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Patchwork field emission properties of lanthanum monosulfide thin films

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The field emission properties of lanthanum monosulfide (LaS) films, deposited on Si substrates by pulsed laser deposition, have been thoroughly analyzed via the scanning anode field emission microscopy technique. Using the conventional Fowler-Nordheim relation, the work function of LaS thin films has been extracted from the slope of the plot $\ln(J/F^2)$ vs $1/F$, where J is the field emission current density and F is the local applied electric field. The threshold for an emission current density of 1 mA/cm^2 occurs around a $230 \text{ V}/\mu\text{m}$ electric field applied across the vacuum gap. This leads to an outstanding, reproducible effective work function value of $\sim 1 \text{ eV}$ across a 1 cm^2 sample area. © 2006 American Vacuum Society. [DOI: 10.1116/1.2354161]

I. INTRODUCTION

In the past, Modukuru *et al.* reported the successful growth of bulk samples of lanthanum and neodymium monosulfides (LaS/NdS) using the sesquisulfide route.¹ Powder x-ray diffraction scans of the samples were obtained and indicated the successful growth of the cubic phase of LaS and NdS with a rocksalt structure. The Kelvin probe technique was used to measure the work function of these bulk samples in air and the best work functions measured to date were found equal to 2.6 and 2.7 eV, for LaS and NdS bulk samples, respectively.² More recently, the first successful deposition of LaS thin films on Si substrates using pulsed laser deposition (PLD) was reported through a collaboration between the University of Cincinnati and the US Air Force Research Laboratory.³

We report in this article a systematic field emission (FE) study from these deposited thin films of LaS on Si by scanning anode field emission microscopy (SAFEM). The experimental results indicated that the LaS surface presented an effective surface barrier for FE in the range of 1 eV over zones that represent only $\sim 1/1000$ of the whole surface area. These patchwork zones were “burned out,” i.e., lose their low effective work function properties, after extracting FE current densities greater than $\sim 50 \text{ A/cm}^2$.

II. EXPERIMENTAL RESULTS

A. LaS thin film cathode fabrication

The PLD technique was used to deposit LaS films on Si wafers. The values of deposition parameters (chamber pressure, substrate temperature, substrate-to-target separation, laser energy, repetition rate, and spot size on the target) leading to a successful growth of films in their cubic rocksalt structure were identified.³ The resulting films, with a thickness up to 100 nm, are golden yellow in appearance with a mirrorlike surface morphology and have a sheet resistance around $0.1 \Omega/\text{sq}$. X-ray diffraction analysis of thick films (about $1 \mu\text{m}$) shows a lattice constant of $5.863(7) \text{ \AA}$, which is close to the bulk LaS value. High resolution transmission electron microscopy revealed the films to consist of nanocrystalline regions, as can be seen in Fig. 1.

B. Field emission measurements from the flat LaS thin film cathode

We use the SAFEM technique (Fig. 2) to extract the FE current from the planar LaS thin film cathodes. The methodology is described in detail in Ref. 4. Hereafter, we outline the main features of the technique.

The SAFEM technique was used to measure the current-voltage (I - V) characteristics at different surface locations and at different temperatures of a LaS thin film with an area of about a 1 cm^2 .⁴ For one location, the full set of measured I - V characteristics (total measured current versus applied voltage) for different values of d , the distance between the cathode surface and the probe ball, were then analyzed in

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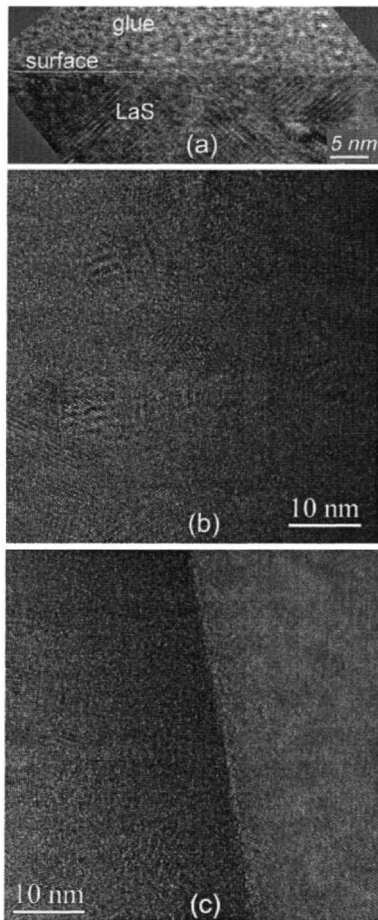


FIG. 1. HRTEM images of (A) top, (B) middle, and (C) interface of a LaS thin film grown on a (100) Si substrate. The admixture of nanocrystalline phases with different orientations and amorphous material throughout the entire cross section of the film can clearly be seen.

order to extract the current density J versus actual applied field F (J - F data) within the approximation that the LaS surface is a plane.

