

SYMPOSIUM R

Electron-Emissive Materials and Vacuum Microelectronics

April 25 – 27, 2000

Chairs

Kevin L. Jensen

Naval Reserach Lab
Code 6841 ESTD
Washington, DC 20375-5347
202-767-3114

Dorota Temple

Electronic Tech Div
Microelectronics Ctr of NC
Research Triangle Pk, NC 27709-2889
919-248-1945

William A. Mackie

Linfield Research Inst
McMinnville, OR 97128-6894
503-434-2432

Robert Nemanich

Dept of Physics
North Carolina State Univ
Raleigh, NC 27695
919-515-3225

Junji Itoh

Electron Devices Div
Electrotechnical Lab
1-1-4 Umezono
Tsukuba, 305-8568 JAPAN
81-298-545503

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* Invited paper

SESSION R1/Q1: JOINT SESSION:
FIELD EMISSION AND DISPLAY APPLICATIONS

Chair: Dev Palmer
Tuesday Morning, April 25, 2000
Franciscan II/III (Argent)

8:30 AM *R1.1/Q1.1

FIELD EMISSION FROM CARBON SYSTEMS. John Robertson, Engineering Dept, Cambridge University, Cambridge, UNITED KINGDOM.

Nano-crystalline diamond, diamond-like carbon and carbon nanotubes can each show field emission at low applied electric fields. The initial work on diamond was motivated by its negative electron affinity and the expected low barrier for electron emission. However, electron energy distribution measurements show that the emission barrier is of order 4-5 eV, the work function, and the energy distribution width shows the presence of large local fields, of order 1000 V/um. In polycrystalline diamond, scanning tunneling microscopy measurements show that emission arises from grain boundary regions. These results suggest that the only common mechanism which can explain the facile emission from these systems involves field focusing and field enhancement to negative space accumulated at grain boundaries or conductive emission channels, or to the tubes in the case of nanotubes. Other mechanisms do not give sufficient barrier lowering. Consequences of this mechanism are discussed. The mechanism places requires the emission sites to be <10 nm in diameter, so the local emission current density is actually high.

9:00 AM *R1.2/Q1.2

APPLICATIONS OF ION TRACK LITHOGRAPHY IN VACUUM MICROELECTRONICS. R.G. Musket, Materials Science and Technology Division, Lawrence Livermore National Laboratory, Livermore, CA.

When a high-velocity (i.e., typically > 0.1 MeV/amu) ion passes through a material it can change the properties of the material within a cylindrical zone centered on the essentially straight trajectory of the ion. The electronic bonding, phase, and density are among the properties modified in the zone, which is called a latent nuclear, or ion, track. Because the diameters of latent ion tracks are typically less than 20 nm, selective chemical etching is generally employed to improve the detection and assessment of the tracks. Historically, etched nuclear tracks have been used mainly for nuclear particle identification, geochronology, measurement of extremely low-dose radiation levels, and creation of membrane filters. This presentation will provide an introduction to the basic concepts involved in the creation and etching of ion tracks to make masks for lithographic processes. Examples of documented applications in microtechnology and in vacuum microelectronics will be given. In particular, the role of ion track lithography in a novel process for producing cathode arrays with individual emitter structures having gates with < 300 nm diameters will be described. Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract #W-7405-Eng-48.

9:30 AM R1.3/Q1.3

SURFACE MODIFICATION OF Si FIELD EMITTER ARRAYS FOR VACUUM SEALING. M. Nagao, T. Matsukawa, S. Kanemaru, J. Itoh, Electrotechnical Laboratory, Ibaraki, JAPAN; H. Tanabe, Dai Nippon Printing Co., Ltd. Chiba, JAPAN; T. Kobayashi, Musashi Institute of Technology, Tokyo, JAPAN.

Vacuum sealing is one of the most important issues for vacuum microelectronics device. It is well known that emission characteristics are worse in vacuum package than that in ultra high vacuum (UHV) condition. This is due to poor vacuum in package and also due to heating treatment in vacuum packaging process. In the present study, the affect of the heating process on silicon field emitter arrays (FEAs) is investigated, and we tried surface modification to avoid the degradation of emission characteristics in heating process. Emission characteristics of Si FEAs in UHV condition were measured before and after heating process at the temperature of 300 degrees centigrade. Emission current dropped significantly by the heating process. The emission current recovered to the initial level by dipping the Si FEA in 1% hydrofluoric acid for 15 sec. This indicates that the deterioration of the emission characteristics by heating process is due to oxidation of the Si emitter surface. Therefore, it is essential to prevent the emitter surface from oxidation. We tried surface modification of coating the emitter surface with carbon by exposing the emitter to CHF₃ plasma in order to avoid the oxidation. Generally, CHF₃ plasma is used for etching SiO₂ and it is known that Si surface is covered with carbon polymer by exposing CHF₃ plasma. Si FEAs were exposed to CHF₃ plasma for 10 sec to be covered with carbon polymer thin film. Emission characteristics of the carbon

coated emitters were measured before and after heating process. As the result, no deterioration of emission characteristics by heating process was observed.

10:15 AM R1.4/Q1.4

SURFACE TREATMENT ON SILICON FIELD-EMISSION CATHODES. M. Hajra, N.N. Chubun, A.G. Chakhovskoi and C.E. Hunt, Electrical and Computer Engineering Dept. University of California, Davis, CA.

Arrays and single-tip n-type silicon and polysilicon micro-emitters have been formed using a subtractive tip fabrication technique. Following fabrication, several different surface treatments have been attempted for comparison. The objectives of these treatments include stabilization of the emission, lowering the effective workfunction, and reducing low-frequency noise. Treatments we have to consider include anodization of the Si tip, coating of the emitter tip with GaN or other nitrides, coating the tip with native or deposited HfC layer, or over-coating the tip with an amorphous or nanotube carbon layer. The tips were evaluated using I-V measurements in the diode configuration. A flat Si anode, spaced nominally 1um from the cathode, was used. The field emission characteristics are measured in a high vacuum chamber at a pressure of 10-8 Torr. The results suggest that the emitters benefit from seasoning or conditioning, for optimal performance, low noise, minimum work function and maximum reproducibility and reliability over the lifetime of the cathode.

10:30 AM R1.5/Q1.5

FABRICATION AND CHARACTERIZATION OF SINGLY-ADDRESSABLE ARRAYS OF POLYSILICON FIELD-EMISSION CATHODES. N.N. Chubun, A.G. Chakhovskoi and C.E. Hunt, Electrical and Computer Engineering Dept., University of California, Davis, CA.

Polysilicon is a candidate material for field-emission microelectronics devices. It can be competitive for large-size, cost-sensitive applications such as flat-panel displays and micro electro-mechanical systems. Singly-addressable arrays of field-emission cells were fabricated in a matrix configuration using a subtractive process on Polysilicon-On-Insulator substrates. Matrix rows were insulated polysilicon strips with emission tips; and matrix columns were thin-film, gold-gate electrodes. Ion implantation has been used to provide a required conductivity of the polysilicon layer. To reduce curvature radius of a tip, a sharpening oxidation was used. The final device had polysilicon emission tips with end radii smaller than 15 nm, surrounded by gate apertures of 0.4 um in diameter. Field emission properties of the cathodes were measured at a pressure of about 10-8 Torr, to emulate vacuum conditions available in sealed vacuum microelectronics devices. It was found that an emission current of 1 nA appears at a gate voltage of 30 V and can be increased up to 1uA at 70 V. Over this range of current, no semiconductor deviation from the Fowler-Nordheim equation is observed. I-V characteristics measured in cells of a 10x10 matrix, with a cell spacing of 50 um demonstrated good uniformity and reproducibility. Electron-optic properties of a single-cell emitted electron beam were investigated and will be discussed.

10:45 AM R1.6/Q1.6

NITROGEN CONTAINING HYDROGENATED AMORPHOUS CARBON PREPARED BY INTEGRATED DISTRIBUTED ELECTRON CYCLOTRON RESONANCE (IDECR) FOR LARGE AREA FIELD EMISSION DISPLAYS. N.M.J. Conway, C. Godet, Lab. PICM, Ecole Polytechnique, Palaiseau-Cedex, FRANCE.

Amorphous carbon (a-C) based films have shown considerable promise as potential cold cathode materials for flat panel display applications. We report results of the characterisation and field emission properties of nitrogen containing hydrogenated amorphous carbon (a-C:H:N). These were grown at high rates(3-12Ås⁻¹) using acetylene gas in an integrated distributed electron cyclotron resonance (IDECR) reactor. Unlike the ion beam deposition techniques commonly used to produce a-C(:H) field emitters, the IDECR is easily scalable to the large areas required for many flat panel display applications. Furthermore, the addition of nitrogen, which has been shown to reduce the field required for emission in a-C(:H), can be achieved efficiently as the electron resonance condition results in high ionisation of the nitrogen gas. We have found that nitrogen incorporation increases with increasing flow of nitrogen gas up to atomic percentages of ~30%. Field emission measurements, using a parallel plate configuration, showed that the addition of nitrogen improved the emission properties of the films, resulting in low onset fields of ~8-10Vµm⁻¹. To further understand this effect, UV-visible ellipsometry was used to study the optical properties. These could be modelled accurately without incorporating a roughness layer into the model, suggesting that all films are smooth in character. A decrease in the refractive index was observed with increasing nitrogen content, which correlates with the

measured decrease in density from 1.7gcm^{-3} to 1.3gcm^{-3} . The optical (E_{04}) gap was also found decrease from 1.4eV to 1.0eV, whilst electrical measurements showed an increase in conductivity and a decrease in the activation energy. These results all point towards an increase in the number of sp^2 sites upon addition of nitrogen, which might be expected to lead to a higher electron affinity and poor emission, contrary to the improvement in emission observed. Possible reasons for this will be discussed.

SESSION R2/Q2: JOINT SESSION:
FIELD EMISSION
DISPLAY/CATHODOLUMINESCENCE

Chair: Troy A. Trottier
Tuesday Afternoon, April 25, 2000
Franciscan II/III (Argent)

1:30 PM *R2.1/Q2.1

CARBON NANO TUBE FEDS FOR LARGE AREA AND FULL COLOR APPLICATIONS. J.M. Kim, N.S. Lee, W.B. Choi, D.S. Jung, I.T. Han, J.H. Kang, H.Y. Kim, S.H. Park, S.S. Hong and H.R. Jang, Samsung Advanced Institute of Technology, The National Creative Research Initiatives, Suwon, KOREA.

Single wall nano tubes of about 2 μm in length are refined and coated with lines of 240 on the 9 inch diagonal glass plate by squeeze and spray method as electron sources. On the other glasses, the R,G,B color phosphors are coated on the 576 lines. With the vacuum gap of 200 μm , the FED panels are fully sealed and the color images on the 9 inch FED panel are first demonstrated. The electrical and optical properties are fully studied in diode mode and unique version of triode mode. The reliability of carbon nano tube based FEDs are fully with the correlated mechanism analysis with phosphors in the narrow vacuum gap.

2:00 PM R2.2/Q2.2

LOW TEMPERATURE CVD CARBON NANOTUBES ON GLASS PLATES FOR FLAT PANEL DISPLAY APPLICATION. Yonhua Tzeng, Chao Liu, Calvin Cutshaw, Department of Electrical and Computer Engineering, Auburn University, AL; Zheng Chen, Space Power Institute, Auburn University, AL.

The application of carbon nanotubes as the electron emitters for plasma displays requires that the carbon nanotubes be deposited on large-size and inexpensive substrates such as glass plates. Low-temperature chemical vapor deposition processes have been developed for coating of carbon nanotubes on glass plates. Substrates were heated by a heater at a chamber pressure between 10 and 760 Torr. Hydrocarbon mixtures were used as the carbon source for nanotube deposition. Carbon nanotubes deposited on glass plates were examined by a phase-contrast optical microscope, and SEM. An ultra high vacuum chamber was used to characterize the electron emission properties of these carbon nanotube coatings. A one millimeter diameter tungsten rod with a hemispherical tip and a glass plate coated with aluminum were used as the anode and placed at a distance between 50 and 300 micrometers from the nanotube coatings to measure the current-voltage characteristics of the carbon nanotubes. Electron emission from carbon nanotubes deposited on glass plates started from a turn-on electric field of about 4-6 volts per micrometer. Details of the deposition process and electron emission characteristics of the carbon nanotube coatings fabricated by the low-temperature CVD process will be presented.

