CHARACTERIZATION OF DIELECTRICS ON THE "TIPS OF NEEDLES"

John J. Hren, Victor V. Zhirnov, Zlatko Sitar, & Gregory Wojak
Dept of Materials Science and Engineering
North Carolina State University, Raleigh, USA

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Abstract: Ultra sharp needles are commonly used as electron sources in transmission electron and as probes in several scanning tunneling microscopies to characterize the atomic structure of surfaces and to probe local electronic properties. The physical basis for such measurements has evolved from much earlier research on field electron emission, which continues to this day. Recent attempts to develop miniature field emission based devices (i.e. Vacuum Microelectronics) have led to studies of thin dielectric coatings, which were found to considerably improve both the emissive properties and "ruggedness" of the emitters. In trying to understand the underlying Physics, extensive measurements have been reported on the energy distribution of the field emitted electrons (FEED), as well as the nanostructure of the coatings and their underlying interfaces with the needle shaped substrates (HREM). In turn, these techniques can also be employed more widely as an analytical strategy to determine the correlation between electrical properties and structure of nanometer scale films and particles deposited onto the tips of needle-shaped emitters. Further information on the same specimens can be also obtained by field emission microscopy (FEM), by using such probes in an STM mode, by studying the controlled effects of high electric fields on chemical reactions,or on the structure of ferroelectric or magnetic coatings, etc. Controlled deposits of either nanoparticles or films also offer a unique opportunity to directly probe property changes of a given material during the transition from classical to quantum An important advantage is the ability to achieve truly direct correlation between properties and nanostructure, since no further specimen preparation is required for HREM studies and specimens may be easily transferred from one instrument to another. Examples will be given of the information obtained from thin films & particle deposits of: nanodiamond, aluminum and boron nitride, and aluminum oxide.

Vrednotenje dielektričnih materialov na merilnih konicah

Ključne besede: AFM spektroskopija sile atomske, upodabljanje molekul, ločljivost atomska, SPM mikroskopija s sondo skanirno, AP sonde atomske, konice igel, spektrum površine, FEM mikroskopi emisije polja, FIM Mikroskopi z ioni polja

Izvleček: Ultra ostre konice danes pogosto uporabljamo kot izvore elektronov v transmisijskih elektronskih mikroskopih ali pa kot merilne konice v različnih rasterskih tunelskih mikroskopih z namenom vrednotiti atomsko strukturo površin ali meriti lokalne elektronske lastnosti vzorca. Fizikalne osnove tovrstnih meritev so se razvile iz zgodnjih raziskav poljske emisije elektronov, ki se nadaljuje še danes. Najnovejši poskusi razviti miniaturne elektronske komponente na osnovi poljske emisije (novo področje imenovano vakuumska mikroelektronika) so privedli do raziskav tankih dielektričnih prevlek, za katere se je ugotovilo, da bistveno izboljšajo emisijske lastnosti in robustnost emiterjev. Z namenom razumeti fizikalno ozadje tega pojava, je bilo opravljeno veliko število meritev energijske porazdelitve emitiranih elektronov (FEED), kakor tudi nanostrukture prevlek in površin pod njimi oz. podlag v obliki konic (HREM).Opisane tehnike lahko uporabimo tudi širše kot neko vrsto analitične strategije za ugotavljanje korelacij med električnimi lastnostmi in strukturo filmov in delcev na nanometrskem nivoju nanešenih na emiterje v obliki konic. Dodatno informacijo o vzorcih lahko dobimo z uporabo poljske emisijske mikroskopije (FEM), z uporabo istih konic v STM načinu dela, ko lahko študiramo kontrolirane vplive visokih električnih polj na kemijske reakcije ali celo na strukturo feroelektričnih ali magnetnih prevlek. Kontrolirani nanosi bodisi nanodelcev ali filmov ravno tako ponujajo enkratno priložnost direktne meritve sprememb lastnosti materiala pri prehodu iz klasičnega v kvantno stanje. Zelo pomembna prednost je možnost doseči resnično direktno korelacijo med lastnostmi in nanostrukturo, saj ni potrebna nobena dodatna priprava vzorca za HREM preiskave, vzorci pa se tudi zlahka prenašajo iz enega instrumenta v drugega. V prispevku so podani primeri preiskav in dobljene informacije na nanešenih filmih in delcih in sicer nanodiamanta, aluiminija, borovega nitrida in aluminijevega oksida.

