



METHOD OF APPLYING A COATING TO A SUBSTRATE

Field of the Invention

The invention relates to coatings, and methods of applying same, for substrates used for
5 integrated circuits and MEMS.

Background of the Invention

Micro-structure devices such as integrated circuits and MEMS devices function in
confined spaces having small interstitial spaces between said devices. As a result,
10 contact between adjacent devices through electrostatic attraction is a common problem.

On contact between adjacent devices, it is also common for adhesion to occur as
providing low friction, non-interactive surfaces to said devices is not common. In fact,
with the materials used, "stiction" can occur in so far as a degree of adhesion adds to the
15 friction between adjacent devices. To this end, the surfaces are subject to abrasion and
can subsequently fail.

It is not practical to provide mechanical means to assist in the reduction of friction such
as a bearing nor is it economic to increase the interstitial space, as size must be kept to a
20 minimum to maintain the small size of the overall device.

It is, therefore, an object of the present invention to provide a means to reduce the
abrasion of a micro scale device through contact with similar adjacent devices.

25 Summary of Invention

In a first aspect, the present invention provides a process for applying an abrasion
resistant coating to a substrate, comprising the steps :

Preparing a substrate for the application of a thin alkyl monolayer

Immersing the substrate in a solution bath including said alkyl under first predetermined
30 conditions to form the alkyl monolayer on the substrate;

Preparing the layered substrate for the application of an organic acid overcoat;



Immersing the layered substrate in a solution bath including said organic acid under second predetermined conditions to form the organic acid overcoat on the substrate to provide the abrasion resistant coating.

- 5 It has been observed that the stiction problems of the prior art are related to the hydrophilic nature of the surface materials. This is found to be inversely proportional to abrasion resistance. Thus, in addressing the abrasion resistance of the substrate surface, a key factor will be an observance of the hydrophobicity of the surface. In the present invention, the final organic acid overcoat is highly hydrophobic, and, in
10 combination with the alkyl monolayer, reduce the friction problems of the prior art. It has been observed that this is a result of the methyl groups at the terminal ends of the organic acid being highly inert and not usually prone to molecular attraction.

- In broad terms, the invention relates to an architecture and method of lowering
15 resistance by means of treating a surface with the formation of monolayers upon a substrate, such as in one embodiment, a silicon based enclosed assembly. This invention enables active lubrication which aims to prevent stiction behavior between two or more surfaces upon contact during a sliding mechanism.

- 20 Such thin coating can be applied to a range of hard coating surface such as, metal oxides, ceramics and steel. Further, in a preferred embodiment, the adhesion characteristics may be improved further by regulating the thermal treatment conditions for enhancing the integrity of the thin coatings based on the intended application.

- 25 The method of the present invention involves multiple thin monolayers bonded to the surface of the intended substrate to minimise wettability of said surface. In so doing, the surface minimises stiction which leads to the reduction in adhesion caused by capillary action or electrostatic attraction.

- 30 Such architecture permits dynamic lubrication of the components which are subject to adhesion and abrasion. As a consequence, the contact surfaces have lower frictional resistance which improves wear resistance.

In a preferred embodiment, the organic acid may be octadecanoic acid also known as Stearic Acid (STA). In a further preferred embodiment, the alkyl monolayer may be Amino-Propyl-Tri-Methoxy-Silane (APTMS). Alternatively, the alkyl monolayer may include any such alkyl compound having an amine chain group, for example, Poly-Ethylene-Imine, Poly-Styrene etc.

Thus, in a most preferred embodiment, APTMS may be applied to the substrate with an STA overcoat which in combination, increase the hydrophobicity of the device and provide a low friction and low stiction surface which overall improve abrasion resistance.

In a more preferred embodiment, the substrate to which the layers are added may be treated, rinsed and dried ready for immersion in a bath of the alkyl monolayer. In this embodiment, the bath may comprise a $3 \times 10^{-3} \text{ m}^3$ bath of APTMS with Toluene to which the substrate may reside for at least 6 hours. This process of organic molecules may be attracted towards the substrate surface and self-assembled themselves chemically onto the intended surface, forming a permanent thin monolayer on said surface. In a further embodiment, following immersion the substrate having the monolayer formed on it, may be rinsed in, for instance, toluene and methanol to remove any unbonded molecules.

