Characterising the deposition of diamond-like carbon on a conducting platinum substrate

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Abstract— **This investigation was to look at characterising depositions of diamond like carbon (DLC) on a conducting substrate. In order to reduce the number of experiments carried out, a statistical determination of experiment (SDoE) was to be used, and the three parameters (beam current, deposition time and voltage) were to be compared with conductivity measurements to determine any relationship. After many changes to the experimental method itself, it was not possible to make conductivity measurements using the desired method and so the experiment ended with no conductivity measurements, but some interesting observations and should provide a good guide for any who might wish to perform similar work in addition to suggesting some slightly different and potentially fascinating branches of research.**

I. INTRODUCTION

Electron-beam-induced deposition (EBID) of carbon on a conducting substrate is a common technique to construct carbon nano-structures. This process is generally conducted inside a scanning electron microscope (SEM), however can only be conducted in some of the older machines as will soon become apparent.

EBID in an SEM basically involves using an SEM which has a diffusion pump on it to achieve the vacuum that an SEM normally operates in. The pump itself creates a vacuum in the chamber of the SEM, however because of the diffusion pump, some hydrocarbon molecules remain in the chamber. These molecules are from the pump itself. When the SEM is turned on, the electron beam used by the SEM impacts upon some of the hydrocarbon molecules and in doing so decomposes them into hydrogen atoms and chains of carbon. The hydrogen atoms remain in the chamber or are pumped out, maintaining the vacuum, however the carbon atoms are attached to the surface that the SEM is scanning at the point where the electron beam strikes the surface. Thus, by changing where the beam is pointing on the surface, one can create different structures on the surface that the SEM is 'looking' at. Additionally, if the beam were to remain in the same place, then there would be a 'tower' of carbon built up.

Traditionally a SEM with a diffusion pump is quite an old model as of recent years they have become less fashionable and been replaced by newer models with a different type of pump. The diffusion pump is noisy and in the past the fact that it contaminates the vacuum of the SEM has been seen as a reason not to use such a machine. Of course for EBID, the diffusion pump is essential as it is this pump that provides the material with which structures can be produced.

The carbon is referred to as diamond like carbon (DLC), as the layers produced have a structure and properties similar to diamond. Thus, DLC is normally characterised as being an electrical insulator (hence its use in metal-insulator-metal, or MIM diodes as discussed later on). It is also very hard (like diamond) and this opens up many possibilities in particular in the fields of nanotechnology and nanophysics.

EBID has previously been used to deposit many different structures onto a conducting substrate. If the microscope is put into an in-line scanning mode, then wire-like structures are produced. In an area scanning mode, a flat plane can be produced which can be used in the likes of a (MIM) diode. If however the electron beam is left in one place, then one manages to keep building further layers of carbon on the same spot and hence a tower of carbon is formed. All of these have previously been accomplished [1].

There is one use of DLC that is of particular interest. Using the SEM to deposit all of the carbon in one place builds up a tower of carbon as already mentioned. If this tower is placed onto the tip of an atomic force microscope (AFM) then it can be used as the tip of the microscope itself. The advantages this brings are that it generally is narrower, with a smaller radius of curvature and has a greater aspect ratio compared with the standard tip and as a result better resolution can be achieved. Indeed it is possible to purchase these DLC tips for an AFM however they are often over $100 each, making them quite expensive.

There are three operating parameters to consider when depositing DLC using a SEM. These are the beam current (I), voltage (V) and deposition time (t). Previous studies have been conducted on the effects of varying these parameters on the geometry and composition of the DLC structures produced [1], [2].

The effect that deposition time had in the studies was unsurprising. If the beam is on for a greater amount of time, then more of the structure was built up. So in the case of the towers, a greater deposition time leads to higher towers. The beam current changed the aspect ratio of the towers. For a lower beam current it was found that the aspect ratio of the towers was greater. This can be seen in Fig. 1. It was thought that this was for two reasons. Firstly, higher beam currents cause localised heating and hence re-evaporation of the carbon from the surface, stunting vertical growth. Secondly, the higher beam current causes greater scattering of the electrons when they reach the surface and this encourage lateral growth of the construct.

