Electron transport in discontinuous metal thin films

James E Morris
Department of Electrical & Computer Engineering, Portland State University, Portland OR, United States of America
E-mail: jmorris@pdx.edu

Keywords: discontinuous thin films, electron tunneling, electrostatic activation, contact injection, nanoparticle self-assembly

Abstract
The structure and basic experimental electrical properties of vacuum evaporated discontinuous (island) metal thin films of discrete metal nanoparticles on insulating substrates are briefly reviewed. Then the widely accepted Neugebauer and Webb (N&W) electrostatically activated electron tunneling conduction model is covered (with enhancements) before the numerous discrepancies between this model and experimental observations are identified, e.g. minimal substrate bias effect, non-linear field distribution, anomalous AC effects, asymmetrical contact effects, and switching. A modified model, based on contact electron injection and extraction, and computer simulations are introduced which explain these discrepancies at a qualitative level. However, quantitative experimental verification of the model is not possible without stable, reproducible films of known structures. The paper concludes with a review of possible preparation techniques which could yield satisfactory samples, especially self-assembly of organically protected metal nanoparticles. One of these has already demonstrated electrostatically activated conduction.

1. Introduction

One can only imagine the initial reactions of the earliest thin film researchers measuring the resistances of (continuous) metal thin films on insulating substrates when resistivity at very small (ultrathin) thicknesses not only seemed anomalously high, but seemed also to display semiconducting properties. Such films would also have displayed colors which possibly suggested their discrete metal island structures to those familiar with the work of Lord Rayleigh and Maxwell-Garnet [1, 2] on colored glasses, e.g. ‘gold glass.’ Such structures would be verified later with the development of electron microscopy.

Gorter [3] and Darmois [4] were the first to propose an electrostatic origin of the ‘semiconductor’ activation energy $\delta E$ as that necessary to charge a spherical island of radius $r$ by removing the electronic charge $q$ to infinity, where $\varepsilon$ is the effective dielectric constant and $C$ is the system capacitance. Other conduction models have been proposed, e.g. by Hartman [5], Wei [6], Herman & Rhodin [7], Milgram & Lu [8] and Tick & Fehlner [9], but agreements with experiment were generally regarded as lacking and it was the electrostatic charging model with inter-island charge transfer by electron tunneling which was generally accepted by the mid-1970s. Nowadays, of course, the concept of the coulomb block (CB) and single electron transistor (SET) has cemented the electrostatically activated tunneling model in place. For this reason, only variations of this model are considered here.

$$\delta E = \frac{q^2}{4\pi\varepsilon r} = \frac{q^2}{2C}$$

(1)

In the 1970s, research in discontinuous metal thin films (DMTFs) was primarily driven by their potential applications as strain gauges [10–19] or for hydrogen detection [20–27], and later for more varied applications [28, 29]. These and subsequent work also have current significance to the understanding and development of CB devices, SETs and quantum dot cellular automata, e.g. in the use of a chain of metal nanoparticles (figure 1) in a SET to reduce $C$ and increase $\delta E$ to enable operation at higher temperatures.
Readers are referred to the earlier review paper [30] which duplicates most of section 2 below and some of section 3, but at much greater length and detail, and subject to 1977’s understanding of the field.

The primary motivation for this review is to challenge a new generation of researchers to take advantage of techniques of fabrication, simulation and characterization to move the field forward in both understanding and applications.

2. 2. Basic structure and properties

Typical DMTF structures as shown in figure 2 (by Kazmerski and Racine (K&R) [31]) are formed by the vacuum deposition of a metal on an insulating substrate. These are usually (but not always) gold on glass, where the nucleation and growth of metal islands/nanoparticles is governed by the weak adhesion of the metal atoms to the substrate. Note that there is already some coalescence of the initial nuclei at 1 nm thickness in figure 2(a), with secondary nucleation evident at 4 nm and 6 nm until the film nears metallic continuity at 15 nm.

Note the relatively clear areas surrounding the larger islands where secondary nucleation can take place where initial nuclei have coalesced into larger aggregates. In figures 2(a) and (c) rings of secondary nuclei can be identified surrounding these larger aggregates due to a ‘capture distance’ resulting from surface diffusion. These capture distances increase with temperature as a consequence of the surface diffusion constant’s temperature dependence. Figure 3 illustrates the process. Figure 3(a) shows three established nuclei which would absorb all atoms deposited within the capture distance X/2, whereas 3(b) shows the possibility of secondary nucleation in areas exposed by island coalescence.

Computer simulations of the development of aggregated (coalesced) islands and secondary nucleation islands have been presented in [32].
Figure 2. DMTF nucleation and growth of Au on glass at nominal thicknesses (a) 1 nm, (b) 4 nm, (c) 6 nm and (d) 15 nm. Deposition at 0.05 nm sec$^{-1}$. Reprinted from [31], with the permission of AIP Publishing.
Figure 4 shows the variation of island radius $r$ and separation $s$ with nominal thicknesses corresponding to figure 2. The essential point to note here is the relatively constant island separation of approximately 2 nm over a wide range of thickness due to the capture distance.

The ‘semiconductor-like’ variation of electrical conductance $\sigma$ with absolute temperature $T$ is demonstrated by the Arrhenius plot of figure 5 which gives a relationship of the form

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right)$$

(2)

where $k$ is Boltzmann’s constant.

