Studies on Measuring Surface Adhesion Between Sidewalls in Boron Doped Ultrananocrystalline Diamond Based Microelectromechanical Devices

Federico Buja¹, Jaap Kokorian¹, Anirudha V. Suman², and W. Merlijn van Spengen^{1,3}*

¹TU Delft, Delft, The Netherlands

²Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL, USA

³Also with Falco Systems, Amsterdam, The Netherlands

*(f.buja@tudelft.nl)

Abstract

In this study, we have investigated the adhesion phenomena between two sidewalls in boron-doped ultrananocrystalline diamond (B-UNCD) micro-electro mechanical systems (MEMS) in humid and dry environment. We have developed and built B-UNCD MEMS test devices, in order to assess the tribological properties of diamond micro devices *in-situ*. Using these devices, we have been able to measure the adhesion force with approximately 15nN resolution, by monitoring the displacement optically with a precision of 4 nm. In case of testing in dry atmosphere, virtually no adhesion (<18 nN) was observed between the sidewalls. After testing in humid air over 55 000 cycles, increased adhesion force up to 128 nN was measured. A rare observation of capillary neck formation between sidewalls at high contact force, in humid air is

observed which is most probably caused by precipitation of carbon contamination. This contamination layer can be easily removed by oxygen plasma exposure but thereafter highest adhesion force of 260 nN adhesive force was measured. Our studies demonstrate that micromechanical devices fabricated based on diamond represent a great alternative over polysilicon based devices in terms of reduced adhesion and thus long term reliability, which is a significant step forward in developing diamond based MEMS.

1. Introduction

Ultrananocrystalline diamond (UNCD) is already known for its unique mechanical, physical and tribological properties, making many characteristics that are close to that of natural crystal diamond available for custom applications [1-4]. An interesting possibility is to make use of its properties in micro and nanotechnology, especially for the fabrication or customization of microelectromechanical systems (MEMS) [5-7]. MEMS is a fast growing new technology with promising potential in many fields, from aerospace to medicine and many others [8-11], but these tiny devices are currently still susceptible to detrimental micro-scale tribological phenomena [12]. The use of many types of micro-devices and the implementation of complex motions, such as rotation or sliding, is hindered by these limitations, due to the inherent surface and structural properties of silicon [13]. Due to a large surface-to-volume ratio, effects such as adhesion dominate the behaviour of contacting micro-scale objects. It is of fundamental importance to fully understand the physical, chemical and mechanical phenomena that occur when two micro-mechanical components make contact. One of the most catastrophic failure

mechanisms in MEMS is stiction, which is the unwanted adhesion of compliant microstructures that undergo interfacial interactions such as electrostatic, van der Waals (vdW), Casimir and capillary forces [14-16]. Silicon has been a choice of material to a large extent for the microfabrication of MEMS until now, due to ease of surface micromachining process and low stress in this material. However, for MEMS involving contacting surfaces, tribological properties, especially adhesion and friction becomes very important and therefore, have been at the centre of the attention and carefully studied [17, 18]. The versatility of employment for which these systems can be used, lies mainly in the choice of their material properties, such as hardness, electrical conductivity, inertness and many others. Indeed, a wide range of structural choices and coatings related to tribology has been tested already for the development of different types of MEMS, in order to broaden the spectrum of applications. Silicon Carbide (SiC) [19], self-assembled monolayers (SAMs) [20] and diamond-like-carbon (DLC) [21, 22] are a few examples that could solve contact related issues in MEMS. Instead of applying a protective coating to the silicon only, another solution is using a new structural material.

In this work we present the study of adhesion tests performed between two boron-doped ultrananocrystalline diamond based (B-UNCD) MEMS sidewalls. The possibilities given by the fabrication of a diamond micro-tribotester are twofold: first, it is possible to study the adhesion properties and interaction of diamond surfaces at the nano scale, and second, to observe, *in situ*, the benefits that this material can provide to MEMS technology. In order to develop micro-devices that can perform complex motions, like repeated sliding or contact, we have considered and utilized B-UNCD as structural material and built a MEMS actuator to explore properties such as adhesion and friction at MEMS length scale. In the current paper, we report, *in-situ* observations of the effect of adhesion between two B-UNCD MEMS sidewalls. The information

gained from this research can be of great importance for the successful development of flat MEMS devices that rely on side contact for their functioning.

2. The MEMS adhesion test device

2.1 Fabrication

For this research a fully diamond based Chevron-type thermal micro actuator has been utilized as platform for measuring the adhesion phenomena between a pair of etched B-UNCD sidewalls. The films utilized were a 3 μm -thick boron doped Aqua type layer (Advanced Diamond Technology, Inc.) and grown with hot-filament chemical vapour deposition (HFCVD) technique on top of a 4" p-type silicon wafer with a 1 μm thick thermal SiO_2 layer.

Fig.1

Chevron actuators rely on the Joule heating effect to provide a linear displacement of a central moving shuttle, of which the far end is the sidewall of interest (Fig. 1). The detailed description

of a conductive UNCD MEMS actuator like this, is given elsewhere [23]. The fabrication of the micro-device was carried out in a class 100 cleanroom, with standard lithographic processes and conventional hard mask deposition techniques (Fig. 2). A 1 μm thick aluminium hard mask has been sputtered to transfer the photolithographic pattern onto the 3 μm thick B-UNCD layer. The etching has been performed using an oxygen plasma with 500 W RF power. A 500 nm thick gold layer was eventually evaporated onto the B-UNCD contact pads in order to provide ohmic contact with probe needles or aluminium bond wires. Fig. 3 shows a cross section of the stack of layers utilized in the micro-fabrication process.

