservoir 17 with gaseous medium may be mobile.

[0025] The coating parameters to be obtained on the object to be coated are adjusted by selecting the distance of the needle 11 from the object and the amount of liquid to be supplied via the valve 15, by selecting the opening pulse length (manually or automatically).

[0026] Fig. 2 schematically shows a diagram of sealings between individual elements of the system according to the embodiment of Fig. 1. The following sealings are used:

- CF class (ConFlat), i.e. with very high tightness, dedicated to ultra-high vacuum, according to ISO 3669:2020;
- SW class (Swagelok standard, these are high-tightness connections, suitable for liquids and gases)
- KF class (with medium tightness, according to ISO 2861:2020)
- LL class (Luer Lock, i.e. with low tightness, used for components requiring cyclic replacement due to ease of use, according to ISO 80369-7:2021)

[0027] In particular, to maintain high vacuum conditions, it is advisable that the injection chamber 9 be separated from the pumping chamber 2 and the user chamber 8 by ConFlat class gate valves, as well as that the manipulator 12 and the linear movement system 13 provide a ConFlat class tightness.

[0028] The tip of the needle 11 can be mounted using a connection with a tightness of LL to CF, as the linear movement system 13 provides a CF class tightness.

[0029] The use of Swagelok connections (and valves of this standard) at the connection of the elements 6, 4b and the chamber 9 results from the need to use elements with a smaller internal cross-section. The effective pumping speed (EPS) is, in practice and to the greatest extent, a function of the cross-sectional area at the narrowest point of the system and the length of that narrowing. In the present device, the influence of the narrowing length is not of much importance as all the elements are close together. However, the cross-section is of great importance. The smallest internal diameter available in the CF standard is DN16CF (i.e. a nominal diameter of 16 mm), while in the SW standard, it is possible to use pipes with an internal diameter of 3 to 4 mm. This combination of cross-sections and valves allows so-called differential pumping and precise control until the valve 7a, which connects the chambers 2 and 9 (where the cross-section is already considerably larger, for example, nominally equal to 63 mm - DN63CF), is fully opened. When this valve is fully opened, it is possible to pump at the full efficiency of the turbomolecular pump. For example, the turbomolecular pump can also be connected with a DN63CF connector - in this situation, pressures of E-9 mbar and below are easily achieved.

[0030] The SW connections, in turn, are used under ultra-high vacuum conditions. Because at the point of their use, there are small cross-sections and a metal-to-metal sealing (in particular, a clamped conical sleeve), it is possible to work with pressures of E-9 mbar and below. In practice, connections of this type exhibit so-called infiltration rates of 10E-11 mbar *l/s, i.e. comparable to the CF standard.

[0031] The system shown in Fig. 1 can be used as follows. At first, the valve 7b in the second module (B) that separates the user chamber 8 from the injection chamber 9 is closed. At this stage, the valves 6 and 4b in the first module (A) and the valves 4c, 4d, 4e, 15 located in the third module (C) are closed, the third module (C) being thus isolated from the second module (B). In the user chamber 8, the user creates or maintains, by any known means, ultra-high vacuum conditions, i.e. p < 9E-9 mbar. In the user chamber 8, there is the object. Before starting the operation, the valve 4a and the valve 7a in the first module (A) are opened. A pump set consisting of the dry pump 5 and the turbomolecular pump 3 is activated. The chambers 2 and 9 are pumped out of the atmospheric pressure level and a vacuum of p < 9E-9 mbar is then generated. Pressure measurement in the chambers 2 and 9 is carried out continuously by the wide-range vacuum gauges 1. At this stage, the pressures in the user chamber 8 and in the injection chamber 9 are in the same range, i.e. p < 9E-9 mbar. The valve 7b is opened and the object prepared for coating is then moved from the user chamber 8 to the injection chamber 9 using the manipulator 12. Then, the valve 7b between the chambers 8 and 9 is closed and the pressure in the injection chamber 9 is set at p < 9E-9 mbar. Subsequently, the valve 7a is closed, cutting off the first module (A) from the second module (B), resulting in a gradual increase in pressure in the injection chamber and setting the pressure in the chamber in the range of 1E-1 > p > 9E-9 mbar, for example to a vacuum of E-5 mbar. The increase in pressure in the chamber 9 is due to the lack of access to the first module (A) and the establishment of the related equilibrium (static vacuum). The third module (C) is then pumped until the pressure is below 1E-1 mbar, by opening the valve 4e connected to the pump 19, which has the ability to determine the pressure. The first sequence is then carried out, wherein the liquid in the syringe 14 is refilled, the valve 4e is closed, the valve 4c is opened, the liquid is introduced into the reservoir 18 and the valve 4c is closed; the valve 4d is then opened and the pressures in the injection chamber 9 and the reservoir 18 are equalized - the final pressure depends on the amount of liquid introduced and its physical characteristics, and will generally be between 1E-1 and 1E1 mbar; the valve 4d is then closed. A second sequence is then carried out, wherein the liquid in the syringe 14 is refilled, the valve 4c is opened, the liquid is introduced into the reservoir 18 and the valve 4c is closed; after that the valve 4d is opened and the pressure in the reservoir 18 is increased by a controlled, gradual supply of gaseous medium induced by the pulsed operation of the valve 15 (the valve 15 is a normally closed valve). For example, the gaseous medium can be supplied at a pressure of 5 bar. Using the manipulator 12, the object is placed in position for liquid application. As a result of the pulsed operation of the valve 15, the liquid is discharged (injected) through the needle 11 towards the object. At the end of the object spraying process (the end of operation of the valve 15), the pressure in the chamber 2 is in the range of 1E-1 > p > 5E3 mbar. In the next step, a differential pumping stage takes place using the first module (A) and supportively the third module (C). To this end, the valves 4b and 4e are opened and the injection chamber 9 is pumped to a pressure below 1E-2 mbar using the dry pumps 5 and 19. The valves 4b and 4d are then closed and the valve 6 is opened until the pressure reaches below 1E-3 mbar. The valve 6 is a valve with a smaller cross-section than the valve 7a and is also more accurate than the valve 7a in terms of controlling its opening. Opening of the valve 6 means that the chamber 9 is gradually pumped by the turbomolecular pump 3 and, at the same time, there is no possibility of damage and stopping of the pump due to overloads that could arise from the pressure difference in the chambers 2 and 9. When a pressure of p < 1E-3 mbar is reached, the valve 7a gradually opens and, when it is fully opened, the turbomolecular pump 3 pumps the system, i.e. the chambers 2 and 9, to a pressure below 9E-9 mbar. The pressure in the injection chamber 9 is therefore low again, and the object can thus be brought out into the user chamber 8 by opening the gate valve 7b, while maintaining high vacuum conditions.

