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BIOLOGICAL MOLECULES USING FIELD DESORPTION
MICROSCOPY AND FIELD ION MICROSCOPY OF DIAMOND

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CURRENT RESEARCH TOWARDS
IMAGING BIOLOGICAL MOLECULES USING FIELD DESORPTION
MICROSCOPY AND FIELD ION MICROSCOPY OF DIAMOND

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I. PRESENT RESEARCH AND BACKGROUND MATERIAL

Work is currently in progress investigating the possibility of imaging large organic and biological molecules in a modification of field desorption microscopy (FDM).⁽¹⁾ A field ion microscope (FIM) is being converted to an FDM by installation of a chevron channeltron electron multiplier array (CEMA), commonly called a chevron channel plate.⁽²⁾ The chevron CEMA has a gain of over 10^7 and can thus produce enough light from single field desorbed ions to be readily photographed. In field desorption microscopy,⁽¹⁾ a fine metal tip is subjected to positive electric fields high enough to field evaporate the metal as positive ions. These ions follow the field lines radially away from the tip and strike the CEMA. One therefore gets a greatly magnified image of the tip by field evaporated ions. The magnification, M equals $R/\beta r$ where R is the tip to screen distance, typically 5-10 cm, r is the tip radius, typically 100 - 1000 Å and β is an electrostatic compression factor due to the field lines being slightly compressed at the tip. Magnifications of over 10^6 are easily obtained and at low temperatures, metal atoms field evaporating from adjacent lattice positions on the tip will strike the CEMA within separate areas. Therefore the resolution is less than 3 Å.

A large amount of work has been done attempting to image molecules on tips by FIM and field emission microscopy (FEM).^(3,4) In FEM, the resolution is normally limited to about 25Å due to the large transverse momentum of the emitted electrons. The images of molecules

obtained have therefore been of low resolution and hard to interpret due to effects which are still controversial in interpretation.^(3,4) By reversing the field and adding an imaging gas one would hope to be able to get high resolution FIM images of adsorbed molecules. It turns out however that the molecules are pulled off the tips in fields of approximately +100 to +200 MV/cm.^(3,4,5) In FEM which uses fields of -30 to -50 MV/cm this is manageable. In FIM, the best resolution is obtained using helium imaging gas which has a best imaging field (~ 440 MV/cm) well above the desorption field of the molecules. By substituting lower ionization potential imaging gases, the field can be lowered. Thus FIM images of molecules have been obtained with H_2 and Hg^(3,4) which require fields of ~ 200 MV/cm and 80 MV/cm respectively. The resolution is not very good however; one only sees diffuse patches of light with no structure. Even if one gets some direct image of a molecule via FIM, the fields are so high that the molecule will be severely distorted and possibly dissociated. The imaging gases which field ionize at low fields all produce low resolution FIM images. In addition, these gases are usually highly chemically reactive at the imaging field.⁽³⁾

Other attempts have been made to shadow molecules on a tip with vapor deposited metal atoms⁽⁵⁾ or encasing molecules in an electroplated deposit on a tip.⁽³⁾ By field evaporating the deposit until a cavity with an enclosed molecule is uncovered, one might hope to see an outline of the molecule by imaging of the surrounding matrix atoms. Again however, the resolution is not very good because of the uncertainty of the metal atoms to reliably encase the molecule.

II. EXPERIMENTAL METHOD

We are attempting a different technique in which one can hope to combine low fields and high resolution. The field evaporation fields of some alkali metals have been calculated to be below 50 MV/cm.⁽⁶⁾ It is possible that this value can be lowered even more if H₂ gas is present, by hydrogen promoted field evaporation.⁽³⁾ If a large molecule is on the surface of an alkali metal coated tip, we hope to field evaporate the metal and thus throw out a shadow of the molecule. At these low fields, the binding force of the molecule to the metal should, in principle, keep it attached while the surrounding metal field evaporates. It is also possible that metal will field evaporate underneath the molecule and accelerate through it if the molecule has an open structure and thereby show some internal molecular structure. Since the alkali metals have such low ionization potentials and are in a closed shell configuration when in the +1 field evaporation charge state, it seems unlikely that the ions will chemically react with the molecules at the low ion energies present immediately above the tip. The resolution of the image is expected to be of atomic or near atomic dimensions.

The micrographs will probably be made in the following manner. A tungsten or platinum tip will be field evaporated to a smooth endform of radius 500 - 1000 Å. In vacuum, the tip will then be dipped in a molten bead of alkali metal which has biomolecules inside or on the surface. The tip, with the metal coating, will then be field evaporated while shadows of surface molecules are looked for. By taking a motion picture of the evaporating metal pattern and integrating the appropriate

frames, the molecular shadow image will hopefully be obtained. It is uncertain whether it will be better to field evaporate using D.C. or by repetitive nanosecond pulses.⁽³⁾ The alkali metals which are under consideration are cesium, rubidium, and potassium. Sodium and lithium have melting points which are high enough that thermally induced damage to the molecules during deposition is likely. At low temperatures, the alkali metals get much stronger than at room temperature, as is characteristic of BCC structures. Thus, it isn't expected that there will be problems with the metals yielding at the relatively low evaporation field stress.

The proposed microscope appears to have several attractive features. It has the relatively low field needs of FEM while still possessing the high resolution of FIM. Another feature is that while internal structure may be obtained with high contrast as is possible with a transmission proton microscope, it doesn't have the problem of radiation damage to the molecules by high energy ions. Of course, this same problem plagues electron microscopy which also has a contrast problem.

III. PREVIOUS WORK WITH DIAMOND TIPS

This work is an extension of previous attempts at molecular imaging using FIM of diamond tips which will be briefly described. This work started out as an attempt to produce FIM images of diamond. While graphite has been imaged previously, there is apparently no literature on diamond imaging.

Diamond tips were prepared by fracturing of flawed jewelry stones. Looking through the fragments, it was possible to sometimes find a fragment sharp enough for FIM imaging. The low temperature conductivity of the diamond was improved by irradiating the stones beforehand with deuterons at the 88" cyclotron. This process induces a green coloration due to electronic defect levels generated in the bandgap. While the images were irregular due to the uneven endform of the tip, certain regions showed some crystallographic regularity. It was noticed that it was easy to see atoms of adsorbed air moving around on the tip using He imaging gas. This is quite difficult to observe on metal tips. One possible explanation was that adsorbates are more strongly bound to the diamond surface than to a metal which suggested organic molecule imaging. Another possible explanation of the adsorbed air imaging is that the best imaging field of helium above diamond is less than it is above a metal tip.

Benzene was admitted at about 10^{-6} Torr to the microscope and it was possible to see fuzzy spots which sometimes appeared to be doughnut like suggesting we were possibly seeing the ring structure of the molecule. Napthalene was then tried and a few double rings were

observed. It is not clear at the present time whether these shapes represent the molecular structures or are artefacts which have been observed in other experiments.⁽⁴⁾ These questions will hopefully be resolved with further experimentation. A more complete report will be published on diamond imaging.

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