Fig.2

The release step has been performed by immersion in buffered hydrofluoric acid (BHF) for 160 minutes (the time needed to under-etch the 15 μm of SiO_2) followed by a further 30 minutes immersion in tetramethylammonium hydroxide (TMAH) to isotropically etch the silicon substrate and allow any contingent accommodation of the internal stress gradient of the B-UNCD layer, which could otherwise make contact with the silicon underneath.

2.2 Mechanical characterization of the B-UNCD MEMS test device

In the Chevron micro thermal actuators, the force output is proportional to the number of beams, while the displacement is proportional to their length [24]. We have made the choice to separate the head from the rest of the moving body, with a foldable spring, to increase the force sensitivity and hence have a clearer view of the ‘jump’ caused by adhesion and the effects arising from any surface modifications (see later in section 3.2, 3.3 and 3.4). For this research we have utilized a V-shaped Chevron actuator with 250 μm -long beams. We characterized the mechanical properties of the device in two steps: 1. a finite elements (FE) simulation, implemented for the calculation of the exact spring constant of the foldable spring system and 2. a displacement detection of its beams, in order to extract the contact force acting between the sidewalls when an adhesion test is performed. In Fig. 4 the maximum simulated displacement of the micro-structure components is shown, from which it was possible to extract the spring constant of the foldable beams. We applied a fix constraint to the moving body while keeping the head free to displace under an applied load. A 100 nN load was applied onto the moving head in the x-axis direction. The resulting displacement of the moving part of the actuator was 21.9 nm, which corresponds to a foldable beam spring constant of 4.56 N m^{-1} . The material parameters used in the computation

were: Young Modulus of 750 GPa, Poisson's ratio of 0.057 and a density of 3300 kg m^{-3} [25]. A quick analytical calculation of the spring constant confirmed that the simulated value is in the right order of magnitude. In the real experiment, this stiffness, utilized as a 'known' parameter, is of primary importance to determine the force of contact of the actuator's head.

Fig. 3

In the plot of Fig. 4 we report the method with which we can assess the force acting between the counter-surfaces during the adhesion experiments. The displacement of the device was accurately monitored by means of a home built optical setup for measuring sub-nm in-place displacements, of which the description is given elsewhere [26]. When the voltage is increased between two electrodes, the micro-actuator moves forward, until the counter-surface is engaged. Before contact occurs, the body of the actuator and its head, separated by the foldable spring, move together, so the difference between their relative displacement values is zero. Once the surface of the moving head touches the fixed counter-surface position in front, the beams start approaching each other. This is visible as a tilted line (the displacement decreases almost linearly with the voltage) in the voltage-displacement curve. The maximum force applied to the surface can then be extracted by multiplying the relative displacement at any given voltage (vertical component of the tilted line) with the spring constant of the foldable beams. The total uncertainty of the force depends on the combined uncertainty of the spring constant calculation and the uncertainty of the displacement measurement.

In the same way, the adhesion force generated at the sidewalls interfaces can be assessed. Once the moving head, returns towards its starting position, it is held at the contact position for a longer time. While the moving shuttle moves backwards, the beams forming the foldable spring open apart, until the force generated overcome the adhesive interaction. At that point, the ‘pull-off’ occurs. This effect is already observable in Fig. 4, highlighted in the dashed circle. During the adhesion experiment, the displacement of the head has been directly observed by dedicated markers position on the part of the actuator that experiences the pull-off effect (Fig. 1).

Fig. 4

2.3 Functionalization of the MEMS surface

It is understood that as-grown UNCD irrespective of its growth method, either MPCVD or hot filament CVD (HFCVD) is normally H-terminated due to the presence of even small percentage of hydrogen (mostly comes from decomposition of CH_4) during the growth process. In HFCVD growth the hydrogen content can be higher [27]. However, we can assume that this will not

influence the adhesion phenomena between the sidewalls, since the surfaces under investigation underwent etching processes that have altered their terminations anyway. Most likely, during pattern transfer in RIE, the surface is passivated with the oxygen ions produced in the plasma during the etch process. The subsequent immersion in BHF and TMAH inevitably affect the chemical composition of the surface by reacting the exposed oxygen or hydroxyl terminations. Therefore we cannot know exactly the real chemical passivation of the 'pristine' surface of the devices, but we could verify the adhesion properties of the as-etched B-UNCD MEMS. The results could be later compared with the outcome from the treated devices, in order to proof or discard possible benefits due to a selected passivation. In order to explore the effects of the surface functionalization on the adhesion phenomena, we utilized a low pressure plasma chamber (Diener Electronic) to treat the diamond MEMS device samples. The functionalization is achieved through an ion bombardment of the surface, produced by a DC discharge in an oxygen medium. The plasma treatment is generally used to remove residual organic impurities or weakly bounded organic contaminations and modify the wettability in order to render a surface more or less hydrophobic. Also, given the fact that the power was set to 10 W, only few nanometers of the upper surface of the diamond layer were affected by the ions bombardment. Therefore we did not run the risk of undermining the stability and change the characteristics of the bulk structural material.