[0032] In the above method, differential pumping is used, with the use of different valve cross-sections: the valve 6 connects the chambers 2 and 9 through a small cross-section channel, while the valve 7a connects the chambers 2 and 9 through a large cross-section channel, where the EPS is close to the maximum value provided by the pump. Immediately after the injection, the chamber 2 has a pressure of p < 9E-9 mbar, while the chamber 9 has a pressure of 5E3 mbar > p > E-1 mbar. With such a high differential pressure, the valve 7a could be damaged and the turbomolecular pump could be "throttled" (a rapid increase in pressure in the chamber 2 would cause the turbomolecular pump to decelerate rapidly, the pump impeller would experience overloads so great that it would stall, in extreme cases the impeller arms could be twisted or the bearings could be knocked out). For this reason, differential pumping was used. In the present system, differential pumping is first carried out with the dry pumps, which are resistant to overloads associated with differential pressure (these are the valves 4b and 4d). When they are closed and the valve 6 is opened, the turbomolecular pump 3 is already used through a narrow channel. There is little pumping efficiency here, so the pump is not subjected to high overloads associated with pressure difference. When the pressure reaches a sufficient level to open the valve 7a, i.e. p < 1E-3 mbar, this valve is opened and the chamber 9 is pumped with its full capacity (maximum EPS) by the turbomolecular pump 3.

First embodiment

[0033] The system was prepared to apply ethanol 99.8% to the surface of the object in the form of single-crystal rutile TiO_2 (011), which is a test sample. The system, consisting of the modules A, B and C, was connected to the user chamber 8 containing a scanning tunnelling microscope to allow observation of the object and a component that allows thermally programmed desorption to be carried out to prove that ethanol was applied to the sample as a result of the process. Fig. 3A shows the surface of a 100x100nm object before ethanol application, imaged with a scanning tunnelling microscope (It = 2pA, U = 1.7V)). It shows the local density of unoccupied electronic states on the surface. The procedure was carried out as discussed above. The needle 11 was maintained at a distance of 20 mm from the surface of the object. In the first sequence, 0.2ml of ethanol was consumed, so that the pressure in the injection chamber 9 relative to the reservoir 18 with liquid was equalized to 1.5E0 mbar prior to spraying. In the second sequence, i.e. the sequence wherein liquid is injected towards the sample, 0.2 ml of ethanol was consumed, and the solenoid valve 15 was controlled with 150 ms pulses, delivering a total of 3 pulses every 2 seconds. Once the liquid had been applied and the pressure in chamber 9 had settled at 2E2 mbar, pumping was started according to the procedure described above. After pumping out the chamber 9, when a pressure of p < 9E-9 mbar was reached, the sample was brought out to the user chamber 8, where the imaging was performed again with the scanning tunnelling microscope. Fig. 3B shows the surface of a 100x100 nm sample with ethanol applied (imaging parameters: It = 2pA, U = 1.7V), whereas Fig. 3C shows a magnified view of the portion indicated by a rectangle in Fig. 3B, with dimensions of 30×30nm (imaging parameters: It = 3pA, U = 1.7V). From Fig. 3B, 3C it can be seen that the maximum molecular multilayer was obtained, as otherwise it would not be possible to measure with the STM microscope with the quality and resolution presented. The surface is evenly covered, with additional agglomerates (Fig. 3B - arrows) and defects that are probably impurities (Fig. 3C - arrow). The said agglomerates and defects occur randomly on the surface of the sample, but their number is small and their occurrence on a molecular or nanometric scale is inevitable.

[0034] Furthermore, to confirm the presence of ethanol molecules on the surface, thermally programmed desorption (TPD) was performed on the sample in the user chamber. While the sample was gradually heated at a controlled rate, a signal was collected from a mass spectrometer positioned directly above the sample surface. This resulted in plots of I(T), i.e. the equivalent intensity of a given atomic mass as a function of temperature T. The result is shown in Fig. 4A which shows the TPD signal collected simultaneously for masses of 31, 45 and 46 amu, the atomic mass of the ethanol molecule is 46.07 g/mol - the existence of a distinguishable maximum when testing the mass of 46 amu is clear evidence that ethanol is present on the surface of the prepared sample. The liquid application method according to the invention therefore ensures even coverage of the sample on a microscale - it can be assumed that a constant degree of coverage θ is achieved every time for the same application parameters.

[0035] Therefore, the experiment was extended to include a series of TPD measurements with different sample heating rates, the result of which is shown in Fig. 4B. This allowed temperatures (Tpeak) corresponding to the maximum desorption at a given heating rate of the sample to be determined. Using the assumptions of the HRV (heating rate variable) method (Fig. 4C), the desorption activation energy Edes and the value of parameter v (pre-exponential factor) were determined for an ethanol molecule on rutile TiO2 (011).

Second embodiment

[0036] An ethanol solution was made that comprises tin phthalocyanine (SnPc) molecules having a structure as shown in Fig. 5D. Because phthalocyanines are poorly soluble in ethanol, the solution was supersaturated and settled down - thus obtaining a mixture with the maximum SnPc concentration under normal conditions.

[0037] The reference sample was the ethanol-applied sample described in the first embodiment.

[0038] In the next stage, the rutile crystal obtained in the first embodiment was purified. Then, using the same application parameters as in the first embodiment, a solution of ethanol and SnPc molecules was introduced onto the surface.

[0039] In this embodiment, it was possible to carry out an additional specialized study of the samples using secondary ion mass spectrometry (SIMS). This method allows the chemical composition of the surface to be accurately inspected, the local concentration of a selected component to be determined, depth profiles to be made and chemical mapping (distribution of a given mass over a selected area of the surface) to be carried out. Figs. 5A and 5B show dependences of signal intensity (counts) for masses characteristic for the SnPc molecule, in the case of ethanol (Fig. 5A) and the solution of ethanol and SnPc molecules (Fig. 5B), respectively. As is evident from the data presented, selected molecules were successfully applied to the surface of the sample. The signal in the experiment was collected from randomly selected areas of the sample with dimensions of 500 × 500 μm. The images can be interpreted as chemical maps for the peak of 632 amu - Fig. 5C. According to the accompanying scale, the brighter the spots on the map, the higher the concentration of molecules. It can be seen that, in addition to the bright agglomerates of molecules, individual points can be seen throughout the area - these are nanometre-sized clusters of molecules.

