Review of Scientific Paper “Contact Electrification Using Force Microcopy”

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***Abstract* — Charge exchange is a mechanism previously explored and theorized about for thousands of years by macroscopic level observation and instrumentation which has proven insufficient. This paper reviews a technique which approaches the problem using a higher resolution method to track and measure charge states on materials.**

***Index Terms* — Triboelectric, charge microscopy, metal-insulator contact, force microscope**

I. BACKGROUND AND INTRODUCTION

The paper “Contact Electrification Using Force Microscopy” describes a new methodology in order to more closely study the process of exactly how charges are exchanged between two different materials that come into physical contact with each other. This property, known as the triboelectric effect, has been observed since the days of a particular Greek scholar known as Thales of Miletus (6th – 7th Century BC) who observed the electrification of materials rubbed with amber. It was he who first coined the word electricity from the Greek work for amber: “elektron”. [10]

The types of triboelectrification are broadly divided into the metal on metal, metal on insulator and insulator on insulator. In the work of J.R. Harper during the 1960’s, it was discovered that when two metals touch, the charge is equalized when the Fermi levels of the respective materials match each other.[9] However in the case where at one or both of the materials is insulating, the process of charge exchange has been controversial.

Some researchers claimed that only the last metal touched determined the net charge on the insulator whereas others apparently observed a cumulative effect with each metal contact. Discerning which theory is correct depends on understanding how the individual charge sites work which has been a problem of area resolution. These experiments were conducted at relatively macroscale (millimeter) regimes which can suffer from net charge inaccuracies. The findings of this paper have found further information that can only be discerned with measurements on a smaller scale.

The modified force microscope employs a piezoelectrically driven lever on which is mounted a thin nickel wire that has been bent 90 degrees downward to an electrochemically etched tip. The piezo element is driven by an oscillator at just above 25 kHz with part of the signal being split into a lock-in amplifier which compares the phase of the signal with that of an optical interferometer sensor that monitors the movement of the lever/tip assembly.

While in operation, the tip is oscillated at just above the resonant frequency (as approaching the surface begins to change the spring constant and dampen the movement) while the AC bias frequency is kept below the tip frequency (to avoid constructive interference in the signal to the Servo Electronics) but above the feedback loop frequency response rate. [1] (probably to avoid creating a false reinforcement in the feedback loop which could cause unpredictable or uncontrollable behavior and oscillation)

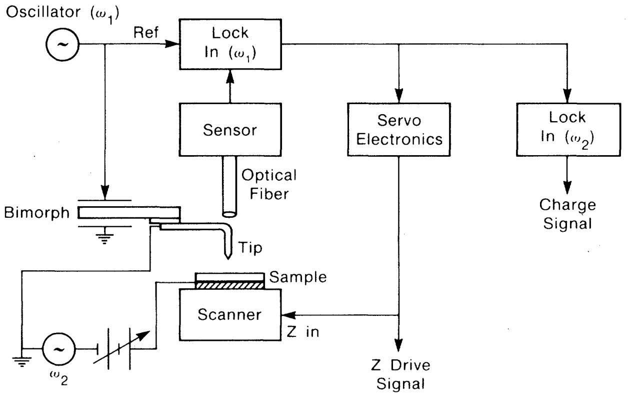

FIG. 1. Block diagram of the force microscope.

FIG. 1. Force Microscope Block Diagram from Reference [1]