FE from the LaS film presents the following main properties [all of them were systematically observed for different samples (2) and from independent measurements over different locations (7) spreading across the entire 1 cm^2 sample area].

- (1) *FE behavior for total emission current up to a limit value of a few microamperes.* A characteristic J - F variation is shown in Fig. 3 and is typical of a conventional field emission behavior, i.e., a linear variation of $\ln(J/F^2)$ vs $1/F$. The J - F variations are reversible as long as the total FE current is lower than $\sim 1 \mu\text{A}$. The electric field F across the vacuum gap needed to observe an emission current density of $1 \text{ mA}/\text{cm}^2$ was found to be around $230 \text{ V}/\mu\text{m}$. An immediate reaction to such FE behavior for so low values of the applied voltage is to question the flatness of the surface of the cathode. In other words, one must consider the possibility of local corrugations introducing a field enhancement factor γ during the conversion of the applied voltages to electric field values.⁵ In such a case, the assumed value of

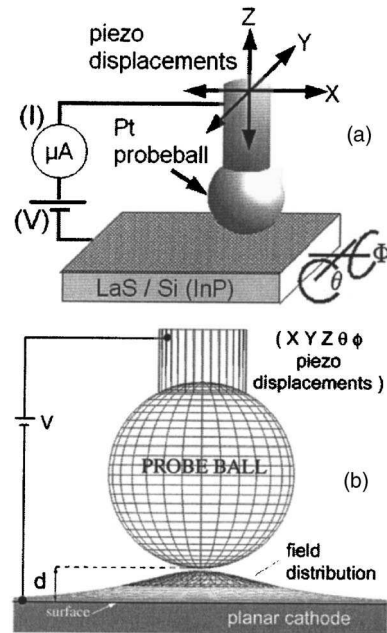


FIG. 2. (a) Schematic representation of the SAFEM. All five mechanical displacements are piezodriven motors with nanometric resolution. (b) The exact field distribution is numerically calculated for each value of applied voltage V and distance $Z=d$. It allowed the extraction of the current density J vs actual applied field F (J - F data) from the full set of measured I - V characteristics for different values d (Ref. 4).

$230 \text{ V}/\mu\text{m}$ would be wrong. To confirm or invalidate this possibility a thorough investigation of the flatness of the LaS thin films by atomic force microscopy (AFM) was carried out over the entire surface area of the samples ($\sim 1 \text{ cm}^2$). The average root-mean-square (rms) variation of the film surface roughness measured over several $1 \mu\text{m}^2$ areas across the entire sample was found to be below 2 nm by AFM. This small rms value is not enough to induce a field enhancement factor of about 10 needed to have FE from a 3.5 eV work function surface. In conclusion, from the AFM measurements, the hypothesis of a planar surface is valid and the values of the electric field extracted from the applied voltage are correct. One can debate about the validity of the conventional Fowler-Nordheim (FN) relation for field emission through a very low surface barrier. However, due to the lack of any other analysis method, we have used the conventional FN relation to extract, from a self-consistent analysis,⁶ the “apparent” surface barrier height (or “effective” work function) of the LaS thin film from the slope of the plot $\ln(J/F^2)$ vs $1/F$. The detailed analysis method was reported in Ref. 4. We call the “effective” work function the value of $\sim 1 \text{ eV}$ obtained with the hypothesis of a flat surface, i.e., assuming γ equal to 1. Moreover, from the analysis of the experimental measurements, exemplified in Fig. 3, within the FN relation and, in particular, with the preexponential term, it appears that only $\sim 1/1000$ of the area probed by the scanning ball is emitting with the effective work function of $\sim 1 \text{ eV}$. This fractional area is a mean value that was obtained by fitting the experimental I - V measurements