[0040] Additional STM mapping was carried out to support the above conclusion. For comparison purposes, the results obtained for ethanol (Fig. 6A, a sample size of 100x100 nm, It = 2pA, U = 1.7V) and the solution of ethanol and SnPc molecules (Fig. 6B, a sample size of 100×100 nm, It = 2pA, U = 1.7V) are collated. Upon application of the solution of ethanol and SnPc molecules, an ethanol-specific structure forms on the surface (indicated by the rectangle in Fig. 6B) and clusters of molecules (diameter < 20 nm) are visible. The poorer quality of the map seen in Fig. 6B is associated with the presence of agglomerates formed by SnPc molecules which are unstable under scanning conditions.

[0041] The embodiments presented here relate to tests on the surface of single-crystal rutile TiO_2 only to illustrate the effects obtained by the method according to the invention. However, this method does not have any limitations related to the application of liquids to other surfaces of metals, semiconductors and insulators.

Claims

1. A vacuum system for applying a liquid to an object, the vacuum system comprising:

- a first module (A) for generating a vacuum;
- a second module (B) with a user chamber (8) and an injection chamber (9) for applying the liquid to the object under vacuum conditions; and
- a third module (C) comprising a set of components for preparing the liquid and supplying the liquid to an injection needle (11);
- wherein the first module (A) is tightly connected to the second module (B) and the second module (B) is tightly connected to the third module (C);

the vacuum system **characterized in that**:

- the second module (B) is connected to the third module (C) via a sealed linear movement system (13);
- wherein the injection needle (11) passes through the sealed linear movement system (13) to inject the liquid prepared in the third module (C), so that the injection needle (11) protrudes from the linear movement system (13) into the interior of the injection chamber (9) in the second module (B) and is movable in the horizontal axis relative to the object (10) located in the second module (B) onto which the liquid from the injection needle (11) is to be sprayed.

2. The system according to claim 1, wherein the sealed linear movement system (13) is a linear bellows manipulator.

3. The system according to any of previous claims, wherein the injection chamber (9) comprises a manipulator (12) for rotating the object.

4. The system according to any of previous claims, wherein the second module (B) further comprises a user chamber (8) separated from the injection chamber (9) by a vacuum-tight gate valve (7b).

5. The system according to claim 4, wherein the manipulator (12) to move the object between the user chamber (8) and the injection chamber (9) is externally controlled.

6. The system according to any of previous claims, wherein the injection chamber (9) is separated from the user chamber (8) by a high-tightness gate valve (7a) mounted on a ConFlat class fitting.

7. The system according to any of previous claims, wherein the injection chamber (9) is separated from a pumping chamber (2) in the first module (A) by a high-tightness gate valve mounted on a ConFlat class fitting.

8. The system according to any of claims 1 to 7, wherein the linear movement system (13) is mounted on a ConFlat class fitting.

9. A method for applying a liquid to an object in the vacuum system according to any of claims 1 to 8, the method comprising:

- in the injection chamber (9) in the second module (B), generating vacuum conditions with a pressure of p < 9E-9 mbar;
- moving the object from the user chamber (8), with pre-generated pressure of p < 9E-9 mbar, to the injection chamber (9);
- closing the valve (7b) that separates the injection chamber (9) from the user chamber (8);
- preparing the liquid to be injected in the third module (C);
- equalizing the pressure between the injection chamber (9) and a reservoir (18) with the liquid to a value between 1E-1 and 1E1 mbar;
- spraying the object with the liquid using the injection needle (11), and adjusting the spraying parameters while spraying, by adjusting a distance of the injection needle (11) from the object and parameters of a pulsed operation of a valve (15) supplying a gaseous medium to the reservoir (18) with the liquid;
- after the spraying is finished, sealing the injec-

tion chamber (9) against the reservoir (18) with the liquid, reducing the pressure in the injection chamber (9) to below 9E-9 mbar and opening the valve (7b) that separates the injection chamber (9) from the user chamber (8); and

- moving the object from the injection chamber (9) to the user chamber (8).