2.4 Sidewall surface roughness characterization

The morphology of the contacting bodies is of primary importance for the understanding of the adhesion effect, because at micro-scale no surface can be regarded as being smooth. It has been

shown that the surface roughness plays a key role in contact phenomena at the micro-scale [28] and that it is reasonable to describe them with an adhesion model of a multi-asperity contact [29]. When two micro-fabricated surfaces come into contact, the real area of contact A_R is determined by the amount, heights and depths of the peaks and valleys that constitute the surface and that eventually touch each other when contact occurs. The real contact area is always smaller than the apparent contact area A_C . The exact description of surface roughness is quite involved. E.g. *Bush et al.* [30] considered a rough surface as a random anisotropic distribution of asperity radii, with a Gaussian distribution of the heights of the asperities. However, for general engineering applications, especially in micro-fabrication, it is recognized that the etching processes produce non-Gaussian surfaces and an asymmetric asperity distribution [31]. This means that, only through an empiric approach in observing adhesion effects, we can have a realistic idea of what is the role of the uneven surfaces under observation. In order to verify the etch profile of a B-UNCD sidewall we scanned a sidewall of the device with an atomic force microscope (AFM) in non-contact mode. To provide easy access to the scanning AFM tip, we broke a slender beam and flipped it (Fig. 6), to expose its lateral side on top. The analysed etched sidewall roughness is representative and comparable to the one of the entire device, also at the contact point. The etch step observable on the sidewall in Fig. 6, is due to a momentary plasma failure during the process.

Fig. 5

The results obtained from the sidewall analysis (Fig. 5B) reveal a surface roughness (S_a) of the scanned area of 6.23 nm. The scan has been performed on $1 \mu\text{m}^2$ area enclosed by the edge of the beam and the central division line. This means that the AFM did not measure the difference in height due to the two etching steps, but only the roughness caused by the oxygen ions bombardment and the effect of the continuous etching process.

3. Results

3.1 Overview of the measurements

With the MEMS adhesion sensor device type of Fig. 1, we have investigated the adhesion between the B-UNCD device sidewalls under cyclic loading conditions, with different load forces and under different environmental conditions. In this section we report these measurements and discuss the results for every experiment individually. First, we have investigated the adhesive contact in dry environment (section 3.2). Then we have performed adhesive experiments between pristine B-UNCD surfaces in ambient environment (section 3.3). In the end we performed experiments with devices of which any non-UNCD carbon contamination had been thoroughly removed by oxygen plasma cleaning (section 3.4). Finally, we will discuss the surface damage and carbon-containing meniscus formation phenomenon that occurs at excessively high load in humid environment (section 3.5) after repetitive 55 000 contact cycles. To our knowledge this has never been observed in detail before, and it clearly places a (high) upper limit on the load conditions for which B-UNCD can be used in MEMS.

3.2 Adhesion testing in dry environment

The phenomenon of adhesion between B-NCD MEMS sidewalls has been also observed in a dry atmosphere, in which case presumably the water meniscus formation cannot occur. The samples have been wire bonded with a conductive glue, in a 26-pin DIL (dual in-line) package and placed inside an environmental chamber. The chamber was baked at 120 °C and simultaneously evacuated in order to evaporate and remove any condensed water. After this process, we could obtain an almost totally dry environment by flushing and filling the chamber with argon, at a

temperature of 30 °C. In order to observe the development and change of the phenomenon of adhesion in time, we performed again a high number of cycles measurement, up to a total of 50000, monitoring and recording the displacement of the sensor's head every 2000 cycles. In Fig. 6, we report only one cycle for simplicity, because no differences were recorded between the beginning and the end of the experiment. We have not averaged, but reported the middle cycles of ten recorded, since all of them were exactly overlapping. From this result we get several indications of how the dry atmosphere plays a role in modifying the adhesive behavior of contacting B-UNCD surfaces. The force applied by the shuttle to the counter-surface has been kept constant throughout the entire experiment, at a value of 424 nN (a little higher than in the following measurements). By looking at the plot of Fig. 6, we can observe a pull-in effect occurring when the surfaces are separated only by 10 nm, corresponding to an adhesive force of 32 nN only. We believe that this phenomenon has been caused by the electrostatic attraction between the two contacting bodies, since in the environmental chamber it was not possible to ground the counter-surface. For typically atomically flat surfaces, the van der Waals force is an order of magnitude lower than the force due to capillary adhesion at 1 nm separation distance, and it falls off with the third power with distance, where capillary adhesion falls off with the second power, as long as there is water between the surfaces [32]. Because our surfaces are much rougher than 1 nm, we expect the van der Waals contribution to be insignificant, as long as there are capillary or electrostatic effects, although they may be partly responsible for the 'meniscus force' mentioned in section 3.5. With a maximum sensitivity of 4 nm, it is not possible to estimate quantitatively the contribution of van der Waals forces. We have also observed that the meniscus formation in the pull-in and snap-off effects is absent, because of the lack of

condensing vapor in a dry environment and because no more adhesion is measured in the backward motion of the sensing head than in the forward motion.

Fig. 6

According to the experiment performed, the diamond surface could sustain 50 000 cycles in a dry environment, showing no adhesion and no measurable surface modification.