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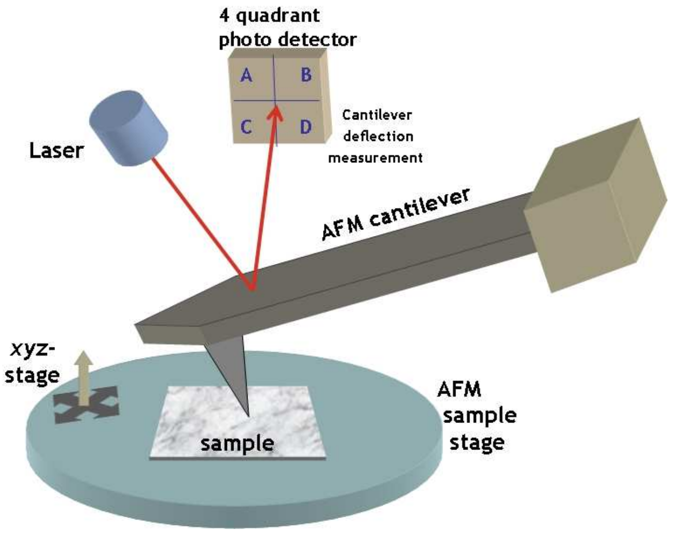

FIG 1A. Atomic Force Microscope Illustration by Kristian Molhave on Wikipedia[2] from Reference [2]

The basic setup of the instrument closely resembles that of an AFM in tapping mode, but with a direct optical fiber sensor (as opposed to a laser reflecting off of a cantilever) monitoring the tip movement and with an extra AC bias voltage that is connected to an electrode beneath the dielectric sample. [2]

The clever part of this setup is the isolation of the AC bias frequency through a second lock-in amplifier which is able to distinguish between charge and sample topography. As the tip passes over a charged area, then Qs (charge of the sample) will be non-zero which means then that the force gradient will add in the sine term of the AC bias signal and the resultant phase will reflect the polarity of the charge.

Electrically, this process has some similarities to how Keithley CV (Capacitance - Voltage) packages work. Four probes ganged in pairs of two are connected to a capacitive sample with a sourced DC voltage time swept across a user-selectable range while an AC bias signal rides on top of the DC signal. The resulting graph shows the change in capacitance (charge capacity) at different DC values.

For the dielectric, PMMA (Poly methyl methacrylate also known under brand names such as Lucite, Plexiglas, etc.) was chosen, which is a broad family of thermoplastic polymers used in everything from optical disks to submarine windows. [3]

II. EXPERIMENTAL RESULTS

After the tip contacted the surface of the PMMA for a few seconds, what was apparently a triboelectrically induced charge was left behind on the sample in a radius roughly 10 microns across. This is in comparison to the tip radius (that was alluded to towards the end of the paper) of 100 – 200 nm, so the charge area left behind was much larger by 3 orders of magnitude.

[The calculated surface area of the charge was ~ 80 microns in comparison to the tip contact area of approximately 0.07 microns]

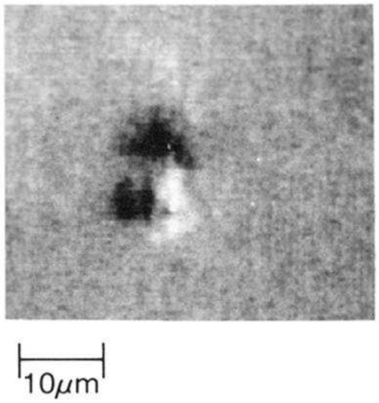

FIG. 3. The charge image of the PMMA surface after it had been contacted by the Ni tip. The black regions are negatively charged and the white regions positively charged.

FIG. 3. Bipolar Charged area ~10 um from Reference [1]

This charged area exhibited both positive and negative polarities coexisting side by side.

III. SIGNIFICANT RESULTS

The charge resolution of the modified force microscope is impressive, with 0.02 VDC corresponding to 3 +/- 1.5 electrons. This offers the capability of measuring a few subatomic particles with an output signal of tens of milliVolts, which is an amount easily seen by an inexpensive DVM. (Digital Voltmeter) Also, this is very close to the absolute limit of charge measurement, which is 1 electron or 1.6 X 10^{-19} Coulombs.