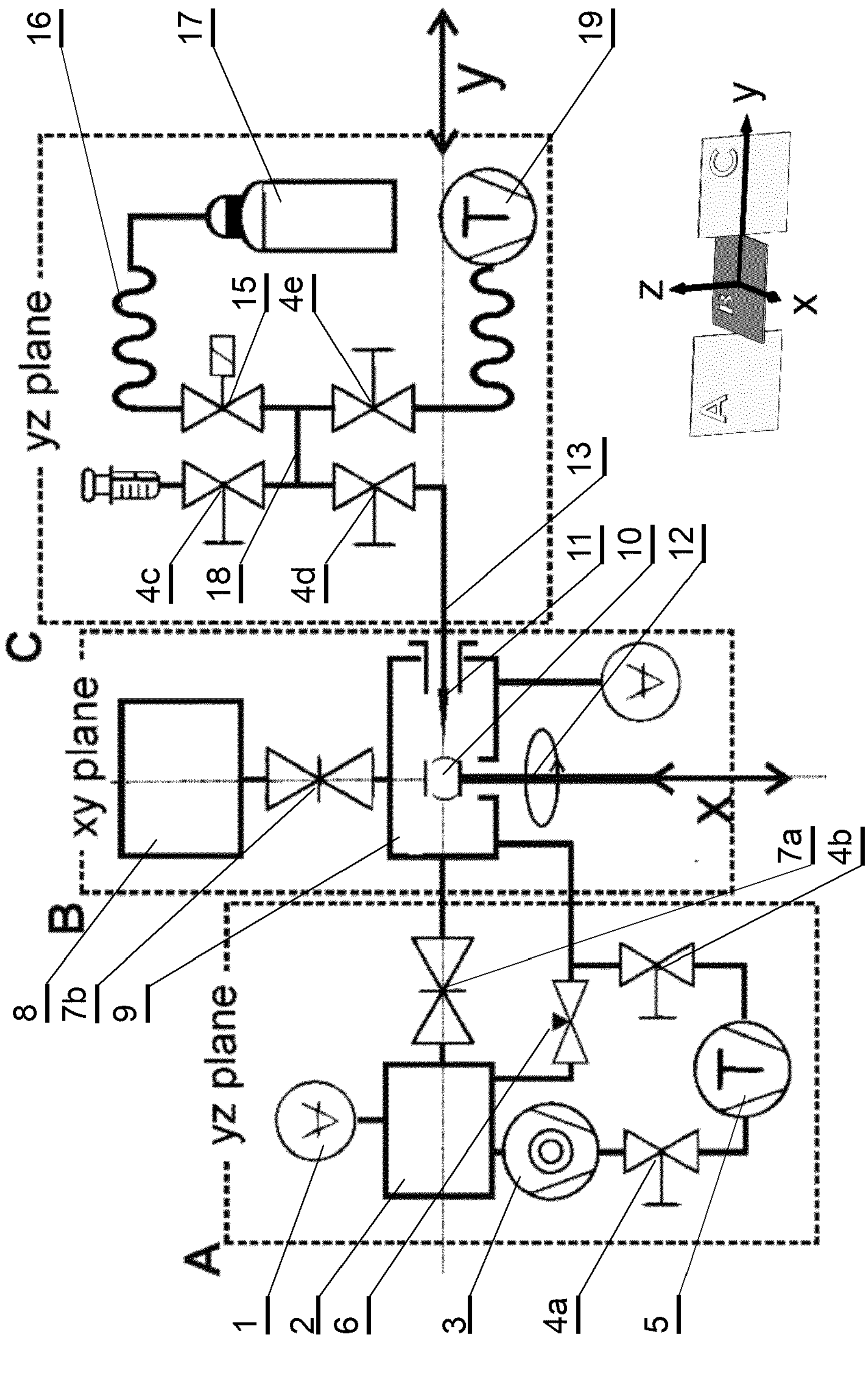

A
B
C
yz plane
xy plane
yz plane
x
y
z
1
2
6
3
4a
5
8
7b
9
7a
4b
4c
18
4d
13
11
10
12
15
4e
16
17
19
T
T