3.3 Experiments of adhesion between B-UNCD sidewalls in uncontrolled humid environment

In all the normal experiments performed with the manufactured B-UNCD adhesion sensors, the forces of contact were always kept below $0.5 \mu\text{N}$. Furthermore, we have to consider the non-perfect alignment between the moving shuttle and the counter-surface, due to the out-of-plane

deformation caused by the stress gradient. Therefore, we estimate that the apparent contact ranges from $0.1 \mu\text{m}^2$ to $1 \mu\text{m}^2$. All the samples used for the experiments, were cleaned in a nitric acid bath (HNO_3 99%) at room temperature for 20 minutes, in order to remove any possible organic contaminations deposited on the surface. In Fig. 7A, we show the result of the very first contact between two B-UNCD sidewalls in normal ambient (humid) testing environment. By monitoring the displacement of the foldable beams with the aforementioned optical displacement detection technique (see section 2.2), we have calculated that the force applied during the adhesion test was 320 nN.

The adhesion force can be estimated by looking at the backward displacement of the moving shuttle and measuring the length of the sudden jump of the sensing head; by multiplying it with the spring constant of the foldable beams, we obtain the adhesive force acting between the MEMS sidewalls [33]. We grounded both the shuttle and the counter surface of the devices used in our experiment, in order to avoid electrostatic attraction of the sidewalls, which could be confused with capillary attraction at the contact points. Therefore, in these type of plots, when visible, a pull-in ‘jump’ has to be interpreted as a formation of a water meniscus (or, less likely, van der Waals molecular force) between the approaching asperities. Normally this can be observed only when the surfaces are a few nanometers apart. Considering the mild hydrophobicity of B-UNCD [34] and the particular conditions of an unprotected environment, it is possible that a meniscus is formed between the approaching asperities, dragging the surfaces towards each other. In the adhesion measurements shown in Fig. 7A and Fig. 7B there is no clear evidence of such an event occurring. The two plots show the adhesion force before and after 55 000 contacts respectively. The effect of repeated contact has been evaluated by running a long-range experiment, with the aim to observe any modification on the surface due to plastic

deformation. In the plot of Fig 7B, we can observe that the adhesive energy remains virtually unchanged, with no significant differences. Considering that the contact force was kept constant and the apparent area of contact did not vary, even after 55 000 cycles, it fair to assume that, at a relatively low force, the diamond surface does not undergo any modification. This is consistent with the plastic deformation model we will present in section 4, where we show that the expected material loss due to plastic deformation would be unnoticeable in this force range.

A

B

Fig. 7

The resolution of the optical measurement when used with these partially transparent diamond devices is roughly 4 nm. From the plots of Fig. 8 we can estimate an adhesive force at the beginning and at the end of the measurement of respectively 132 nN and 128 nN and they were calculated observing the length of the snap-off sudden jump. The difference with the displacement position at which the ram should have been, is directly translated into the force holding the device to the surface, obtained by multiplying the snap-off length for the foldable spring constant of the actuator. In a humid environment, the meniscus formation between mating surfaces can be formed at different distances, depending on the degree of relative humidity (RH). In this case, where RH is unknown but certainly present, the formation of a water meniscus causes the adhesion force to disappear at a certain distance, greater than the distance at which vdW interaction would have a comparable strength. In fact, for distances bigger than 0.5 nm, capillary forces are stronger than vdW forces and they operate up to the break of the meniscus. In addition, large areas like a MEMS sidewall (if compared to an AFM tip) make capillary forces much more influent at greater distances. The actuation voltage and displacement were kept constant in the two cases. The absolute difference between the values visible on the horizontal and vertical scale bars is caused by the different voltage at which the recording of the data was initiated (offset) and slight drift of the microscope optics during the long cycle measurement.

3.4 Treatment with oxygen plasma of the B-UNCD sidewall surfaces

It has been reported in literature that a modification in the diamond termination can influence the surface and electrical properties of the material [35-37]. It has also been shown that increased hydrophobicity helps to prevent stiction [38] and that the contact area (stiction reducing bumps

[39] or even high surface roughness) counts when reducing adhesion phenomena. The interaction of diamond surfaces that have been passivated with atomic species also results in enhanced hydrophobicity or hydrophilicity and negative or positive electron affinity. On the surface, different dipole moments between the carbon and the passivating atomic species change the surface properties and thus change the interaction of diamond MEMS sidewalls. Experiments on passivated poly-crystalline diamond films have been performed by M.C. Salvadori *et al.* [40] using a plasma gun to bombard the surface with the desired ion species. In our experiment we applied the same concept to functionalise the B-UNCD surface with oxygen, in order to explore its effects to the adhesion phenomena. In order to replace the natural terminations of diamond with the desired species, the samples have been treated for 60 minutes in a 10 W RF plasma.

In order to understand the surface affinity with water, we measured the contact angle of a water droplet on the upper side of the B-UNCD layer. In Fig. 8 we show the effect of the oxygen plasma cleaning on the behaviour of a water droplet on the surface. The treatment increases the surface energy of diamond so that it becomes completely hydrophilic: the water spreads completely across the film.

A partially hydrophobic behavior is observed for the untreated diamond layer. No contact angle can be measured if we treat the diamond with oxygen plasma, indicating that the surface has become completely hydrophilic. In the case of hydrophobic surfaces that are surrounded by a vapor that can 'capillary condense', a concave meniscus can form. During adhesion tests, a capillary condensation at the contact asperities would be then confined to a smaller area compared to a hydrophilic surface, where the low surface energy would cause the water molecules to spread across a bigger area.