2:15 PM R2.3/Q2.3

FABRICATION OF NANOCRYSTALLINE DIAMOND ARRAYS FOR FIELD EMISSION DEVICES. A.H. Jayatissa, A.R. Krauss, T. Corrigan, A. Sumant, D.M. Gruen, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL; O. Auciello, Materials Science Division Argonne National Laboratory, Argonne, ILL; R.P.H. Chang, Materials Science and Engineering Dept, Northwestern University, Evanston, IL.

It has been shown that nanocrystalline diamond (NCD) has attractive properties as an electron field emission material because of its low emission threshold voltage (2-5 V/micron), and chemical and thermodynamic stability, although the electron emission mechanism is not fully understood. In order to use NCD in electron emission displays, it will be necessary to deposit the electron-emissive coating on a conductive layer on a glass substrate. The deposition area must be patterned to provide row and column addressing of individual pixels. We have deposited patterned NCD coatings on Ti and Mo patterned films using stripe and island geometries for both the metallization layer and the NCD coatings. Feature resolution of ~ 100 nm has been demonstrated for the NCD patterning, and NCD islands ranging in diameter from 2 to 100 microns have been fabricated. The electron emission uniformity has been studied using a phosphor screen

tester, photoelectron emission microscopy (PEEM), and field electron emission microscopy (FEEM), to determine the emission current density and emission site location as a function of NCD feature size and separation.

Work supported by the U.S. Department of Energy, BES-Materials Science under contract W-31-109-ENG-38 and USIC CRADA C9501500, and the Office of Naval Research under contract #N00014-97-F-0905. The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory (Argonne) under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

2:30 PM R2.4/Q2.4

EPITAXIAL OXIDE THIN-FILM PHOSPHORS FOR LOW VOLTAGE FED APPLICATIONS. Yong Eui Lee, David P. Norton, J.D. Budai, Miyoung Kim and S.J. Pennycook, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; Philip D. Rack and Michael D. Potter, Advanced Vision Technology, Inc., W. Henrietta, NY.

Oxide thin-film phosphors are attractive for low voltage field emission display applications due to their thermal stability and excellent luminescent properties. Nevertheless, improvements in luminescent efficiency and brightness are needed. For cathodoluminescence (CL), the utility of the phosphor depends upon multiple interrelated properties such as spectra response, charge carrier transport and chemical stability. Current research in luminescent thin-film displays is focused on use of polycrystalline phosphors that do not adequately satisfy the required criteria and limit performance of these devices. It has recently been reported that epitaxial thin-film phosphors can exhibit superior PL and CL luminescent intensity as compared to randomly-oriented polycrystalline deposits. We have investigated the epitaxial growth and properties of Li-doped ZnGa_2O_4 and Sr_2CeO_4 phosphors on (100) MgO and (100) YSZ single crystal substrates, respectively. Those films exhibit blue CL efficiencies of up to 0.28 lm/W at 1kV, 4.5 micro-A/cm². The photoluminescent properties of epitaxial Li-doped ZnGa_2O_4 and Sr_2CeO_4 will also be discussed, including the role of Li in ZnGa_2O_4 . These results are useful not only for developing high performance phosphors, but also in understanding the fundamental properties of crystalline phosphor films. This research was sponsored by the Office of Science, U.S. Department of Energy under contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp..

3:15 PM *R2.5/Q2.5

MECHANISMS AFFECTING EMISSION IN RARE-EARTH-ACTIVATED PHOSPHORS. David R. Tallant, Carleton H. Seager and Regina L. Simpson, Sandia National Laboratories, Albuquerque, NM.

The relatively poor efficiency of phosphor materials in cathodoluminescence with low accelerating voltages is a major concern in the design of field emission flat panel displays operated below 5 kV. Our research on rare-earth-activated phosphors indicates that mechanisms involving interactions of excited activators have a significant impact on phosphor efficiency. Persistence measurements in photoluminescence (PL) and cathodoluminescence (CL) show significant deviations from the sequential relaxation model. This model assumes that higher excited manifolds in an activator de-excite primarily by phonon-mediated sequential relaxation to lower energy, emitting manifolds in the same activator ion. In addition to sequential relaxation, there appears to be strong coupling between activators, which results in energy transfer interactions. In terms of phosphor efficiency, some of these interactions appear to be benign, resulting in direct transfer of excitation to emitting manifolds from remote higher manifolds. Because they accelerate the rate of population of emitting manifolds, these effects are observable in the persistence curves of these manifolds. Other interactions negatively impact phosphor efficiency by nonradiatively de-exciting activators. Increasing activator concentration and excitation by CL, as compared to PL, enhances these interactions. The net effect is a significant degradation in phosphor efficiency at low accelerating voltages and useful activator concentrations. I will present phosphor efficiency and persistence data primarily from PL, but with comparisons to CL, which indicate the presence and suggest the nature of these interactions. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000

3:45 PM R2.6/Q2.6

MODELING OF INTERFACIAL SCATTERING EFFECTS DURING LIGHT EMISSION FROM PHOSPHOR THIN FILMS FOR FIELD EMISSION DISPLAYS. Rajiv Singh, Kyu-Gong Cho,

It has been experimentally shown that the light trapping due to internal reflection effects from a smooth surface is reduced as the surface becomes progressively rougher. Although this phenomenon is qualitatively understood, there has been a lack of detailed analysis of the scattering phenomenon which affects the light emission from thin film phosphors. Factors which affect the brightness of thin film phosphors such as thickness, microstructure, wavelength, and dimensions of the surface roughness, type of substrate used (and thus the interface formed), in many cases, cannot be independently varied, thus making it difficult to quantitatively interpret the solutions. Furthermore, as the wavelength of the surface roughness is smaller or has the same dimensions of the wavelength of the emitted radiation, classical theories based on rectilinear propagation of the light cannot be used without gross simplifications. Some simplified models have been suggested to predict the brightness of the thin film phosphors as a function the effect of bulk and surface structure, however they do not take into account complex surface scattering-based effects. To overcome the deficiencies of the earlier work, we have developed a new model which incorporates diffraction related surface scattering effects. The results have been obtained experimentally from deposition of $Y_2O_3:Eu$ thin film phosphors with different thickness (and surface roughness) values on various substrates. Indeed, the model supplies an integrated solution for predicting the cathodoluminescent properties of thin film phosphors considering the most primary parameters affecting brightness of the thin film phosphors.

4:00 PM R2.7/Q2.7

CATHODOLUMINESCENCE DECAY MEASUREMENTS OF EMISSION FROM Eu AND Tb RARE-EARTH IONS AT LOW ELECTRON BEAM ENERGIES. C.H. Seager and D.R. Tallant, Sandia National Laboratories, Albuquerque, NM.

Most conventional phosphors used in cathode ray tubes have efficiencies which decrease almost linearly as function of beam energy for E less than 5 keV. It is commonly thought that this is due to the non-radiative recombination of beam-created electrons and holes in a near-surface dead layer or at the free phosphor surface itself. In this work we have measured the cathodoluminescence (CL) decay of excited Eu and Tb rare earth ions in commercial and experimental powders of Y_2O_3 and Y_2SiO_5 over a range of beam energies from 0.8 to 4 keV. CL measurements were directly compared to photoluminescence (PL) persistence data obtained from the same emitting states. We find that, in general, the initial CL decay process is faster than that seen in PL, and that the decay rate depends significantly on beam energy. These effects are most noticeable for the higher excited states of these ions and for activator concentrations > 2 at%. Accompanying measurements over the same beam energy and activator concentration range show that the beam energy dependence of the CL efficiency is noticeably stronger at higher activator concentrations. Several explanations for these data are examined, and we introduce a model which assumes that: 1. Low energy electrons, because of their large stopping power, have a high probability of producing densely spaced excited activators, particularly at high activator concentrations, and 2. Activator-activator (non-radiative) quenching is enhanced when nearby rare-earths are both excited. This model attributes much of the decay rate dependences on E , and at least some of the beam energy dependence of CL efficiency on interaction effects, rather than energy losses which occur before activators are excited. *Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

4:15 PM R2.8/Q2.8

EFFECTS OF VACUUM PARTIAL PRESSURES ON ELECTRON STIMULATED SURFACE CHEMICAL REACTIONS ON COATED AND UNCOATED CATHODOLUMINESCENT PHOSPHORS. Paul H. Holloway, Wiets Roos, Billie Abrams and Joe Thomes, University of Florida, Gainesville, FL.

Electron beam stimulated surface chemical reactions (ESSCRs) have been shown to lead to degradation of cathodoluminescent (CL) phosphors. We have studied in detail the effects of various gaseous partial pressures on the processes leading to degradation. We have demonstrated that either high partial pressures of H_2 or H_2O will cause degradation of ZnS P22 phosphors, but the ESSCR is very different. Degradation is much more severe and occurs at lower coulombic loadings when partial pressures of $\sim 10^{-8}$ Torr of H_2O are present. This partial pressure was controlled over a wide range by back filling the vacuum chamber from a stainless steel vessel containing H_2O isolated from the vacuum by a leak valve. Hydrogen partial pressures of $\sim 10^{-7}$ Torr were sufficient to result in degradation by an ESSCR in which H_2S was speculated to be formed. It was shown that the presence of SiO_2 coatings could accelerate this process, and a mechanism involving the formation of hydroxyl radicals will be

discussed. The implications of ESSCRs for FEDs will be discussed. This work supported by DARPA through the Phosphor Technology Center of Excellence.

4:30 PM R2.9/Q2.9

NANOFUNCTIONALIZED SULFIDE BASED POWDERS FOR FLAT PANEL DISPLAY APPLICATIONS. Michael Ollinger, Valentin Craciun, Rajiv K. Singh, Dept of Materials Science and Engineering, University of Florida, Gainesville, FL.

Sulfide based phosphor materials have been routinely utilized in cathode ray tube displays (CRT), electroluminescent (EL) displays, and have been explored for field emission display (FED) applications due to their high luminescent efficiencies in comparison to oxide based phosphors. However, the sulfide-based phosphors are prone to degradation of the cathodoluminescent properties caused by the interaction of the e-beam with the adsorbed residual gases on the particle surface of the phosphors. To overcome this critical issue we have synthesized nanofunctionalized phosphor powders, which are formed by coating a very thin film onto the surfaces of the phosphor powders using a novel atomic flux coating technique. This technique uses a 248 nm wavelength excimer laser, with a pulse duration of 25 ns operated from 5-15 Hz at energies between 2-5 J/cm², which strikes a solid target under a high vacuum (10^{-5} Torr) and creates a plume of atomic species. These species or nanoclusters are then deposited onto the host particles that are being mechanically agitated during deposition for coating uniformity. The coating material should be a low Z material, electrically conducting, transparent, and chemically stable. Characterization of the brightness and degradation was performed using cathodoluminescence (CL), the stoichiometry and chemical composition of the particle surface was studied using x-ray photoelectron spectroscopy (XPS), and the presence of the coating was seen using Auger Electron Microscopy (AES). The effect of different coatings on the brightness and degradation characteristics of $Y_2O_2S:Eu$ has been investigated and a degradation mechanism has been proposed.

4:45 PM R2.10/Q2.10

THE EFFECT OF MICROSTRUCTURE ON THE BRIGHTNESS OF PULSED LASER DEPOSITED $Y_2O_3:Eu$ THIN FILM PHOSPHORS. Kyu-Gong Cho, Dhananjay Kumar, Zhan Chen, Rajiv Singh, Department of Materials Science and Engineering, University of Florida, Gainesville, FL; Gary Russel and Brent K. Wagner, PTCOE, Georgia Institute of Technology, Atlanta, GA.

In order to investigate the effect of microstructure on the brightness of thin film phosphors, $Y_2O_3:Eu$ thin film phosphors were prepared using pulsed laser deposition. To experimentally deconvolute the effects, the $Y_2O_3:Eu$ films of controlled thickness and microstructure were prepared on the various substrate materials such as amorphous quartz, (0001) sapphire, (100) lanthanum aluminate ($LaAlO_3$), and (100) silicon wafers. Cathodoluminescent brightness and efficiency of the films were obtained in both transmission and reflection mode. The $Y_2O_3:Eu$ films deposited on the quartz substrates showed the maximum brightness followed by the films on (0001) sapphire, (100) lanthanum aluminate ($LaAlO_3$), and (100) silicon substrates. The role of interface scattering of the emitted light on the film brightness will be discussed together with changing surface roughness and film thickness.