2.1. Electrostatically activated tunneling

Neugebauer and Webb (N&W) [33] developed the widely accepted concept of electrostatically activated tunneling between islands. The basic premise is that the number of charged islands $N$ is given by the Boltzmann distribution.

$$N = N_\infty \exp\left(-\frac{\Delta E}{kT}\right)$$

(3)

where $N_\infty$ is the total number of islands. Conduction occurs by electron tunneling between these $N$ charged islands and the neutral islands. The tunneling term is

$$\sigma_n = \frac{\lambda 4\pi mq^2}{h^3 B} \frac{\pi BkT}{\sin \pi BkT} \exp\left(-A\phi^{1/2}\right)$$

(4)

where $B = (A/2)\phi^{1/2}$, $A = 4\pi s (2m)^{1/2}/h$, $\lambda$ is a constant and $m$ is the effective electron mass, $h$ is Planck’s constant and $\phi$ is the effective tunneling barrier height.
The second element of the N&W model is that $\delta E$ is modified from equation (1) to

$$\delta E = \frac{q^2}{4\pi\varepsilon} \left( \frac{1}{r} - \frac{1}{r + s} \right) = \frac{q^2}{2C}$$

(5)

where

$$C = 2\pi\varepsilon r(1 + r/s)$$

(6)

is the capacitance between the island and the rest of the film a distance $s$ (the capture distance) away. This recognizes that the island charge needs to be transported a distance $s$ away, not to infinity.

Figure 6 compares experimentally determined values of $\delta E$ with the expected variation with $r$ and $s$, from the published results of several researchers, i.e. K&R (figures 4 and 5) [31], Hill (H) [34], Herman and Rhodin (H&R) [35], Tick and Fehlner (T&F) [9], and Morris (M). The solid lines represent equation (5) with $\varepsilon_r = 1$ and 10. All points should fall between these limits and closer to $\varepsilon_r = 1$ than 10.

Clearly, conduction between the larger aggregate islands must take place through the smaller secondary islands and presumably authors would report those sizes for bimodal distributions, but this point is not explicitly made. The K&R line suggests $\varepsilon_r < 1$, which is not physical. $\delta E$ is calculated for each point from figure 5 with $r$ and $s$ taken from the corresponding points in figure 4. A possible explanation of the anomaly could be that $r$ and $s$ were determined for the coalesced islands rather than for secondary nucleations. If so, secondary island sizes would push the K&R plot in figure 6 to the right, towards the $\varepsilon_r = 1$ line. By contrast, figure 7 [36, 37] shows good agreement with equation (5) with $\varepsilon_r \approx 1.2$ for sputtered Al films with $r$ and $s$ measured by AFM (see below.)

Apart from this point, there are clearly differences between the best line plots for the different researchers represented in figure 6, and the question arises as to which island sizes have been measured and whether these are the islands actually determining the measured $\delta E$ values. Hill pointed out that if electrical contacts are deposited prior to the DMTF deposition, radiation from the thermal source (which was generally used) will heat the contacts more than the (glass) substrate and create a thermal gradient adjacent to the contacts which will affect the nucleation and growth of films there [38]. All the depositions which provided the data for figure 6 were performed with pre-deposited electrodes [9, 31, 34] except for H&R [35] for which this information is not given.
It is visually evident that the film structure adjacent to the electrical contacts is different from that in the ‘bulk’ of the film, away from the contacts, but the usual assumption has been that this is due to diffusion of contact material under the deposition mask. But the higher temperature in this region would promote higher atomic surface diffusion constants which would lead to mobile adatom depletion immediately adjacent to the contact due to contact capture and larger tunneling gaps. There is little evidence of the structure at the contacts for the simple reason that the preparation of samples for electron microscopy is extraordinarily difficult. Parallel deposition on carbon-coated copper grids does not give a realistic picture [21, 39] and SiO2 coated grids, which should be better, were not generally available when this work was done. Most coated the DMTF with carbon and floated samples off the substrate in water, aided by the surface tension. But this turned out to be impossible for areas immediately adjacent to the contacts, with the only solution to use a soluble substrate [40]. The net effect has been that published structures have been from the center of the films while (it will be argued below) the structure determining electrical properties is that at the contacts.

The atomic force microscope (AFM) can give additional information and is non-destructive. Two examples are presented below in figure 8 for sputtered Al films where high temperature deposition (at 773 K) maintains the discontinuous structure longer than for other films discussed here. The AFM’s z-axis resolution should provide a means of direct measurement of island eccentricity from the curvature of the surface. Combined with the height measurement, this could also provide a measure of the island-substrate contact angle assuming oblate ellipsoidal shapes (see below.) But the AFM has its limits. The physical size of even ultra-fine tips prevents m from reaching down through nm-scale gaps to secondary nuclei between coalesced islands.
2.2. Non-ohmic effects

The observation of non-ohmic effects in DMTFs provided a litmus test for earlier models and established N&W’s electrostatically activated tunneling model as the front runner. The field-dependent activation energy is similar to the Schottky effect as shown in figure 9 [41] in which the reduction of $\delta E$ with electric field $F$ and the development of a maximum is illustrated, with $\delta E$ eventually going to zero.

$\delta E$ in equation (5) is modified to

$$
\delta E = \frac{q^2}{4\pi \varepsilon} \left( \frac{1}{r} - \frac{1}{r + s} \right) - (2r + s)qF
$$

for $F < \frac{q}{4\pi \varepsilon r (r + s)^2}$ and for higher fields to

$$
\delta E = \frac{q^2}{4\pi \varepsilon r} + \left( \frac{r}{s} (2r + s)qF + \left( \frac{q}{4\pi \varepsilon} \frac{2r + s}{s} qF \right)^{1/2} \right)
$$

Figure 8. Two AFM images showing the growth of sputtered Al films. Reproduced with permission from [36]. The z-axis markers are 20 nm.
until \( \delta E \rightarrow 0 \) when \( F = (q/4\pi \varepsilon)/r^2 \), which corresponds to the CB turn–on condition at \( T = 0 \) K. Plots of these equations (figure 10(a)) [41] compared favorably in general shape to experimental plots (figure 10(b)) [42] which also show the expected inflection as the dependence of \( \log (\sigma/\sigma_0) \) (which corresponds to \( \delta E \)) goes from the linear dependence on \( F \) to \( F^{1/3} \). Experimental variations of \( \delta E \) with field also match theory [43] or at least display a linear dependence on \( F^{1/3} \) (figure 11) [34].