Fig. 8

It has been shown by Lafeng and Regnier [41] that adhesion force increases in presence of meniscus action in higher humidity and higher shape index.

In order to investigate the effect of the oxygen passivation on a longer term, we have performed a high number of repeated contacts, maintaining the force constant. The aim of the test was to observe any contingent surface modification and conclude if the material underwent to any local phase transformation due to interaction with the plasma. The measurements carried out on the sidewalls of the B-UNCD adhesion sensor, reveal an initial change in adhesive force after oxygen passivation of sidewalls terminations. We kept a constant normal force of 320 nN at the contact point between the surfaces, in order to compare the results with the un-treated test. We measured the adhesive force at the beginning and at the end of a long run of 50000 cycles. In the plots of Fig. 9A we show the initial snap-off that was observed. The force of adhesion between

the sidewalls increased to 260 nN. Its higher magnitude, when compared to the un-treated B-UNCD sidewalls, is most probably due to the formation of a thin liquid layer on the diamond surface, which increased the number of ‘wet’ asperities that make contact. The same device was used after 50 000 cycles to measure the adhesive force between the sidewalls. The snap-off length decreased by 40% (Fig. 9B), leading to an adhesion force of 160 nN. Given the fact that the device used is different from the un-treated experiment, and that there is always some statistical variation in adhesion between different devices, the force found in the latter case matches the forces that were measured when the diamond surface was not treated within good approximation. We believe that a repeated contact between oxygen terminated asperities, which undergo chemical, physical and mechanical interactions at every cycle, bring back a local hydrophobic condition on the surface in contact, where new carbon atoms engaging contact are exposed and interact with the environment, which was first only passivated with hydroxyl groups.

A

B

Fig. 9

3.5 Observed undesirable effect in diamond adhesive contact

At higher loading forces that reported above, we sometimes do observe significant damaging of the surface. In Fig. 10A and Fig. 10B we show the adhesion curves of two samples analyzed in unprotected testing environment, at room temperature. We have to mention that during those tests, the environmental conditions were particularly extreme, being hot and humid days during the summer. During the backward motion, the shuttle is released by the surface in a gradual manner: instead of a sharp snap-off from the counter-surface, the trend of the motion follows a curved shape, in which individual jumps are visible.

Fig. 10

Fig. 11

The image in Fig. 11 demonstrates how a capillary neck was formed during a repeated impact of two B-UNCD sidewalls in an humid un-protected environment. Even with a normal optical microscope, it was possible to observe the real-time development of this neck between the sidewalls.

This condition is not related to the data shown in Fig. 10, but confirms an effect observed in real-time in B-UNCD MEMS when no particular care is given to the environmental conditions under higher load conditions. A range of forces between $0.5\ \mu\text{N}$ and $5\ \mu\text{N}$ were applied when these rare adhesion curves were observed. The possible explanation of this effect lies in a particular phenomenon that occurs at the surface of B-UNCD. We believe that a thin layer of a hydrocarbon/amorphous carbon (a-C) mixture surrounds the bulk diamond and interacts with the same compound that covers the counter-surface. When the two bodies come into contact under a high compressive force, the hydrocarbon/a-C is squeezed and mixed in between. The interaction

of the two layers and the presence of water molecules eventually causes the carbon atoms to aggregate together. The formation of chains or bundles of hydrocarbon/a-C during the backward motion can be the origin of the phenomenon seen in the plot. The deformation of these entities, their different lengths, strengths and positions determine many individual snaps-off that, occurring at different times, build up the gradual pullback visible in during backward motion. The presence of a thin layer of superficial amorphous carbon or environmental organic impurities on the sidewalls can be the result of the etching process, releasing and handling in an un-protected environment. This effect was previously observed in [42], where the measured adhesion curves revealed a gradual snap-off. When cleaned, in oxygen plasma, the effect was not visible anymore, leading us leading us to suppose that a superficial amorphous carbon layer was causing this effect. After more investigation, we can conclude that this effect occurs when a higher loading force is applied and under special, seldom environmental conditions. Because carbon nanoparticles are highly hygroscopic [43], any unwanted deposition of a-C compounds on the surface would result in an agglomeration of more particles in a matrix of water. This would explain the occasional ‘huge’ adhesive force observed in some of these un-treated B-UNCD devices that we have used for testing. The meniscus volume is much larger than the volume of the material removed from the surface.

4. Discussion: a simple model for the assessment of material loss due to plastic deformation

At relatively low load (sections 3.2 - 3.4) conditions we have observed no damage to the contacting B-UNCD surfaces, indicating that the material is very suitable for application in MEMS where surfaces can (or should intentionally) come into contact. The question that remains

is up to which load these conditions hold, as we occasionally see significant damage under higher load (section 3.5).

In order to estimate the amount of material that is removed during the contact between two microscopically rough surfaces, we have modeled the system as a contact between a flat, infinitely hard surface, and a rough one, of which the mechanical properties are those of the two original surfaces combined. If the surfaces of the two bodies, 1 and 2, have a height distribution function with standard deviation σ_1 and σ_2 , the standard deviation of the height distribution $h(x)$ of the 'combined' surface is $\sqrt{\sigma_1^2 + \sigma_2^2}$. Because in this research the two surfaces are made of the same material, the hardness of two surfaces combined is the same as the hardness of a single surface.