SESSION R3: FUNDAMENTAL PROCESSES

Chair: John Robertson
Wednesday Morning, April 26, 2000
Franciscan III (Argent)

8:30 AM *R3.1

THEORY AND MODELLING OF FIELD-INDUCED ELECTRON EMISSION. Richard G. Forbes, University of Surrey, School of Electronic Engineering, Guildford, Surrey, UNITED KINGDOM.

The intentions of this paper are to restate our current understanding of the basic theory of cold field emission (sometimes called Fowler Nordheim emission), and to present a broad review of our current understanding of the physical mechanisms possibly involved in the field induced emission of electrons from semiconductors and from amorphous quasi-dielectric films, such as diamond-like carbon films. The following topics, amongst others, will be covered. - Formulation of elementary, standard and generalised versions of the Fowler-Nordheim (FN) equation, in modern notation; classification of the different versions of the FN equation, and of different electron emission regimes; interpretation of FN plots. - Basic theory of field emission from semiconductors and related materials, including the theory of field emission energy distributions, the origin of voltage and field-dependent distribution shifts and shape changes, and the validity of using energy distribution data to derive estimates of the value of

the surface electric field. - Main alternative models of conduction in semiconductors and amorphous materials. The paper will review the main alternative models for field-induced emission from diamond-like carbon films and related materials, including models that treat the emitter as a multi-layer system in which the film and the adjacent layers are not homogeneous, and will identify some strong and weak points of these models. To conclude, the paper will assess various methods of predicting high local electric field values at a material surface, and re-state some of the anomalies that need to be resolved before it can be said that we truly understand the electron emission process from carbon-based films and related materials.

9:00 AM R3.2

THE EFFECTS OF CONDITIONING ON I-V INSTABILITIES AND HYSISTERIS FOR MOLYBDENUM, SILICON, AND PLATINUM FIELD EMITTER TIPS. Gregory Wojak, Victor Zhirnov, Jerome J. Cuomo, John J. Hren.

Although sharp molybdenum and silicon tips are the basis for most field emission arrays being developed today, very little data has been published about effects seen during their conditioning and successive operation that do not follow classical Fowler-Nordheim behavior. This usually is the result of the emission characteristics being the statistical mean of all the contributing emitters in a large array. However some applications, such as electron sources for SEM's, do not require large arrays of emitters. The main barrier to the use of field emission cathodes in low power applications lies in the difficulty of obtaining stable and reproducible emission characteristics. In such an application, the cause of these instabilities must be understood and addressed. It has usually been assumed that vacuum conditions are the primary factor, if not the only factor affecting emission performance. This assumption does not hold for emission carried out under the conditions normally in use for commercial applications. In this study single field emitter tips made of molybdenum, silicon, and platinum where subjected to a range of vacuum pressures (10^{-6} to 10^{-9} Torr) and conditioning procedures, peak currents, conditioning times, and anode-cathode distances were adjusted. Resulting data shows changes in I-V characteristics, such as variable hysteresis, which cannot be attributed only surface to contamination due to adsorbates. Instead, these results suggest the presence of a surface charge, most likely in the native oxide or at the metal oxide interface. These results will be presented along with some suggestions for minimizing the deleterious effects of trapped surface charge.

9:15 AM R3.3

SIMULATION OF THE INFLUENCE OF INTERFACE CHARGE ON ELECTRON EMISSION. Kevin L. Jensen, Jonathan L. Shaw, ESTD, Naval Research Laboratory, Washington, DC.

Diamond is a promising material for electron sources. One method of injecting charge into the diamond conduction band is through a tunneling interface. We have shown previously that a purely geometric model of internal field emission is inadequate explain experimental data¹. In the present work, we have developed a general method for estimating electron transport and energy distributions through semiconductor interfaces when a charged particle modifies the tunneling barrier. A coulomb potential within the Schottky barrier enhances the transmission probability and therefore total current and energy distributions. Another system where charge plays a similar role is the SiO₂-vacuum interface, for which experimental data exists². The model applies equally well to both systems. Here, we shall model the effects of the addition of a coulomb potential inside a thin SiO₂ coating over silicon. The mathematical model is implemented by numerically solving Schrodingers Equation for a piece-wise linear potential using a newly developed Airy Function approach designed for semiconductor interface and field emission potentials. The electron supply function is obtained from a simple model relating the field within the dielectric to the electrochemical potential. A qualitative comparison to experimental energy distribution findings is obtained by developing an analytical model of the field emitter tip from which current-voltage relations may be found. From simulation, we observe a general enhancement of emitted current due to barrier lowering, but also the introduction of resonant peaks due to levels within the coulomb potential. We discuss the model predictions in light of the experimental findings.

¹K.L. Jensen, et al., MRS Abstracts (April 5-9, 1999, San Francisco) C6.3.

²J. Shaw, et al., Tech. Dig. of the 12 IVMC (July 6-9, 1999, Darmstadt, Germany) p158.

10:00 AM R3.4

OBSERVATION OF HOT ELECTRON FIELD EMISSION. Jonathan Shaw, Naval Research Lab., Washington, DC.

Energy distribution measurements of the beam emitted from coated Si Field Emitter Arrays show a small fraction of the emission occurs at energies well above the Fermi level. This unusual behavior gives a clue

about the role of transport and surface states in field emission from wide gap semiconductors. The arrays were coated with 5nm of ZnO ex-situ and coated with an additional thin layer of Ti in-situ. The as-deposited ZnO coatings produced broad energy distributions with peak energy shifting lower linearly with gate voltage. A very small fraction of the energy distribution occurred above the Fermi level. The characteristics were stable over time. Such behavior is consistent with emission from ZnO gap states that shift to lower energy as band bending in the ZnO increases with gate voltage. After coating with Ti, the energy distributions became sharp, showing crisp thresholds at the Fermi energy and falling off exponentially at low energy. The peak energy did not shift with gate voltage. Such distributions are similar to clean metals. The current obtained after Ti coating was reduced at low voltage but increased more rapidly with voltage, consistent with using a higher work function and larger area in the Fowler-Nordheim equation. Exposure to UHV for many hours reduced the current but the slope and the energy distributions remained the same. The Ti coated surfaces exhibited enhanced emission at energies above the Fermi level. The intensity of this emission just above Ef was about 1% of the maximum intensity, and fell off at the rate of one decade per volt above the Fermi level.

10:15 AM R3.5

A NOVEL APPROACH FOR TRUE WORK FUNCTION DETERMINATION OF ELETRON-EMISSIVE MATERIALS BY COMBINED KELVIN PROBE AND PHOTOELECTRIC EFFECT MEASUREMENTS. Bert Lägél, Iain D. Baikie, Konrad Dirscherl, U. Petermann, Robert Gordon Univ, Dept of Applied Physics, Aberdeen, UNITED KINGDOM.

For the development of new electron-emissive materials knowledge of the work function (ϕ) and changes in ϕ is of particular interest. Among the various methods, the ultra-high vacuum (UHV) compatible scanning Kelvin Probe has been proven to be a superior technique to measure work function changes due to e.g. UHV cleaning processes, chemical contamination, thermal processing etc. with high accuracy ($<1\text{meV}$) [1] The Kelvin Probe measures local work function differences between a conducting sample and a reference tip in a non-contact, truly non-invasive way over a wide temperature range. However, it is an inherently relative technique and does not provide an absolute work function if the work function of the tip (ϕ_{tip}) is not known. In this paper, we present a novel approach to measure ϕ_{tip} with the Kelvin Probe via the photoelectric effect, thus providing the true work function of the sample surface with an accuracy of approx. 50meV. We demonstrate the application of the technique by in situ work function measurements on evaporated layers of the low work function material LaB₆ on a Re substrate and follow the work function degradation of LaB₆ due to the adsorption of gas molecules on its surface. Thus, the extended Kelvin Probe method provides an excellent tool to characterise and monitor the stability of low work function surfaces.

[1] I. Baikie, U. Petermann, B. Lägél, Surf. Sci. 433-435, 249 (1999).

10:30 AM R3.6

Transferred to R5.16.

SESSION R4: FIELD EMITTER ARRAYS
Chairs: Lalitha Parameswaran and Jong Duk Lee
Wednesday Afternoon, April 26, 2000
Franciscan III (Argent)

1:30 PM *R4.1

Mo AND Co SILICIDE FEAs. Jong Duk Lee, Byung Chang Shim and Byung-Gook Park, Seoul Nat'l Univ, School of Electrical Engineering, Seoul, KOREA.

Metal silicides including Ti, Co, Nb, Mo, Pd, Ta and Pt were previously reported in the various literatures to improve electron emission characteristics of Si FEAs. The advantages of silicide emitters have been mentioned as lower effective work function, higher electrical conductivity, and better chemical and thermal stability than those of silicon emitters. However, due to different emitter structure design and silicide formation process, the emitter materials including silicide phase and emitter structure including tip radius are not same. Thus, the results presented in the literatures are not always consistent. Therefore it is still important to study effective work function, and emission current characteristics for the silicide emitters, especially Mo and Co silicides.

To obtain the effective work functions, slopes of Fowler-Nordheim (F-N) curves are drawn and tip radii are accurately measured by field emission scanning electron microscopy (FESEM). To investigate emission current fluctuation and stability, the emission current fluctuation at a fixed gate bias and emission current change depending on the vacuum pressure are investigated. In this study, Mo silicide and Co silicides are formed on the gated

single crystal silicon(c-Si), polycrystalline silicon(poly-Si) and amorphous silicon(a-Si) FEAs. The silicide formation is confirmed and the I-V characteristics are obtained.

From the slopes of F-N plots and tip radii, the calculated effective work functions of c-Si, poly-Si and a-Si FEAs are 4.06 eV, 3.44 eV and 3.62 eV, respectively. Whereas, those of Mo silicide FEAs based on the same Si FEAs are 3.13 eV, 2.45 eV and 2.91 eV, respectively. In the case of Co silicide FEAs based on the same Si FEAs, the effective work function are 2.56 eV, 1.74 eV and 2.16 eV, respectively. The emission current fluctuations of the c-Si, poly-Si and a-Si FEAs normalized with average anode current at a fixed gate bias were ranging from -99.9 % to +164.2 %. Whereas, those of Mo silicide FEAs based on c-Si, poly-Si and a-Si were ranging from -10.6 % to +10.5 %. Those of Co silicide FEAs based on c-Si, poly-Si and a-Si were ranging from -12.3 % to +14.9 %. It is remarkable that the fluctuations from silicide emitters are reduced by about one tenth comparing with the silicon emitters. This phenomenon is mainly due to work function reduction and inertness to the gas molecule of the silicides.

As a test of inertness of Mo and Co silicide emitters to air molecules, the emitters were operated at high vacuum level of 10^{-9} torr and increased air pressure up to 10^{-6} torr and then the vacuum level increased to 10^{-9} torr again. The emission currents of the silicides gradually decreased and remained constant, and then back up to the original current level. On the other hand, those of Si FEAs inconsistently changed.

2:00 PM *R4.2

STABILIZATION OF EMISSION CURRENT IN SILICON FIELD EMITTER ARRAYS. D. Palmer, D. Temple, J. Mancusi, L. Yadon, and D. Vellenga, MCNC Materials and Electronic Technologies Division, Research Triangle Park, NC.

Several schemes to minimize emission current noise in cold cathodes have been explored in the literature. Of these schemes, the most prevalent are passive stabilization, most often embodied by incorporation of a resistor or resistive layer into the cathode, and active stabilization, most often embodied by incorporation of a MOSFET or other type of transistor in the cathode circuit. Passive stabilization seeks to control the emission current by reducing the applied voltage as the emitted current increases. This scheme is only partially successful, because the emitted current tends to be an exponential function of the applied voltage, while the resistor can provide only a linear reduction in voltage as a function of the emission current. In other words, it is mathematically impossible for the stabilization to keep up with the fluctuations in emission. Active stabilization represents an improvement over passive stabilization, in that the transistor element is used as a current-limiting element in the circuit. In this scheme, the transistor limits the supply of electrons to the cathode, which in turn limits the emission current. In other words, the cathode can only emit electrons if electrons are available. Under these conditions, the cathode is said to be operating in supply-limited mode. This operating mode for cold cathodes is analogous to space-charge-limited mode for thermionic cathodes. In this mode, the stability of the emitted current is directly dependent on the stability of the current-limiting element, which can vary greatly depending on external factors such as temperature, supply voltage variations, and others. MCNC has developed additional improvements to this scheme that eliminate the long time scale variations in emission current. Measurements will be shown that indicate this technique may represent a significant advance in the effort to enable the use of cold cathodes in practical applications.