In a preferred embodiment, the APTMS coated substrate may then be immersed in a solution comprising at least STA with a dehydration reagent which in a further preferred embodiment, may be N, N'-Di-Cyclohexyl-Carbo-Diimide (DCCD). The use of the dehydration reagent may accelerate the reaction between the alkyl monolayer and the organic acid overcoat and so assist in the formation of the dual layered structure.

Description of Preferred Embodiment

It will be convenient to further describe the present invention with respect to the accompanying drawings and examples which illustrate possible embodiments of the invention. Other embodiments of the invention are possible and consequently, the

particularity of the accompanying drawings and examples is not to be understood as superseding the generality of the preceding description of the invention.

Figure 1 shows a detailed cross-section of the coated substrate according to the present invention.

Figure 2 is a graph providing rate of change of the coefficient of friction according to experimental data.

It has been observed that surface hydrophobicity is directly proportional to the friction generated between two sliding surfaces. With appropriate combination of thin coating layers on substrates, it is possible to create desirable anti-stiction film characteristics that reduce and possibly eliminate adhesion between two microstructure surfaces, and also markedly reduce the premature failure of the components when the interstitial spaces are very small.

The coating comprises one alkyl monolayer 102, particularly, Amino-Propyl-Tri-Methoxy-Silane (APTMS) and organic acid overcoat 103, particularly, Octadecanoic Acid, alias Stearic acid (STA). Such layered coatings are applicable for most substrates 101 commonly used for MEMS devices, such as Silicon, Metal oxides, Metal, Glass, polymer, etc, as shown in Fig. 1. The determination of a suitable substrate material will include an assessment of smooth surface roughness, hard surface texture, and heat resistance capability.

The process of the present invention commences with the substrate, for example, Silicon, glass, metal, metal oxide coated, polymer, etc, being cleansed with soap water, followed by a subsequent rinse with acetone and distilled water. This process effectively removes most surface contaminants, such as fingerprints, dirt particles, grease, etc. Next, the substrate surface is chemically treated in order to promote good adhesion of monolayers. Here, the intended substrate surface is immersed in a warm mixture bath of 60°C, containing Sulphuric acid (H_2SO_4) of 98% concentration, and Hydrogen peroxide (H_2O_2) of 30% concentration, in volume ratio of 7:3. At least 50

minutes immersion duration is recommended for removal of residual tough stains on substrate from previous cleaning processes, which is not desirable for further chemical bonding. Again, the intended substrate surface is rinsed with acetone and distilled water after removing from the mixture bath, and blow dry using Nitrogen (N₂) gas.

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When the treated substrate is dried and cleaned, and then immersed in a bath solution, containing $3 \times 10^{-3} \text{ m}^3$ of APTMS with Toluene, for at least 6 hours. In this process, organic molecules are attracted to the substrate surface and self-assemble themselves chemically onto the intended surface, forming a permanent thin monolayer on the intended surface. Following the immersion, the substrate is rinsed with toluene and methanol to remove any molecules that attached to the intended surface by physical attraction during the formation of monolayer. Blowing with N₂ gas is also useful to dry the substrate. Post thermal annealing at 100°C for 10 minutes is recommended to strengthen the binding of monolayer on intended substrate.

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Likewise, this APTMS coated substrate is then immersed in a solution of dilute STA and N, N'-Di-Cyclohexyl-Carbo-Diimide (DCCD) in n-hexane for at least 24 hours for promoting surface hydrophobicity. In this process, DCCD does not react with the coated monolayer, but operates as a dehydrating reagent to accelerate the reaction between STA and APTMS, for forming a dual layered structure. The resulting surface is subsequently rinsed with n-hexane and acetone after the coating, and dried using N₂ gas.

The thickness of each layer is in the range 5~15nm, and the adhesion between these layers is further enhanced by means of exposing the intended surface to 50°C, in a vacuum oven, for 20 hours, that brings about good covalent bonding within these coated films.

Hydrophobicity properties of the surfaces are as follows:

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Test structure	H2O Contact angle, θ
Si	21°~29°

Si/APTMS	62°~66°
Si/APTMS/STA	101°~103°

It is observed that APTMS and STA effectively reduces the wettability of the substrate, which aids in reducing adhesion related friction problems. This is due to the methyl groups at the terminal ends of the STA layers being highly inert, and so less prone to molecular attractions.

Figure 2 shows the graphical results of tests applying a Silicon-Nitride ball probe with 0.05N axial loading and rotating at 100 rpm through a cycle of radius 2.5mm:

Test structure	Time before visible scratch marks appear on surface
Si, without annealing	<1 sec
Si / APTMS / STA, without annealing	~4,000 sec
Si / APTMS / STA, with annealing	~20,000 sec

Annealing the film layers will tend to cause strong binding of Silicon-Oxide between Silicon surface and APTMS monolayer, leading to very rigid molecular covalent bonding structure that can withstand larger physical loading.

