Multi-Electrode Localized Electrochemical Deposition MELED

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Herein we attempt to extend the versatility of Localized Electrochemical electro-Deposition by experimental analysis of deposition produced by a multielectrode probe. Unlike previous devices that implement LED, the device here uses a multielectrode end tool that consists of a linear array of platinum-iridium wires, 25 μm in diameter. While variations in electic potential across the electrode array did produce mulimodal deposition, the rate of this deposition and potential for inter-electrode short circuit limits the usablity of this process. The cental problem is the extreme nonlinear relationship between electric field strength and deposition rate at the surface of the substrate. Futher research is required to deterimine if single electode deposition field refinement is possible and if a multielectrode probe provides any advantagous sensing capiblities.

I. MOTIVATION

Microstructure construction via Localized Electrochemical Deposition (LED) was first proposed little more than a decade ago[4][1]. Since that time, several experiments and devices have used this technology to successfully implement LED. So far, many complex microstructures have been constructed. These include springs, walls, and tubes (see figure 1)[1]. Much research has also been spent in an attempt to produce higher qualitity depositions. It has been found that increased ion concentration and the use of proprietary plating additives can reduce the porosity of grown copper columns[3].

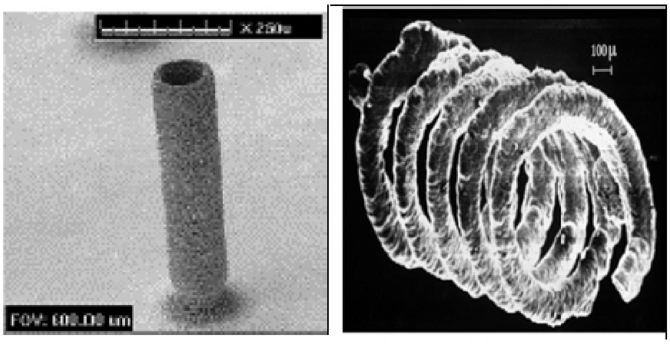

FIG. 1: Complex structures created using single electrode LED.[1]

Despite these successes, the methods of LED still remain in the experimental and development stages. Issues that limit this method are repeatability, resolution, and the geometric complexities of structures constructed. It is highly desirable to surmount these challenges because of the geometric capabilities available with LED microfabrication[1]. Multi Electrode Localized Electrochemical Deposition (MELED) is an attempt to overcome some of these challenges by providing extended multimodal sensing and deposition fields.

II. RATIONALE

In the well established LED setup, a micrometer scale conducting wire (electrode) is placed in an electrolytic solution within less than one electrode wire diameter away from the conducting substrate. The application of a electric potential between the the electrode and the substrate produces an extremely large and localized electric field (10^5 V/m)[6]. The electric field exerts a force on the ions causing them to migrate towards the surface of the substrate. Previous research has established that the electrochemical deposition profile conforms to the local electric potential gradient at the surface of the substrate[7].

For deposition to occur, metal ions (Cu 2^+) in the electrolyte must move through the solution, through the double layer of ions that surrounds the charged solid substate, and bind to the metal crystal substrate. Logically this implies that the eventual binding location of the ion is dependent on more than simply the local electric field. In total there are four factors that determine the mass transport of ions to the substrate. These factors are diffusion, convection, induction and migration. Although all these factors effect the quality of deposition, experimentation has determined that *migration*, ion motion produced by the electric field, determines the *rate* of deposition.

$$\overline{n} \cdot v_s = \frac{M_k i_n}{\rho z F} \tag{1}$$

Based upon previous assumptions, deposition rates at the substrate can be approximated locally using Faraday's law (Equation 1)[7]. This equation gives the velocity of growth (v_s) normal to the substrate surface for the deposition current density i_n. While such a formulation is desired, the difficulties in computing the current density makes this equation more useful in qualitative analysis of experimental data rather than a modeling of the natural process[7]. Although attempts have been made to simulate the LED process, complixites such as the double layer and deposition crystalization places limits on the prediction of the exact deposition profile.