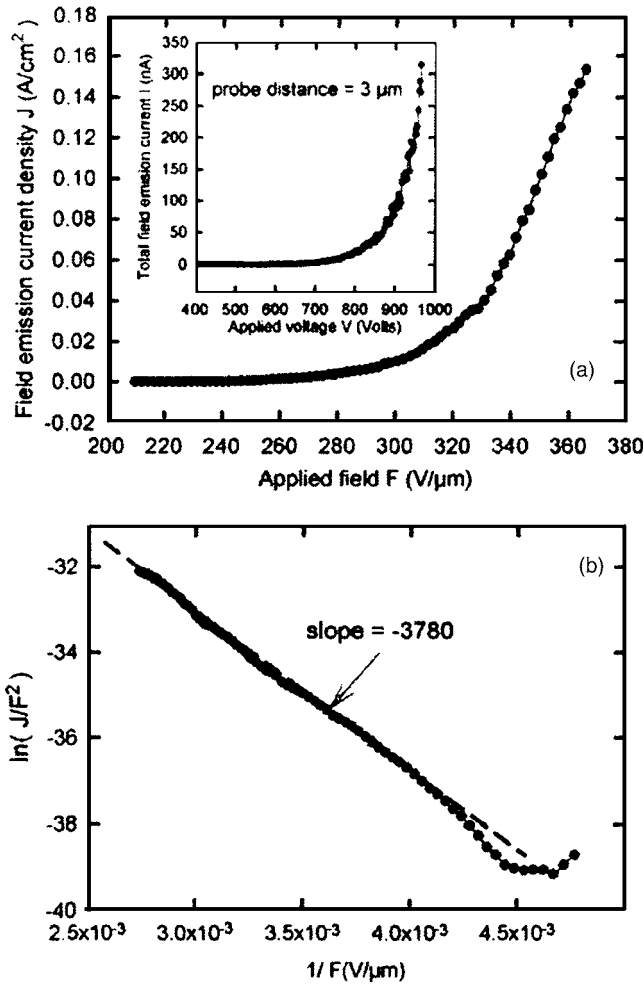


FIG. 3. (a) Characteristic J - F plot obtained from I - V measurements at different cathode-probe ball distances. The inset is a I - V plot for a SAFEM probe distance of $d=3 \mu\text{m}$. (b) The same data plotted as $\ln(J/F^2)$ vs $1/F$.

with the preexponential term of the Fowler-Nordheim relation calculated by integration of the current density over the active field emission area. These analyses have taken into account the field distribution over the cathode surface due to the spherical geometry of the probe ball.⁴

- (2) *Burnout behavior.* For higher values of the emitting current, when $I > I_{BO}$ with I_{BO} in the range of microamperes, a sudden current blackout happens. Figure 4(a) is a characteristic example of such a behavior with a value of the $I_{BO}=0.5 \mu\text{A}$. This sudden and irreversible blackout of the FE current happens due to a sudden increase in the apparent surface barrier of the emitting zone. This is a nonreversible surface evolution. We call the resulting emission area a *burnout* area. In order to estimate the value of the current density J_{BO} leading to the blackout, we have divided the total blackout current I_{BO} by 1/1000 of the probe surface defined by numerical simulations. Different measurements give J_{BO} values between 50 and 100 A/cm^2 .

A comparison between the two $\ln(I/V^2)$ vs $1/V$ plots, measured successively for the same area before and after a burnout, gives a ratio of 8.82 for the slopes [Fig. 4(b)]. This