This is a notable improvement over the earlier version of the electrostatic force microscope constructed by Stern and Rugar; in their paper they describe the ability to detect as few as 100 electrons with a spatial charge resolution of about 1 micron.[8]

Not only was the resolution itself remarkable, but it also revealed the presence of bipolar charges being left at the point of contact. These charges would last for a period of several days, during which they would slowly dissipate. The bipolar charge pattern was unexpected due to the extent of the area covered by the charges. Given that the conditions of surface resistivity were high enough to allow for the charges to expand across the surface, then they should also allow for the charges to recombine, which they did not do immediately.

This particular finding underscores the need for higher resolution imaging in order to document more detailed data which can assist in formulating more accurate theories. Cruder instruments such as an electroscope can only measure area charge on the order of millimeters at best, in which case the bipolar nature of the charge would be lost in the "noise" of an overall net charge.

A more extreme analogy would be tasking the ancient Greeks with discovering the components of an atom using only a mortar and pestle. But despite the relative lack of modern instrumentation, certain philosophers and thinkers came astonishingly close to the truths of the universe; in some cases even thousands of years before there was equipment and methodology developed to verify these theories.

Mankind had to start somewhere and wrong ideas often lead others to the right answer.

As an additional note, according to the previous work by Stern and Rugar, PMMA and sapphire were capable of holding a charge for up to weeks, whereas other materials such as mica and quartz would lose this charge within minutes and/or seconds. Therefore the composition of the sample material greatly governs the charge behaviors and longevity.[8] This also undoubtedly led to the selection of PMMA as a suitable test material.

The authors speculated that an electrical breakdown at the tip as the surface is separated from it may explain the residual bipolar charges as a result of overcompensation from the possible resulting discharge. While the paper was not clear on the matter of overcompensation, what seems to be implied is that a nano-sized lighting bolt is ejected in order to balance charge, but the resulting spike in energy may dislodge electrons (and leave resulting holes) in an uneven surface distribution.

If such a discharge were occurring, it would be interesting to see a time lapse view of the signal as the tip is moved away from the surface, though perhaps such an event would be so brief in duration that it may have been beyond the time domain resolution of the equipment.

However, a figure from the earlier Stern and Ruger paper did show a time lapse progression of charge dissipation on PMMA over the period of an hour starting at the top left and gradually dying off. The dimensions of the inset image are 24 microns X 5 microns.

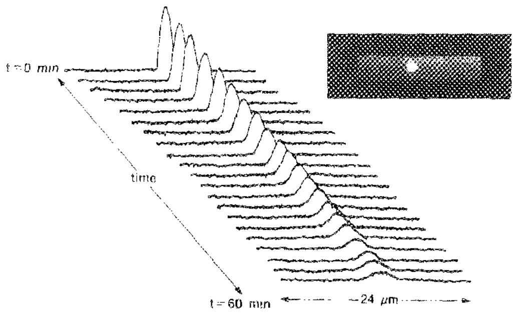

FIG. 2. Contours of constant force gradient taken at 3 min intervals over the center of a region of deposited charge on PMMA. The initial peak height corresponds to a 0.5 μm increase in tip-to-sample separation. Inset: Gray-scale image of a negatively charged region. The two-dimensional scan range is 24 μm × 5 μm.

FIG. 2. Force Gradient vs. Time Graphic from Reference [8]

IV. MAJOR CONCLUSIONS

Did a deeper understanding of the triboelectric effect on metal-insulator result from this methodology? The paper focused mostly on the resolution achievement as a STEP towards solving the mystery rather than solving the mystery itself.

In this case, the sequential papers written by Stern and Rugar reflected an EVOLUTION of approach and refinement in their instrumentation. Not only in terms of detecting smaller amounts of charge (fewer electrons) but also in imaging smaller areas of charge. (as little as 200 nm across as opposed to the 1 um resolution of their earlier instrument)

The experimental results of seemed to raise even more questions, particularly about the nature of the bipolar charge regions of contact. What about recombination? Is this the mechanism by which charges dissipate / decayed away from the PMMA? The fact that it took several days could imply external factors such as recombination with electrostatically charged dust particles and/or water adsorption.