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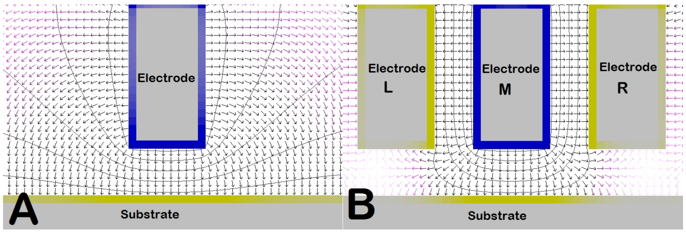

FIG. 2: Rational behind MELED. Case A is the field surrounding a single electrode that is near the surface of the substrate. Case B is the same electrode now surrounded by other electrodes with opposing potentials. This causes a dramatic change in the local field near the substrate and would appear to increase the locality of the field strength.

The rationale behind MELED is the realization that the effective electric field at the substrate can be manipulated directly by the use of mulitiple electrodes at different potentials (see figure 2). Based on the previous discussion, the goal of this manipulation is to change the local deposition rate. Prior to experimentation three hyposthises were formulated to verify general assumptions about MELED.

1. Changes in size and relative position of deposition can be produced by a variation of static voltages on the electrodes.
2. Changes in the deposition shape can be produced by electrode voltage variations with respect to deposition height.
3. Sensing of newly formed depositions can be achieved by detecting variations in current vs applied voltage through each electrode while passing the probe over the substrate.

Many experiments were carried out in attempt to verify these claims, the results of which appear in this paper. Although claim 1 was definitly verified, deposition rates and interelectrode short circuits make MELED unusable for case of the setup presented here.

III. SETUP

A. Substrate Preparation

The substrate required preparation not only to establish deposition but also for a baseline in the analysis phase. In all of these experiments a copper substrate was used. The edge of deposition was polished like a dull knife. Meaning that there was a very flat 100μm thick edge to deposite microstrures along. This allowed for a reduction in dimension of the experimental problem to that of a 1D heightfield. It also allowed for the viewing and measuring of the microstructures with a optical microscope by placing them upon a glass slide. As suggested by previous experiments, the edge was prepared via 600 grade waterproof polishing paper to provide a 1μm smooth horizontal baseline[3].

B. Apparatus

The appuratus was only required to produce deposition profiles to verify the general claims in this paper. As such, the device that was constructed had only two degress of freedom. These axis were controlled via linear stages connected to stepper motors. This motors could be stepped manually or by microprocessor control. A series of glass slides sandwiched togther functioned as both the basin for electrolye solution and the substrate sample holder. The probes where constructed by arranging one and three 25μm Pl-Ir wires on a glass slide under a light microscope. The final configeration of these wires was made fast by sandwiching another glass slide over top and using clear epoxy as a binding agent. See figure 4 for multielectrode arrangment . The result was a glass probe that could move in 2D but was constrainted to always be above the flat copper substrate in the third dimension (see figure 3).

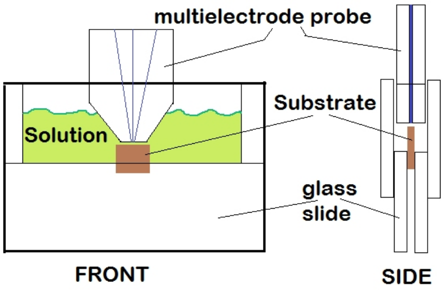

FIG. 3: Experimental setup of probe, solution basin and substrate holder.

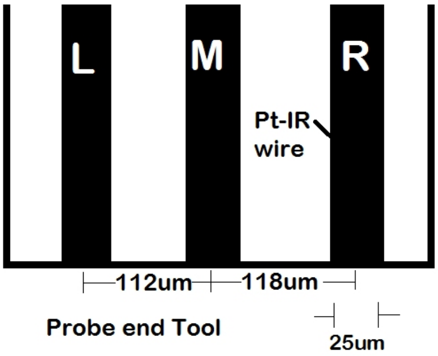

FIG. 4: MultiElectrode probe end tool. Dimensions experimentally measured. L R and M labels for Left Right and Middle electrodes respectively.

C. Plating Solution

The solution for electrochemical deposition is composed of 500 mol/m^3 copper sulfate and 380 mol/m^3 sulfuric acid[6]. The basic chemistry of the electro plating process appears in figure 5. The sulfuric acid is merely acting as a catalyst.