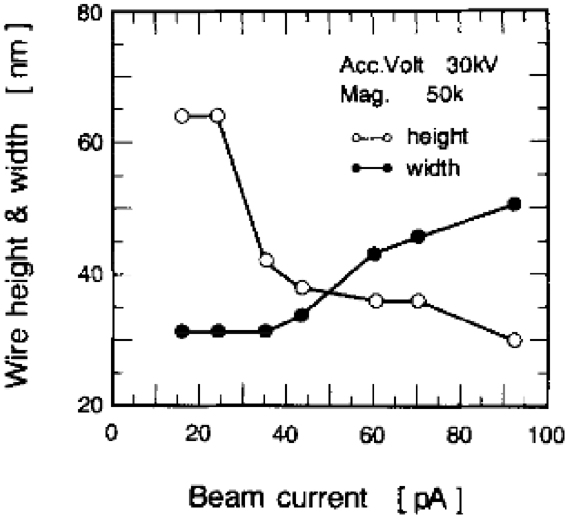

Fig. 1: The effect on the beam current has on the height and width of a carbonaceous carbon deposition [1].

In the case of the voltage, it was found that this altered the composition of the carbon. DLC is characterised by the ratio of different types of bonds within the material. Essentially the carbon forms either the type of bond associated with diamond or that associated with graphite (sp^3 and sp^2 respectively). If one takes a ratio of the numbers of these bonds as sp^3/sp^2, then it is clear that the higher this ratio is, the more of the bonds are diamond like and the lower this ratio, the more that are graphite-like (by 'graphite-like', the weak bonds that adhere one layer of graphite to another are referred to). As graphite is an electrical conductor but diamond is not, it would be reasonable to think that any change in the sp^3/sp^2 ratio would indicate a change in conductivity of the sample. The voltage was found to indeed alter this ratio, with higher accelerating voltages leading to higher ratios and to greater electrical insulating properties (high resistance) [2].

When conducting an experiment, it is often the case that some of the experiments possible are very unlikely to yield any results. These are normally the experiments involving the extreme conditions. For these cases a statistical design of experiment (SDoE) can be used. The basic idea of this is that there is a lower probability of extreme events occurring and so these events can be discounted without significant loss of data. This basic idea can be seen in Fig. 2.

Fig. 2 shows an example of how a SDoE works. It allows one to ignore the extreme (unlikely) experiments (shown as red), thus reducing the numbers of experiments required. Fig. 2 only shows two variable inputs (x and y) and this produces a 3-D space (as the output is included also). Our experiment has 3 variables which leads to an experimental space that cannot be visualised as it is a 4-D space, but the principle is the same. This technique was chosen for this experiment because of the number of trials that would be necessary otherwise.

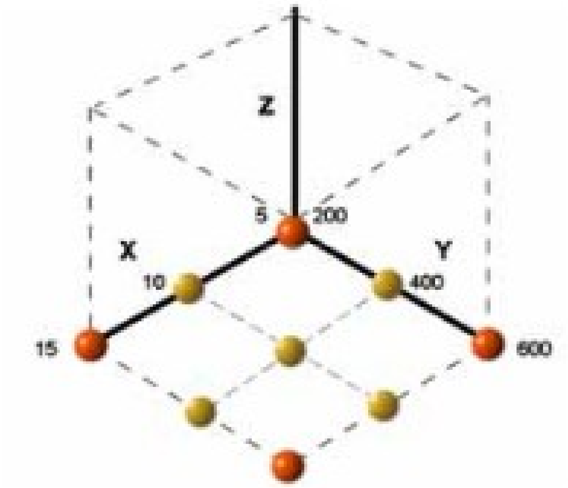

Fig. 2: A 3-D experimental space demonstrating the principles of SDoE. [3]

II. Experimental Method

The intention of this experiment was to characterise the parameters for the deposition of DLC and to then perform conductivity measurements. As such, the first step of the original experiment was to obtain some AFM cantilevers (one to use and a couple in reserve) and then sputter coat them in copper. This would allow the cantilevers to conduct, which would be necessary for the conductivity measurements. The layer sputter coated onto the cantilevers was intended to be about 100nm thick, which required about a half hour to coat. In reality it was slightly over 100nm, but this was a fairly arbitrary choice of thickness. It was simply chosen because it should ensure that the cantilevers conducted. A conducting substrate would then be used to deposit a series of DLC towers on them, with the SEM using operating parameters determined by using a statistical design of experiment.