2:30 PM R4.3

SOLID STATE FIELD CONTROLLED ELECTRON EMISSION: AN ALTERNATIVE TO THERMIONIC AND FIELD EMISSION. Vu Thien Binh, J.P. Dupin, P. Thevenard and J.C. Plenet, Univ Lyon 1, Lab Emission Electronique, DPM-CNRS, Villeurbanne, FRANCE.

Considering the different applications that used electron beams, an ideal cathode can be outlined and characterized by the following main factors: -Room temperature operating condition. -Possibility of a fast modulation of the emission. -Small operating voltage. -High brightness and efficiency. -Insensitivity to medium or poor vacuum conditions. -Long life-time and reproducible operating conditions. -High throughput and ease of fabrication. Possibility of realization of a novel cathode that combined most of these characteristics will permit a breakthrough in the applications of electron beams to emerging technologies like flat panel displays, parallel e-beam lithography and vacuum microelectronics devices. Moreover, it could be a possible candidate for the replacement of the present thermionic cathodes considering the gain in the energy consumption. A new concept of electron emission from metallic surfaces covered with ultra-thin films of large gap semiconductors, called solid state field controlled electron emission (SSE), is presented. The SSE concept is based on a serial process with an electron injection through a solid state Schottky junction followed by the electron emission from a

field-controlled negative electron-affinity surface. Experimental results from ultra thin layer of TiO₂ deposited with various techniques on Pt surfaces are presented and discussed within the SSE model. This cathode matches some of the cited characteristics that are of interest for some industrial applications.

2:45 PM R4.4

PROGRESS AND PERFORMANCE OF ZIRCONIUM CARBIDE FIELD EMITTER ARRAYS. W.A. Mackie, K.S. Lee, Tianbao Xie and P.R. Davis, Linfield Research Institute, McMinnville, OR.

Field emission arrays may find varied applications from the video displays to microwave devices, and spacecraft charge dissipation and propulsion systems. Many of these uses would require high currents per tip and operation in adverse vacuum conditions. These requirements necessitate robust cathode materials. Our work focuses on the use of transition metal carbides for field emission sources. Here, we report on vapor deposition of zirconium carbide emitter cones in the conventional field emission array geometry. We deposit these carbide emitters via physical vapor deposition from crystalline zirconium carbide sources. Use of this material has required changes in the array fabricating technique that we will report. The emission properties of arrays formed in this way will also be reported. In general, zirconium carbide has an electronic work function approximately 1 eV lower than molybdenum, a common FEA emitter material. This has translated into a measured lowering of turn-on voltages by 45% and an increase in emission stability. Extraction voltages in the 35-65 volt range are reported for solid carbide emitter cones in the FEA geometry. Emission at relatively high individual tip currents and at poor vacuum levels will also be presented and discussed. These carbide cone arrays could lead to extremely robust electron sources and open the use of FEAs to a variety of applications. This work supported in part by DARPA High Definition Systems.

3:30 PM *R4.5

APPLICATION OF FIELD EMITTER ARRAYS TO MICROWAVE POWER AMPLIFIERS. D.R. Whaley, B. Gannon, C.R. Smith, C.M. Armstrong, Northrop Grumman Corporation, Vacuum Electronics Research Development and Engineering, Rolling Meadows, IL; C.A. Spindt, SRI International, Menlo Park, CA.

With the recent advances in field emitter array (FEA) technology, current densities as well as total currents from planar arrays have reached values meeting or exceeding many moderate power TWT beam requirements. The development of a robust high current density (>10 A/cm²) cold cathode source, such as the FEA, would offer many advantages for both pulsed/CW and gated operation over current thermionic cathode technology. This development program is designed to be implemented in several stages including both simulation and analysis of the electron optics and gated RF performance as well as pulsed and finally gated experimental demonstration of FEA operation in a TWT microwave power amplifier. The new FEA electron gun structure uses a series of shaped electrostatic lenses to overcome the problems associated with inherent defocusing of high current density FEA electron beams. In TWT geometry, confinement and focusing of the FEA beam is complicated by the low magnetic field at the cathode surface, the non-convergent nature of the emitted beam, high emittance, and high pre-acceleration current density. Unlike space-charge limited thermionic cathodes, FEA emitters can be operated at any current below the operating current. The electron gun and magnetic field structure accommodate all modes of operation by producing laminar, non-scalloping, electron beams for low current as well as full current operation. RF gated emission from such emitters has been simulated using actual emission current profiles. TWT circuits have been designed for use with a wide range of prebunching current ratios. Results show significant improvement in many RF characteristics over those of a thermionic beam including efficiency, linearity and harmonic power generation. A complete FEA-TWT microwave power amplifier has been designed, fabricated and tested using Spindt-type FEA cathodes from SRI. The new electron gun design proved to successfully extract and focus the electron beam and excellent beam propagation characteristics were measured along the length of the TWT helix structure. Current operation has exceeded 30mA with stable FEA emission observed at all times. Beam emission and focussing characteristics as well as RF performance of the FEA-TWT will be presented.

4:00 PM *R4.6

FIELD-EMITTER-ARRAY COLD CATHODE ARC PROTECTION METHODS - A THEORETICAL STUDY. Lalitha Parameswaran, R. Allen Murphy, MIT Lincoln Laboratory, Lexington, MA.

Field-emitter arrays (FEAs) are desirable for use as electron emitters in microwave-tube amplifiers because they can provide such advantages as higher efficiency and faster turn-on over their thermionic counterparts. Calculations have shown that Spindt-type metal and semiconductor emitters operate well below intrinsic current limits due

to thermal effects, even for high-current applications such as klystrodes, twystrodes, and traveling-wave amplifiers. Nevertheless, the primary barrier to FEA utilization in such applications is premature failure due to arcing, which is thought to be produced by ionization of gas molecules and/or desorbed contaminants, exacerbated by a poor vacuum environment. Additionally, emission current stability and noise are also of importance. Lifetime and stability issues have been largely resolved for less stringent applications, such as flat-panel displays, through the use of integrated passive resistors that provide current-limiting. However, such an approach is not directly amenable to operation at high frequency and current density. Other more complex approaches such as the incorporation of active control in the form of integrated transistors, have also been demonstrated, but again, only for FEAs used in displays. This paper will review some of these schemes in the context of their efficacy in improving lifetime and stability of FEA cold cathodes in high-frequency applications. A theoretical analysis will be given of the effect on high-frequency performance of incorporating arc protection structures into Spindt-type metal FEAs. Specifically, two approaches will be considered: passive protection schemes such as the use of a modified thin film resistive layer, and active schemes such as FETs and saturated current limiters (such as the VECTL developed by NEC).

This work was sponsored by the Department of the Air Force, and the Naval Research Laboratory.

4:30 PM R4.7

FIELD EMISSION CATHODES AND ELECTRIC PROPULSION SYSTEMS. Colleen M. Marrese, Advanced Propulsion Technology Group, Thermal and Propulsion Engineering Section, Jet Propulsion Laboratory, Pasadena, CA.

Microscale propulsion systems (<10 mN) are being developed for picosatellites (<1 kg) and for primary propulsion and attitude control and for much larger spacecraft which require continuous drag or torque compensation. The development of the thrusters is currently limited by the cathode technology. The electron sources are required for propellant ionization and ion beam neutralization. Conventional hollow and filament cathodes cannot be scaled down in power and size to be compatible with microscale propulsion systems. Field emission cathodes are being considered as the electron source in EP systems because they are easily scalable in size and power and do not require propellant. The primary challenges with integrating these technologies is cathode lifetime in the hostile environment created by EP systems. The details of different thruster environments and the demands on the cathode performance will be discussed in this paper. FE cathode configurations, operating voltages, and materials required to meet these demands will also be discussed.

4:45 PM R4.8

SPACE BASED APPLICATIONS FOR FEA CATHODES (FEAC). B.E. Gilchrist, Univ. of Michigan, Dept. of Electrical Engineering and Computer Science, Ann Arbor, MI; K.L. Jensen, J.G. Severns, Naval Research Laboratory, Washington, DC; A.D. Gallimore, Univ. of Michigan, Dept. of Aerospace Engineering, Ann Arbor, MI.

Cold cathodes such as field emitter arrays offer the potential to benefit or enable space-based applications of critical commercial, government, or military importance by providing an electron source that is low power, low cost, requires no consumables, potentially robust as well as highly reliable. Applications that would especially benefit from such cold cathodes include low power electric propulsion (EP) thruster technology, electrodynamic tethers (ED) for propellantless propulsion in low-Earth orbit, and spacecraft negative potential charge control. In controlled environments, field emitter arrays have shown substantial capability, but have failed in harsher environments more typical of space applications. We argue that a combination of localized arc suppression coupled with a low work function, but nevertheless robust, coating such as zirconium carbide would provide the needed ruggedness to withstand energetic ions, oxygen fluxes, and adsorbates typical of a spacecraft environment. In this work, we present a survey of the requirements and capabilities of FEACs based on an analytical model of FEA performance. From it, we ascertain the relative advantages of FEACs as a function of materials, geometry, and space charge limitations, for ED, EP, and spacecraft charge control. We identify what is required of FEACs in terms of emission performance and lifetime, as well as what configurations and operating conditions are required. We have found that arc-protected and coated FEACs that can operate in a 1-10 microTorr pressure environment with current densities of less than 0.1 Amps/cm² and gate voltages between 50-100 Volts, would enable reliable, low-cost devices capable of operating in the required space environment.

Wednesday Evening, April 26, 2000
8:00 PM
Metropolitan Ballroom (Argent)

R5.1

SILICON FIELD EMISSION ARRAYS COATED WITH A CoSi₂ LAYER GROWN BY REACTIVE CHEMICAL VAPOR DEPOSITION. Byung Wook Han, Hwa Sung Rhee and Byung Tae Ahn, Korea Advanced Institute of Science Technology, Dept of Materials Science and Engineering, Taejon, KOREA; Nam Yang Lee, Orion Electric Co., Information Display Research Institute, Suwon, KOREA.

The low turn-on voltage and stable emission current are important factors of the electron source in the emissive flat panel displays (FPDs). Silicon emitters have been intensively studied by many researchers due to the extensive knowledge about the process compatibility with integrated circuits. However, silicon emitters have problems such as relatively poor electrical and thermal conductivities and thin oxide layer that grows on the surface. To solve the problems in the silicon emitter tip, we modified emitter tips by coating CoSi₂. The CoSi₂ layer was in-situ deposited on silicon emitters at 600 ~ 650°C with cobalt metallorganic source by reactive chemical vapor deposition. CVD commonly offers advantage such as a conformal deposition on the emitter tips and a uniform deposition over a large area. The Co film was deposited from cyclopentadienyl decarbonyl cobalt, Co(η^5 -C₅H₅)(CO)₂, at 110 mTorr with 10scmm H₂ carrier gas. The deposition time was 15min and thickness of CoSi₂ layer was 300-350Å. The resistivity of CoSi₂ layer was about 17.3 μΩcm. The emission characteristics of CoSi₂ coated field emitters were improved. The enhanced emission properties were due to the increase of emission area by the formation of CoSi₂ on silicon emitters from Fowler-Nordheim plot. And emission current fluctuation decreased due to the chemically stable surface properties of CoSi₂. A further study of emission current degradation with time is under investigation.

R5.2

FIELD EMISSION CHARACTERIZATION OF UNDER-GATE TRIODE TYPE CARBON NANOTUBE BASED FLAT PANEL DISPLAY. J.H. Kang, Y.S. Choi, J.H. Choi, W.B. Choi, D.S. Chung, H.Y. Kim, N.S. Lee, J.M. Kim, Display Lab., Samsung Advanced Institute of Technology, Suwon, KOREA.

Carbon nanotube has attracted much attention for application to the electron emission source of the field emitter due to its high aspect ratio and small tip radii of curvature with high chemical stability and high mechanical strength. There have been many efforts to apply carbon nanotubes to a field emission source, but they were restricted within diode type. In this study, we present new structure of triode type using single walled carbon nanotubes as electron emission source of field emission display (FED). At first, gate was patterned on the glass, and cathode pattern which contains carbon nanotubes was separated from gate pattern by cured polyimide. The panel was fabricated by semiconductor processes and slurry squeezing techniques. Gate and cathode electrode were patterned by metal deposition and photolithography processes, and carbon nanotube pattern was formed by squeeze printing method, respectively. Field emission properties of our prototype of triode structure panel were investigated by means of I-V measurement, current stability, and brightness. We observed that the emission current and brightness of our flat panel display were controlled by relatively low gate voltage under consistent anode bias.