Fig. 1

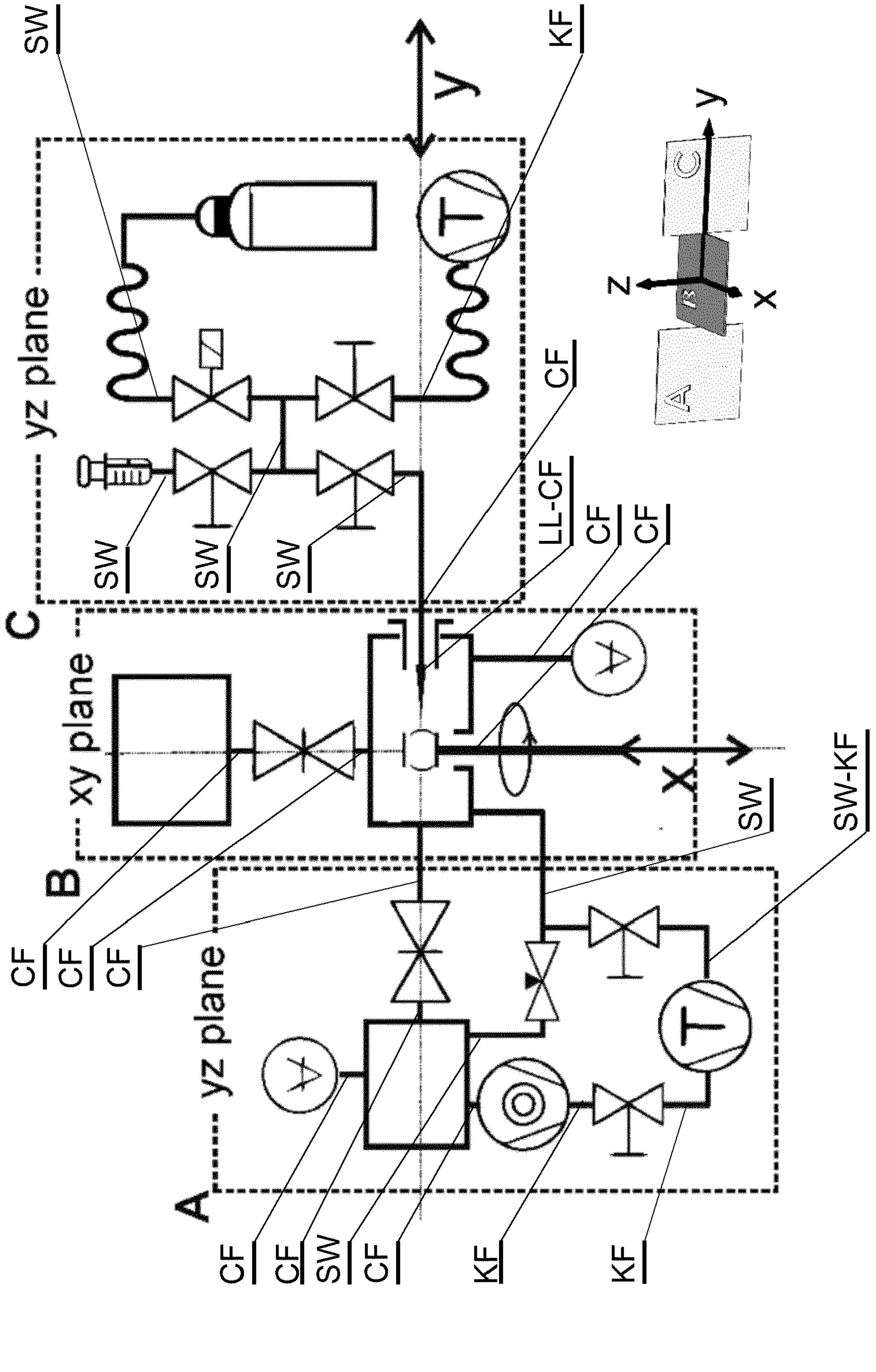


Fig. 2

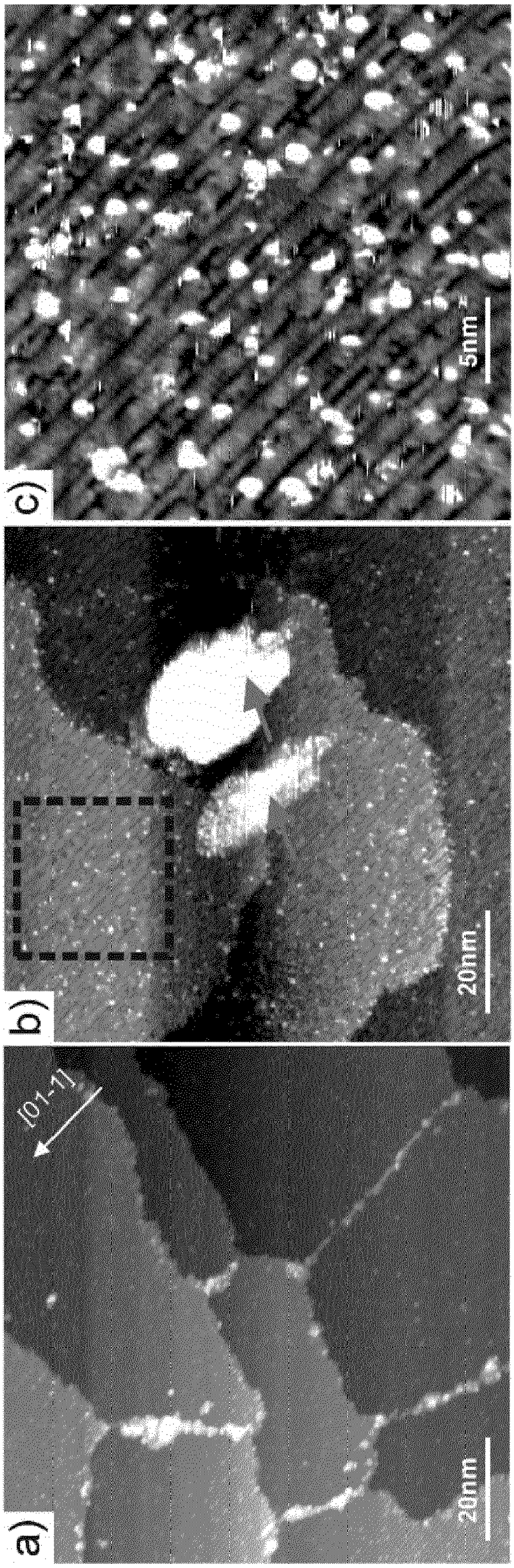


Fig. 3A

Fig. 3B

Fig. 3C

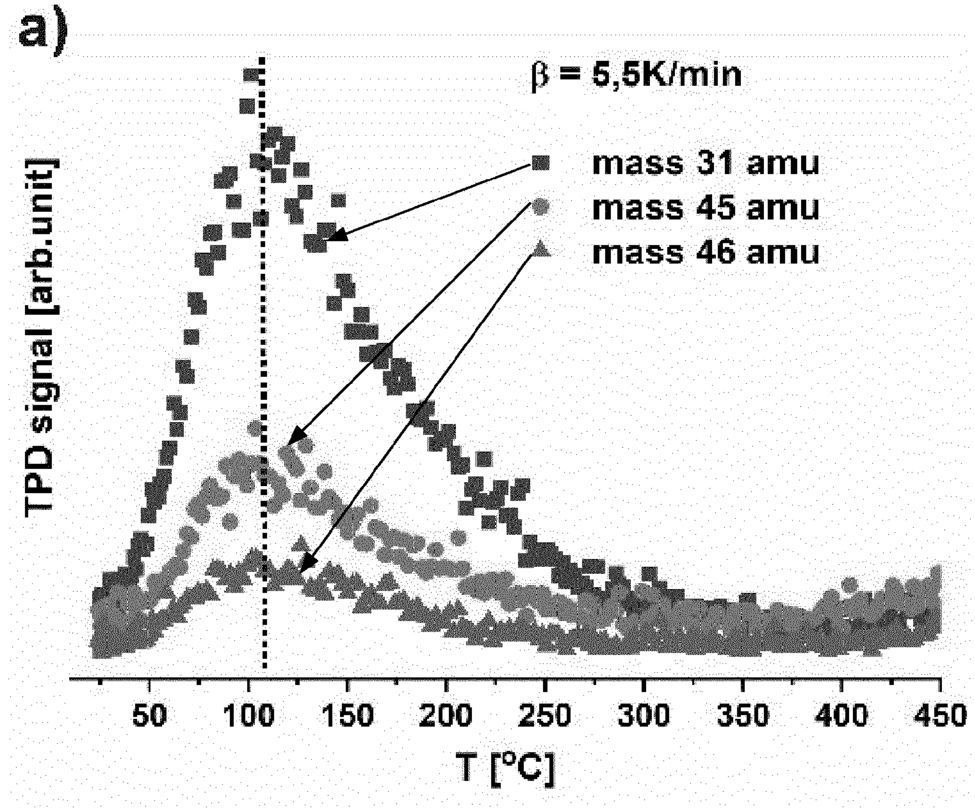

a)
β = 5,5K/min
mass 31 amu
mass 45 amu
mass 46 amu
TPD signal [arb.unit]
50 100 150 200 250 300 350 400 450
T [°C]

Fig. 4A

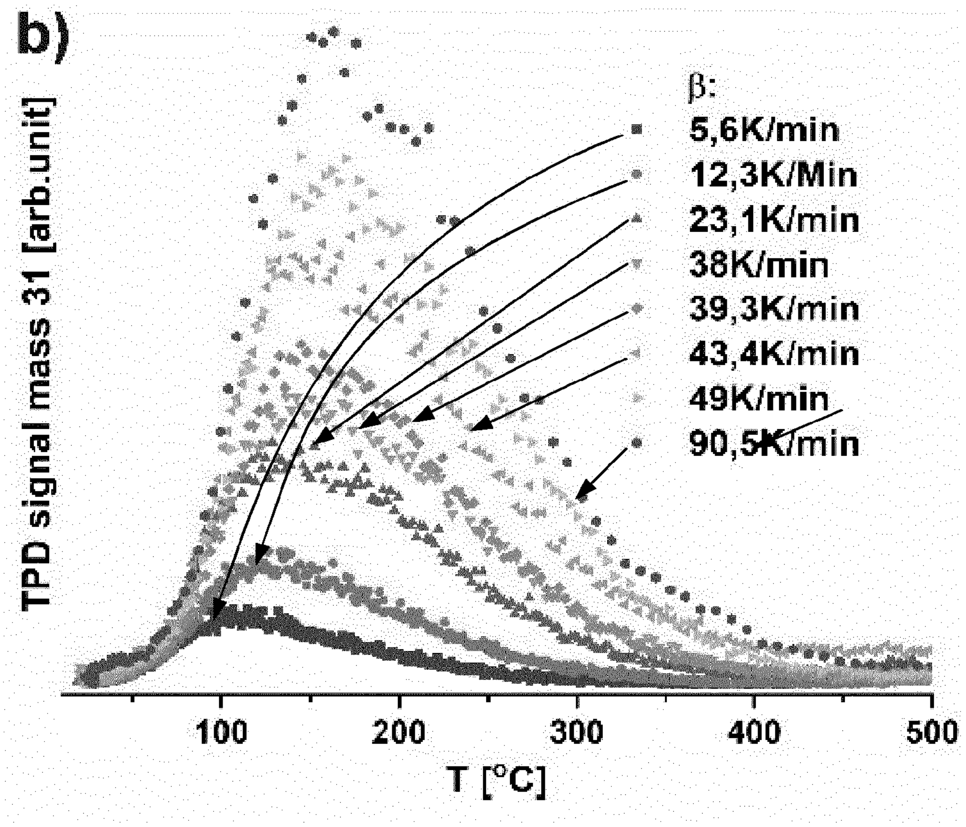

b)
β:
5,6K/min
12,3K/Min
23,1K/min
38K/min
39,3K/min
43,4K/min
49K/min
90,5K/min
TPD signal mass 31 [arb.unit]
100 200 300 400 500
T [°C]