Using a SDoE, we established that the different experiments we needed to carry out numbered 13, and they can be seen in table I. For each parameter, the lower number is that below which no interesting change was expected, the higher a value above which no interesting result was expected and the middle value what was considered a sensible value that might be of interest. In this way it should be possible to map (generally) the changes had by the three parameters. This specifically is something that does not seem to have been attempted before. It should be noted that the unusual figure for voltage of 19 kV was implemented because this was the highest value that the SEM would use and still give confidence that the electron beam was not spreading out significantly.

Table I – the experiments carried to be carried out as determined by the SDoE

Voltage (kV)	Beam Current (pA)	Deposition time (s)
10	50	3
19	50	10
19	5	10
10	5	20
3	50	10
3	5	10
19	20	20
10	5	3
3	20	3
19	20	3
10	20	10
3	20	20
10	50	20

The substrate used was a broken conducting cantilever placed so that the platinum backing was facing upwards. This was adhered to the SEM stub using conductive tape and to ensure that there was an electrical connection between the substrate and the stub, a silver solution was then applied over the edge of the substrate This silver solution can be seen together with the substrate in Fig. 3.

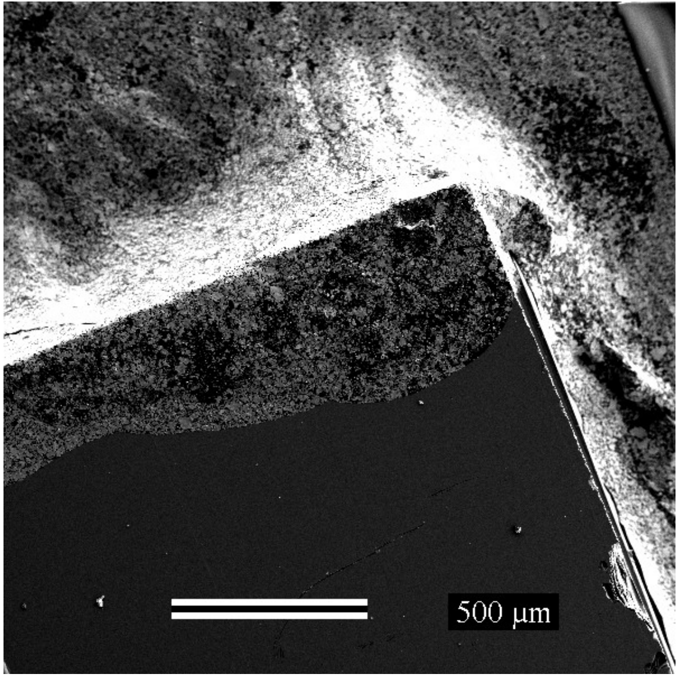

Fig. 3: An SEM image of the substrate used, together with the silver solution (which can be seen along the top edge of the substrate).

The depositions themselves were made with the SEM beam focussed on a single point. The AFM was then used to try and find the depositions and would have been used for conductivity measurements of the towers. This was not possible for reasons that shall be discussed later, and so a slightly different method was used.

The alternative method used was to compensate for the fact that the towers could not be found. Thus, both as a proof of concept (to demonstrate that the SEM was actually making depositions) and to obtain some results for the experiment, the experiment was altered so that large (diameter ~2µm) discs were deposited instead of towers using a programme to deposit them in a pattern of four depositions in a line.