Introduction

Since the mid 1980's, ultra sharp needles have been used as probes for a variety of scanning probe techniques primarily to study a spectrum of surface or near surface features. A seemingly endless variety of such techniques is constantly being invented. Their attractiveness includes: simplicity, high resolution, adaptability to a variety of environments, etc. Only rarely is the probe itself employed as the object of analysis, and then usually to aid in the interpretation of some surface feature. On the other hand, the tips of sharp needles have been the primary object of FEM, FIM, and Atom Probe (AP) studies for many decades. Electron microscopic techniques (SEM, TEM, HREM, ELS, EDS) have been frequently combined with the FIM &/or AP on studies of the tips of needles. In fact, it is very desirable to combine the strengths of the above methods into a powerful analytical strategy that offers unique prospects in studies of thin dielectric films or nanoparticles. The present paper will briefly review some of the features of each relevant technique, describe examples where several modes of analysis have been combined to advantage, give recent results from extensions of this approach, and finally suggest prospects for further extensions, particularly for nm scale dielectric films and particles.

Field Emission, Field Ionization, and the Atom Probe

Field electron emission was the basis for very early attempts to develop a point projection electron microscope or Field Emission Microscope /1/. Attempts to image molecules were made very early and had some success, but the resolution was limited by the transverse spread of the emitted electrons to ~2nm and the high electric fields (~10^9 V/m) affected the molecular deposits. A point projection microscope with higher resolution was soon developed by E. W. Mueller, by simply reversing the bias on the needle, cooling the specimen to cryogenic temperatures, and field ionizing an inert gas, e.g. He or Ne, leaked in as a background gas at pressures of ~10^{-4} Torr. Mueller thus achieved true atomic resolution for the first time (Fig1d) with a Field Ion Microscope (FIM) /2/. But the electric fields required were another order of magnitude higher (~10^{10} V/m), so high that the tip of the needle could be made to field evaporate. The bulk and shear stresses induced by these electric fields were correspondingly high (~1/10 the bulk modulus) and could distort or eliminate features of interest (e.g. point defects, dislocations, boundaries, etc) /3/. However, field evapo-ration could be employed in a pulsed mode (using voltage or laser pulses) to make the needle a controlled source of ions for a time-of-flight (TOF) mass spectrometer that achieved single ion sensitivity and became known as an Atom Probe /4/. If a heavy liquid on the surface of a needle was desorbed by field evaporation, it became the source for a focused ion beam or FIB. By substituting a sensitive two dimensional detector, such as a channel plate, just in front of a phosphor screen, the features of both atomic imaging and TOF spectrometry could be achieved. Such a combined instrument became known as an Imaging Atom Probe /5/.

Surface Studies using Field Electron Emission

Once it became clear that the field emission electron microscope (strictly FEEM but almost always abbreviated FEM) had physically insuperable limita-tions on its resolution (~2nm) and specimen configuration (the tip of a needle of radius <10^{-6} m), it was only infrequently used for its original purpose. But at the same time it became obvious that the FEM was a powerful tool to study the surfaces of conductors and semiconductors /9/. Surface studies, however, required vacuums of ~10^{-11} Torr to permit a sufficient interval to conduct useful experiments and UHV conditions were (and are) not easy to achieve and maintain. But once achieved, such vacuums permitted studies of the properties of truly clean surfaces of most metals and some semiconductors for the first time. The practical consequence was the development of the first experimental tool of the new field of Surface Science and the incentive to develop an entire array of new techniques for surface characterization (e.g. AES, SIMS, etc).