Fig. 4B

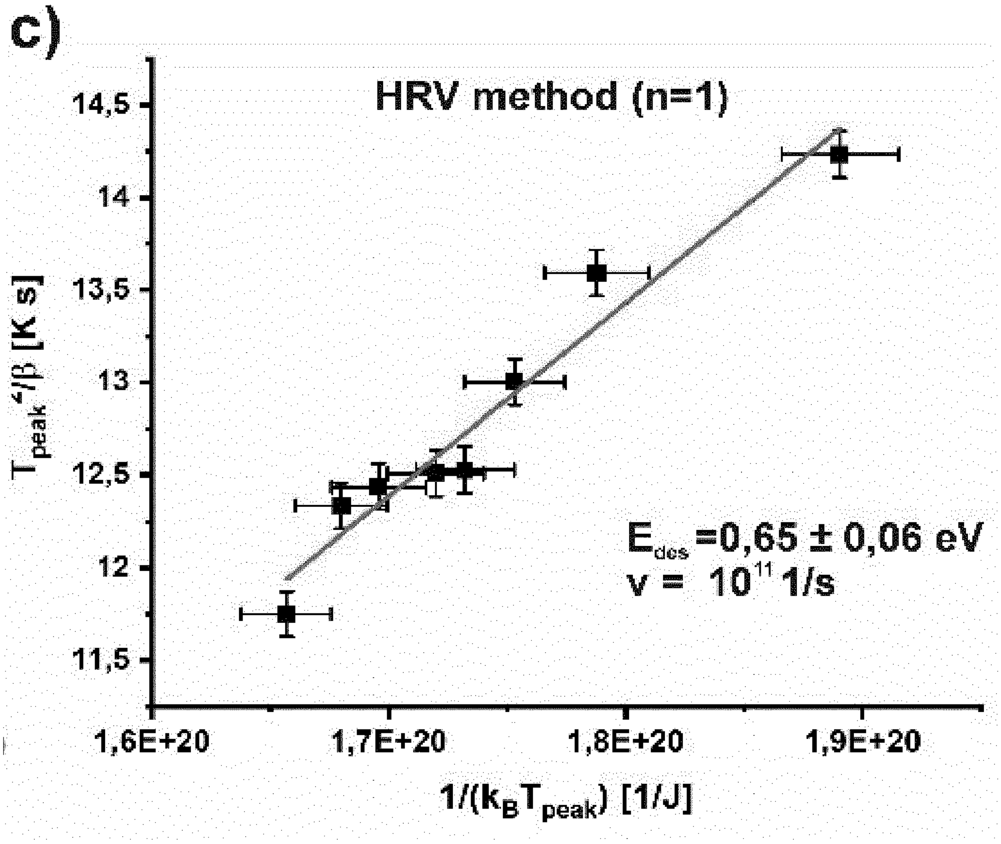
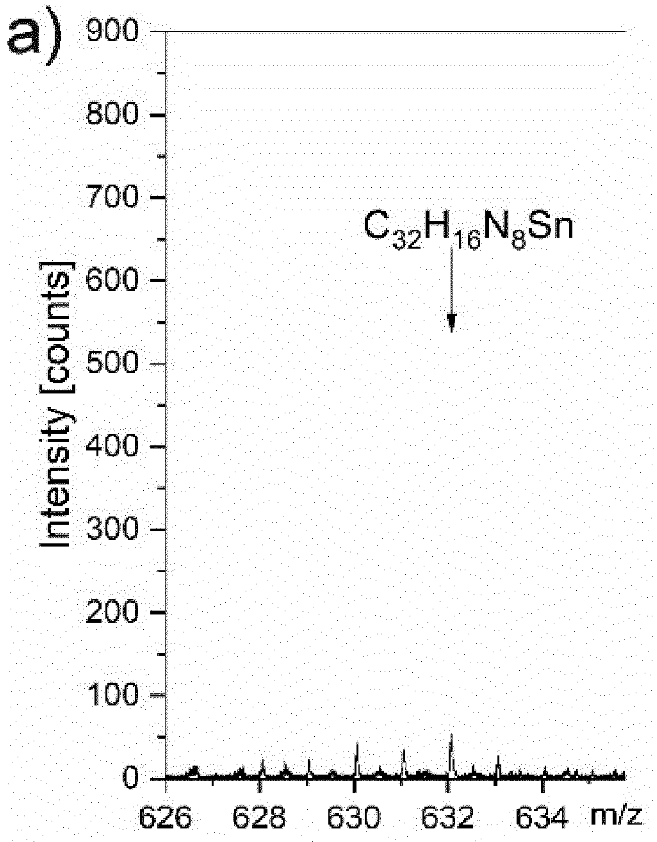
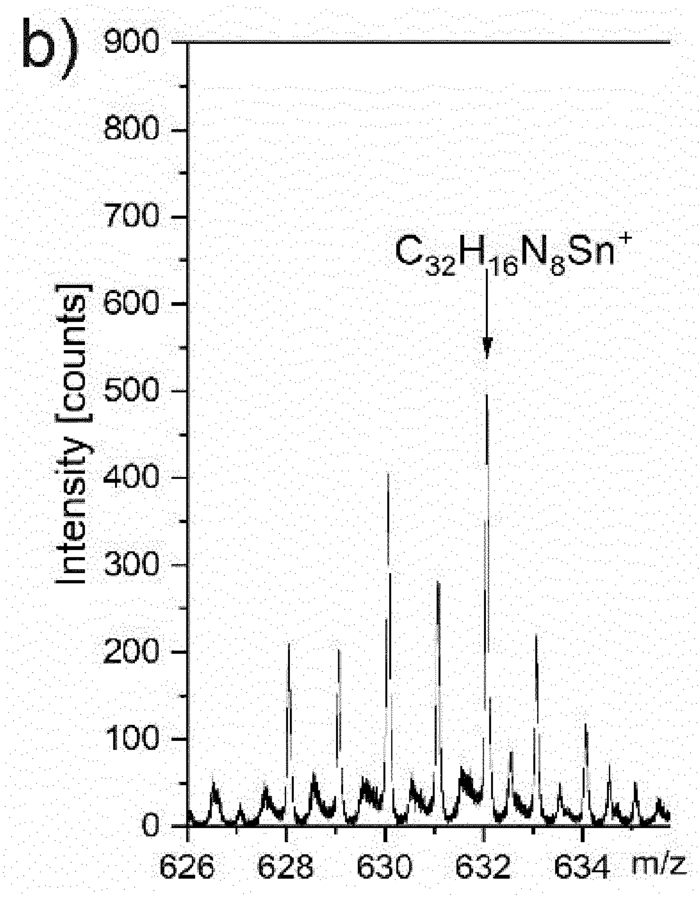