This change in method also had the effect of changing the parameters. Using the SEM on a programme to deposit over an area meant that the changeable parameters were voltage, beam current and dose. The dose is essentially the charge per unit area that was deposited. Now, the beam current and voltage were varied between depositions at 50 pA and 10 kV for the first deposition and 20 pA and 3 kV for the second and with the dose taking values of 10^4, 10^5, 10^6 and $2x10^6$ µCcm^{-2}. Resistance measurements were then made of these discs and of the substrate, using a conducting cantilever loaded into the AFM after the failure of the sputter coating. The conductivity measurements were made using a (very sensitive) multimeter using this to measure the resistance between the substrate and the AFM cantilever in contact mode. An image of the connections made to allow this can be seen in Fig 4. In the event, more force was required than contact mode would provide in order to get a resistance reading and so the cantilever was manually lowered onto the sample until a reading was obtained.

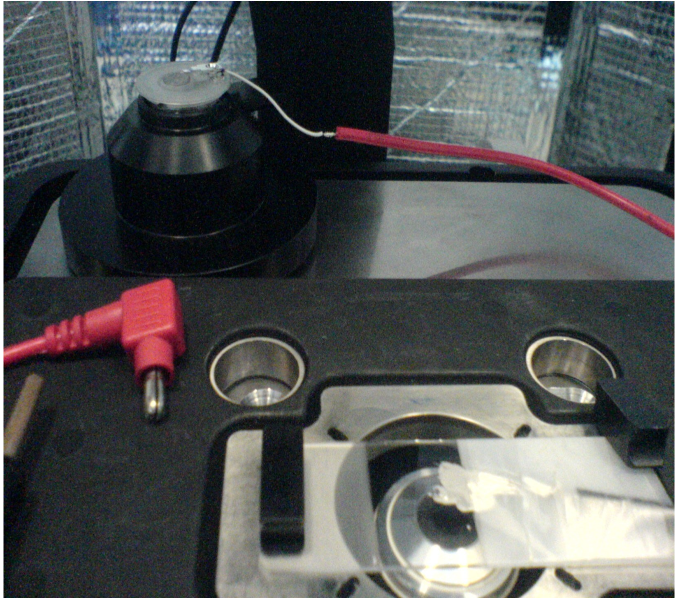

Fig. 4a: The general experimental set up for the resistivity measurements. The end of the red wire that can be seen was plugged into the multimeter and likewise, the wire coming from the sample on the glass slide leads to a probe that also went to the multimeter.

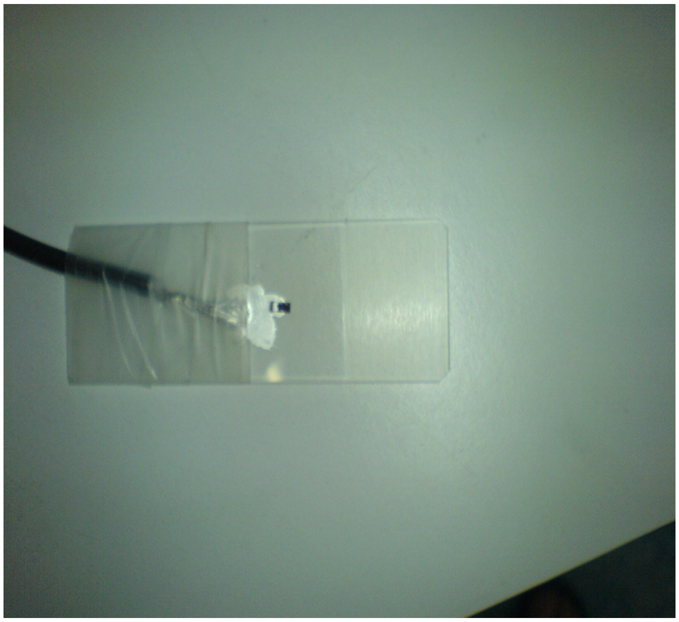

Figure 4b: An image of the sample on a glass slide with a wire that leads to the multimeter and the silver solution used to establish an electrical connection between the two.

III. Results and Analysis

Not originally intended as a stage in the experiment that would yield results, the fact that the sputter coater deposited a coating on the AFM cantilevers that had a black metallic finish is in itself of interest. As we were using a copper target, it would seem that this black substance was probably copper (II) oxide, also known as cupric oxide and having the chemical formula CuO. There had been problems with the plasma arcing in the sputter coater and presumably the oxide layer had formed when the target was in storage/being fitted. The sputter coating process itself is conducted in an oxygenless environment so it would not have formed during this process. Many of the common oxides of copper will still conduct (which was one of the reasons that copper was selected, so if there were any oxides it should still conduct) so it was surprising that this one did not. With 30V placed across it with crocodile clips it still did not show any sign of conduction (it was connected to a sensitive multimeter which when measuring resistance never showed any figure other than one that was too high for it to read).