Attempts to clean the (approximately) hemispherical tip of the needle-shaped specimens by heating in UHV conditions, yielded surfaces that were not smooth at the atomic level, but developed flat facets dominated by the closest packed (or lowest energy) planes. The FEM images from such specimens gave a magnified image of the relative probability for electron emission over a range of orientations. The relative size of these facets reflected their relative surface energy, detailed specimen geometry, the applied field during heating, the ultimate temperature and time, background gases & pressures (even at <10^{-11} Torr), etc. By placing a moveable aperture placed near the magnified FEM image and measuring only those electrons that passed through, the Fowler-Nordheim equation could be applied to deduce the work functions of different crystalline orientations and the effects of adsorbates, atomic order, defects, etc. Significantly different values were obtained for different orientations and surface effects, so that the very meaning of the work function became an object of scientific study. Adsorbates, not surprisingly, were found to also react anisotropically; indeed they could alter the measured work function, quite dramatically Atomic and molecular adsorbates could also be viewed directly by the FEM, even as they migrated on specimen surfaces, even at cryogenic temperatures. Thus as many questions as answers emerged. Were these effects due to the experimental conditions or were they fundamental properties? It became obvious that even more data was required from the tips of needles, under closely controlled conditions. But in addition, independent data from the other characterization tools of surface science now became essential.

The Field Emission Energy Distribution (FEED)

Significant new data came first from an obvious extension of the evolving methods of FEM. A more comprehensive theory of the energy distribution of the field emitted electrons was developed and applied to the methods already well known for measuring data for Fowler-Nordheim plots. Adding an electron spectrometer behind a phosphor viewing screen with an aperture and the capability of translating the image (e.g. by deflection) permitted the measurement of both I-V data and the emitted energy distribution of the emitted electrons. With this capability, theory could truly be tested against experimental data. Not only could an understanding of the fundamental physics thus be improved, but the distribution of the electron supply (i.e. the band structure) of the electron source could be measured directly. And the influence of crystallographic orientation, adsorbates, disorder, alloying, defects, etc could now be investigated independently and quantitatively. This experimental approach became known as the Field Emission Energy Distribution (FEED) and has continued to evolve until the present. However, FEED has remained noncommercial; that is, FEED systems have not become very common surface science tools and each remains custom made for the needs of a specific researcher /6/.

Scanning, Transmission and Analytical Electron Microscopy

Researchers conducting Material Science studies of grain boundaries, defects, or precipitates by FEM, FIM and FEED techniques soon recognized that both the Scanning Electron Microscope and Transmission Electron Microscopes (SEM and TEM) were invaluable ancillary tools /7/. This coupling was especially fortuitous for TEM users, since the tips of needles de facto made excellent specimens which required no further preparation. The preparation of representative TEM specimens has always been a fundamental barrier to the correlation between the microstructures and properties. How could you be certain that the microstructural features you observed in a TEM specimen were directly related to the phenomena under investigation, when by the very act of preparing the specimen you were forced to remove most of the material surrounding features of interest? Is the volume of material remaining representative of the bulk specimen properties? By using a needle as the specimen, FEM and/or FIM related analytical methods could be applied first, then viewing the very same specimen in a TEM and/or SEM with no preparation steps between, you can be quite confident of the relationship and relevance of the two sets of data. Of course, all of the ancillary analytical techniques available with TEM or SEM (e.g. EDS, ELS, SE or BSE, etc) can be also brought to bear. A pertinent example comes from some recent studies of oxide films on Al needles . A controlled electric field, inherent to the needle shape, was used to first damage the oxide. The damaged oxide was later exposed to a corrosive environment, which led to the initiation of corrosion at the damaged site. These corrosion products were then analyzed by TEM and ELS. Earlier studies by FIM, IAP, and TEM of the structure and composition of grain boundaries, precipitates, and interfaces, effectively demonstrated the advantages and simplicity of obtaining combined information from specific sites /7/.