### 2.3. Modified theory for oblate islands

Everything above is based on the assumption of spherical islands, but it was realized that with a calculated contact angle for gold on glass of 136° [44] (idealized), reality should fall somewhere between spherical and hemispherical. But there are additional complications.

Norrman and Andersson noticed that the nanoparticle islands as viewed by transmission electron microscopy (TEM) seemed to be elongated and modeled them as prolate ellipsoids [45]. They analyzed the statistical distributions of eccentricities, major and minor axis lengths, island separations and center-to-center distances, but without correlating island dimensions with separations.
Hill demonstrated that the island dimensions as seen by TEM vary as $m^{\frac{1}{2}}$, where $m$ is the deposited mass (figure 12) rather than as $m^{\frac{1}{3}}$ as they would for spherical islands, and that the islands are better approximated as oblate ellipsoids, or even as discs, since this is the dominant eccentricity.

For the model shown in figure 13, equations (7) and (8) become (for eccentricity $e$):

$$\delta E = \frac{q^2}{4\pi e R} e \left[ \sin^{-1} e - \sin^{-1} e \frac{1 - p}{1 + p} \right] \frac{1}{1 - p} qRF$$
for

\[ F < F_{\text{min}} = \frac{q}{4\pi \varepsilon R^2} \frac{4p}{1 + p} [(1 + p)^2 - e^2(1 - p)^2]^{1/2} \]

where \( p = s/R \), \( R = 2r + s \), and

\[ \delta E = \frac{q^2}{2} \left[ \frac{\sin^{-1} e - \sin^{-1} \sqrt{1 - e}}{(1 - p)R + 2x} \right] = \frac{qFe}{p} \]

for \( F_{\text{min}} < F < F_{\text{max}} = \frac{q}{4\pi \varepsilon R^2} \frac{4p}{(1 - p)^2 \sqrt{1 - e^2}} \)

where

\[ x = \frac{Re(1 - p)}{2\sqrt{2}} \left[ \sqrt{1 + \frac{2ap}{\pi \varepsilon F}} (1 - p)^2 R^2 e^2 - \sqrt{2} \right] \]

and \( \delta E = 0 \) at \( F = F_{\text{max}} \).

Direct observation of the oblate nature of the islands is not easy, but can be done by the technique developed by Fathy (ASU HREM Facility) and Morris [47], shown in figure 14. The larger islands seen by this technique are significantly flattened with major:minor axis ratios on the order of 10:1 and contact angles of \( \sim 136^\circ \) by eye.

Figure 15 demonstrates that the Au-glass contact angle is \( >90^\circ \) and shows that larger islands can overlap smaller (secondary nucleation) islands [48].

2.4.2.4 The granular film model

Many have proposed island/gap correlations for electron hopping models and derived theoretical values for \( n \) where \( \sigma \) is of the form

\[ \sigma = a \exp \left( \frac{b}{T^{1/n}} \right) \]

but while different data seemed to support some theoretical values of \( n \), no consensus emerged and it is clear that hopping models are not feasible for the tunneling distances required.

However, the modified electrostatically activated tunneling model as proposed by Abeles et al [49–51], who coined the term ‘granular metals’ to include both DMTFs and ‘cermets,’ (metal-ceramic composites) gained considerable traction. The basic premise is that the nanoparticle dimensions \( r \) and gaps \( s \) scale so \( s/r = \) constant = \( f \). In this case equation (5) can be rewritten as

\[ \delta E = \frac{q^2}{4\pi \varepsilon} \frac{f^2}{(1 + f)} \]

and combining equations (2) and (4) as

\[ \sigma = \sigma' \exp \left( \frac{\delta E}{kT} \right) \]

\[ = \sigma' \exp \left( \frac{q^2}{4\pi \varepsilon} \frac{f^2}{(1 + f)skT} \right) \]
\[ \sigma' = \sigma_0 \exp(\alpha s + \frac{\beta}{s kT}) \]

where
\[ \sigma' = \sigma_0 \exp(\alpha s) \quad \text{and} \quad \beta = (q^2/4\pi\phi)f^2/(1 + f) \]

\( \sigma \) is a maximum when \( [\alpha s + \beta/skT] \) is a minimum, when
\[ \alpha - (\beta/kT)/s^2 = 0, \quad \text{i.e. when } s = (\beta/\alpha kT)^{1/2} \]
and substituting back

$$\sigma = \sigma' \exp -2\frac{(\alpha \beta)}{kT}$$

which suggests a linear log $\sigma - 1/T^{10}$ relationship. The experimental evidence presented, however, is all for cermet with nothing to support the applicability to DMTFs. Adkins has criticized the theory generally, (with others,) but more specifically for DMTFs [52–57], for which figure 4 clearly demonstrates that the constant $s/r$ premise is fallacious.

There is evidence of curvature in some wide temperature range experimental Arrhenius plots which is indicative of some form of percolation. This issue should be tackled again when the basic conduction mechanism is confirmed, as proposed here.

3. Inconsistent experimental results

The brief review above has emphasized that DMTF conduction is understood to take place by electrostatically activated electron tunneling and has presented the standard evidence to support this conclusion, and some to support minor modifications to the basic model to accommodate increased understanding of the DMTF structure. But there are many experimental inconsistencies with the basic view of the model which is based on equation (3) and the notion of a fixed distribution of charged islands across the bulk of the film. Conflicts between this model and experiment are reviewed in this Section prior to the presentation of a modified theory which seems to resolve all discrepancies.