c)
HRV method (n=1)
E_{des} =0,65 ± 0,06 eV
v = 10^{11} 1/s
T_{peak}^{2}/β [K s]
14,5
14
13,5
13
12,5
12
11,5
1,6E+20
1,7E+20
1,8E+20
1,9E+20
$1/(k_B T_{peak})$ [1/J]

Fig. 4C



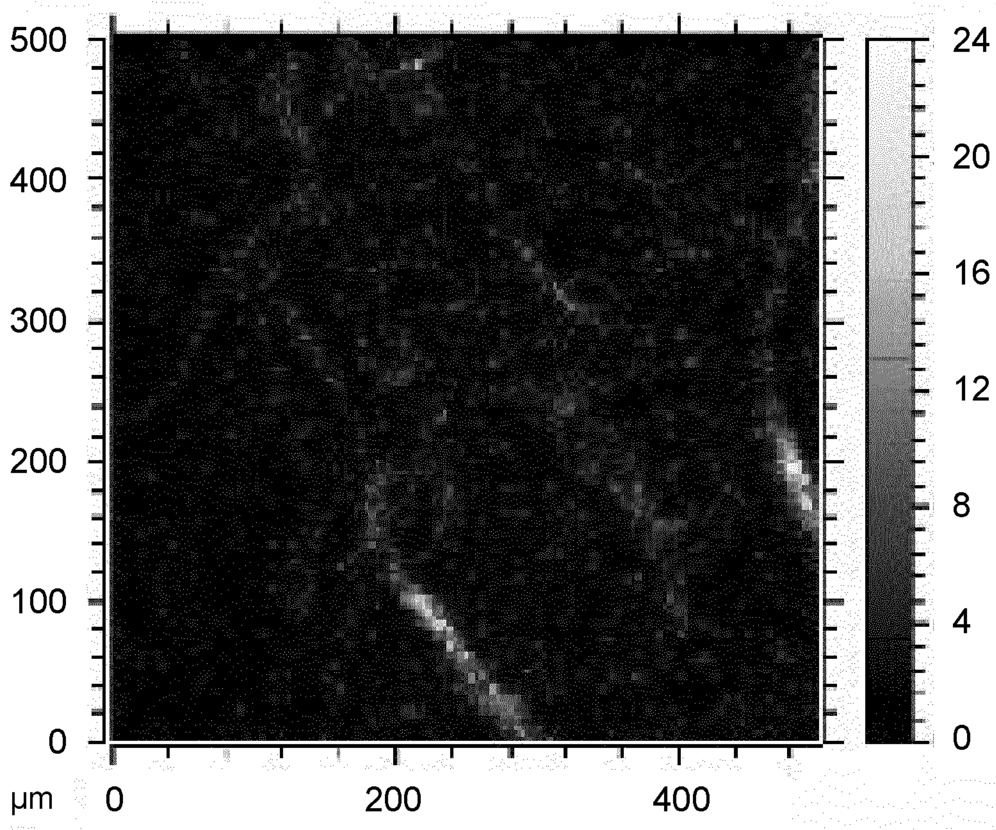
a)
Intensity [counts]
900
800
700
600
500
400
300
200
100
0
626
628
630
632
634
m/z
$C_{32}H_{16}N_8Sn$

Fig. 5A



b)
Intensity [counts]
900
800
700
600
500
400
300
200
100
0
626
628
630
632
634
m/z
$C_{32}H_{16}N_8Sn^+$