Scanned Probe Techniques

Scanning tunneling microscopy, STM evolved quite naturally as variations on the utility of FEM continued to develop. Since the current of emitted electrons was exponentially sensitive to the electric field, which in turn was determined by the applied potential and specimen geometry, why not vary one while keeping the other fixed as a sensing device? Indeed, several kinds of sensors with impressive sensitivity were shown to confirm this as a viable approach. Why not then a device where a sharp needle at constant potential could be used as a probe to slowly scan very near a roughened surface, which should yield large variations in current that could be used to map surface topography? Or as a variation, a constant current is maintained, while the varying potential would reflect topography? These were the kinds of thinking that went into early versions of the development of a Topografiner, as it was called. But this concept did not work as well as hoped because of complications arising from the sensitivity to external vibrations, which then affected the needle to surface spacing. Indeed overcoming this vibrational barrier led to the development of the first STM and a Nobel prize in the mid 1980s. The pleasantest surprise from this achievement was the excellent lateral resolution obtained with the STM, a capablity of resolving the dimensions of a single atom! Indeed this development opened the floodgates to the emergence of many variations on the STM, which are still emerging and referred to as Scanning Probe Microscopes (SPMs).

But common to all SPMs is a probe comprised of the tip of a needle and many are compatible with studies by FEM, FIM, AP and consequently the TEM, SEM, and AEM in combination. It is this formidable combination of techniques, that rely upon or can easily be used to analyze the tips of needles that we direct this paper. We argue that this combination of analytical techniques is unique in special abilities to characterize thin films and nanoparticles, especially dielectrics, which are major objects of modern research in Materials Science. Furthermore, coated needles have the potential for significant direct and indirect applications, e.g. in Vacuum Microelectronics or Nanolithography, or as intense electron sources for microwave communication. Also because of their very scale, the results obtained from their study are applicable to a wide spectrum of novel nanoelectronic devices now under intense development.

Examples of combined studies on the tips of field emitters

Some examples of the analytical approach promoted here are presented to illustrate its power and potential. The objectives of these studies were not to develop analytical tools, but rather to better understand field emission and thereby develop stable, intense electron sources for Vacuum Microelectronic applications. Field emission sources suitable for all such applications are required to operate at vacuum levels much poorer than those required for FEM studies (e.g.at ~10^{-6} Torr rather than 10^{-11} Torr). In addition, such emitters should be easy to fabricate, uniform in their properties, inexpensive, and highly reliable. Considerable progress has been made to achieve these aims in the last decade, most of which has come from understanding why coating needle-shaped emitters of silicon and molybdenum with carbon-based films and fine particles, as well as those of several other wide band gap dielectrics, substantially enhances and stabilizes emission, even under these very modest vacuum conditions. Some examples of the analytical methods employed for these studies and some of the pertinent results are summarized in the following.

Diamond and Amorphous Carbon Coatings on Si and Mo Emitters

The tips of needle-shaped silicon field emitters were coated with nanocrystalline diamond using "biased-enhanced" microwave plasma CVD /8/. Field emission from these emitters was enhanced by several orders of magnitude and the emission stability was significantly improved, as compared to uncoated silicon emitters. Transmission electron microscopy of the interfaces between the diamond deposits and the silicon substrate (Fig. 1) revealed that a thin (5-10 nm) silicon carbide phase formed, even though the maximum temperature during the deposition was limited to 500-600°C.