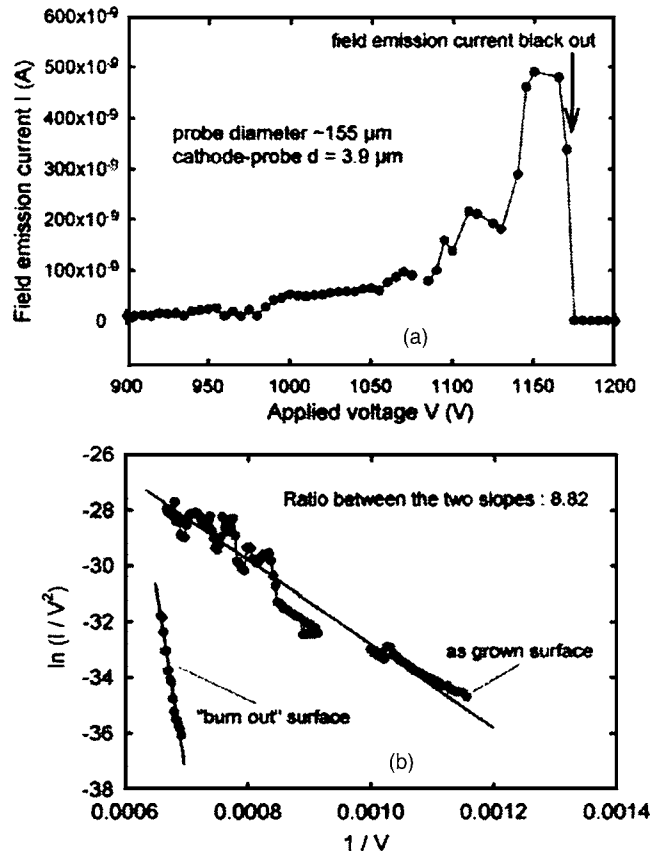


FIG. 4. (a) I - V characteristics showing the field emission current blacking out after reaching a value of $0.5 \mu\text{A}$. For field emission kept under $0.5 \mu\text{A}$, the I - V variation is reversible. After the blackout, there is an irreversible change of the surface, which we call “burnout” surface. (b) Fowler-Nordheim plots of the same area. The as-grown surface corresponds to a reversible FE with a current less than $1 \mu\text{A}$. The burnout surface corresponds to the same zone after a sudden blackout of FE when the current is over the $1 \mu\text{A}$ range.

means that the apparent surface barrier of the burnout surface can be estimated to be $\sim 3.5 \text{ eV}$ compared to the as-grown surface, which has an effective value of $\sim 1 \text{ eV}$ as shown earlier. This value is comparable with the Kelvin probe measurements and also with the thermionic and photoemission measurements performed on the as-grown surface. The surface barrier deduced from our analysis within the Richardson-Dushman relation of the thermionic data from the same samples has a value between 2.7 and 2.8 eV. Photoemission currents were also measured when the as-grown LaS surface was irradiated with 455 nm photons.

After a first blackout and still maintaining the probe ball at the same position, i.e., the same (X, Y) locations and same distance d of the SAFEM probe above the sample, a FE recovery takes place for higher applied voltage. In the example shown in Fig. 5, the cathode-probe distance was $4.25 \mu\text{m}$ and the first blackout happens at $\sim 1500 \text{ V}$ with $I_{BO}=1.5 \mu\text{A}$. Pushing the voltage up to $\sim 2200 \text{ V}$, a FE current can be obtained resulting in a conventional Fowler-Nordheim behavior until a second blackout occurs at an overall current of $\sim 2 \mu\text{A}$ for an applied voltage of $\sim 2400 \text{ V}$.

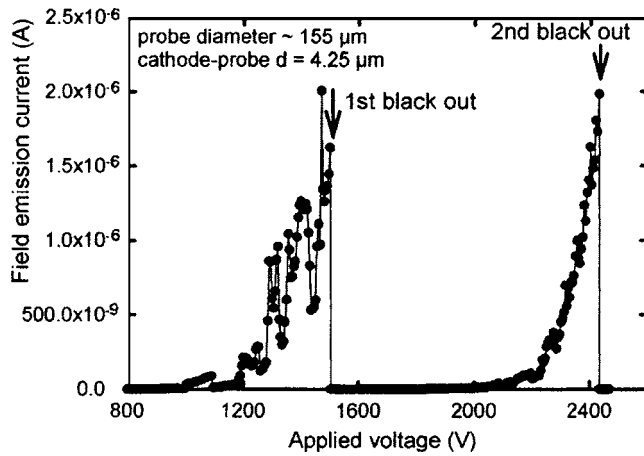


Fig. 5. I - V characteristics from a fixed position of the LaS surface showing two successive blackouts of the FE current when increasing the applied voltage.

This behavior could be the result of the presence of adsorbed species on the surface and the formation of nanoprotusions under the presence of a high electric field, a process well known for metallic tips and repeatable as long as the tip is reexposed to a new adsorption. In the experiment with LaS, when a surface was “burned out” it was no longer possible to observe again an effective work function of ~ 1 eV. This irreversible behavior is incompatible with the nanoprotusion formation from adsorbed species. This is the reason that we have not considered the hypothesis of patchwork nanoprotusions due to adsorption to explain the observed I - V characteristics of the LaS surface. Although no scanning electron microscopy observation of the burnout areas has been done, a visual examination of the surface gave no sign of any surface damage.