During the contact, when the two bodies are crushed together, the highest points that touch each other will deform plastically and/or elastically. We consider the simplest case, in which the deformation is considered to be fully plastic. This assumption allows us to calculate the 'bearing area': the smallest area of the surface that can withstand the normal load F_N . The progress of plastic deformation will continue up to this point, after which the displacement of the material will be stopped because the surface will develop enough strength to sustain the load. The bearing area will then be equal to the real area of contact, A_R , which is given by:

$$A_R = \frac{F_N}{H} \quad (1)$$

Where A_R (m²) is the real area of contact, F_N (N) is the normal load and H is the hardness. In order to evaluate the fraction of the surface in actual contact, we have to consider the ratio of the real area

A_R and the apparent contact area A_C , the latter being the one seen in contact if looking at the system from a macroscopic point of view.

If, from an infinite distance ($-\infty$), we bring the flat surface in contact with the rough counter-body that has a height distribution function $h(x)$, there will be a plastic deformation of the asperities, up to a certain position x_b , that corresponds to the point where the bearing area is large enough to sustain the load. For simplicity, we assumed a Gaussian height distribution function $h(x)$.

The position x_b is defined by the fraction of the area that is really in contact, the ratio of A_R and A_C , as

$$\int_{-\infty}^{x_b} h(x)dx = \frac{A_R}{A_C} = \frac{F_N}{HA_C} \quad (2)$$

To calculate the volume of material that has to be plastically removed to move from $-\infty$ to x_b , we have to note that the distribution of the amount of new surface displaced at every height x is $A_R \cdot h(x)$. The volume corresponds to the amount of that surface multiplied by the distance between the surface and x_b , integrated over all distances. The total volume removed, V is correspondingly:

$$V[m^3] = A_R \int_{-\infty}^{x_b} (x_b - x)h(x)dx \quad (3)$$

The last two equations are readily evaluated numerically. Note that x_b is a function of A_C , which is just to say that the bearing area height depends on the total apparent contact area.

For the case of the B-UNCD adhesion sensor, the roughness of the individual surfaces is 6.23 nm (AFM measurement of Fig. 5), making the standard deviation of the combined surfaces 8.81 nm.

The indentation hardness H is taken as 28 GPa, and the apparent contact area A_C is varied from $0.01 \mu\text{m}^2$ to $10 \mu\text{m}^2$. Fig. 12 shows the removed volume V due to plastic deformation as a function of normal load. Considering the high surface roughness of the bodies in contact and an out-of-plane shift of the moving shuttle, we can assume, in the worst condition, a real contact area of $0.01 \mu\text{m}^2$. In this case, from Fig. 12A and Fig. 12B we can evaluate the effect that the contact force can have on the surface modification process. In fact, by applying a higher loads, a point is reached at which a grain can be removed, therefore more amorphous carbon can come loose and aggregate to form a carbon capillary neck.

Fig. 12

Because a single carbon atom has a diameter of around 0.35 nm and a typical UNCD grain has dimensions ranging from 5 nm to 15 nm , we can estimate the lowest possible onset of wear, depending on whether single atoms or complete grains are removed.

5. Conclusions

UNCD (ultrananocrystalline diamond) is a novel material with high potential for use in MEMS technology. We have developed MEMS adhesion sensors based on boron-doped UNCD (B-UNCD) as the structural material.

With these sensors, we have experimentally investigated the adhesion phenomena that occur when two B-UNCD sidewalls make contact, under different environmental conditions.

The contact force applied during most tests has been fairly low, in accordance with typical loads expected in functioning MEMS devices, from a minimum value of 320 nN to a maximum of 424 nN. The load forces and adhesive forces were monitored by looking at the displacement of the front spring (foldable beams) with a house-built optical measurement setup. It has been observed that the B-UNCD MEMS in humid air tend to stick to each other, generating an adhesive force of about 130 nN, presumably due to the creation of water meniscus between the sidewalls asperities. When treated in an oxygen plasma for 60 minutes, the material becomes more hydrophilic, therefore increasing the adhesion further, due to more meniscus formation. Additionally, we have also reported the infrequent observation of the catastrophic formation of a carbon-containing capillary neck at higher normal force conditions (0.5-2 μ N), observed in adhesion measurements as well as with scanning electron microscopy. The effect occurs infrequently, but if it occurs, it increases the adhesive force generated at the interface enormously. Therefore, it places an upper limit on the contact force at which the B-UNCD material can be successfully applied. To estimate the smallest contact force for which the effect might occur, we have presented a simple analytical model based on calculating the maximum

volume of material that might be plastically deformed at a certain contact force, depending on the surface roughness and the hardness of the B-UNCD material.

The main result of this study is that, at low contact force, the B-UNCD is virtually indestructible, and that it can hence be used as a replacement structural material for (poly-) silicon MEMS. However, in humid environment, after prolong operation, at high contact forces, higher adhesion force is observed in diamond and capillary necks were observed between the sidewalls in contact. Future studies involving H-termination are required to see how these devices will behave in dry and humid environments.

Acknowledgements

This work was sponsored by the Dutch funding agency NWO-STW in the ‘vidi’ program under ref no. 10771. Use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

Figures Captions

Figure 1: (A) 3D sketch of the adhesion sensor utilized in our research. (B) Scanning electron micrograph (SEM) image of the released device with description of its fundamental components.