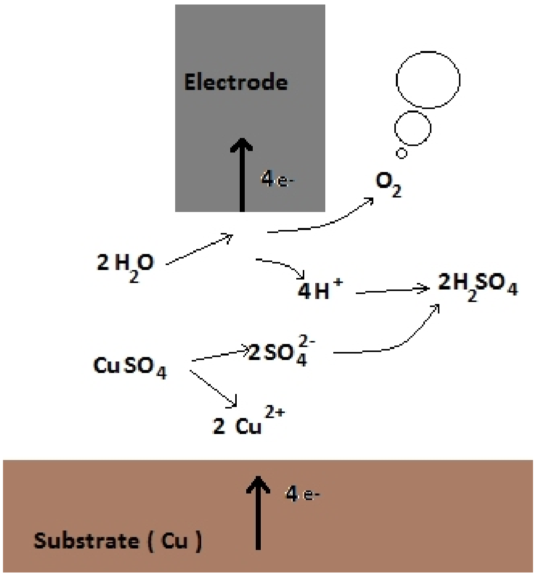

FIG. 5: Chemical process underlying copper electroplating.electrode LED.

D. Control and Measurement

During all experimentation the stepper motors were used to position probe and substrate. The steppers base step is known to be 200 steps per revolution. Based on multiple measurments, each step corresponds to 6μm±0.5μm. Manually positioning was done with base steps, thus resulting in low accuracy. Positioning with microcontroller can be done in up to 24nm precision at 50,000 steps per revolution. During manual control current and voltage measurments were made with standard mulitmeters. The accuracy of these readings greatly exceeded their stablity thus uncertianty was based on variations in value. The DAQ microprocessor used (NI-USB-6008) is limited to 12 bits accuracy but this was only used when stepper motor control was required.

All analysis of microstuctures created was performed using digital photography via a standard optical microscope. By measuring the pixel dimensions of known size objects a μm/pixel value was computed for each image. This gave dimensional uncertianty to within %4, not including inaccuracies with interpixel measurements.

IV. PROCESS AND RESULTS

A. Testing

Prior to any MELED expertimentation a series of tests were preformed with the single electode probe to confirm expectations based on previous work. The first test involved merely deteriming the conductivity of the solution at various applied potentials when the probe was seperated from the substrate by effectively infinite distance. The results of this experiment appear appear in Table 1[2].

Table 1:Current and Deposition dependent on Voltage.

E(V)	I(mA) ref.	Rate(μm/min) ref.	I(mA) Verified
2.8	0.008	<5	0.117
3.0	0.090	<40	0.177
3.2	0.120	86	0.250
3.5	0.225	332	0.378
3.8	0.300	741	0.508
4.0	0.390	751	0.612
4.5	0.520	867	0.726

The second test was intended to simply to establish single probe deposition. The probe was placed within ≈6μm of the substrate surface and a voltage of 4.00V±0.02V was applied between the substrate and the probe. At some point current rose abruptly and a short circuit resulted. By manually moving the probe up in steps of the stepper motor when the short occured a very small low quality microcolumn was constructed (see figure 6). This positive result concluded the reference tests.

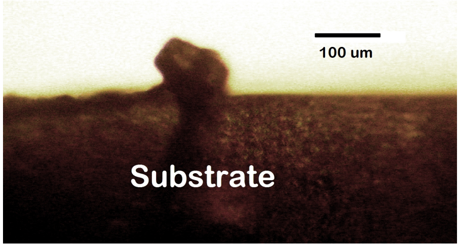

FIG. 6: Very small microcolumn created using a single electrode probe. The height of this column is about 60μm.

B. MultiModal Deposition

A set of experiments were carried out to determine if variations in potential on each electrode could produce multimodal deposition and what the nature of deposition is for the field interference. It was first hypothesised that the potential on L/R electrodes of the three electrode probe might screen the potential of the M electrode. This idea was tested for the probe head set at infinite distance from the substrate. The results of this test appear in Table 2. As can be seen in the table the current through the M electrode is actually larger for voltages that would be preceived as shielding. When looking at the probe post-experiment plating had occured on the L/R electrodes. This explains the high current for what should be shielding potentials. This undesired plating prevents the application of any sustained relative potential between electrodes that exceeds the electrolye voltage threashold.

Table 2: Voltage on L/R vs Current through M.