As an aside the cantilevers that had been sputter coated (and were now of no special use as they did not conduct) were placed in the AFM to see if they could still be used as normal AFM tips. Cantilevers usually have a frequency of about 170 – 180 kHz, however the sputter coated tips had a frequency of about 270 – 280 kHz. This indicated that the cantilevers were slightly heavier, which was no surprise, but still perfectly usable as AFM cantilevers.

When the discs were deposited (the alternative method after the initial method failed), they were found looking as seen in Fig. 5. Of note is the visibility of only one of the discs on the height trace but the positions of all 4 being present on the phase trace. This would appear to indicate that the dose in the other cases was not high enough to create a structure, however the electron beam did interact with the surface, hence the deposition sites being visible in the phase trace. It can also be seen that each of the positions where we tried to deposit discs vary in the amount they show up on the phase trace, with the higher doses showing up much more. It should be said at this point that the doses are slightly out of order. The two highest doses are the other way around. So the doses are in ascending order form left to right except that the highest two are the other way around making the highest dose the third from the left (the one with a tower) and the second highest dose the furthest to the right. There is a spike in the height trace near to the lowest dose position, however it does not quite match in position to the position of this on the phase trace so appears to be nothing to do with the depositions. Note that the apparent valley seen in Fig. 5 is nothing important. It is only noticeable because of the scale. This shows this shape in the substrate but it only changes the height of the substrate by a few nanometres over a lateral distance of twenty microns. It is actually a very gradual feature.

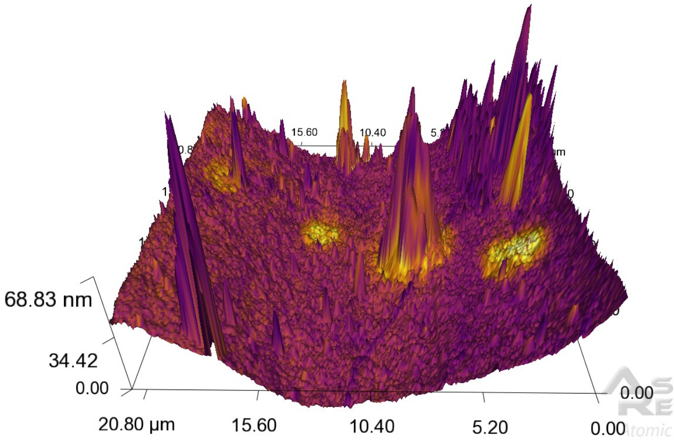

Fig. 5: An overlay of the phase trace over the height trace of one of the two sets of 4 discs. The height trace is represented by the actual topography of the image and the phase by the colour.

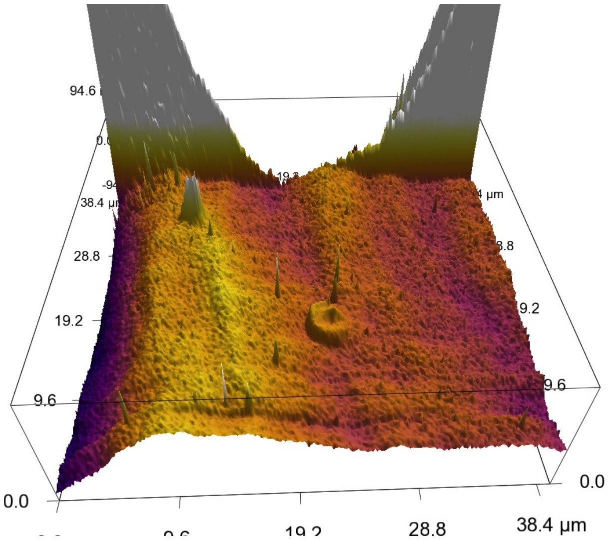

Fig. 6: A height trace of the deposition area showing both depositions.