III. FIELD EMISSION MODEL

Our interpretation of the FE behavior from the LaS film takes into account two facts: (i) the high-resolution transmission electron microscopy (HRTEM) observations of the LaS film indicated a polycrystalline layer with nanometric crystallites (Fig. 1); and (ii) the work function of the LaS surface is dependent on the crystallographic orientation. Calculations indicate that some orientations can have a work function less than 1 eV, for example, it gives a value of 0.9 eV for the $\langle 100 \rangle$ direction.^{7,8} Measurements of the work function of bulk samples, which contain polycrystalline grains with many different crystallographic orientations, have been reported to be in the range from 2.6 to 3.0 eV.² Our interpretation is therefore based on a patchwork distribution of the work function at the surface of the LaS film due to its polycrystalline structure. Nanocrystals having the $\langle 100 \rangle$ orientation perpendicular to the surface and outcropping it are believed to be responsible for the low work function of ~ 1 eV recorded using the SAFEM technique. They are surrounded by nanocrystals presenting other crystallographic orientations and amorphous zones that will have a work function in the range of 2.6–3.5 eV. Field emission current will then

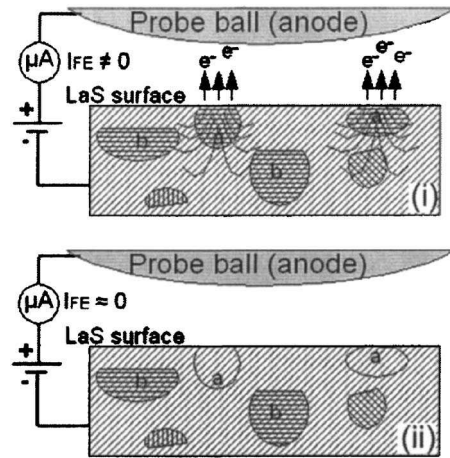


Fig. 6. (i) Schematic representation of a patchwork FE through nanocrystallites (a) having low work function [crystallites (a) and (b) have the same orientations but (b) are FE inert because they are embedded in the layer]; the lines surrounding the nanocrystallites (a) schematically represent the current lines of the emitted electrons. (ii) The crystallites (a) have undergone crystallographic modification due to the FE high current density. Their outcropping surfaces no longer have low work function values.

preferentially be extracted from these $\langle 100 \rangle$ areas [Fig. 6(i)]. According to our analyses this ratio is about 1/1000 of the surface area. When the total FE current goes beyond the $1 \mu\text{A}$ range, the FE current density transiting through these areas reaches values in the range of 100 A/cm^2 that can produce enough internal heating, i.e., energy absorption, to activate a crystallographic rotation/modification of the $\langle 100 \rangle$ nanocrystals, accompanied by a sudden disappearance of the low work function patchwork area. Most of the surface will then have a work function in the range of 3.5 eV, leading to a blackout of the FE current when the same applied voltage (~ 1500 V) is maintained because it is not enough to have FE from a 3.5 eV work function surface [Fig. 6(ii)]. In concrete terms and for comparison, having a cathode-probe distance of $4.25 \mu\text{m}$ (experimental condition of Fig. 5) and a value of the work function of 3.5 eV, it needs an applied voltage of 5600 V (i.e., an axial local field of $1350 \text{ V}/\mu\text{m}$) to extract a total FE current of $\sim 1 \times 10^{-10}$ A.

The multiple blackouts of the FE current shown in Fig. 5 can also be explained by this model if one considers the electric field distribution under the probe ball. As the burnout zone is localized only for an area where $J_{\text{local}} > J_{\text{BO}}$, the first one is then a circular zone around the axis of the probe ball where the highest field distribution is present. After the first blackout, this zone now is having a work function of ~ 3.5 eV, it will have observable field emission only for a local field exceeding $1350 \text{ V}/\mu\text{m}$ (i.e., 5600 V for the applied voltage). However, by increasing the applied voltage from 1500 to less than 5600 V the patchwork areas having an effective work function of ~ 1 eV within the annular region surrounding this burnout area will emit when the local fields become greater than the threshold value of $\sim 230 \text{ V}/\mu\text{m}$. The corresponding FE current from these patchwork areas will increase with the applied voltage following the FN relation until the second blackout occurs