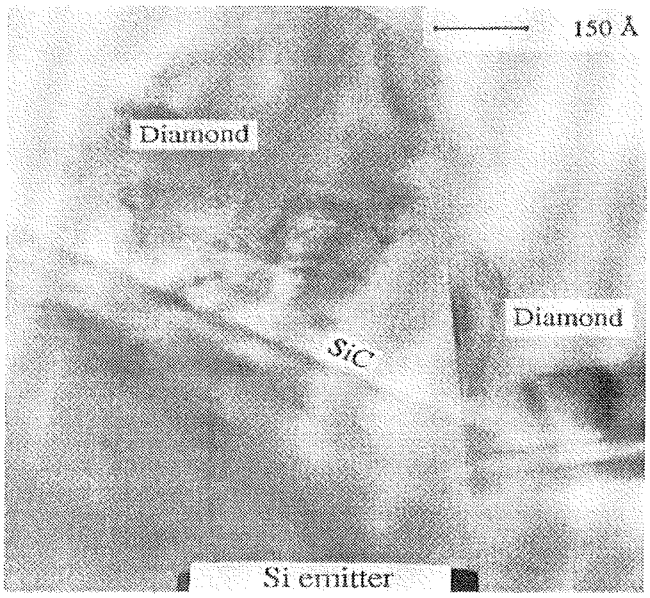
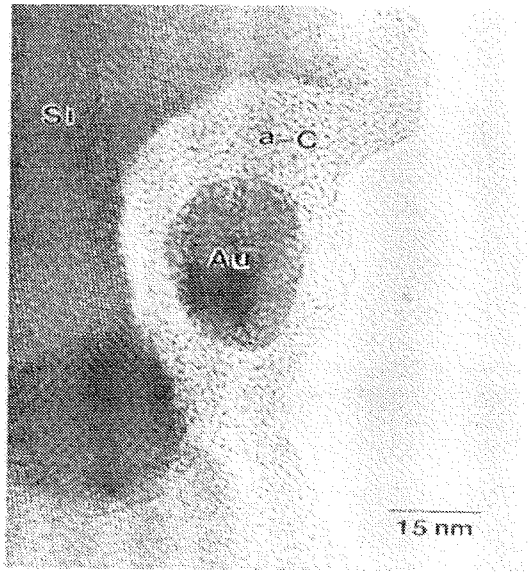


Figure 1 TEM of SiC nucleated at Si-diamond interface.

An attempt was made to achieve similar improvements in emission using what was thought to be "diamond-like" amorphous carbon deposits on silicon needles. The deposits were smooth and were deposited near ambient temperature. However, it became obvious that the emission currents were actually reduced. A TEM study of the coatings using ELS of the coating/silicon interfaces showed the coating to be comprised mainly of sp2 bonded C rather than the sp3 bonding. TEM (Fig 2) and ELS also revealed another unexpected result. There were ~10-20 nm sized crystals of Au present at the film-silicon interface /9/. The presence of these Au nanoparticles appeared to be a result of the method by which the silicon needles were originally grown and then precipitated during their storage and deposition treatments.

Parallel studies on needle-shaped Mo field emitters, examined several methods of depositing coatings. It was discovered that thin, extremely adherent layers of crystalline diamond powder could be deposited onto the tips of needles by dielectrophoresis, an especially simple and inexpensive, ambient coating technique /10/. Surprisingly, emission was further enhanced, even without thermal treatment; however, a low temperature (~400 °C) anneal in a hydrogen ambient, yielded even better emission and improved the emission stability. The thickness and uniformity of the deposits could be quickly checked by the SEM (Fig 3a) and the interface between the diamond deposits and the Mo substrate was observed by TEM to be surprisingly intimate (Fig 3b), but could be further improved by a low temperature anneal, which nucleated a nm scale molybdenum carbide interface layer.

The energy distribution of the field emitted electrons (FEED) from the dielectrophoretic diamond coatings on Mo also gave valuable information about the mechanism of the observed enhancement in emission /11/. FEED measurements were taken before and after



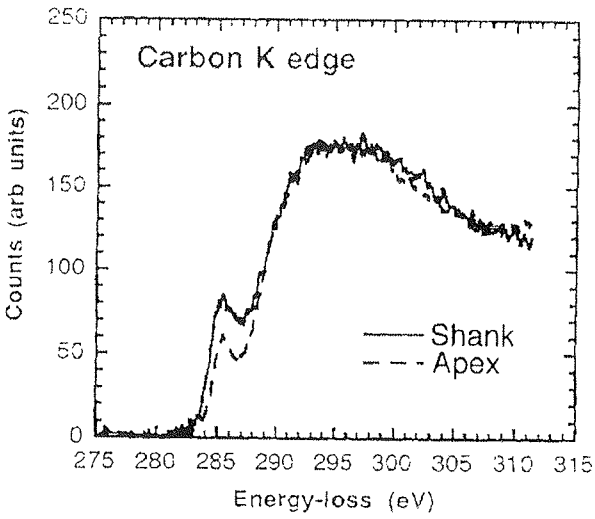


Figure 2. (a) TEM Au precipitates in amorphous C deposit (b) EELS spectra at apex and shank of amorphous C deposit.