Fig. 6 shows a height trace of the whole area of both depositions. In each case, only one disc is really visible, with one being seen in the top-left of the scan and one further towards the bottom of the scan. This second disc is slightly flatter than the first, and about 35 nm high, while the first is about 75 nm high. This can be seen from Fig. 7. It can be seen however that only the highest dose disc is showing up on the height trace.

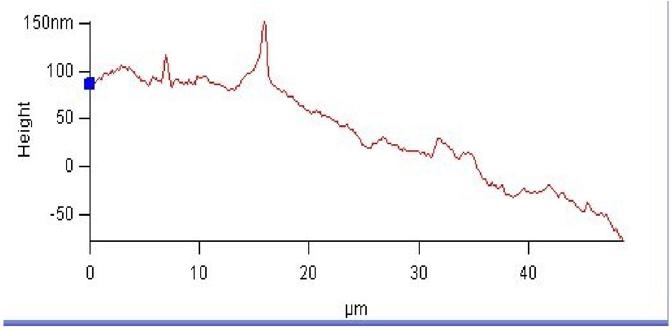

Fig. 7: Showing the heights across the scan area. The peak of the first deposition can be seen at ~ 15 µm along the plot and that of the second can be just seen at about 32 µm.

One feature of interest in Fig. 6 is that there appears to be a line of peaks (including the obvious disc), which seem slightly too regular to be naturally occurring features on the surface. They are also in the same orientation as the depositions for that group. This might indicate that there were some (very small) depositions made at these locations, however the face that these features do not appear with the first deposition seems to imply that if it is possible to make depositions at these lower doses, it is not a reliable process. Either way, the two main depositions were the most likely to yield meaningful and reliable conductivity measurements. Even comparing the two definite depositions they are quite different. The first is taller and has a far greater aspect ratio. The second is closer to that expected from depositions of discs, i.e. it is shorter and more squat, with a flattened top.

An explanation of the difference in heights of the two discs could lie in the parameters used. Between the two depositions, both the accelerating voltage and beam current were altered. The beam current should not make any difference as the machine uses a dose (the same between the depositions), which is a charge per unit area, so a higher beam current will simply result in shorter deposition times. This leaves the accelerating voltage. This would also not be expected to make a difference (see calculation based on bond enthalpies in the discussion), and the fact that the accelerating voltage does in fact make a difference would seem to indicate that the process of EBID is not quite as simple as previously thought.

The resistance measurements themselves were then conducted over a series of points that were located both on the substrate and the discs themselves. There were originally 7 locations chosen. Three of these were on the substrate and 2 were on each of the towers. The locations of these points can be seen in Fig. 8.

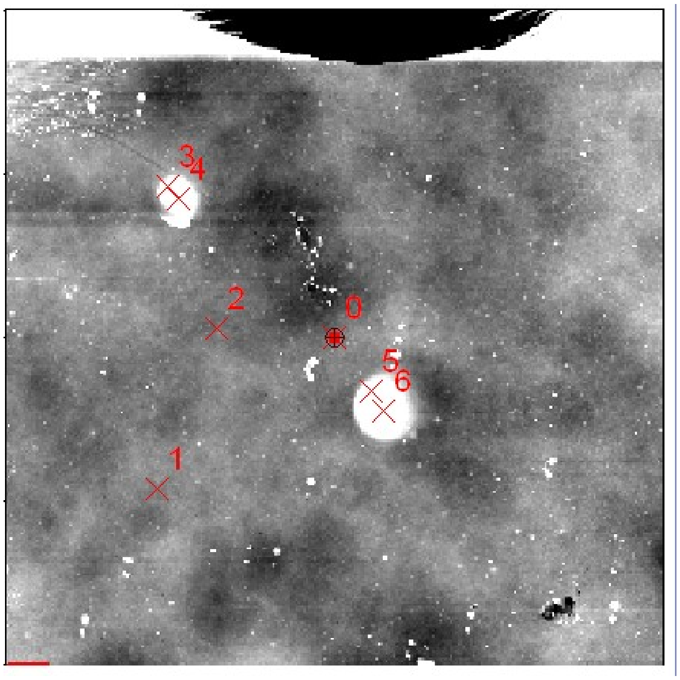

Fig. 8: A height trace of the deposition area (the same areas as shown in Fig. 6), with the locations of the measurements marked on.