E(V±0.02V) L/R	I(mA±0.05mA) M
0.0	0.252
0.52	0.188
1.05	0.177
1.58	0.172
2.03	0.149
2.54	0.162
2.96	0.110

A second experiment was carried out to determine the viability of claim 1. In this experiment the three electrode probe was zeroed at the surface of the substrate and then was manually set to a distance of 90μm$\pm 4\mu$. Voltage on L/R electrodes was set to 3.64V±0.02V and the M electrode was allowed to float (aka not connected). In the second trial the M electrode was set to 2.22V±0.02V. The resulting depositions for both trials appear in figure 7.

The trial 1 establishes mulitmodal deposition. Maximum height of deposition is 60μm$\pm 2\mu$m. This corresponds to a deposition rate of 0.067μm/s in an electric field strength of 4.02×10^4 V/m. This is roughly one tenth the normal electric field used in standard LED but corresponds to one hundredth the normal deposition rate. This indicates the high degree of nonlinearity between potential gradient and rate of deposition.

The second trial had nearly identical deposition rate (0.04μm/s) of the lowest point between the L/R electrode. However the deposition rates at the peaks was greatly different between the two trials. The deposition rate of the peaks on trial 2 is estimated to be 0.107μm/s. This increased rate of deposition indicates that the applied potential at M might be increasing the electric field density at electrodes L and R.

Based upon these results, experiments were conducted to futher determine what effect multimodal fields have on deposition. A two electrode (dual) probe was placed 30μm away from the substrate surface. Three deposition trials were conducted the results of which appear in figures 8, 9 and 10. In trial #2 the 2.81V potential and 210 seconds was selected based upon previous experiments that resulted in shorting occuring between the two electodes or substrate.

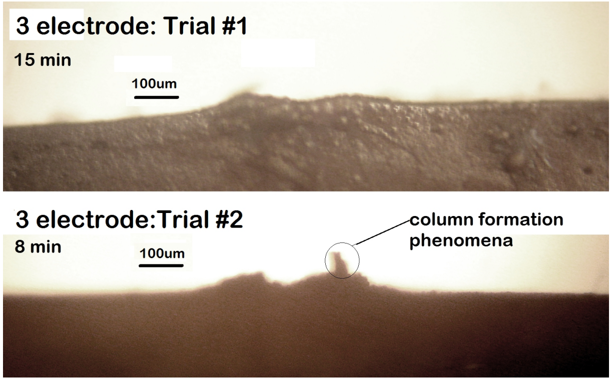

FIG. 7: MultiModal deposite formation via multielectrode probe. Electrode distance was confirmed to be the peaks in deposition height. In trial #2 the deposition short ciruited due to the rapid onset of growth via column formation on the R electrode.

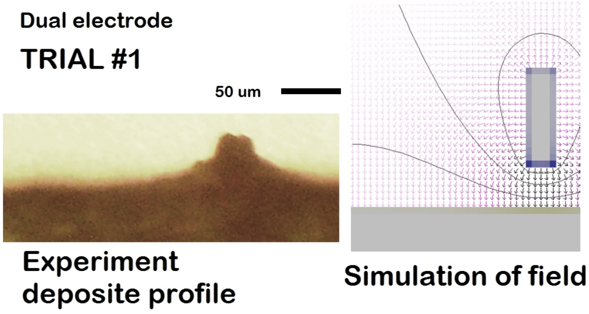

FIG. 8: Single electrode deposition from a height of $\approx 30\mu$m. In this preliminary trial the M electrode was set at a potential of 3.62V and the L electrode was allowed to float (aka not connected). The result was single modal deposition that later led to column formation phenomena.

C. Substrate Scanning

Since electrodepostion is such an inaccurate process it is highly desired to determine current substrate profile to use predictive corrective methods to achive final deposite. It was first hyposthesised that scanning across the substrate at less than electrolye potential threashold would produce fluctuations in current that would correspond to deposition height. However this was found experimentally to not be the case. There is no noticable increase in current as the probe descends to the surface of the substrate at less than threashold voltage. At greater than threashold voltage there is an extreme nonlinear corrospondence between distance from substrate surface and current through electrode. This nonlinearity makes it nearly impossible to perform surface scans for any distances much less that electrode diameter.

Table 3: AC at distance D from substrate.