Film destruction starts to occur at around 4,000 sec, showing noticeable scratch track on the surface of non-annealed SAM coating. This demonstrates the 'soft' bonds between the silicon substrate and APTMS monolayer that causes the film to suffers from abrasion wear despite the relatively lower coefficient of friction. Conversely, the annealed sample shows no peak in coefficient of friction through the abrasion test to above 20,000 sec, implying improved wear resistance characteristics resulting from thermal treatment of SAM coating.

CLAIMS

1. A process for applying an abrasion resistant coating to a substrate, comprising the steps :
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Preparing a substrate for the application of a thin alkyl monolayer
Immersing the substrate in a solution bath including said alkyl to form the alkyl monolayer on the substrate;
Preparing the layered substrate for the application of an organic acid overcoat;
10 Immersing the layered substrate in a solution bath including said organic acid to form the organic acid overcoat on the substrate to provide the abrasion resistant coating.
2. The process according to claim 1 where the alkyl monolayer is Amino-Propyl-Tri-Methoxy-Silane.
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3. The process according to any one of the preceding claims wherein the alkyl bath comprises $3 \times 10^{-3} \text{ m}^3$ of Amino-Propyl-Tri-Methoxy-Silane with toluene.
4. The process according to claim 3 wherein the substrate has a residence time in
20 the alkyl bath of at least 6 hours.
5. The process according to any one of the preceding claims wherein the substrate immersing step is followed by the steps of rinsing in toluene and methanol, and blow drying with nitrogen.
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6. The process according to any one of the preceding claims, wherein the organic acid overcoat is stearic acid.
7. The process according to claim 1 wherein the solution bath comprises a solution
30 of dilute stearic acid and N,N'-Di-Cyclohexyl-Carbo-Diimide in n-hexane.

8. The process according to claim 7 wherein the coated substrate has a residence time in the organic acid bath of at least 24 hours.
9. The process according to any one of the preceding claims wherein the layered
5 substrate immersing step is followed by the steps of rinsing in n-hexane and acetone, and blow drying with nitrogen.
10. The process according to any one of the preceding claims wherein preparing the substrate comprises the steps of cleansing the substrate with soap water, rinsing with
10 acetone and distilled water, and treating the substrate by immersion in a bath of 98% concentration of sulphuric acid and 30% concentration hydrogen peroxide in a ratio of 7:3 by volume.
11. The process according to claim 10 wherein the immersion in the sulphuric acid
15 and hydrogen peroxide bath is at a temperature of 60 degrees and for a residence time of at least 50 minutes.
12. The process according to any one of the preceding claims wherein preparing the substrate is followed by the step of rinsing in acetone and distilled water, and blow
20 drying with nitrogen.
13. The process according to any one of the preceding claims wherein the substrate material comprises any one of silicon, a suitable metal oxide, a suitable metal, glass, quartz or a suitable polymer.
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14. The process according to any one of the preceding claims wherein the layered substrate immersing step is preceded by the step of annealing the layered substrate at 100° for 10 minutes.
- 30 15. The process according to any one of the preceding claims wherein the final step of the process comprises exposing the final surface to 50°C in a vacuum for 20 hours.

16. The process according to any one of the preceding claims wherein the thickness of the monolayer and the thickness of the organic acid overcoat are both in the range 5 nm to 15 nm.

5 17. An abrasion resistant element, comprising

a substrate;

a thin alkyl monolayer applied directly to the substrate, and;

an organic acid overcoat applied directly to thin alkyl monolayer to provide the abrasion
10 resistant coating.

18. The element according to claim 17 wherein the alkyl monolayer includes Amino-Propyl-Tri-Methoxy-Silane.

15 19. The element according to claim 17 or 18, wherein the organic acid overcoat is stearic acid.

20. The element according to any one of claims 17 to 19 wherein the substrate material comprises any one of silicon, a suitable metal oxide, a suitable metal, glass,
20 quartz or a suitable polymer.

21. The element according to any one claims 17 to 20 wherein the thickness of the monolayer and the thickness of the organic acid overcoat are both in the range 5 nm to 15 nm.

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22. An abrasion resistant element resulting from the process according to any one of claims 1 to 16.

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