After taking some measurements at these locations, a further scan of the area was performed and it was found that the sample had moved. Thus, three further locations were chosen (7, 8 and 9). The scan performed also showed how the surface was being altered by the measurements being made. This scan is shown in Fig. 9. 7 and 8 were at the locations where it was thought the discs would be now and point 9 was on the substrate. Once again, measurements were made. A scan was once again completed part way through, however again the sample had moved. The results of all the measurements can be seen in table II.

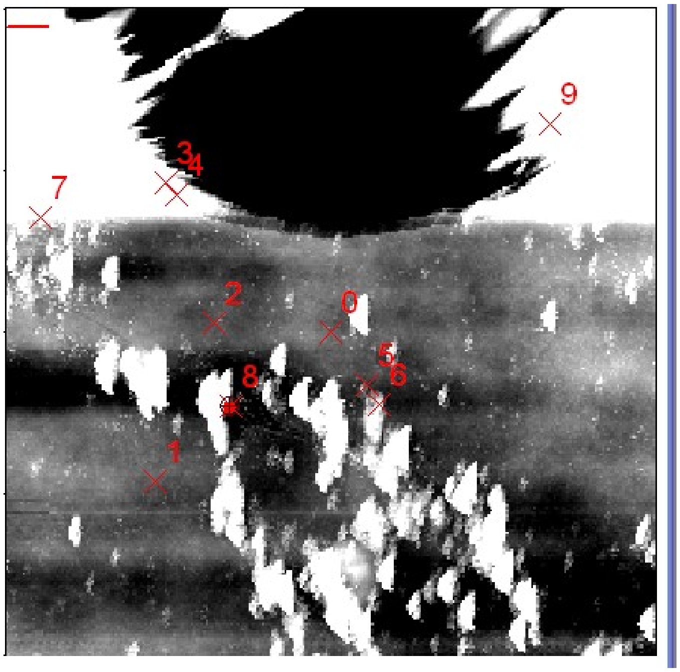

Fig. 9: A height trace showing both the movement of the sample and the locations of all of the measurement points.

Table II – resistance measurements

Location	Resistance (MΩ)		
0	7.7913	7.7886	
1	7.7927	8.44	7.7960
2	7.8	7.7901	
3	7.793	7.7890	
4	8.7	7.789	
5	7.7917	7.7887	
6	7.9060	7.790	
7	7.7900	7.7886	
8	7.8021	7.7933	
9	7.7896		

Note: Each measurement is accurate to the number of significant figures that it is quoted to.

Performing a simple calculation to obtain the mean of all values that should have been taken on carbon and those taken on the substrate it is easy to see that these results tell us nothing. Even excluding the extreme values (8.44 for location 3 and 8.7 for location 4) one obtains that the mean resistance for the first deposition is 7.789 MΩ ± 0.0007, for the second deposition 7.820 MΩ ± 0.0005 and for the substrate 7.819 MΩ ± 0.05. Thus it can be seen that from these values, the resistance value for the DLC (so DLC plus that of the substrate) is really no different from that of the substrate alone. This makes no sense at all, as regardless of how much resistance the carbon discs should have, it should add to the resistance of the base. So, these results do not say anything (presumably mainly because the sample moved). Note, that the mean values above have been conducted using the first 6 values only as these are probably more reliable as for those measurements taken at locations 7 – 9, finding the depositions was more difficult.