3.1. Experimental resistance comparison with theory

Tunneling currents calculated by equation (4) require extreme values of the effective electron mass (e.g. $\sim m_e/1000$ [30] where $m_e$ is the electron rest mass) to match measured DMTF values, whereas values of $0.4m_e$ [34] and $2.8m_e$ [10] have been obtained experimentally by other means.

3.2. Bias effect

For a regular film of 3 nm diameter islands with 3 nm gaps, say, $N_{\infty} = 1.235 \times 10^{16}/m^2$, $\delta E$ is 0.64 eV for $\varepsilon_r = 1$ so the number of charged islands is $9.4 \times 10^9/m^2$, giving a surface charge of $1.5 \times 10^{-13} C m^{-2}$. If a ‘gate’ bias is added as shown in figure 16, the film can be charged to $3.5 \times 10^{-9} C m^{-2}$ per volt, for a 1 mm thick substrate of $\varepsilon_r = 4$, charging $2 \times 10^{11}$ islands/m$^2$ per volt, i.e. roughly $2 \times 10^9$ times the equilibrium Boltzmann values per volt. That ratio can change very quickly for other parameter assumptions, but the point is that one should be able to easily swamp the equilibrium charged islands with injected charge with reasonable values of $V_{BIAS}$. The definitive experiments were performed by Adkins et al. [58, 59] where $V_{BIAS} = 1 V$ only produced a 1% change in conductance for an estimated one injected elemental charge (positive or negative) per island. Even less change was observed by Morris at higher voltages [60]. Hill [61] observed more significant changes, but attributed these to substrate effects.

3.3. Electric field distribution

Borziak et al [62] measured the potential distributions across DMTFs with a technique based on shifts in a TEM image [63]. Their results generally show minimum electric fields in the bulk of the film, away from the contacts, with larger values towards the contacts. The assumption was that these effects were due to structural variations along the film but the deviations from linearity in figure 17(a) suggest the existence of space charges in the film [64]. The implication in the text is that the L and R contacts for figure 17(a) are identical and of type a in figure 18. ‘Homogeneous’ contacts were defined by scratching a channel in a continuous film, whereas the ‘inhomogeneous’ contacts of figure 18(b) were obtained by contact diffusion under a shadow mask. The film in figures 17(b) and (c) are ostensibly ‘symmetrically’ inhomogeneous, i.e. with identical inhomogeneous contacts. However, the difference with reversed polarity does not support that, so given the observation that ‘the potential
drop was always large at the positive electrode it is hypothesized that the L contact is higher resistance than the R contact, e.g. with slightly larger gaps and/or smaller islands.

AFM probing of a discontinuous film confirms the different structure close to a contact. Figure 19 shows smaller islands with wider gaps close to the contact as compared with those further into the film. The electric field would be greater close to the contact than further away.
3.4. AC effects: capacitance

For an ideal DMTF consisting of a regular array of identical islands and gaps the electrical properties of the overall film would be representative of the properties $R_g$, $C_g$, $R_b$ of the single island-gap combination (figure 20 [65]) of the series/parallel combination of a square film. The frequency characteristics of a typical DMTF are presented in figure 21. From the corner frequency $\omega_1 = 5 \text{ rad s}^{-1}$, $R_g = 10^{10} \Omega$, and $C_g = 20 \text{ pF}$. But from equation 1 and $\delta E = 0.86 \text{ eV}$, $C_g \approx 10^{-19} \text{ F}$. This enormous discrepancy suggests that the capacitance measured by the frequency response might be between the film and a contact with the number of islands along the contact equal to $20 \times 10^{-12}/10^{-19} \approx 2 \times 10^8$ making the ‘cell’ $R_g = 2 \times 10^{18} \Omega$ with dimension $(r+s)$ along the 2.5 cm
contact c.0.1 nm (0.2 nm for two contacts) . . . plausible, but not a complete match unless the contact is ‘fractal-like’ due to diffusion under the shadow mask.

Note that $R_b$ in figure 21 does not display a consistent temperature dependence, but a positive (metallic) temperature coefficient of resistance was found in [66].

3.5. Asymmetrical films: diode effect
With asymmetric inhomogeneous contacts (figures 16(b) and (c)) the I–V characteristic shown in figure 22 can be characterized as displaying a ‘diode effect’ [30, 65].

3.6. AC effects: asymmetrical films
Asymmetrical inhomogeneous contacts can be fabricated by deposition with one contact region shadowed by the pre-deposited contact as shown in figure 23. The equivalent circuit suggests that most of the resistance is concentrated in two dissimilar contact regions, with two different parallel capacitances, with an intervening smaller resistance representing the center area of the film.

For more extremely offset depositions (figure 24) an apparent resonance effect develops due to a ‘pseudo-inductance.’ Just as the current builds with time after the application of a voltage in a regular inductor, the pseudo-inductive current increases with time as the number of injected charge carriers increases.

It would be interesting to see how these effects (and the resistances in figure 23(c)) vary with temperature.

3.7. Switching effects
Switching effects have often been observed in DMTFs, and in the analogous 3D cermet structures, as shown in figure 25. These effects are often destructive, lasting only a few cycles, presumably due to thermally induced structural changes. Hence the use of the cermet example here to represent reversible high-to-low resistance switching, where switching was observed without failure for hundreds of cycles. Repeatability suggests changes in the electronic conduction mechanism rather than structural changes, but note changes in threshold voltages between cycles.

Figure 26 shows schematically the observation of similar high-to-low switching at low frequencies in asymmetrical DMTFs with an inhomogeneous electrode, formed this time by high current breakdown of quasi continuous films. The switching thresholds are random, so switching does not occur in every cycle, despite the uniform sinusoidal input. These films also display a diode effect, (see figure 22.)