Further experiments with different environmental conditions and time lapse images would seem to be the next logical step for this work. A possible precaution would have been to have conducted the experiment in a sort of clean room which could filter out potentially charged dust particles.

V. DISCUSSION POINTS

Q: What nanoscience or nanotechnology principles have

been applied in the work?

A: Nanoscale instrumentation and the electrical properties of materials at the quantum scale.

Q: What makes the work nanoscale?

A: For a work to qualify as nanoscale, at least one of three structural dimensions must be in the sub 100 nm regime. This is an example of a 1 – 3 D nanoscale implementation as at least the Z height above the sample must fall within this range for the instrument to work. The scanning in X and Y may also fall into the nanoscale depending on the resolution sought.

While the smallest defined areas of charge were in the 200 nm range, the technology required to acquire this data were nickel tips about 150 nm in radius with a scanning height (tip to sample distance) of only 50 nm high, which puts at least the Z dimension in the nanoscale regime.

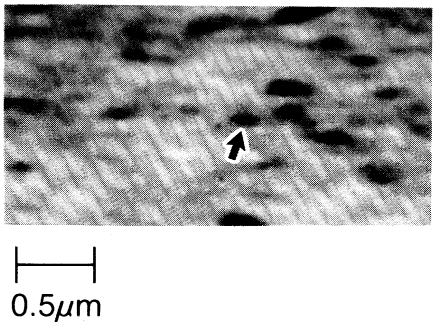

FIG. 4. The charge image for an oxidized Si surface after it had been bombarded by 0.3-μm polystyrene spheres. The smallest, well defined, negatively charged (black) regions are approximately 0.2 μm in diameter. One such region is marked by the arrow.

FIG. 4. Resolution of Charge (200 nm) from Reference [1]

Q: What fields of study are applied in the work and how?

A: Mechanical engineering is used in the design of the apparatus; specifically in the piezoelectric bimorph drive which moves according to the applied oscillator signal and in the Z drive for the scanner which maintains proper tip to sample height.

Material science played a role in the design/geometry of the scanning tip and selection of the dielectric sample for proper planarity, stability and resistivity.

The principal of optical physics was utilized in the employment of an optical-fiber interferometer to detect small changes in the lever motion that follows the tip oscillation.

Electrical engineering knowledge was critical for the control of the scan head by piezoelectric drives, design of the oscillators and frequency selection as well as the demodulation of the sensor output for proper amplifier lock-in and charge signal measurement.

Q: What history impacts the work?

A: The invention of the STM (Scanning Tunneling Microscope) in 1981 gave rise to the science of SPM.[4] (scanning probe microscopy) The digital control of the tip / sample scanner and display were made possible by the advances in computing at that time. (ENIAC or other vacuum tube based technology would probably not have been feasible)

Only a few years before this publication, the AFM (Atomic Force Microscope) was invented in 1986. [3]

Q: What nanotechnology was used in conducting the work?

A: Force microscopy (similar to AFM tapping mode) and the imaging of electrostatic charge through nanoscale Z tip to sample heights.

Q: What nanotechnology solution might be enabled by the work, perhaps in the next decade or so?

A: Given that this paper was originally published in 1989 and it is now the year 2010, this is could be answered by that has arisen out of this work in the past twenty years and / or what may continue to arise. The ability to image charge in a sample is one of many analysis methods in research, research & development and pure production scale FA (failure analysis) in the $250 billion dollar per year semiconductor industry.

The apparent descendent of this work appears to be the EFM, or Electrostatic Force Microscope. It operates on the same principle as a non-contact AFM and takes advantage of the fact that electrostatic forces have a longer range (up to 100 nm) than Van der Waals intermolecular forces.

Q: How might the work impact society?

A: As discussed above, it already has in by enabling the continuation of Moore's Law (which states that the number of transistors for a given device can double every 18 months) through improved failure analysis techniques.