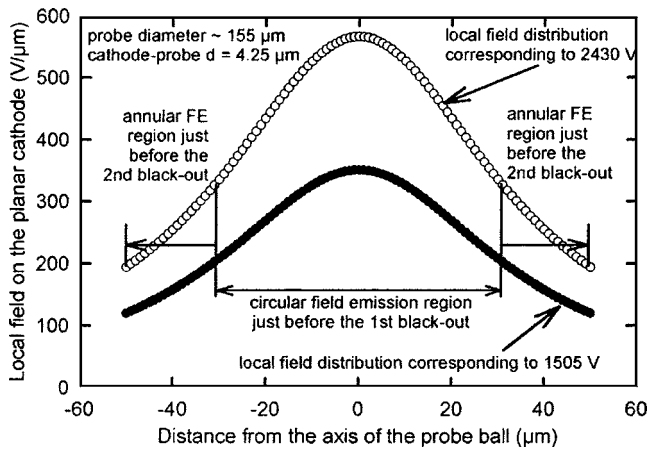


Fig. 7. Field distributions over a planar cathode for two values of applied voltages corresponding to the blackout voltages of Fig. 5. The distance d of the cathode probe is $4.25 \mu\text{m}$. The estimated field emission areas before and after the first blackout are also indicated.

when the current density over this annular region reaches J_{BO} . With regard to this analysis, in Fig. 7 we have plotted the calculated field distributions over the cathode surface for two values of the applied voltage corresponding to the blackout situations of Fig. 5, i.e., for 1505 and 2430 V, respectively. In the same figure, we also report the sizes of the first (circular) and the second (annular) emitting areas corresponding, respectively, to before the first and second blackout. These areas were estimated by fitting the experimental values of Fig. 5 with the Fowler-Nordheim model and the difference in areas was the result of the field distribution over the ball anode. This figure also clearly indicates that for applied voltages up to 2430 V only the area with an effective work function of $\sim 1 \text{ eV}$ can emit, i.e., justifying the model of FE from $\langle 100 \rangle$ nanocrystallites located in the annular shape emission area after the first blackout.

IV. CONCLUSIONS

Scanning anode field emission microscopy (SAFEM) was used to measure the field emission properties of lanthanum monosulfide (LaS) films (with thickness up to 100 nm) deposited on Si substrates by pulsed laser deposition. A thorough AFM investigation of the flatness of the surface allows one to discard the possibility of field enhancement by a surface corrugation. By using the conventional Fowler-Nordheim relation, the effective work function of LaS thin films has been extracted from the slope of the plot $\ln(J/F^2)$ vs $1/F$ and found to be around 1 eV when measured at different locations across a sample area of 1 cm^2 . The threshold for an emission current density of 1 mA/cm^2 occurs around

a $230 \text{ V}/\mu\text{m}$ electric field applied across the vacuum gap. The I - V characteristics are reversible as long as the FE current is lower than $\sim 1 \mu\text{A}$. For higher values of the emitting current, a sudden current blackout happens. Such an emission area is called a *burnout* area. An interpretation of these results is given based on a patchwork distribution of the work function at the surface of the LaS film due to its polycrystalline structure, as revealed by HRTEM measurements. Nanocrystals having the $\langle 100 \rangle$ orientation perpendicular to the surface and outcropping it are believed to be responsible for the low work function of $\sim 1 \text{ eV}$ recorded using the SAFEM technique. Our future efforts will be aimed at growing thinner monocrystalline LaS films with the $\langle 100 \rangle$ orientation to avoid the burnout regime of operation of the LaS films. In addition to field emission analysis for a very low surface barrier, further studies and analyses are also needed to answer the following questions. What is the uniformity of the spatial distribution of the nanocrystallites, for the electron emission occurs dominantly from the low work function regions? What is the mechanism that triggers the local phase transformation of the outcropping patchwork area? What is the behavior of electron emission from patchwork nanoscale areas with low apparent surface barrier completely surrounded by areas with high surface barrier,⁹ and in particular on the role of the applied high electric field on the apparent surface barrier?

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⁵The field enhancement factor γ due to a local corrugation is a function of the ratio (total corrugation height L /corrugation apex radius a) [C. J. Edgcombe and U. Valdrè, *J. Microsc.* **203**, 188 (2001)]. This effect is of importance, in particular, for L equal or greater than r , with r well under $1 \mu\text{m}$.

⁶Iterative calculations have been done in order to take into consideration the variations of the Nordheim parameters with the work function and FE applied field.

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