In the author’s experience, low-to-high resistance switching is invariably due to localized high current thermal effects changing preferred percolation paths and usually leads to the permanent higher resistance or film destruction. Borziak et al, however, reported stable low-to-high switching (figure 27) lasting for hundreds of stable cycles [65]. They postulated instability in the space charge indicated by the non-linear potential distribution as the cause.

4. Revised conduction model
So far, it has been established in section 2 that the mechanism of electrostatically activated tunneling hits the main points of agreement between theory and experiment, but in section 3 that it fails in many other
disagreements. Clearly there is a need for a modified model and the results in sections 3.3 to 3.6 point to contact injection as a starting point. Most treatments in the literature implicitly focus on electrons as charge carriers, i.e. the distribution of negatively charged islands, but it is axiomatic that there are positively charged islands too.

Figure 28 breaks the conduction process into multiple components. Electron transfer is from left to right for the electric field shown and solid arrows indicate the electron transfer under consideration at each location and the energy level at which it takes place, while the vertical arrows indicate the Fermi level shift in each island due to the tunneling process and δE shifts. In figure 28(a) the islands in question are initially uncharged, so these are the carrier generation processes: charge injection at the electrodes and charge separation in the center, analogous to electron-hole pair generation so we can use the term ‘hole’ for the movement of the positive charges. The higher potential barrier for the tunneling electron in hole injection than for electron injection makes this a higher component of the overall resistance and a higher field is required at equilibrium to maintain charge equality in the film. These are all activated processes but charge separation in the center of the film requires more energy to charge two islands, and of course the most likely result would be immediate recombination, so this process could be neglected, but is included in these simulations. In figure 28(b), the islands are initially charged so these represent charge extraction at the electrodes and recombination at the center, and are not thermally activated, unless the substrate’s high frequency dielectric constant comes into play [30]. Figure 28(c) shows ‘drift’ of the electrons and ‘holes’ in the bulk of the film with no increase in system energy.

With charge pair generation, recombination and ‘drift’ in the center of the film are analogous to electron-hole pair behavior in a semiconductor, so the central region’s behavior could be characterized by standard semiconductor theory, but with different dynamics characterizing each individual process, e.g. [30, 64, 71, 72] for charge separation.

Figure 23. (a) Asymmetric inhomogeneous deposition, (b) admittance Bode plot for L = 1 in, (c) equivalent circuit from (d) the Cole-Cole plot. Reproduced with permission from [67].
4.1. Simulation results
Simulations have been run for the model described above for an artificially ideal structure of $10^4$ islands in a $100 \times 100$ array. The islands are all 3 nm in size with 3 nm gaps, except for an anomalous row of 1 nm islands.
adjacent to the left hand electrode 5 nm away. The islands are considered to be spherical in the calculation of \( \delta E \) and cubic for tunneling current calculations.

4.1.1. Case A
Case A is shown in figure 29 with \( V = 10^{-4} \)V so \( eV \ll kT \ll \delta E \) at 300 K, with the results shown in figures 30–32. The potential distributions are shown for the center column of islands, two columns close to the edges, and the average over all columns along the film, whereas the charge distribution shows the total positive and negative charges for each transverse row. The potential distribution is non-linear indicating the existence of net space charges in the film, particularly at the positive electrode where a concentration of positive charges is evident. The maximum field is at the positive contact as observed experimentally (section 3.3) despite the larger gap at the negative end. The higher field at the positive end is attributed to the greater potential barrier seen by tunneling electrons for hole injection than that at the negative end for electron injection.

4.1.2. Case B
Case B covers the opposite polarity as shown in figure 33, with the simulation results shown in figures 34 and 35. Comparison of figure 34 with figure 31 shows that essentially the full applied voltage is dropped at the positive
end where the smaller island and larger gap exacerbate the difference in hole and electron injection rates. Now the space charge at the positive end is larger and primarily electrons.

4.1.3. Diode effect
Varying the voltage across the film yields the diode-like characteristic shown in figure 36, where the approximate 10:1 resistance ratio very nearly matches that observed by Borziak et al (figure 22) [30, 64].

4.1.4. Pseudoinductance
For the simulations’ initial conditions, one should ‘seed’ the film with equal numbers of positively and negatively charged islands, according to equation (3). But for $10^4$ islands and $\delta E = 0.255$ eV (for $r = 1.5$ nm, $s = 3$ nm) at 300 K, that would mean 0.036 islands, so the steady state Boltzmann distribution is increased to ‘a few’ randomly placed charges. (‘a few’ ranging from one to three pairs.) The current response to a voltage step is shown in figure 37, where the initial current at time $\sim$ps corresponds to the N&W value using the Boltzmann number of charge carriers, (or ‘a few’) whereas the steady state value at $t >$ ns corresponds to the steady state simulations of figures 29–35. (The discontinuity at time equal to 1 ns is due to a change in the simulation timestep.) The increasing current is due to the increasing numbers of injected carriers and the establishment of the steady state potential distribution, i.e. the pseudo-inductive effect in section 3.6, also explains section 3.1.
4.1.5. Switching

The simulations above were programmed with each interisland gap represented by a calculated tunneling resistance and $\delta E$. These first simulations ran as an R-C network until stopped at a fixed time step (initially 1 ps.) Then the islands’ charges were rounded up or down to integral values of the electronic charge and the charge field distributions found for these values. Then the simulation was restarted using the values when it was stopped. Obviously, this is not physically realistic, and a second set of simulations was run using a Monte Carlo random single electron transfer model [36] for an approximately 1 μm long film. The results were qualitatively similar to those obtained with the previous model, so only the switching simulation will be presented here in figures 38–40.