Figure 2: Process flowchart. The conductive B-UNCD wafer was processed in a class 100 cleanroom. The diamond layer is etched using oxygen based plasma and released in BHF and TMAH at 80 °C.

Figure 3: Finite elements simulation of the maximum displacement of the diamond actuator. To simulate the spring deformation caused by the contact, a 150 nN load was applied in the positive x-axis to the head, while keeping the rest of the body behind the foldable spring constrained.

Figure 4: Plot of the differential spring deformation used to calculate the contact force. The beams 1 and 2 move together when the voltage is increased (the line is not perfectly aligned to zero because of a mild effect of out-of-plane buckling due to thermal expansion). Upon contact, the differential displacement is measured and translated into loading force.

Figure 5: (A) SEM image of a broken B-UNCD beam after the etching process. The sidewall has been analysed with an AFM in non-contact mode, to avoid the wear of the tip. It is clearly visible a double-etch step; (B) AFM scan of the sidewall. The scanning tip has been maintained in the area between the middle etch line and the edge of the beam.

Figure 6: (A) Plot of the adhesion effect between B-UNCD sidewalls in argon filled environment. The curve does not change during the cyclic experiment and zero adhesion is virtually visible in the plot; (B) Zoom-in of the contact region. A pull-in effect is visible when the ram is few nanometer apart from the counter-surface. This is attributed to electrostatic attraction.

Figure 7: (A) Adhesion between B-UNCD sidewalls in un-protected humid conditions at its first contact. The snap-off jump corresponds to an adhesive force of 132 nN; (B) Adhesion between B-UNCD sidewalls in un-protected humid conditions after 55000 cycles. The snap-off jump corresponds to 128 nN adhesion force.

Figure 8: (A) Contact angle measurement on a B-UNCD surface; (B) The water droplet after oxygen plasma treatment is not visible anymore due to the hydrophilicity of the surface.

Figure 9: (A) Adhesion between oxygen cleaned B-UNCD sidewalls in un-protected humid environment, at first contact. The adhesive force has increased to 260 nN, compared to 132 nN for the untreated case; (B) Adhesion between oxygen cleaned B-UNCD sidewalls in un-protected humid environment, after 50000 cycles. The adhesive force decreases to 160 nN.

Figure 10: (A) In the plot is shown the adhesion observed in similar conditions, in which is clear that the snap-off does not occur sharply, but dynamically in time. This effect has been observed only in micro-actuators that did not undergo an oxygen plasma cleaning process; (B) Zoom-in on the adhesive effect occurred in a similar device, under the same ambient conditions.

Figure 11: Effect of capillary formation between two un-cleaned B-UNCD MEMS sidewalls.

Figure 12: Removed volume V due to plastic deformation as a function of F_N and A_C ; (B) Removed volume V due to plastic deformation as a function of F_N and A_C , when a lower load is applied on the surface.

References

1. N. Kumar, et al., Tribological properties of ultrananocrystalline diamond films in various test atmosphere, Tribology International, 44 (2011) 2042-2049.

2. O. A. Shenderova and D. M. Gruen, *Ultrananocrystalline Diamond: Synthesis, Properties and Applications*. Second ed. 2012: Elsevier.
3. A. V. Sumant, et al., Toward the ultimate tribological interface: Surface chemistry and nanotribology of ultrananocrystalline diamond, *Advanced Materials*, 17 (2005) 1039-+.
4. A. V. Sumant, et al., Ultrananocrystalline diamond film as a wear-resistant and protective coating for mechanical seal applications, *Tribology Transactions*, 48 (2005) 24-31.
5. A. R. Krauss, et al., Ultrananocrystalline diamond thin films for MEMS and moving mechanical assembly devices, *Diamond and Related Materials*, 10 (2001) 1952-1961.
6. A. V. Sumant, et al., Ultrananocrystalline and Nanocrystalline Diamond Thin Films for MEMS/NEMS Applications, *Mrs Bulletin*, 35 (2010) 281-288.
7. A. V. Sumant, et al., MEMS/NEMS based on mono-, nano-, and ultrananocrystalline diamond films, *Mrs Bulletin*, 39 (2014) 511-516.
8. D. Berman and J. Krim, Surface science, MEMS and NEMS: Progress and opportunities for surface science research performed on, or by, microdevices, *Progress in Surface Science*, 88 (2013) 171-211.
9. S. Cass, MEMS in space, *Ieee Spectrum*, 38 (2001) 56-+.
10. X. Lafontan, et al., The advent of MEMS in space, *Microelectronics Reliability*, 43 (2003) 1061-1083.
11. D. Panescu, MEMS in medicine and biology, *Ieee Engineering in Medicine and Biology Magazine*, 25 (2006) 19-28.
12. C. H. Mastrangelo, Adhesion-related failure mechanisms in micromechanical devices, *Tribology Letters*, 3 (1997) 223-238.
13. B. Bhushan, *Advantages and Limitations of Silicon as a Bearing Material for MEMS Applications*, in *Tribology Issues and Opportunities in MEMS*, Springer, Editor. 1998. p. 341-362.
14. D. J. Fonseca, On MEMS Reliability and Failure Mechanisms, *Journal of Quality and Reliability Engineering*, 2011 (2011) 7.
15. R. Maboudian, W. R. Ashurst, and C. Carraro, Tribological challenges in micromechanical systems, *Tribology Letters*, 12 (2002) 95-100.
16. Y. P. Zhao and J. L. Wen, Surface stability of epitaxial elastic films by the Casimir force, *Chinese Physics Letters*, 19 (2002) 1161-1163.
17. B. Bhushan, Nanotribology and nanomechanics of MEMS/NEMS and BioMEMS/BioNEMS materials and devices, *Microelectronic Engineering*, 84 (2007) 387-412.
18. M. P. de Boer, et al., Adhesion of polysilicon microbeams in controlled humidity ambients, *Microelectromechanical Structures for Materials Research*, 518 (1998) 131-136.
19. P. M. Sarro, Silicon carbide as a new MEMS technology, *Sensors and Actuators a-Physical*, 82 (2000) 210-218.
20. R. Maboudian, W. R. Ashurst, and C. Carraro, Self-assembled monolayers as anti-stiction coatings for MEMS: characteristics and recent developments, *Sensors and Actuators a-Physical*, 82 (2000) 219-223.
21. R. A. Singh, et al., DLC nano-dot surfaces for tribological applications in MEMS devices, *Applied Surface Science*, 257 (2011) 3153-3157.
22. N. S. Tambe and B. Bhushan, Scale dependence of micro/nano-friction and adhesion of MEMS/NEMS materials, coatings and lubricants, *Nanotechnology*, 15 (2004) 1561-1570.