Given the shrinking geometries of semiconductor features , SET (Single Electron Transistor) measurements and leakage are a critical research arm to further condense computing power. The extremely high mobility of graphene makes it a strong candidate.[11]

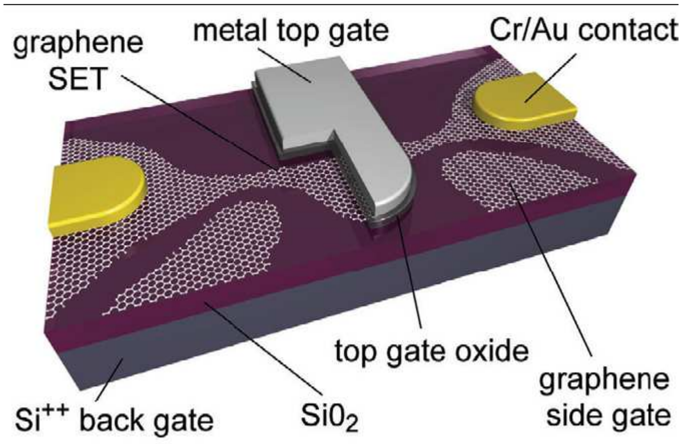

FIG. 5. SET Model from Reference [11] "Graphene single-electron transistors" paper

Through research in ESD, (Electrostatic Discharge) damage to sensitive electronic devices such as MOSFET gates may be further investigated so that additional protective features may be built in.

Developing improved materials for measurement cables such as low noise tri-axial cables can enable lower noise floors for more sensitive signals. (The Keithley 4200 C-V package can measure down into the attoFarad range or $1X10^{-18}$ F) Triboelectric charge caused by bending a cable is one of the many forms of noise that can limit the highest signal to noise ratio.

While coming up with applications, I thought about using electrostatics in conjunction with pharmaceuticals as a type of potential delivery system for biomedical particles. While perusing the Journal of Electrostatics, I found a paper entitled: "Triboelectric Charging and dielectric properties of pharmaceutically relevant mixtures" with implications of determining the moisture content of drug constituents.[5]

Also while researching PMMA, it is now being used in biotechnology for microfluidic lab-on-a-chip devices which employ channels that are 0.1 mm wide for liquid channels. Perhaps altering charge in smaller channels could be an alternate form of microfluidic switching. Furthermore, it was discovered in World War II that PMMA is somewhat biocompatible as shards of it lodging in the eyes of pilots did not experience tissue rejection.[3]

VI. FINAL COMMENTARY

There were some apparent irregularities in this publication that could have been addressed and some improvements which would have clarified and strengthened the data:

1) A photograph of the apparatus with appropriate labeling would have been a good illustration in parallel with the block diagram.

2) Graphs of the signal output could have clarified some concepts of how the two frequencies appeared to the Servo Electronics and the Lock In.

3) The paper only showed representations of the surface after the charge had been applied. Images of before the experiment and in a time lapse sequence (as shown in the figure from their earlier work) after would have made the experimental results more compelling.

4) A legend or scale that corresponded with the magnitudes and polarities of charge would have given a more complete X-Y data set.

5) It would have been helpful to mention the tip diameter during the description of the equipment setup so as to better appreciate the charge dispersion phenomena. The fact that the charged area and the wire diameter were both 10 microns was a bit confusing, and it was only further along in the paper that the tip radius was mentioned.

6) The authors mentioned the bipolar charges at the point of contact never being observed before in tribocharging experiments, and then seemingly contradict themselves in the same paragraph by stating that Lowell and Akande found bipolar distributions of charged regions.[6]

7) Certain control measures did not seem to be closely observed in the experiment. The authors mention variations in temperature, humidity and were a bit vague when mentioning the contact time with the sample was only a "few seconds." While such variables may be only 2nd order effects or less, any perceived looseness in a scientific paper can leave openings for doubt about the care with which the experiment was conducted.

8) While there are numerous pieces of information which could have been added to the paper, it is generally recognized that researchers may purposely keep some details vague in order to maintain future IP (intellectual property) opportunities.

ACKNOWLEDGMENT

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FIGURE REFERENCES

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