R5.3

A CONCENTRIC CIRCULAR TYPE IN-SITU VACUUM SEALED LATERAL FEAs EMPLOYING E-BEAM EVAPORATOR. Moo-Sup Lim, Min-Koo Han, School of Electrical Eng., Seoul Nat'l Univ., Seoul, KOREA; Yearn-Ik Choi, Dep. of Molecular Sci. and Tech., Ajou Univ., Suwon, KOREA.

Vacuum field emitter devices have attracted a considerable interest for high frequency and high temperature applications. Various field emitter structures have been reported. However, most of those devices require an additional vacuum environment and their operating voltages are too high to act as an amplifier. We have reported the in-situ vacuum encapsulated lateral field emitters which does not require any additional vacuum packaging and have a low turn-on voltage (<10 V)[1]. However, the previous lateral FEAs are found to be somewhat unstable for a long period operation because the structure has weak region at the edge of FEAs. The mechanical and electrical stresses may drive that region to have crack and the vacuum sealing is broken in entire FEAs. In this paper, we propose concentric circular lateral field emitter structure which is more stable in fabricating and maintaining vacuum conditions. The new FEAs have concentric circular shape while our previous FEAs are stripe type. The anode is formed at inner circle and the cathode is outer circle respectively. The tips are located between circles, therefore there are no edges in this structure. It is important that this structure has no edge which may

cause crack by mechanical stress and break the sealing material. We use Molybdenum or Silicon dioxide as a sealing material. After fabricating tips, Molybdenum or Silicon dioxide is deposited with e-beam evaporator at base pressure of 1×10^{-7} pressure. It should be noted that the vacuum level of micro-cavity is identical to the base pressure of evaporator chamber[1]. The FEAs which are sealed with Molybdenum has triode characteristics as our previous lateral FEAs. All of the two types of new FEAs show good reproducibility in fabricating and maintaining vacuum conditions. Consequently, we propose and fabricate successfully more stable in-situ vacuum lateral field emitters employing concentric circular shape in order to reduce the stresses between substrate and sealing materials.
[1] C.M. Park, M.S. Lim and M.K. Han, IEEE Electron Device Letters, Vol. 18, No. 11, November, pp. 538 (1997).

R5.4
SILICON FIELD EMITTER ARRAY BY FAST ANODIZATION METHOD. Y.M. Fung, W.Y. Cheung, I.H. Wilson, J.B. Xu, S.P. Wong, The Chinese University of Hong Kong, Department of Electronic Engineering, Shatin, NT, Hong Kong, CHINA.

A new fast fabrication method, two step anodization of silicon with different HF solution was used to form high aspect ratio silicon Field Emitter Array on n-type silicon with resistivity of $0.01 \Omega\text{-cm}$. Silicon oxide mask was used to define the field emitter array. The silicon substrate was pre-anodized with low current density for 1 minute in the dark and then anodize in HF:H₂O:ethanol solution. Finally, the porous silicon was removed by isotropic solution etching. The turn-on voltage of the fabrication field emitters was approximately 27V when the emission current density reaches $1 \mu\text{A}/\text{cm}^2$. This compares with turn-on field of about 35V on silicon tip by using isotropic etching solution of HNO₃. It obtained emitter arrays with good uniformity, reproducibility. Fabrication of an emitter array and its field emission characteristic are reported. The results of fabricated gated structures are also reported.

R5.5
STUDY ON DEPLETION MODE OPERATION OF PROTRUDING-TIP FIELD EMITTER TRIODES. Yong-Chun Luo, Miki Shibata, Hiroyuki Okada and Hiroyoshi Onnagawa, Toyama University, Faculty of Engineering, Toyama, JAPAN.

Depletion mode operation of protruding-tip field emitter triodes has been investigated with numerical calculations and experiments. Potential, electric field distributions and current versus voltage characteristics varied with the emitter tip-height were simulated using Laplace and Fowler-Nordheim equations. In order to realize the depletion mode operation, the gate-anode distance of the protruding-tip field emitter triode was reduced about three microns. In conventional field emitter triode with normal emitter tip height, anode voltage was not influenced on the electric field of the top of emitter tip. While for the protruding-tip field emitter triode, the electric field of the top of emitter tip was largely affected with the anode voltage. Since the gate and anode voltages simultaneously controlled the electric field of the emitter tip, the anode current under zero gate voltage was non-zero value, like as current-voltage characteristics of depletion-mode transistor. From above simulated results, we have explored a possibility of the depletion mode field emitter triode and have been fabricated Spindt-type Mo field emitter triode with different emitter tip height. Experimental results were in good agreement with that of calculation results.

R5.6
FIELD EMISSION STRUCTURE WITH SHOTTKY-BARRIER ELECTRODE. Alexey A. Levitsky, Krasnoyarsk State Technical Univ, Dept of Radioelectronics, Krasnoyarsk, RUSSIA; Andrey P. Genelev, Vladimir S. Zasemkov, Krasnoyarsk State Technical Univ, Vacuum Microelectronics Lab, Krasnoyarsk, RUSSIA.

We analyze a non-traditional version of semiconductor field emission structure, based on silicon cones arrays and destined for application in low-voltage vacuum microelectronics devices. In proposed construction, the gate electrode is used as Schottky-barrier contact on silicon tips. Due to Schottky-barrier contact we have obtained depletion layer in tip body under the gate electrode. Therefore variation of the gate electric potential provides the emitter current modulation. Experimental structures were fabricated with about 28000 silicon cones per 1 mm^2 by reactive ion etching through a silica mask. Using a quasi two-dimensional model, we have computed these emitter structures. The model takes into account non-uniformity of silicon cone cross-section. Here, we study the influence of emitter tips parameters on the structure performance. Initial results prove the possibility of cathode current electric control with the gate electrode potential. Additionally we have obtained some other electric parameters of the emitter with the Schottky-barrier contact. The results of numerical analysis and experimental study provide a guide for design of proposed field emitter structure.

R5.7
MICRO-STRUCTURAL AND FIELD EMISSION CHARACTERISTICS OF NITROGEN-DOPED AND MICRO-PATTERNED DIAMOND-LIKE CARBON FILMS PREPARED BY PULSED LASER DEPOSITION. Ik ho Shin, Taek Dong Lee, Jae Hyoung Choi, Jeong Yong Lee, Korea Advanced Institute of Science and Technology, Dept of Materials Science and Engineering, Taejeon, KOREA.

Effect of nitrogen doping on field emission characteristics of patterned Diamond-like Carbon (DLC) films was studied. The patterned DLC films were fabricated by the method reported previously. Nitrogen doping in DLC film was carried out by introducing N₂ gas into the vacuum chamber during deposition. Higher emission current density of $0.3 \sim 0.4 \text{ mA}/\text{cm}^2$ was observed for the films with 6 at % N than the undoped films but the emission current density decreased with further increase of N contents. Some changes in CN bonding characteristics with increasing N contents were observed. The CN bonding characteristics which seem to affect the electron emission properties of these films were studied by Raman spectroscopy, x-ray photoemission spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). The I(D)/I(G) ratio of the Raman spectra increased and G-band width decreased with the increasing nitrogen content but the both showed a plateau-like region at 4 to 6 at %. The strong decrease of the G-band width and the increase of the I(D)/I(G) were observed at 6 to 9 at % nitrogen. A shift of peak position of the carbon core electron excitation energy towards higher binding energy in the specimen doped with 6 at % nitrogen content was observed. Further increase of nitrogen content resulted in shifts of the C1s peaks towards lower binding energy, e.g. more graphite-like bonding. The deconvoluted IR spectra of the DLC films were in consistent with the Raman and XPS results. The electrical resistivity and the optical band gap measurements supported the above mentioned analyses. Consequently, it is deduced that the enhancement effect on the field emission properties by the incorporation of the nitrogen is restricted by the formation of sp² bond regions. For more detail analyses, DLC films are being investigated by transmittance electron microscopy and electron energy loss spectroscopy.

R5.8
ENHANCEMENT OF THE EMISSION PROPERTIES OF FIELD EMISSION SOURCES FABRICATED FROM RETICULATED VITREOUS CARBON (RVC). A.G. Chakhovskoi, C.E. Hunt, ECE Dept., University of California, Davis, CA; D.E. Booth, LightLab USA, West Sacramento, CA.

Large surface area field emission cathodes made from reticulated vitreous carbon (RVC) were investigated as potential electron sources for various electron-beam applications. In this work we present the results of our study of treating RVC material and measuring electronic performance in diode and triode configuration of field emission sources made from this material. We optimize the emission characteristics of the electron beam using emitters with areas ranging from 5 to 100 mm². The surface morphology of the large area emitters varies with the porosity of the 3-dimensional RVC structure as well as with the direction of the volume compression applied to the carbon foam during the manufacturing process. Treatments which influence the performance of the emitters include cleaning procedures, emission surface treatment using plasma, DC current training and laser beam trimming. Emission current characteristics in the range from 0.1 uA to 200 uA and emission stability characteristics were studied for unfocused and focused beams using differently shaped modulators and grids. Focusing of the beam is obtained by in-situ variation of the distance between emitter, modulator and phosphor screens. The results are compared with computer simulations and with measurements using carbon surface-oriented nanotube emitters. Experimental prototypes of cold light-emission sources with brightness up to 20,000 cd/m² were fabricated and studied.

R5.9
PHOTOEMISSION PROPERTIES OF CVD DIAMOND WITH DIFFERENT MICROCRYSTALLINE STRUCTURE. S. Salvatori, G. Conte, M.C. Rossi, University of Roma Tre, Dept. of Electronic Engineering and INFN, Rome, ITALY; F. Pinzari, CNR-IMAI, S. Monterotondo, Rome, ITALY.

Polycrystalline diamond offers new perspective as electron emitter, exhibiting negative electron affinity (NEA) when its surface is in a reduced state. Such a property makes this material very attractive for the realization of field-emission displays, as well as photoemissive devices, where UV radiation with energy above diamond band gap can directly excite electrons from the valence band to the vacuum level. However, electron emission from diamond surfaces appears to largely depend on the material properties. In this context we present a study on the correlation between electron emission properties and film microstructure by comparing the spectra of CVD diamond films with different morphologies. Both crystalline quality of cubic diamond and

the amount of non diamond phases, evaluated by Raman spectroscopy, largely affect the photoemission intensity and spectral distribution, whereas its energy threshold is affected to a lesser extent. In particular, experimental data suggest that different types of transition occur over different spectral ranges which extend well below the diamond band gap. Such results are discussed in terms of optical excitation of electron from defect states, either located within diamond grains and at the grain boundaries, or related to the diamond surface. Results on the photoemission yield modifications induced by hydrogen and oxygen termination of the diamond surface are also presented and discussed.

R5.10

Abstract Withdrawn.

R5.11

INVESTIGATION ON ELECTRON FIELD EMISSION BEHAVIOR OF TETRAHEDRAL AMORPHOUS CARBON. J.P. Zhao and Z.Y. Chen, Ion Beam Laboratory, Shanghai Institute of Metallurgy, Chinese Academy of Sciences, Shanghai, CHINA and Shikoku National Industrial Research Institute, Takamatsu, JAPAN.

Tetrahedral amorphous carbon (ta-C) films have been synthesized by using hyperthermal carbon species during filtered arc deposition (FAD) process. Systematic investigation on electron field emission behavior of large number of ta-C samples was conducted using parallel plate diode configurations, in which smooth mirror quality ta-C film coated Si wafer and a metal plate were used as cathode and anode, respectively. The spacing between anode and cathode was about 70 μm . Field emission measurements were performed at a pressure of 1×10^{-6} Torr and room temperature. Testing was done on five different areas of each sample to gauge the repeatability of the results. Total six series of ta-C samples were prepared and investigated: 1) ta-C with various sp^3 content; 2) ta-C with different thickness; 3) multilayer ta-C with different layer number and thickness per layer; 4) annealing of as-deposited ta-C; v) nitrogen doping in ta-C by ion implantation at various ion energy and dose; 5) ta-C prepared at various deposition rate. As-deposited ta-C exhibited a bandgap of ~ 2.4 eV and an effective emission barrier as low as 0.06 eV. Threshold electric field of 15 V/ μm and high emission current (20-40 μA) can be obtained in as-deposited film. Based on the systematic study of six series of ta-C samples, threshold electric field as low as 5 V/ μm , which is comparable to that of diamond, was achieved, and we found that deposition condition and post-treatment may have obviously influence on the electron emission behavior of ta-C. Moreover, Fowler-Nordheim relation was observed in all samples. Conclusively, we considered that to obtain high current emission at low electric field from ta-C, the presence of both sp^3 and sp^2 bonded carbon is necessary. As far as emission mechanism is concerned, we suggested that sp^3 and sp^2 sites might play different role in electron emission process.