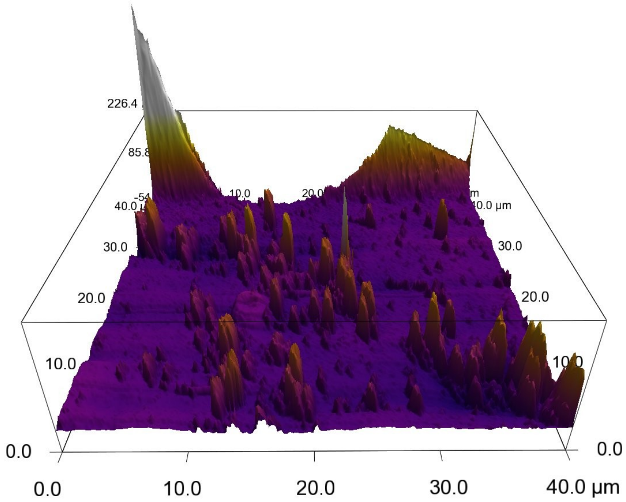

Fig 10: A 3-D height trace of the deposition area after the resistance measurements were made.

Fig. 10 shows the area after the resistance measurements. It can be very simply contrasted with Fig. 6. It is unsure exactly what the new features are, although some of them are probably parts of the DLC discs that have broken off. There is however not enough mass for all of these features to be caused by this. Any roughness of the surface brought about by the technique would be seen as a depression, so it is not this. The only other cause that it might be is a piece debris that the AFM cantilever has picked up, although if this were the case, the features would surely not have as much space between them as they do. Thus, what all of the additional features are for certain is unknown. One thing for certain is that in order for this experiment to have been altered to allow more resistance measurements, the depositions would have to be made again on a different part of the surface as this is probably far too rough to be of any further use.

IV. Discussion

The fact that the sputter coating produced a layer that was quite so insulating was of some interest. It was unexpected and as such warrants some more work to see if the conductivity of the layer actually matches the known conductivity of cupric oxide. Indeed some more investigation into how the layer was actually produced would be interesting as such a good insulating layer could be of use in a variety of other experiments.

With it clear that the depositions appear to be highly dependent on the dose delivered, the question arises as to whether altering some of the other parameters (say the voltage) would have changed the depositions. This question can be easily answered with a simple set of calculations.

The bond enthalpy of a C-H bond is 413 kJ/mol. Dividing this value by N_A gives the energy per bond required as 6.86×10^{-19} J, or 4.28 eV. Thus, 4.28 joules of energy would be required per coulomb of charge to break these bonds. Considering the operating voltage is 3 kV, which corresponds to supplying 3000 joules per coulomb, it can be seen that the energy of an impact is not the issue. A collision between an electron from the electron beam and a hydrocarbon molecule will break the C-H bond with ease. Thus, the issue is one of particle density.

The SEM operates in a vacuum, with only a few hydrocarbon molecules from the diffusion pump and the electrons from the SEM beam occupying the chamber (ideally). With a pressure perhaps in the realm of 3 mtorr, there will not be many particles in the chamber. Thus, the issue is not making the collisions energetic enough to react but rather managing to have enough collisions to obtain the desired carbon chains. Thus, increasing the dose (the charge the beam is releasing per unit area) leads to a larger deposition as there are more electrons for the hydrocarbons to react with. It would be interesting to see an investigation into how exactly the deposition varied with size. In this experiment, just doubling the dose was the difference between no deposition at all and one ~ 35 nm in height (as the second, squatter deposition was).

Having said this however, the accelerating voltage was also changed and would seem to be the only variable changed and so the only one capable of explaining the difference in heights between the two depositions. This is in contradiction to the above calculation which demonstrates that the energy provided by even the smaller of the two accelerating voltages is more than enough to break any C-H bonds present (it is an order of magnitude larger in fact). This contradiction leads to the conclusion that the process involved in EBID is more complicated that the model depicted thus par in this investigation. Any further work that investigated this aspect would be of great interest.

Ultimately, if this experiment were to be conducted again, kelvin probe microscopy (KPM) would probably be a good choice of method to take the conductivity measurements. This would get around the whole problem of the sample moving that was encountered in this study.

V. CONCLUSION

Although this investigation did not successfully obtain the results hoped for, it has laid the foundations for further study in a range of areas. It would be possible to attempt to conduct this experiment again with corrections made to avoid the problems encountered, especially using KPM. One could look into the layering of the insulating layer present from the sputter coating, or try and characterise the deposition height as a function of dose. Perhaps more fundamentally, one could try and investigate the processes behind EBID itself as our current knowledge base on this subject would appear to be lacking.

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