D(μm ±10%)	I(mA±0.1mA)
0.0	1.2
6	1.0
12	0.5
18	0.4
24	0.35
∞	0.35

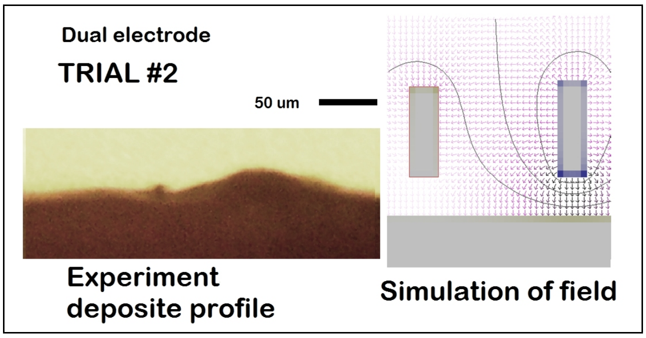

FIG. 9: The field interference between two electrodes (L and M of the multiElectrode probe) and the resulting depostion for a duration 210 seconds. For this trial L was set at 2.81V and the M was set at 3.62V. This is in contrast to trial #1.

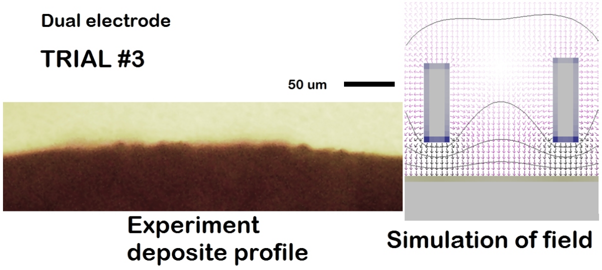

FIG. 10: Additive field interference for two electrodes both set at 3.62V. The deposition profile is unexpectedly broad with little evidence of multimodal structure.

In order to overcome the high degree of nonlinearity in sensing a different approach was taken using a, zero DC offset, sinisodial alternating voltage (AC) as the applied potential. The AC is intenteded to reduce the potential barrier at the electrode and substrate caused by the double layer. The AC version scanning will also prevent unintended mutilation of newly formed deposite. The AC scanning test was done on a flat substrate using a single electrode for voltages between 0.5V-4.0V. The AC frequency was set to 1kHz as suggested by reference experimentation[4]. During the scanning process a small amount of brown colloidal particles precipitated out of solution near the exposed electrode. The colloidal sludge appears to be copper micro particuli generated by the action of the AC. It is unknown as to the actual stucture of this copper sludge but it does present a challenge since it remains suspended out of solution long after the AC has been shut off.

The scanning AC exibited slightly a less nonlinear relationship for the height of probe vs current than the DC version (see Table 3 for 1.0V AC trial). Yet, still, currents at greater than one electrode diameter are equivalent to currents at infinite distance from substrate.

D. Discussion

The results of experimentation clearly indicate that multimodal stuctures can be generated in parallel with multielectrode probes. The difficulty remains in quantifying the interaction between field interference and deposition produced. It was expected that the interelectrode potential would have a much greater effect on deposition profile. However, the experimental results do not appear to indicate any such effects. In the tests involving three electrodes the deposition in the valley between the L/R electrodes does not appear to be negitively effected by the applied potential at M as the rates are the same for both trials. The experiments conducted with the dual electrodes also do not indicate any measurable interelectrode field effects that negitivally effect deposition rates. In figure 9 it appears that the 2.81V on the L electrode is contributing to a broading of deposition beneth the M electrode (In contrast to figure 8). It would appear as though the multiple electrodes can only have a additive influence to deposition growth. This essentially means that multielectrode probes produce no additional functionaliy over single electrode probes used in standard LED.

It is important to note that the conclusions here are only based upon the experimental setup used, in particular the multielectrode probe used in the tests. Though negative electric field effects on deposite growth could not be noticed for dual electrodes separated at a distance of $\gtrsim$2 electrode diameters this does not indicate that a smaller seperation would not exibit these effects. However, interelectrode short ciruits are common at the current separation parameters and it can only be speculated that these shorts would increase in rate as the seperation distance is reduced. A proposed mechanism for this senerios is depicted in figure 11. A smaller distance between the electrodes would mean a greater electric field densitiy (V/m) and therefore a higher depostion rate on the offending electrode. While switching between electrodes to reverse the undesired plating might be possible it remains to be seen if this could be made into a practical process.