R5.12

LARGE AND STABLE FIELD-EMISSION CURRENT FROM HEAVILY Si-DOPED AlN GROWN BY MOVPE. Makoto Kasu and Naoki Kobayashi, NTT Basic Research Laboratories, Kanagawa, JAPAN.

Aluminum nitrides show very small or negative electron affinity, so they are promising for field-emission devices such as flat panel displays and high-frequency micro vacuum tubes. The AlN reported hitherto was not intentionally doped. We report that the electron emission current from AlN depends greatly on the Si-dopant density and that heavily Si-doped AlN has a very low turn-on electrical field, and large and extremely stable emission current. Heavily Si-doped AlN ($2.5 \times 10^{20} \text{ cm}^{-3}$) and GaN ($1 \times 10^{19} \text{ cm}^{-3}$) were grown at 1100 and 1000 $^{\circ}\text{C}$, respectively, by low-pressure (300 Torr) MOVPE. The substrates were n-type ($1 \times 10^{18} \text{ cm}^{-3}$) 3.5 $^{\circ}$ -misoriented (0001) 6H-SiC. The sources were TMA, TMG, NH_3 , and SiH_4 . The Si-dopant density was measured using SIMS. The probe-surface distance was fixed at 1.8 μm . The W probe was disk shaped, 2 mm in diameter. The I-V curves showed that electrons were emitted via the Fowler-Nordheim tunneling. The turn-on electric fields (defined as 0.1 nA) were 50, 94, and 150 V/ μm for AlN, GaN, and Si, respectively, indicating that the energy barrier of AlN is the lowest of the three. Further, the barrier height for AlN decreased with the Si-dopant density (N_d). The turn-on electrical fields were 50, 106, and 217 V/ μm for $N_d = 2.5 \times 10^{20}$, 7.5×10^{19} , and $2.5 \times 10^{19} \text{ cm}^{-3}$, respectively, indicating that AlN electrons at the donor level might be emitted directly into the vacuum. The maximum currents (current densities) were 150 μA (4.8 mA/cm^2), 19 μA (0.6 mA/cm^2), and 1.9 μA (0.06 mA/cm^2) for AlN, GaN, and n $^+$ -Si, respectively, probably because that the AlN bonds are the strongest. The emission current from the AlN was very stable. The fluctuation was only 3% over 20 min compared to 27% for Si. In conclusion, heavily Si-doped AlN showed a low turn-on electrical field, and very large and stable current density.

R5.13

CHARACTERIZATION OF FIELD EMISSION PROPERTIES OF SiCN NANORODS AND NANOWIRES. F.G. Tamtair, H.C. Cheng, National Chiao Tung Univ, Dept of Electronics Engineering, Hsinchu, TAIWAN; S.W. Chang, Dept of Physics, National Taiwan Univ, Taipei, TAIWAN; C.Y. Wen, L.C. Chen, Center for Condensed Matter Sciences, National Taiwan Univ, Taipei, TAIWAN; J.J. Wu, K.H. Chen, Inst of Atomic and Molecular Sciences, Academia Sinica, Taipei, TAIWAN.

Field emission properties of SiCN nano-rods and nano-wires have been investigated. These nano-sized materials were synthesized by using a novel two-stage process. First, a (SiCN) buffer layers were deposited on Si substrates using ECR-CVD. Then, the substrates were transferred to a microwave plasma CVD reactor for the growth of nano-rods and nano-wires. The nanorods were grown under the following condition: a microwave power of 2 kW, reaction gases consisted of N_2 , H_2 , CH_4 , and SiH_4 with flow rates of 80, 80, 20 and 4 sccm, respectively. On other hand, the SiCN nanowires were grown with CH_4 flow rates 40 sccm and the other growth parameters were same as the nanorods'. These micrographs of SEM reveal a high density of quasi-aligned nanorods uniform distribution the entail substrate. The diameters of the nanorods and nanowires were in the range of 30~50 nm and 18~30 nm, respectively. The length of is nanorods 1mm~1.5 mm after 3-hour deposition. An emission current of 1.5 mA/cm^2 at the maximum accessible voltage, which gives an applied field strength of 35 V/ μm was observed from the nano-rods. Furthermore, this material also showed a low turn-on field at 10 V/ μm , which is defined as the applied for an emission current density at 0.01 mA/cm^2 . Remarkably, the F-N plot shows an excellent linear relationship, indicating ideal field emission characteristic. Beside, SiCN nano-rods exhibited rather stable emission current under constant applied voltage. The nanowires also show excellent emission properties. Due to the stable field emission properties and large area growth capability, field emitters of SiCN nano-rods and nanowires are attractive for flat panel display applications.

R5.14

ELECTRON EMISSION OF VERTICALLY ALIGNED CARBON NANOTUBES GROWN ON A LARGE AREA SILICON SUBSTRATES BY THERMAL CHEMICAL VAPOR DEPOSITION. Cheol Jin Lee, Jung Hoon Park, Kwon Hee Son, Dae Woon Kim, Tae Jae Lee, Seung Chul Lyu, Kunsan National Univ., School of Electrical Engineering, Kunsan, KOREA; Seung Youl Kang, Jin Ho Lee, Microelectronics Labs., ETRI, Daejeon, KOREA; Hyun Ki Park, Chan Jae Lee, Jong Hun You, Flat Display Labs., Samsung Display Devices Co., Suwon, KOREA.

We have grown vertically aligned carbon nanotubes on a large area of Co-Ni codeposited Si substrates by thermal chemical vapor deposition using C_2H_2 gas. The carbon nanotubes grown by the thermal chemical vapor deposition are multi-wall structure, and the wall surface of nanotubes is covered with defective carbons or carbonaceous particles. The carbon nanotubes range from 50 to 120nm in diameter and about 130 μm in length at 950 $^{\circ}\text{C}$. It was observed that surface modification of catalytic metals deposited on Si substrates by dipping in a HF solution and/or NH_3 pretreatment is a crucial step for the vertically aligned nanotube growth prior to the reaction of C_2H_2 gas. The turn-on voltage was about 0.8 V/ μm with a current density of 0.1 $\mu\text{A}/\text{cm}^2$ and the emission current density was very high level as about 1.1 mA/cm^2 at 4.5 V/ μm applied field. In this case, the emission current reveals the Fowler-Nordheim behavior.

R5.15

ALIGNED CARBON NANOTUBE FILMS ON SiC WAFERS. Junko Shibata, Toshiyuki Suzuki, Michiko Kusunoki, Tsukasa Hirayama and Noriyoshi Shibata, Japan Fine Ceramics Center, Nagoya, JAPAN.

Application of carbon nanotubes(CNTs) are strongly expected for nanometre-scale engineering and electronics industries. For practical use of CNTs, well-aligned CNT films are in great demand. Recently, the present authors discovered that aligned CNTs were formed on the surface of SiC particles heated at 1700 $^{\circ}\text{C}$ using a laser system attached to a transmission electron microscope(TEM). Furthermore, it was found that well aligned CNTs 3-5nm in diameter and 0.25 μm in length were produced on an α -SiC(0001) wafer only by heating at 1700 $^{\circ}\text{C}$ in a vacuum electric furnace. The growth of CNTs was due to a decomposition of SiC by selective desorption of Si atoms. To investigate the formation mechanism of the large-area nanotube film on a SiC wafer, α -SiC(0001) single-crystal wafers were heated at several temperatures such as 1300,1500 and 1700 $^{\circ}\text{C}$ in a vacuum furnace. These specimens were observed using TEM(Topcon 002B: 200kV) and AFM(SPI3800/SPA300). From these results, it was clarified that nanocaps of graphite 3-5nm in diameter were generated all over the surface of the SiC wafer at the initial stage around 1300 $^{\circ}\text{C}$. The growth is presumably dominated by active oxidation

which is expressed as follows: $\text{SiC}(s) + \text{CO}(g) \rightarrow \text{SiO}(g) + 2\text{C}(s)$. In this reaction, solid SiC is continuously oxidized to form a SiO gas without forming a passive SiO₂ solid film. In this formula, C(s) corresponds to CNTs. From AFM and TEM micrographs observed along the plan-view direction, the density of the CNTs in this film was estimated to be roughly 30billions/mm². The sample SSD(self-organized by surface decomposition) method produces pure and homogeneous CNTs. Moreover, the size and the alignment are easily adjusted on inch-size SiC wafers. These characteristics will be of great advantage for industrial applications.

R5.16

FIRST PRINCIPLE CALCULATIONS OF EMISSION PROPERTIES OF NANODIAMOND CLUSTERS. Denis Areshkin, Donald Brenner, John Hren, North Carolina State University, Raleigh, NC; Victor Zhirnov, Semiconductor Research Corporation, Research Triangle Park NC; Alexander Pal, Troitsk Institute for Innovation and Fusion Research, Troitsk, RUSSIA.

Ab-initio local density-of-states calculations were applied to modeling the electronic properties of spherical nanodiamond clusters (NDC) with diameters of 3-6 nm. Nanocrystalline building blocks provide new opportunities for building electronic devices, because the cluster size plays a significant role in both bulk properties and surface/interface effects. Changes in conductivity, band gap, density of states, dielectric constant and electron affinity can be observed, for example in studies of field electron emission, a promising near-term application. Until now, the electronic/emission properties of NDC have never been studied theoretically, even though they are almost ideal objects for modeling, each containing only 500-10,000 atoms. For such small particles, the surface adsorption may drastically alter the physical properties. Thus, it is possible to control the electronic properties of NDC by control of surface adsorbates. In this work, the influence of different adsorbates (e.g. H₂O, N, and OH) on NDC properties were investigated exploring surface doping, surface passivation, surface barrier height, and electron injection. The effects of different adsorbates on surface barrier height was calculated and compared to experimental data on the electron affinity of NDC. Electron injection into NDC was studied for several doping levels: "intrinsic" ND, moderately nitrogen doped ND with deep acceptor levels, and highly nitrogen doped ND without acceptor levels. There are three possible mechanisms of electron emission through/from ND clusters, depending on the applied field and the diameter of the NDC: (1) double barrier injection, (2) direct tunneling, and (3) resonant tunneling. Conditions for resonant tunneling can occur at $F \sim F_c$, and with the surface barrier above the conduction band minimum (e.g. positive electron affinity). For all mechanisms, the electron injection is characterized by the interface barrier height ϕ_B , and the critical field strength F_c . In addition, values of ϕ_B and F_c were calculated for differing NDC sizes and doping levels.

SESSION R6: DIAMOND AND WIDE BANDGAP

Chair: Otto Zhou
Thursday Morning, April 27, 2000
Franciscan III (Argent)

8:30 AM R6.1

FIELD EMISSION PROPERTIES OF CARBON THIN FILMS. Oliver Groening, University of Fribourg, Fribourg, SWITZERLAND.

With the development of the field emission flat panel display technology the interest in cold electron emitters has seen an important increase over the last decade. In this context carbon thin films have received great attention. For a wide range of different carbon based materials, such as chemical vapor deposition (CVD) diamond, diamondlike carbon (DLC), nanocrystalline (mostly sp² bonded) carbon and nanotube thin films field emission current densities of up to 1 mAcm⁻² where observed for applied electric fields below 0.05 MVcm⁻¹. For comparison it should be mentioned that similar emission current densities in the case of a perfectly flat metal film would be expected at fields of 50 MVcm⁻². The perhaps most important question with regard to the field emission of carbon films is: What is the local field present at the emission site and from what kind of electronic states the electrons are emitted? I-V measurements alone can give us no or only very indirect answers to this question. We will show how the measurement of the field emitted electron energy distribution can give us reliable information on the emitter work function, the local electric field at the emission site and the nature of the emitting electron states. We will further present simultaneous field emission and photoemission measurements and discuss in the case of CVD diamond the possibility of conduction band emission. For CVD diamond and DLC thin film emitter we will give values for the emitter work function and the local electric field at the emission site and relate the electron field emission with the film properties. Due to their geometrical structure (high aspect ration) carbon nanotubes can

generate large field enhancement at their apexes and are therefore also very interesting for field emission cathodes. By field emission spectroscopy we could determine the work function of multiwalled nanotubes (MWNTs) at their apex to be 4.9 ± 0.3 eV, which agrees well with the average work function of 4.8 eV determined by photoelectron emission spectroscopy. For singlewalled nanotubes (SWNT's) we found a lower work function of 3.7 ± 0.3 eV (at the tube apex). We will present a model to explain the lowered work function of SWNT's. We will present field emission spectra of SWNT's at high temperatures of 1300 K and discuss the emission from states well above (>2 eV) the Fermi level.