Figure 38 illustrates a high to low resistance switching event as the voltage across the film is ramped up well beyond the 0.1 mV level used for the previous simulations. There is clearly a current surge at a point >0.8 mV which would inject more carriers into the film. Figure 39 shows the charge distribution prior to switching with the expected Case B negative space charge at the positive contact where the electric field would be a maximum. Figure 40 shows the charge distribution after switching, with no significant space charge at the positive contact indicating the collapse of the high field there. The interpretation is that a tipping point is reached at a critical field where the barrier to hole injection collapses, resulting in the injection of many holes which recombine with the electronic space charge, forcing a redistribution of the potentials along the film.

5. Structural control

Verification of any model of any phenomenon requires experimental confirmation and that requires the ability to either set up a model that accurately represents physical reality or to set up the experiment to match the model’s assumptions. The models above are highly idealized and can be considered successful even if they only provide qualitative agreement with experiment. They are constrained by memory and processing speed restrictions, but can probably introduce some parameter variations, but are unlikely to achieve realistic structures in the near term. The alternative is to create more ideal physical structures for experiments. Even if only one parameter can be accurately controlled, that would remove one random variable and enable more realistic simulations. This Section explores some possible techniques to achieve more controllable structures.
The first sections (5.1 and 5.2) deal with efforts to directly deposit or otherwise control the fabrication of regular DMTF structures. Section 5.3 recognizes that monosized metallic nanoparticles are routinely fabricated by chemical means and reviews some self-assembly techniques to achieve uniform DMTFs.

The target is an array (or line) of metallic nanoparticles of $r \leq 10$ nm and $2$ nm $\leq s \leq 5$ nm.

### 5.1. AFM and similar techniques

It would seem that direct deposition of the nanoparticles on an insulating substrate should be the easiest method and field evaporation of gold and other materials from an atomic force microscope (AFM) tip has been investigated by numerous researchers [73–79] on both semiconducting and insulating surfaces.

The common factor is a negatively biased AFM tip yielding $1–4$ nm thick deposits of $15$ nm and $21$ nm minimum diameter on silicon [73, 74] with similar results on SiO$_2$ (on Si) [75, 76]. The method is slightly varied in [78] where a side counter electrode is deposited on the SiO$_2$ surface instead of using the Si substrate as a back gate electrode which relies on the leakage current through the SiO$_2$.

A somewhat different approach is illustrated in figure 41 [23] which shows a positive AFM tip bias with deposition control achieved by the combination of pulse width timing and diode reverse saturation current. The intention here is to deposit Cr ‘seed’ atoms by field evaporation, and to then deposit the Au DMTF.
Figure 34. Case B log potential distribution along the 600 nm film. Reproduced with permission from [23, 70].

Figure 35. Case B charge distribution along the 600 nm film. Reproduced with permission from [23, 70].
conventionally, with Au islands nucleating only on the Cr seeds, provided they are less than the atomic Au capture distance apart. The Cr would provide adhesion to the substrate, i.e. stability/reliability for the DMTF. (Note that it is claimed [75] that deposition from a positively biased tip is thermal.) The concept of Cr field evaporation from an AFM tip was first demonstrated in 1996 [78], but with essentially no deposition pulse control the deposit was of μm dimensions. Ideally, a 0.4 ns pulse would be required per atom deposited for a diode current of 0.4 nA, (but it was noted that in practice ∼3.5 atoms were deposited per electronic charge.) A further demonstration is shown in figures 42 and 43. Cr has also been deposited with V < 0 but the evidence suggests that the tip came in contact with the GaSb substrate [79].

![Figure 36. Simulated diode effect: V > 0 Case A, V < 0 Case B. Reproduced with permission from [23, 70].](image1)

![Figure 37. Pseudo-inductive rise of the DMTF current from the Boltzmann limited initial value to the simulation’s steady state. Reproduced with permission from [23, 70].](image2)
The possibility exists of using the AFM to ‘dig’ holes in a substrate surface to define nucleation sites for thermal evaporation or other deposition methods. A variation is demonstrated in [76] where the positively biased AFM tip is used to detach a sulphur atom from a MoS$_2$ surface to create a nucleation site on the surface defect.

AFM oxidation of a Si surface to form 5 nm high 10 nm diameter SiO$_2$ nanodots is probably the best-known technique for nanoscale surface modification [80, 81]. The obvious next step to DMTF fabrication is to use the
SiO₂ dots as a nanoimprinting mould, which would have the advantage of mass production potential, but another possibility is suggested in these papers. The SiO₂ actually extends below the Si surface so when an HF etch removes the oxide it leaves etch pits that serve as DMTF nucleation sites.

Hill has observed that Au, for example, nucleates preferentially on positive charges on an insulating substrate surface [82], suggesting the possibility of defining nucleation sites by AFM charge deposition [83–85]. Both positive and negative charges have been successfully deposited by contact electrification and the charge distributions persist for hours, but the charge areas are ~200 nm diameter or more.
Finally, the AFM can presumably be used similarly to the scanning tunneling microscope tip to decompose a metallic carbonyl precursor to achieve chemical vapor deposition of a metallic line (~ 100 nm Ni in [86]) or NPs.

5.2. Other deposition techniques
5.2.1. Laser standing wave fields
Kundt’s dust tube is the classic freshman physics example of aggregation at standing wave nodes in an energy field. Application of the principle has been applied to standing laser waves for the deposition of (continuous) Cr lines [87, 88], but of course the laser wavelengths (~400 nm) rule this out for DMTF purposes which would require orthogonal EUV standing waves for 2D nucleation.

5.2.2. Polarized laser and electric field
Instead of nucleating NPs in a standing wave field, it is possible to reassemble the particles in a previously deposited DMTF into lines under the influence of polarized laser light and an applied electric field [89]. There seems to be no control on s and r which would be subject to the initial distribution, but the organization of the NPs into lines would remove the percolation parameter in standard DMTFs.