deposition and spectra then compared. These measurements revealed that the emitted electrons originated from the diamond/vacuum interface after tunneling from the conduction band minimum of the diamond, but the nature of the Mo/diamond interface also played a significant since role, since it affected the electron supply to the diamond conduction band. A series of FEED studies (Figs 4a and 4b) of BN powders depo-sited by dielectrophoresis onto Mo needles, illustrates its effectiveness in helping to deduce the mechanisms of emission and the basis for the enhancement in emission /6/.

More recently, we have been depositing nanodiamond particles by dielectrophoresis onto Mo emitters, varying the deposition conditions widely. Typical results at very short deposition times are given in Fig. 5. There is a marked preference top deposit at the very tip of the needle, where emission is greatly enhanced.

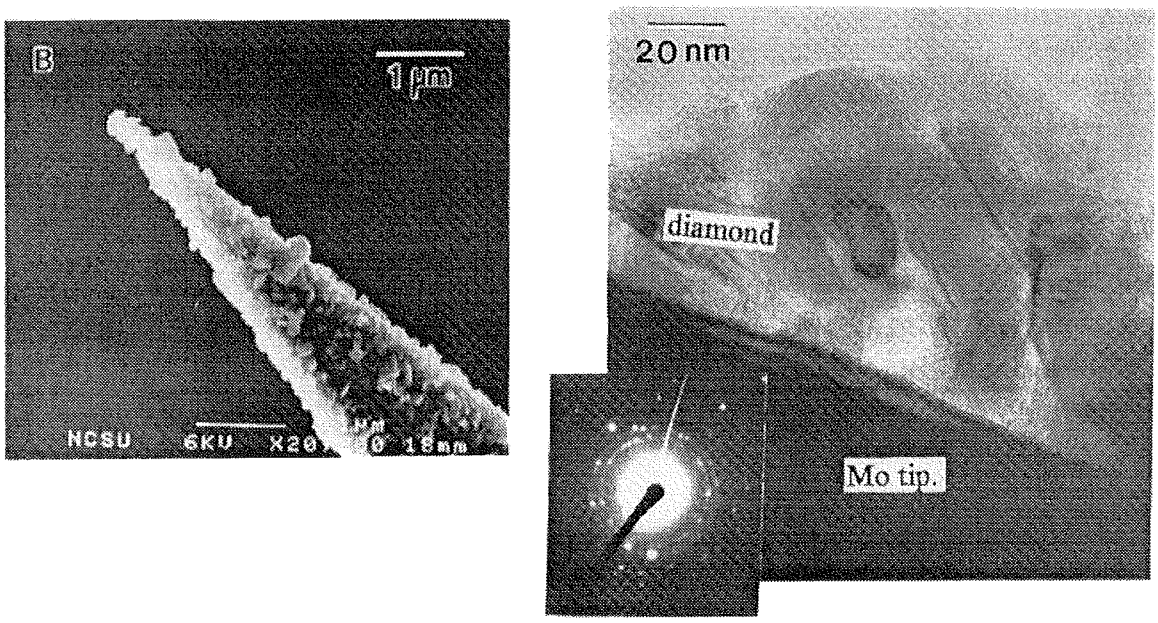


Figure 3. (a) SEM of diamond particles deposited by dielectrophoresis onto Mo needle (b) TEM of the particle-Mo interface of same needle.