8:45 AM R6.2

THE ROLE OF HYDROGEN AND NON-DIAMOND PHASES FOR THE FIELD EMISSION PROPERTIES OF CVD DIAMOND AND DIAMOND GRIT. L. Ley, J.B. Cui, J. Ristein, Inst. of Technical Physics, University of Erlangen, Erlangen, GERMANY.

An anticorrelation exists between the field emission properties and the quality of CVD diamond films and diamond grit. Emitters with larger fractions of non-diamond phases and defects have in general lower threshold fields. Also, hydrogenation improves the emission properties of these materials in all cases. We have elucidated the roles of diamond and non-diamond phases and of hydrogenation in the field emission process of diamond based materials by studying composites of nanocrystalline diamond and nanocrystalline graphite. By systematically varying the graphite content between 0 and 100% we prove that: (1) diamond is not responsible for field emission. (2) For non-hydrogenated composites the field emission is strongly influenced by the conductivity of the graphitic phase. Composites with a graphite content that is higher than the approximately 30% that constitute the percolation threshold for conductivity through a mixed conductor-insulator phase have an emission threshold similar to that of graphite. Below the percolation threshold the emission is limited by the high resistivity of the composite. (3) Hydrogenation improves the surface conductivity of diamond and removes thereby the percolation threshold in the conductivity of the composite. (4) Hydrogenation also transforms the diamond surfaces from PEA to NEA. This effectively lowers the workfunction from 5.0 to about 3.5 eV for those parts of the graphitic grains that are within a few tens of a nm of a diamond surface. It is this effect which leads to a further lowering of the emission threshold after hydrogenation. From these observations we draw the following conclusions. The superior field emission properties of poor quality CVD diamond films and diamond grit are due to the graphite-like non-diamond phases which provide the electrons for emission and in favourable cases a conducting path from the substrate to the surface. The role of diamond is threefold. It constitutes a dielectric matrix for the graphite-like fibers and sheets at the grain boundaries and allows thus for the field enhancement alluded to earlier by others. After hydrogenation, the surface conductivity of diamond ensures the flow of charge from the substrate to the surface in cases where the concentration or connectivity of the graphite-like phase lies below the percolation threshold. The unique property of diamond to attain a very low workfunction in the form of NEA, finally, lowers the field emission barrier of the graphite-like phases at the surface that are in close proximity with diamond substantially below that of graphite.

9:00 AM R6.3

ENGINEERED COATINGS FOR FIELD EMISSION CATHODES. Victor Zhirnov, Semiconductor Research Corp, Durham, NC; Donghun Kang, Gregory Wojak, Jerry Cuomo and John Hren, Dept of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

The procedures for fine tuning parameters for a field emission cathode will be introduced, both in terms of an analytical model and in the desired experimental characteristics. A composite cathode material consists of conductive tip and dielectric coating with controlled thickness, density of traps and electron saturation velocity. Controlling the materials properties of the coatings permits engineering the current/voltage characteristics of such composite emitters, thereby making it possible to fabricate cathodes with the desired characteristics. The cathode parameters in the I-V curve to be engineered are the threshold point (voltage/current), the maximum point (voltage/current), and the transconductance (slope). We will present data on cathodes with optimally controlled transconductance; that is, with current-voltage characteristics consisting of a steep initial slope (high transconductance) followed by a shallow one (low transconductance). Engineering the three critical parameters implies control of the three characteristic points of the I-V curves by controlling the coating parameters. The threshold point is a function of the coating thickness, the density of traps and the concentration of dopants. The transition point is primarily determined by the saturation velocity in the coating, which in turn, depends upon the size of crystallites in the coating and their defect density. The maximum point is determined by the thermal conductivity and the

coating thickness. We have developed two low temperature techniques for the deposition of ultrathin coatings which permit the desired controls: dielectrophoresis of nanodiamond particles and magnetron sputtering of AlN. Experimental results on emitters with such coatings have shown significant improvements in emission. We will present a phenomenological model for emission through dielectric films in the presence of both dynamic and static space charge. This model has been tested against the data from numerous experiments with different coatings. It was found that the model explains well nearly all details of the experimental observations.

9:15 AM R6.4

ANOMALOUS FIELD ENHANCEMENT IN PLANAR SEMI-CONDUCTING COLD CATHODES FROM SPONTANEOUS ORDERING IN THE ACCUMULATION REGION. Griff L. Bilbro, North Carolina State Univ, Dept of Electrical and Computer Engineering, Raleigh, NC; Robert J. Nemanich, Dept of Physics, North Carolina State Univ, Raleigh, NC.

Field emission measurements from planar diamond cold cathodes and other wide band gap semiconducting cold cathodes exhibit Fowler-Nordheim characteristics, but often with anomalously high field enhancement values. We show that anomalous field enhancement values can result from a previously unknown instability in the space-charge layer that accumulates at the surface of a semiconductor in the presence of an external electric field. We extend the conventional analysis of the accumulation region by self-consistently solving Poisson's equation, the drift diffusion equation, and the Boltzmann distribution for time-dependent, three-dimensional perturbations of electric potential and the electron density around the usual one-dimensional equilibrium. We identify certain variations of the accumulation layer that will appear spontaneously to produce variations of electron concentration, electric potential, and electric field at the surface of even a perfectly planar uniform semiconducting cathode in an ideally normal electric field. We find that the spatial scale of these variations is on the order of a Debye length, which is a few nanometers for the AlGaN cathodes being developed at North Carolina State University. We argue that this effect may explain experimental measurements of electron emission threshold voltages that are lower than predicted by UPS measurements of work functions.

9:30 AM R6.5

CARBON BASED MPCVD FILMS AS A LOW TEMPERATURE THERMIONIC-FIELD ELECTRON SOURCE. F.A.M. Koeck, J.M. Garguilo, B. Brown, R.J. Nemanich, North Carolina State University, Raleigh, NC.

Microwave Plasma assisted Chemical Vapor Deposition (MPCVD) has been utilized to synthesize nitrogen doped diamond films for application as a low temperature thermionic-field emission cathode. The critical result of this study is the imaging of electron emission from UV photo excitation and from thermionic-field emission. The samples were imaged in UHV by photo electron emission microscopy (PEEM) using a UV Hg lamp for photoemission excitation. The same instrument was used to obtain the thermionic-field emission electron microscopy images (T-FEEM) at temperatures up to 900°C. The microscope has 10nm resolution. Nitrogen doped diamond films were grown at substrate temperatures from 850°C to 920°C, microwave power of 1300W and 50 Torr chamber pressure using 0.5 vol % methane, 12 vol % nitrogen in hydrogen at a total flow rate of 500scm. The Raman spectra of the films showed a strong diamond peak at 1332cm⁻¹ and weak signal from the graphitic regions in the sample. Field emission could not be measured at room temperature, but the PEEM images showed relatively uniform emission. The PEEM images showed little change as the temperature is increased. At temperatures as low as 640°C the T-FEEM images exhibited strongly enhanced electron emission with increasing temperature. These results indicate a promising new material for the production of low temperature, high brightness electron sources.

10:15 AM R6.6

CAPACITANCE AND TRANSIENT PHOTOCAPACITANCE STUDIES OF TETRAHEDRAL AMORPHOUS CARBON. Kimon C. Palinginis and J. David Cohen, Department of Physics, University of Oregon, Eugene, OR; A. Ilie and W.I. Milne, Engineering Department, Cambridge University, Cambridge, UNITED KINGDOM.

Tetrahedral amorphous carbon (ta-C) has attracted great interest because of its high content of diamondlike sp³ - bonded carbon, usually around 80%. However, the understanding of defect densities and defect distributions in the mobility gap has been difficult since most of the standard spectroscopic methods cannot be applied to such thin films (~100nm). Recently we showed that junction capacitance techniques can successfully be applied to ta-C/c-Si heterostructures to deduce some of their electronic properties [1]. In this paper we present

a study on thin film ta-C deposited on silicon carbide (SiC) substrates. This type of heterostructure enabled us for the first time to apply the transient photocapacitance method to study deep defect transitions in the optical gap of the ta-C. Using this technique we determined an Urbach tail of 250meV in the ta-C. Junction capacitance measured as a function of temperature and frequency revealed a thermal activation process with an activation energy of 0.3eV. Unlike studies of ta-C/c-Si heterostructures this activation process did not show any bias dependence. This indicates that bulk ta-C defects dominate the behavior of the junction capacitance, implying a much lower density of defects at the ta-C/SiC interface. Capacitance profiling revealed uniform defect densities in the ta-C film ranging from 4 x 10¹⁷ cm⁻³ to 8 x 10¹⁷ cm⁻³. We previously obtained a similar density of defect states for ta-C using a crystalline Si substrate. This suggests that the true deep defect density in the optical gap of the ta-C lies indeed in this relatively low range (below 10¹⁸ cm⁻³).
[1] K.C. Palinginis, Y. Lubianiker, J.D. Cohen, A. Ilie, B. Kleinsorge and W.I. Milne, Appl. Phys. Lett. Vol. 74, pp.371 (1999).

10:30 AM R6.7

FIELD EMISSION FROM HETROSTRUCTURED NANOSEEDED DIAMOND AND NANOCLUSTER CARBON CATHODES. B.S. Satyanarayana^{1*}, K. Nishimura², A. Hiraki³, W.I. Milne¹. ¹Dept of Engineering, Cambridge University, Cambridge, UNITED KINGDOM, ²Kochi Prefectural Industrial Tech. Centre, Nunoshida, Kochi, JAPAN, ³Dept. of Electronic & Photonic Systems Engr, Kochi University of Technology, Kochi, JAPAN, *Present address - Dept. of Electronic & Photonic Systems Engr., Kochi University of Technology, Kochi, JAPAN.

There is an increasing interest in carbon based nanostructured materials like the nano-diamond, nanotubes and nanocluster carbon for possible use as electron emitters. The interest stems from the diverse applications such as electron-beam lithography, electron and ion guns, sensors, electron microscopes and microprobes, low & medium power microwave sources and Tera hz communication devices being envisaged for these electron emitters, besides field emission displays. The need is for electron emitters capable of emitting high emission currents at low fields accompanied by a high emission site density. With this aim hetrostructured microcathodes made of nanoseeded diamond and nanocluster carbon films deposited at room temperature on a silicon substrate were studied. The nanoseeded diamond with varying nano-diamond concentration was first spin coated on to the substrate. The nanocluster carbon films were then deposited on the nanoseeded diamond deposited substrates using the cathodic arc process. The hetrostructured microcathodes were observed to exhibit low field electron emission (1μA/cm² emission current at 1.5 - 5 V/μm) and also a resonant tunnelling behaviour. The resonant tunnelling behaviour was observed to be dependent on the nanoseeded diamond concentration.

10:45 AM R6.8

INTEGRATION OF ULTRANANOCRYSTALLINE DIAMOND FILMS ON GLASS SUBSTRATES FOR FIELD EMISSION DISPLAYS. T.D. Corrigan, Argonne National Laboratory, Materials Science and Chemistry Divisions, Argonne, IL, and Northwestern University, Dept. of Materials Science and Engineering, Evanston, IL; O. Auciello, Argonne National Laboratory, Materials Science Division, Argonne, A.R. Krauss, D.M. Gruen, A. Jayatissa, S. Bhattacharya, J. Tucek and A. Sumant, Argonne National Laboratory, Materials Science and Chemistry Divisions, Argonne, IL; R.P.H. Chang, Northwestern University, Dept. of Materials Science and Engineering, Evanston, IL.