Fig. 5B


500
400
300
200
100
0
µm
0
200
400
24
20
16
12
8
4
0

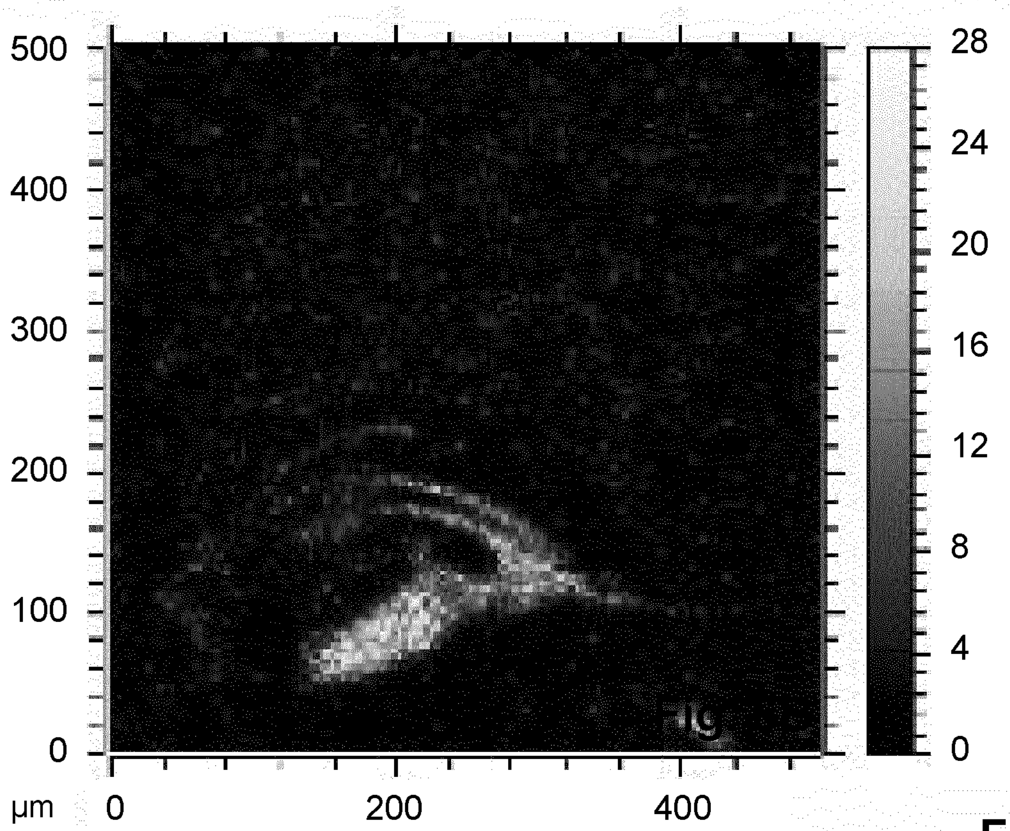

500
400
300
200
100
0
µm
0
200
400
28
24
20
16
12
8
4
0

Fig. 5C

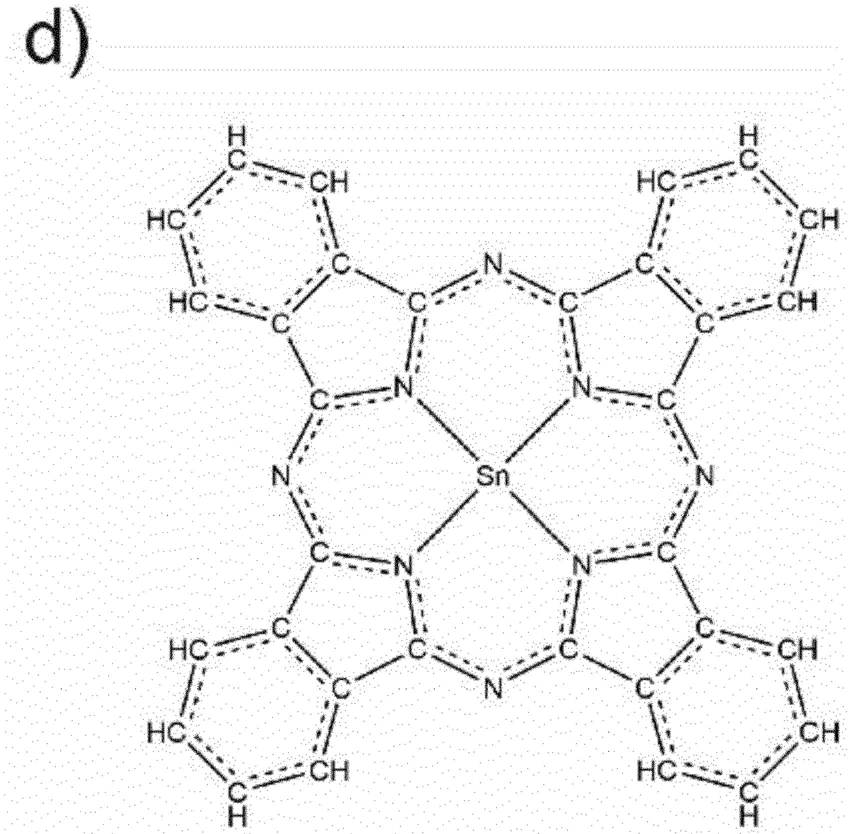
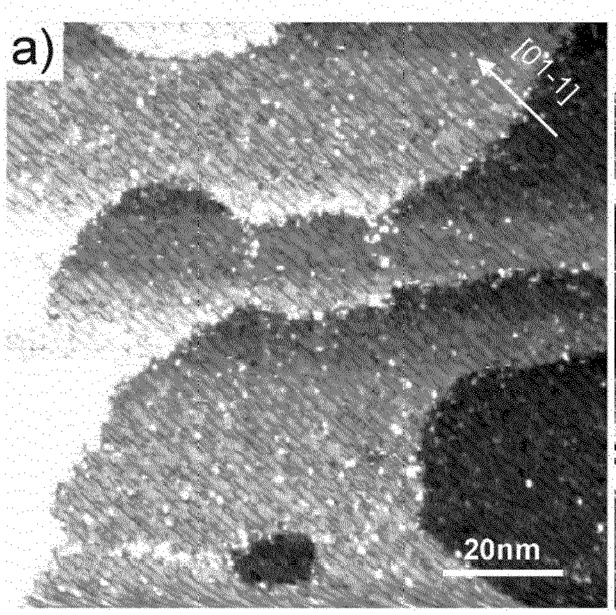


Fig. 5D



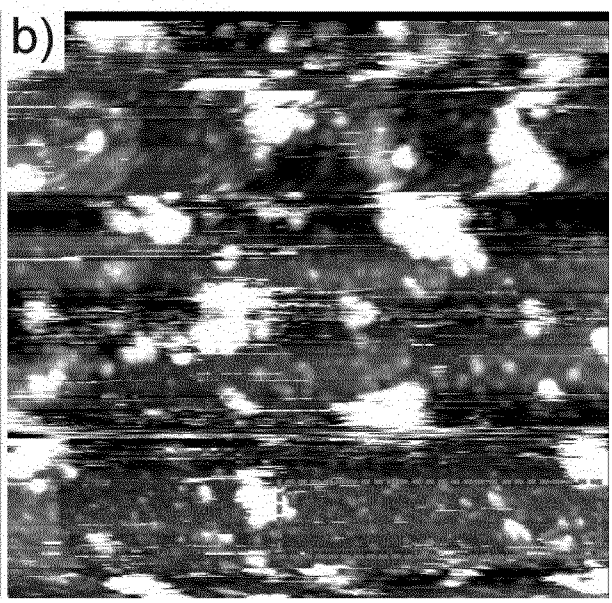


Fig. 6A

Fig. 6B

Europäisches Patentamt
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EUROPEAN SEARCH REPORT

Application Number
EP 23 15 0837

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	CN 210 585 651 U (SHENZHEN XETAR TECH CO LTD) 22 May 2020 (2020-05-22) * the whole document * -----	1,9	INV. B05B16/00
A	US 2014/318452 A1 (STOWELL JR MICHAEL WAYNE [US] ET AL) 30 October 2014 (2014-10-30) * the whole document * -----	1,9	
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TECHNICAL FIELDS SEARCHED (IPC)

B05B

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	13 June 2023	Eberwein, Michael

CATEGORY OF CITED DOCUMENTS

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13-06-2023

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