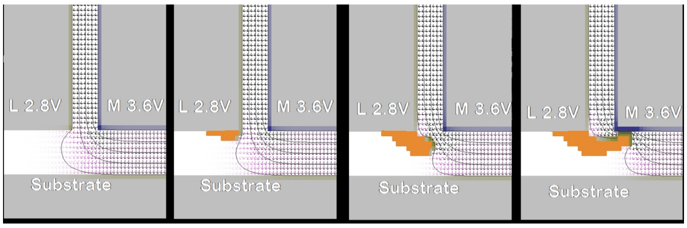

FIG. 11: Suggested mechanism for interelectrode short curcuit between electrodes of different relative potential. Moving from left to right, the deposition (shown in light brown) on one electrode follows the field which grows till contact on the adjacent electrode. This phenomena is noted even for electrode separation $\gtrsim$3 electrode diameters.

The initial experiments were carried out with the hopes of establishing the three initial claims. Measurements using a single probe, both AC and DC, ruled out claim 3 for having any practical significance and the mulielectrode scanning experiments were not carried out. Since intention of claim 2 was dependent upon the postulated negative rate effects of interelectrode fields the establishment of this claim is inconsequential. The possible rates of deposition for time dependent multimodal deposition makes such experiments difficult and error prone.

The extreme nonlinearity of deposition rates with respect to electric fields is the most surprising observation made throughout all experiments in the presented study. This indicates that complexities such as the double layer are having a much greater effect on crystal growth than initially thought. Reference experiments suggest that 10^5V/m at a distance of 3μm achieves high quality rapid deposition[5][6]. Since the double layer can extend up to several micrometers around a charged solid in solution this data indicates that the mechanism of rapid deposition physically interferes with double layer formation. The original hypothesis about MELED relied heavily on the existance of a linear relationship between field density and growth rates. Thus, unfortunatly, the experiments here show negitive results for interelectrode depostion interference.

V. CONCLUSION

Use of multielectrodes for microstucture formation in LED cannot be recommended here as no futher functionality was established over the traditional single electrode process. While the first of the MELED claims, multimodal shapes, was experimentally produced, interfield interference effects on deposition could not be established in any quantitative manner. Increasing the proximity of the electrodes might increase the interference effect, however this would also greatly increase the rate at which a interelectrode short circuit would occur. Since surface scanning at greater than electrode diameter appears to be impossible, single electrode scanning can produce the same measurments as would a multielectrode probe. Also, futher research is required to determine what effect AC current has on the electrolyte since the brown copper sludge produced in the solution should be cause for concern. This paper cannot fully rule out the use of multimodal fields to produce tip refinement but does stress interelectrode short circuiting as a major obstacle to achiving this effect. Finally it is important to note that these conclusions only concern multielectrodes for producing interfield effects. It remains to be seen wether parallel LED, with independent electrodes, can be transformed into a versatile means of microfabrication.

[1] Said, R. A., “Localized electro-deposition (LED): the march toward process development”, Nanotechnology, 15, (2004): S649-S659.

[2] Soel S. K., “Localized Electrochemical Deposition of Copper Monitored Using Real-Time Xray Microradiography ”, Advanced functional materials, 15, (2005): 932-937.

[3] El-Giar, E. M. Said, R. A. ,“Localized Electrochemical Deposition of Copper Microstructures”, Journal of The Electrochemical Society,, 147(2), (1999): 586-591.

[4] Madden, John D., “Three-Dimensional Microfabrication by localized Electrochemical Deposition”, Journal of Microelectromechanical Systems , 5, (1996): 24-32.

[5] Said, R. A., “Adaptive Tip-Withdrawal Control for Reliable fabrication by Localised Electrodeposition”, Journal of Microelectromechanical Systems, 13(5), (2004): 882-832.

[6] Lin, C. S., “Improved Copper Microcolumn Fabricated by Localized Electrochemical Deposition”, Electrochemical and Solid-State Letters, 8(9), (2005): C125-C129.

[7] Said, R. A.,“Microfabrication by localized electrochemical deposition: experimental investigation and theoretical modeling”, Nanotechnology, 14, (2003): 523-531.