5.2.3. E-beam lithography
2D NP arrays have been produced by e-beam lithography [90] but to get down to DMTF dimensions from the e-beam center-to-center spacings of 50 nm will require EUV.

5.2.4. Templated lithography
Pt NPs with \( r \sim 6 \) nm and \( s \sim 13 \) nm were deposited through polystyrene templates [91], so although the NP size is satisfactory, the spacing is too large for tunneling. The pores of anodized aluminum have been used in many other applications, and in [92] the Al surface is etched through the pores to create bowls of controllable depths which form preferential nucleation sites for a sputtered Au film. The Au NPs are stabilized with an epoxy coating and the Al is then etched away to leave the NPs of \( r \sim 25 \) nm and \( s \sim 70–100 \) nm, both too large, on the epoxy surface. Another intriguing concept is presented in [93]. The idea is to self-assemble soluble or otherwise removable spheres in a regular array on the substrate and deposit the DMTF through the periodic gaps, but for \( s \sim 5 \) nm (as a practical tunneling limit) the sphere diameter must be \( \sim 8 \) nm, giving \( r \sim 0.8 \) nm, so the question is whether one can produce suitable monosized 8 nm diameter spheres.

5.3. Self-assembly of colloidal nanoparticles
There are two main problems with AFM deposition techniques, which might be scalable down to acceptable nanoparticle sizes: (1) There has been little work on minimizing island separations, and (2) the serial depositions are not commercially practical unless they can be turned into mass production templates, e.g., by nanoimprinting, which also appears to have separation challenges. Another approach may offer a more promising path than those available to early researchers. Nowadays metallic NPs are available from commercial suppliers, complete with insulating protective coatings which typically have uniform monomolecular thicknesses. These offer the prospect of constant controllable tunneling dimensions when self-assembled into 2D arrays. But so far, the NP dimensions commercially available neither meet the \( r \leq 10 \) nm criterion set above nor can be characterized as ‘monosized.’ The purpose of this Section is to look at some recent research progress towards acceptable sizes by different NP fabrication techniques and coating thicknesses. A review of colloidal particle fabrication has recently become available [94] to supplement an earlier one focused on the self-assembly mechanisms [95], including dendrimer polymers, copolymers, DNA and proteins to control NP spacings. 6.6 nm particle fabrication has been described by NaBH₄ reduction of H₆AuCl₆ [96], which seems to be the usual starting point, with ascorbate and citrate ligands around the NPs (due the addition of ascorbic or citric acid in the fabrication process) instead of the usual thiols.

Tricard et al [97] report 1.1–1.7 nm NPs formed from organometallic precursors, but with a dispersion \(~30\%\). These were stabilized by aryl or alkyl thiol ligands to yield \( s \sim 1.9–2.5 \) nm, and structures displaying CB block properties, i.e., suitable for DMTFs. Li et al [98] studied the use of rigid linkers which gave \( s \sim 1.12 \pm 0.12 \) or \( 11.42 \pm 0.04 \) nm for \( r \sim 2.7 \pm 0.3 \) nm, again suitable for DMTFs.

In an alternative approach [99], Au NPs were precipitated from AuPMe₃Cl (Me = methyl) in Au-peptide rings which self-assembled on a lithographically patterned substrate. The outer ring diameter was 50 nm and the inner (NP) diameter was 15 nm (\( r \sim 7.5 \) nm, \( s \sim 17.5 \) nm) which are too large, but the principle of defining the structure by the dimensions of an organic ring, e.g., urea, has merit providing the rings will self-assemble without lithography.
There are three elements of interest in the use of templated cavities in [100]. First, the reduction of HAuCl₄ results in r ∼ 4 nm NPs in a shell of ∼ 2 nm oleylamine ligands, i.e. s ∼ 4 nm, which would work for DMTFs. Then the self-assembly NP delivery on to the substrate is controlled by the meniscus as the NPs are drawn from the liquid. But the substrate must be patterned by templated cavities, e.g., by nanoimprinting or AFM holes. But the e-beam lithography of hydrogen silsesquioxane used here limits the template to 25 nm period and 10 nm feature size, enabling both single and multi-NP islands, but at unacceptable separations.

Ye et al have reviewed the spontaneous self-assembly of NPs at an oil-water interface and subsequent removal to a substrate surface [101]. There is some emphasis on the control of the interparticle separation in the 0.5–5 nm range. Possibly the simplest method of self-assembly is to allow a random assembly on the substrate to self-assemble in a drop of alcohol which is then allowed to evaporate (in a ‘coffee ring’ effect) [102]. The process should work with smaller NPs than the 13 nm ones used, which were coated with dodecanethiol monolayers. 75–150 nm chains of 13 nm NPs self-assembled with the appropriate concentration of a cationic conjugated polymer (PFP) [103], but contacting the chains would present a challenge. 80 nm cobalt NPs have been aligned into 1D chains with 10 nm gaps (controlled by polyvinylpyrrolidone) in a magnetic field [104], which should make contacts easier. The use of resorcinarene as a stabilizer with 9.2 nm and 35 nm NPs is the focus of [105] which also reports briefly on the use of the oldest self-assembly technique of all: Langmuir-Blodgett compression.

The use of aligned vertical DNA strands to self-assemble at a defined distance above the substrate surface is demonstrated in [106], but the structures in the actual experiment were limited in resolution by the e-beam lithography used to define the underlying substrate patterns.