It has been demonstrated that diamond and other carbon-based thin films provide low threshold field, high current electron emitting surfaces for field emission displays (FEDs). In the case of diamond-based FEDs, it will be necessary to grow diamond films on glass at < 500°C, which is much lower than the temperature needed for growing diamond films by conventional CVD. In addition, it is desirable to shorten the deposition time for cost effective processing. We have demonstrated that we can grow ultrananocrystalline diamond (UNCD) films using a unique microwave plasma technique that involves CH₄-Ar gas mixtures, as opposed to the conventional CH₄-H₂ plasma method. The growth species are C₂ dimers, resulting in activation energies of 6 Kcal/mol and the ability to grow diamond at lower temperatures than conventional diamond CVD. The UNCD films have 2-5 nm grains, as opposed to the micrometer grains characteristic of conventional diamond films. For the work discussed here, the UNCD films were grown with plasma enhanced chemical vapor deposition (PECVD) at low temperatures (350-500°C) on glass substrates coated with Ti and Mo thin films. Raman analysis confirmed the diamond character of the films. We will present results on emission properties of UNCD films selectively deposited in patterned micron-size dots as well as on gated field emitters with geometry equivalent to that needed for gated cathodes for FEDs. Work supported by the U.S. Department of Energy, BES-Materials

11:00 AM R6.9

ANOMALOUS THICKNESS DEPENDENCE OF FIELD EMISSION FROM ALN COATINGS. Donghun Kang, Victor Zhirnov, John Hren, North Carolina State Univ, Dept of Matls Sci & Engr, Raleigh, NC.

A series of "physical insight" field emission experiments were performed using ultrathin (7-20 nm) coatings of AlN deposited onto sharp (50 nm) Mo tip. The current/voltage (I-V) characteristics were analyzed following precise characterization of the emitter, e.g. the film thickness and the precise dimensions of the radii and the nature of the interfaces were examined by high resolution transmission electron microscopy. The I-V characteristics showed three distinct regions, depending upon the thickness of the AlN coatings, D. (1) For $D < 10$ nm, the emission (threshold) voltage increased with thickness, as compared to bare Mo emitters. (2) For $D = 10-15$ nm, the emission threshold dropped drastically with a minimum around 14 nm. (III) For $D > 15$ nm, the threshold voltage increased. The latter increase of the threshold voltage can be explained by the accumulation of negative space charge in the poorly conducting coatings. However, such a model does not explain the presence of a minimum in the dependency of emission voltage on the AlN coating thickness. Several other emission models were critically analyzed for their ability to quantitatively explain the experimental data, which comprised measurements of I-V, the electron energy distribution, and the temperature dependence of emission. The most realistic explanation appears to be the model of impact ionization in the AlN films. It is suggested in this model that holes generated by impact ionization in the AlN coating assist electron emission through the metal-AlN interface because of the reduction of tunneling width. This model can explain both the experimentally observed thickness dependence and the electron energy distribution data. A detailed analysis of the impact ionization model for field emission will be presented, and the model will be applied to predict an optimum thickness for AlN coatings.

SESSION R7: CARBON NANOTUBES AND NANOSTRUCTURES

Chair: Richard G. Forbes
Thursday Afternoon, April 27, 2000
Franciscan III (Argent)

1:30 PM *R7.1

FABRICATION AND ELECTRON FIELD EMISSION PROPERTIES OF CARBON NANOTUBES Q. Zhou, C. Bower, L. Fleming, H. Cui, B. Stoner, Univ. of North Carolina at Chapel Hill; W. Zhu, G.P. Kochanski, S. Jin, Bell Labs, Lucent Technologies.

In this talk we present recent results on controlled synthesis of carbon nanotubes by laser ablation and chemical vapor deposition techniques. Progress in fabrication of patterned carbon nanotube films with controlled orientations will be also presented. The electron field emission properties of different carbon nanotube materials will be discussed.

2:00 PM R7.2

NEW ELECTRON EMISSION DEVICES FORMED WITH NANOTIPPED PLANAR SURFACES PREPARED BY ENERGETIC C₆₀ BOMBARDMENT. P. Thevenard, J.P. Dupin, Binh Vu Thien, S. Purcell, V. Semet, C. Journet, Département de Physique des Matériaux, Université Claude Bernard Lyon 1, Villeurbanne, FRANCE.

A new method is proposed to realize flat-panel displays from original electron emission devices. This method is based on the ability to produce nanotips at the surface of refractory oxides by energetic bombardments with C₆₀ clusters. The goal is to obtain localized electron emitters with a controlled surface concentration in the range 10⁹ to 10¹¹ cm⁻². For this purpose, refractory oxide surfaces covered with a thin layer of metal: 5 nm of platinum, were bombarded with C₆₀ cluster beam at 20-40 MeV. To prevent an overlap of irradiated zones ie to get isolated nanotips, the fluences were kept in the range 10⁹ to 10¹¹ clusters per cm². Protrusions of nanometer sizes (up to 20 nm) were produced. The nanotips were characterized by scanning probe microscopes. They result from the damage created by the high level of electronic energy losses surrounding the particle trajectories (up to 80 keV/nm). Electron emission from these nanotipped surfaces were performed. Above a low threshold field, the current-voltage characteristics showed a two-stage behavior. At high field, the electron emission is very stable even in low vacuum. The electron energy distribution seems characteristic of negative electron affinity emitters.

2:15 PM R7.3

ELECTRON EMISSION FROM MICROWAVE PLASMA CVD

CARBON NANOTUBES. Yonhua Tzeng, Chao Liu, Department of Electrical and Computer Engineering, Auburn University, AL; Zheng Chen, Space Power Institute, Auburn University, AL.

Carbon nanotubes were deposited on substrate using a microwave plasma CVD reactor that was designed and used for diamond deposition. Substrates were heated by the microwave plasma to between 400 and 1500°C at a chamber pressure between 10 and 200 Torr. Hydrocarbon or oxyhydrocarbon mixtures that were used for diamond deposition were used as the carbon source for nanotube deposition. Under an appropriate deposition condition, both diamond and carbon nanotubes can be deposited simultaneously on the same substrate. Carbon nanotubes deposited on solid substrates were examined by a phase-contrast optical microscope, and SEM. Bundled multi-wall carbon nanotubes were visible under a phase-contrast optical microscope. An ultra high vacuum chamber was used to characterize the electron emission properties of these carbon nanotube coatings. A one millimeter diameter tungsten rod with a hemispherical tip and a glass plate coated with aluminum were used as the anode and placed at a distance between 50 and 300 micrometers from the nanotube coatings to measure the current-voltage characteristics of the carbon nanotubes. Electron emission from the carbon nanotubes started from a turn-on electric field of about 4 volts per micrometer. Electron emission current densities on the order of milli-amperes per cm² were measured. Details of the deposition process and electron emission characteristics of the carbon nanotube coatings deposited by the microwave plasma CVD technique will be presented.

2:30 PM R7.4

FABRICATION AND APPLICATION OF MICROSTRUCTURED Ni-C ELECTRODES WITH HIGH-DENSITY CARBON-NANOTUBE COATINGS. Zheng Chen, Space Power Institute, Auburn University, AL; Yonhua Tzeng, Chao Liu and Calvin Cutshaw, Department of Electrical and Computer Engineering, Auburn University, AL.

Fabrication and characterization of carbon nanotubes deposited on microstructured Ni-C electrodes will be presented. The highly effective surface-area of the microstructured Ni-C electrode provides high-density nucleation sites for carbon nanotubes. Ni also serves as a catalyst for the nanotube growth. Hydrocarbon mixtures are used as the carbon source for the chemical vapor deposition process. Carbon nanotubes deposited on microstructured Ni-C are examined using a phase-contrast optical microscope and an SEM. An ultra high vacuum chamber is used to characterize the electron emission properties of carbon nanotube coatings. Phosphor coatings are used to display visible lights which are excited by the electrons emitted from the nanotubes. These electrons are accelerated in a high voltage. The comparison of the turn-on field and visible light intensity between carbon nanotubes grown on flat substrates and microstructured Ni-C will be presented. Application of the microstructured Ni-C electrodes with high nucleation-density carbon-nanotube coatings as electron field emission electrodes are explored.

3:15 PM R7.5

HOT-FILAMENT ASSISTED FABRICATION OF CARBON NANOTUBES ELECTRON EMITTERS. Yonhua Tzeng, Chao Liu, Department of Electrical and Computer Engineering, Auburn University, AL; Zheng Chen, Space Power Institute, Auburn University, AL.

A hot-filament diamond CVD reactor has been used for the deposition of carbon nanotubes on various substrates. Substrates were heated by the hot-filament to between 400 and 1000°C at a chamber pressure between 30 and 200 Torr. Hydrocarbon or oxyhydrocarbon mixtures were used as the carbon source. Carbon nanotubes deposited on solid substrates were examined by a phase-contrast optical microscope, and SEM. Bundled multi-wall carbon nanotubes were visible under a phase-contrast optical microscope. An ultra high vacuum chamber was used to characterize the electron emission properties of these carbon nanotube coatings. A one millimeter diameter tungsten rod with a hemispherical tip and a glass plate coated with aluminum were used as the anode and placed at a distance between 50 and 300 micrometers from the nanotube coatings to measure the current-voltage characteristics of the carbon nanotubes. Electron emission from the carbon nanotubes started from a turn-on electric field of about 4-6 volts per micrometer. Electron emission current densities on the order of milli-amperes per cm² were measured. Details of the deposition process and electron emission characteristics of the carbon nanotube coatings deposited by the hot-filament CVD technique will be presented.

3:30 PM R7.6

EFFECTIVE RADICAL SPECIES IN MICROWAVE ASSISTED PLASMA FOR THE GROWTH OF CARBON NANOTUBE. Y.S. Woo, D.Y. Jeon, Korea Advanced Institute of Science and Technology, Dept of Materials Science and Engineering, Taejeon,

KOREA; I.T. Han, N.S. Lee, J.M. Kim, Display Lab., Samsung Advanced Institute of Technology, Suwon, KOREA.

Carbon nanotubes were deposited on Ni-coated glass substrate using CH₄/H₂/NH₃ gas mixture as a precursor by microwave plasma-enhanced chemical vapor deposition method. By observing the scanning electron microscope, it was found that the density and shape of carbon nanotube as well as the coagulation of Ni film were somewhat different from those formed with CH₄/H₂ or CH₄/NH₃ gas mixture. Using optical emission spectroscopy, the radical components in plasma of CH₄/H₂/NH₃ gas mixture were analyzed and compared with those of CH₄/H₂, and CH₄/NH₃ gas mixture. According to this analysis, it can be concluded that the differences in active radical composition affect the coagulation of Ni film and the growth of carbon nanotube. From this investigation we will suggest the roles of individual radical elements for the growth and etching of carbon nanotube and for the coagulation of Ni film also.

3:45 PM R7.7

FIELD EMISSION CHARACTERISTICS OF SILICON NANOWIRES FILMS. Frederick C.K. Au, K.W. Wong, Y.H. Tang, Y.Z. Zhang, I. Bello, S.T. Lee, Center of Super-Diamond and Advanced Films and Department of Physics and Materials Science, City University of Hong Kong, HONG KONG.

The field emission characteristics of silicon nanowires (SiNWs) films were investigated based on current-versus-voltage characteristics and the Fowler-Nordheim equation. The SiNWs were synthesized by laser ablation method. Pieces of sponge-like SiNWs were grounded to powder, then dispersed and stuck onto a silicon wafer for field emission measurements. Hydrogen plasma treatment by electron cyclotron resonance chemical vapor deposition can possibly removed the oxide layer and improved the emission uniformity of the film. Decreasing the diameter of the silicon nanowires can enhanced the electron field emission.

4:00 PM R7.8

STUDIES OF ELECTRON/ION EMISSION FROM THE PLASMA FORMED ON THE SURFACE OF FERROELECTRICS. A. Dunaevsky, Ya. E. Krasik, J. Felsteiner and S. Dorfman, Department of Physics, Technion, Haifa, ISRAEL.

During last several years a great attention was directed to ferro-emission cathodes. It was shown that application of a driving pulse of several kV to the ferroelectric sample covered at rear side by a disc electrode and at the front side by a grid/strip electrode causes intense electron emission from the front side. Electron current density up to 100 A/cm² was observed. It was demonstrated that such types of cathodes could operate in a high (up to 2 MHz) repetition rate producing uniform electron beams. It was suggested that a fast (units of nanoseconds) polarization reversal of domains inside the ferroelectric causes appearance of extremely high electric field (up to 10⁹ V/cm) at the vicinity of the ferroelectric surface. The high electric field occurs due to a low conductivity of ferroelectric material that does not allow fast redistribution of free charges to compensate the domain charge, which appears as the result of reversal polarization. Carried out experiments showed severe contradictions with the model of ferroemission due to reversal polarization. Indeed, our experiments clearly showed that the source of electrons is a plasma which forms on the surface of the ferroelectric due to non-complete electrical discharge. It was shown that the plasma formation occurs at early beginning of the driving pulse independent on the phase state of the ferroelectric sample and polarity of the driving pulse. Parameters of the plasma and extracted electron beam are presented and discussed.