23. F. Buja, et al., Electrically Conducting Ultrananocrystalline Diamond for the Development of a Next Generation of Micro-Actuators, Sensors and Actuators A: Physical (submitted), (2013).
24. Y. Zhu, A. Corigliano, and H. D. Espinosa, A thermal actuator for nanoscale in situ microscopy testing: design and characterization, *Journal of Micromechanics and Microengineering*, 16 (2006) 242-253.
25. *UNCD Wafers Data Sheet & Technical Knowledge Bank*, Technology, Editor.
26. J. Kokorian, F. Buja, and W. M. van Spengen, In-Plane Displacement Detection With Picometer Accuracy on a Conventional Microscope, *Journal of Microelectromechanical Systems*, (2014).
27. Y. F. Zhang, et al., The roles of argon addition in the hot filament chemical vapor deposition system, *Diamond and Related Materials*, 10 (2001) 1523-1527.
28. P. Attard and J. L. Parker, Deformation and Adhesion of Elastic Bodies in Contact, *Physical Review A*, 46 (1992) 7959-7971.
29. P. Prokopovich and V. Starov, Adhesion models: From single to multiple asperity contacts, *Advances in Colloid and Interface Science*, 168 (2011) 210-222.
30. A. W. Bush, R. D. Gibson, and T. R. Thomas, Elastic Contact of a Rough Surface, *Wear*, 35 (1975) 87-111.
31. D. J. Whitehouse, *Handbook of Surface Metrology*. 1994: Institute of Physics Publishing.
32. R. Maboudian and R. T. Howe, Critical review: Adhesion in surface micromechanical structures, *Journal of vacuum science and technology*, 15 (1997) 1-20.
33. W. M. van Spengen, E. Bakker, and J. W. M. Frenken, A 'nano-battering ram' for measuring surface forces: obtaining force-distance curves and sidewall stiction data with a MEMS device, *Journal of Micromechanics and Microengineering*, 17 (2007) S91-S97.
34. L. Y. Ostrovskaya, et al., Hydrophobic diamond films, *Protection of Metals and Physical Chemistry of Surfaces*, 49 (2013) 325-331.
35. K. Hayashi, et al., Investigation of the effect of hydrogen on electrical and optical properties in chemical-vapor-deposited homoepitaxial diamond films (vol 81, pg 744, 1997), *Journal of Applied Physics*, 81 (1997) 7078-7078.
36. A. R. Konicek, et al., Influence of surface passivation on the friction and wear behavior of ultrananocrystalline diamond and tetrahedral amorphous carbon thin films, *Physical Review B*, 85 (2012).
37. M. I. Landstrass and K. V. Ravi, Hydrogen Passivation of Electrically Active Defects in Diamond, *Applied Physics Letters*, 55 (1989) 1391-1393.
38. P. F. Man, B. P. Gogoi, and C. H. Mastrangelo, Elimination of post-release adhesion in microstructures using thin conformal fluorocarbon films, *Ninth Annual International Workshop on Micro Electro Mechanical Systems*, *Ieee Proceedings*, (1996) 55-60.
39. L. S. Fan, Y. C. Tai, and R. S. Muller, Ic-Processed Electrostatic Micromotors, Sensors and Actuators, 20 (1989) 41-47.
40. M. C. Salvadori, et al., Termination of diamond surfaces with hydrogen, oxygen and fluorine using a small, simple plasma gun, *Diamond and Related Materials*, 19 (2010) 324-328.
41. W. Lefeng and S. Regnier, A More General Capillary Adhesion Model Including Shape Index: Single-Asperity and Multi-Asperity Cases, *Tribology Transactions*, 58 (2014) 106-112.

42. Buja, Federico, et al. "First adhesion measurements of conductive ultrananocrystalline diamond MEMS sidewalls." Nano/Micro Engineered and Molecular Systems (NEMS), 2014 9th IEEE International Conference on. IEEE, 2014.
43. E. Weingartner, H. Burtscher, and U. Baltensperger, Hygroscopic properties of carbon and diesel soot particles, Atmospheric Environment, 31 (1997) 2311-2327.