The most encouraging technology reported produces free-standing DMTFs intended for strain gauge [107–109] and plasmonic [110] applications. The strain sensing dependence on the NP gaps is consistent with that published by others [10, 11, 19] and conduction by electrostatically activated tunneling is largely confirmed [97, 109]. The fabrication sequence is shown in figure 44 from the NP suspension to the test structure. 7 nm NPs were used in [109, 110] while for [107, 108] 14 nm NP nano-cluster wires were formed by a (modified ‘coffee ring’) ‘stop and go’ process implemented at the figure 44(b) step. Within the self-supporting film, the dodecanethiol interparticle gaps were 1.3 nm [109] and estimated as 0.8 nm, 1 nm and 2 nm for the 14 nm wires [107].

5.4. Low temperatures
Most of the NP sizes quoted above are too large for the criterion that δE ≫ kT at 300 K, but there is always the option of using the larger particles at a lower temperature to maintain the δE ≫ kT condition. But figure 45

![Figure 44. Fabrication of free-standing 7 nm Au NP films [109] (With permission).](image-url)
below shows that to maintain the same 300 K $\delta E/kT$ ratio at 77 K allows only a $\sim 2.5 \times$ increase in $r$, e.g. 5 nm to 12.5 nm, but a full order of magnitude increase for 4 K. But tunneling is only weakly temperature dependent, so the same limits on $s$ apply at lower $T$ as for 300 K.

6. Conclusions

A full understanding of electronic transport in DMTFs is important for the design of multiple devices that operate by electrostatically activated tunneling, which has been the accepted model of DMTF conduction since the 1970s following its basic development in the 1960s, largely on the basis of its non-ohmic property. The details of the model have been adjusted, e.g. as knowledge of island shape evolved, but there is continuing uncertainty about whether the relevant island sizes were reported, initially because of secondary nucleation bimodal distributions and subsequently when the importance of islands adjacent to the contacts was recognized.

From section 2, it is clear that a systematic study of island properties is required using a combination of AFM, TEM and SEM, (if adequate resolutions can be achieved,) determinations of island dimensions, substrate contact angles, ellipsoidal eccentricities, nearest neighbor tunneling gaps, etc., and their statistical variations and correlations, for varied deposition temperatures and monitoring fields. These should include areas adjacent to and close to the contacts and far away, and for no contact deposition prior to the film’s. These depositions should be performed by modern controllable sources, e.g. MBE sources in modern ultra-high vaccuum systems. The substrates could be varied to establish their contribution to $\varepsilon_r$ in ambient environments where $\varepsilon_r = 1$.

Conventional atomistic nucleation and growth models typically assume a uniform array of nucleation sites which is difficult to apply to (ideal) glass surfaces, but possibly controlled surface charge densities [48] can act as nucleation site densities. The overriding issue to be addressed in this work is to establish the respective roles of coalesced and secondary islands (especially adjacent to the contacts) in the conduction process. Figure 3(b) suggests that nearest neighbor tunneling would be from large-to-small-to-large islands, but $\delta E$ might change that and perhaps only islands at the contacts determine $\delta E$.

Section 3 enumerated multiple experimental results which are totally inconsistent with the model of sections 1 and 2. All of these deserve further study and verification. Specifically:

- Section 3.2: Would a transient $V_{BIAS}$ step make the bias effect more noticeable?
- Section 3.3: Compare electric field distributions with models (section 4.1) for different experimental island parameters.
- Section 3.4: It is not clear whether the $R_v$ TCR in figure 21 is positive or negative. If negative, weak activation would give added insight into the conduction process in mid-film. (If positive, compare with the metal TCR.)
- Section 3.5: Determine the temperature dependences ($\delta E$) of $R_{on}$ and $R_{off}$ in the diode effects of figures 22 and 26.
• Section 3.6: Determine the temperature dependence of the asymmetrical AC effects in figures 23 and 24, i.e. $\delta E$ and TCR values, and resonant/corner frequencies. The frequency characterization of the pseudo-inductance (figure 24) needs more thought too, (see [67].)

• Section 3.7: Determine the temperature dependences ($\delta E$) of the high and low resistances of switching films (figures 25–27.) Does the driving frequency affect switching (figure 26)?

Likewise, the simulations in section 4 need verification, more effective presentation of the results, (e.g. 100 × 100 2D false color displays of island-by-island charge, field and potential distributions,) as functions of temperature for the steady state and time for the turn-on transient (figure 37). Also, the changes in charge and field should be tracked step-by-step during switching simulations (figure 38). Switching and turn-on transients could be viewed effectively as videos.

Experimental verification of section 4’s model requires more uniform structures than have been available before and section 5 surveys some basic techniques that have been tried (or proposed) in the past. These separate into various direct deposition techniques and self-assembly of commercial or chemically fabricated NPs. Most have not achieved NPs small enough for effective experiments at 300 K, but might be adequate at 77 K or below. An attractive feature of the nanoparticle self-assembly approach is that the monomolecular protective coatings provide a consistent known value of $s$, and that commercial suppliers can provide data on the dispersion of (spherical) nanoparticle sizes. The self assembly process of figure 44 looks the most promising with the basic DMTF property already demonstrated [109]. Whichever fabrication process is chosen, the standard DMTF experiments can be run to verify $\delta E$, $\sigma_o$, non-ohmic, strain, ambient atmosphere, and AC effects, switching, field distribution, etc., all to compare with theory for the ideal structure. In addition to these more obvious experiments, verification of figure 37 would be most interesting and could be demonstrated as a transient response or by extension of the Bode plot of figure 21 to (much) higher frequencies. Then the challenge becomes to modify the ideal uniform (self-assembly) structure to include the non-ideal elements, e.g. island shape, different structures at the contacts, etc., to further verify the theoretical modeling that includes these changes. There is clearly much work to be done!

As a closing remark, although this review attempts to demonstrate the resolution of many questions on DMTF conduction, there are more identified in [30] that have not been covered in this discussion.

Data availability statement

No new data were created or analysed in this study.

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