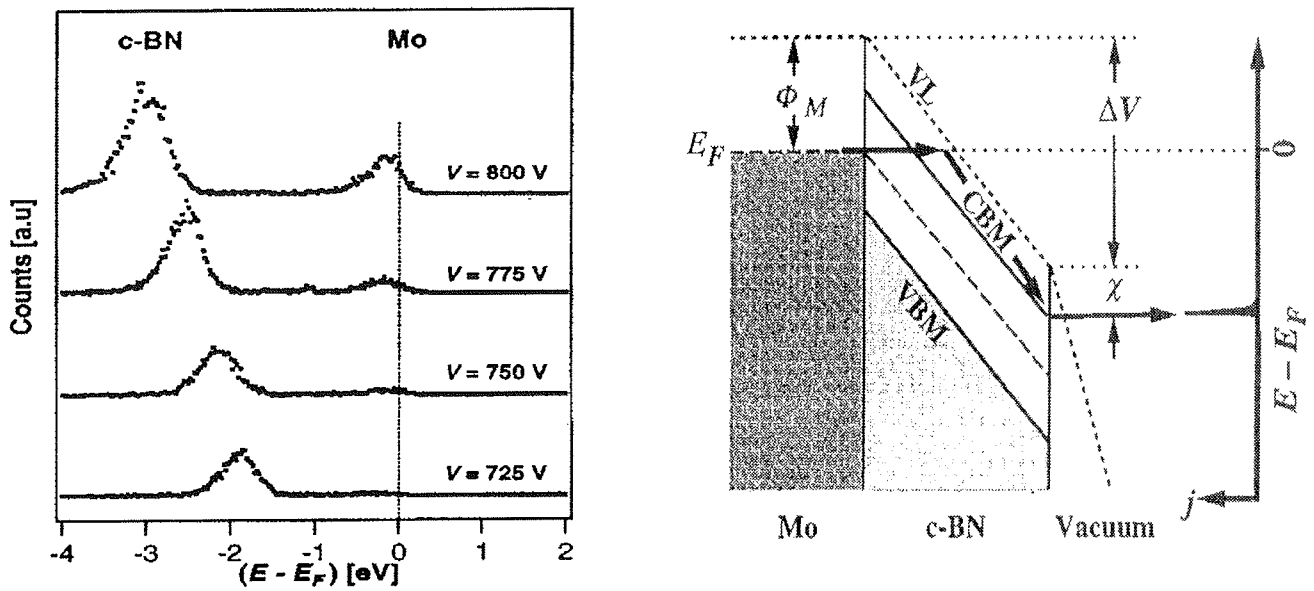


Figure 4. (a) Shift in BN FEED maximum relative to Mo as a function of applied potential, (b) band diagram illustrating emission mechanism.

The potential to study nanoparticles and thin films

No one has reported results from a single material characterized extensively from nanoscale dimension, where "quantum effects" dominate, up to dimensions where the measured properties are identical with those obtained from "bulk" samples. The present methods could achieve this and the experimental data obtained at the "quantum scale" could then be directly compared with first principle theoretical calculation. What other combination of techniques can claim to obtain a comparable result? We suggest that the tip of a needle makes an ideal specimen to achieve such a breakthrough.

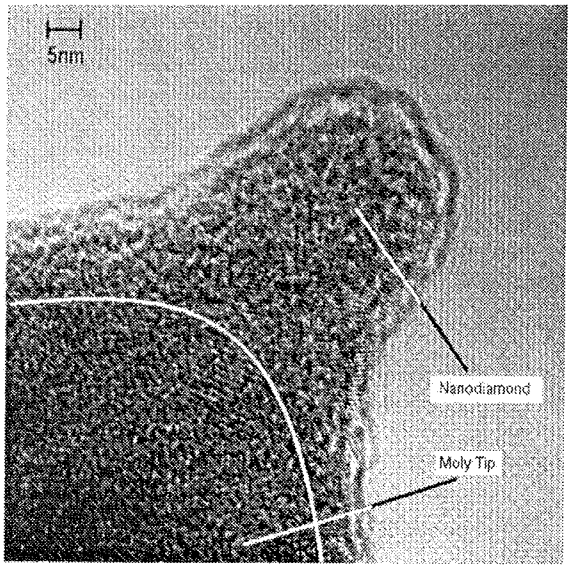


Figure 5 TEM of nanodiamond deposit on Mo needle by dielectrophoresis.

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John J. Hren, Victor V. Zhirnov,
Zlatko Sitar, & Gregory Wojak
Dept of Materials Science and Engineering
North Carolina State University
Raleigh, NC 27695-7907,USA
john_hren@ncsu.edu

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