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Ovshinsky Effect by Quantum Mechanics

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***Abstract*—**Ovshinsky initiated scientific research in the field of amorphous and disordered materials that continues to this day. The Ovshinsky Effect where the resistance of thin GST films is significantly reduced upon the application of low voltage is of fundamental importance in phase-change - random access memory (PC-RAM) devices.GST stands for GdSbTe chalcogenide type glasses.However, the Ovshinsky Effect is not without controversy. Ovshinsky thought the resistance of GST films is reduced by the redistribution of charge carriers; whereas, others at that time including many PC-RAM researchers today argue that the GST resistance changes because the GST amorphous state is transformed to the crystalline state by melting, the heat supplied by external heaters. In this controversy, quantum mechanics (QM) asserts the heat capacity of GST films vanishes, and therefore melting cannot occur as the heat supplied cannot be conserved by an increase in GST film temperature.By precluding melting, QM re-opens the controversy between the melting and charge carrier mechanisms. Supporting analysis is presented to show that instead of increasing GST film temperature, conservation proceeds by the QED induced creation of photons within the GST film, the QED photons confined by TIR. QED stands for quantum electrodynamics and TIR for total internal reflection. The TIR confinement of QED photons is enhanced by the fact the absorbedheat energy absorbed in the GST film is concentrated in the TIR mode because of their high surface to volume ratio. The QED photons having Planck energy beyond the ultraviolet produce excitons by the photoelectric effect, the electrons and holes of which reduce the GST film resistance.

***Keywords*—**Ovshinsky,phase change memory, PC-RAM, chalcogenide, quantummechanics, quantum electrodynamics.

I. Introduction

OVSHINSKY became perhaps the greatest American inventor since Edison by his 1968 discovery [1] that the electrical resistance of ultra-thin films of chalcogenide glassesis dramatically reduced after applying small voltages. Today, Ovshinsky's discovery called the Ovshinsky Effectis central to storage of computer data in phase-change random-access memory (PC-RAM) devices, the most familiar of which being the rewritable CD-RW disks.

The PC-RAM writing and erasing processes are called SET and RESET. With the GST film in the amorphous state, it is generally [2] thought SET occurs by melting to the crystalline state by heating to temperatures above 600 C. SET and RESET are encoded in a binary (0, 1) system,, say 1 corresponding to the low resistance SET state and RESET as a 0 in a high resistance.. Memory is erased in RESET by a applying a lower-intensity heat pulse of long duration to transform the crystalline state back to the high resistance amorphous state. Ovshinsky's [1] submicron 500 nm thin film of amorphous chalcogenide GeSbTe (GST) glasses allowed significant reversible transitions in electrical resistance in less than about 1 microsecond. Today, the GST thicknesses [3] are typically < 50 nm changing GST states in less than 100 nanoseconds, but the mechanism by which the high-resistance GST amorphous state switches to the low-resistance crystalline state is still not understood.

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II. Problem

QMrequires the heat capacity [4] of submicron GST films to vanish, and therefore the heat supplied during SET and RESET cannot be conserved by an increase in GST temperature. What this means is switching from the high to low resistance GST states is not caused by melting from the amorphous to crystalline states. In fact, Ovshinskythought [1] the resistance change was caused by a redistribution of charge carriers– not by melting. By precluding melting, QM has re-opened the controversy between the melting and charge carrier mechanisms underlying the Ovshinsky Effect.

III. Proposed Mechanism

The Ovshinsky Effect occurs by a redistribution of charge carriers as Ovshinsky envisioned, although the lack of heat capacity required by QM was not given as the reason melting does not occur in GST films. Because the supplied heat cannot be conserved by an increase in temperature, QED theory claims conservation proceeds by the creation of photons that producecharge carriers in the form of excitons (holes and electrons) by the photoelectric effect.

IV. Background

QED theory [4] claims space charge is created anytime EM energy of any form is absorbed in nanostructures, and need not be related to nanoelectroncs, e.g., the movement of nanocars[5]upon heating.Nanocars are molecular prototypes of actual cars having wheels on a pair of axles supported on a chassis. Upon laying down a number of nanocars at random on a flat gold surface, the nanocars are observed to move by heating the surface.Electrostatics issuspected, but only QED theory can explain how charge is generated by heating.

Similarly, heat transfer ininterconnects between nanoelectroniccircuit elements is thought[6] to occur by ballistic transport by phonons creating temperatures across the nanocontacts. Only QED theory can explain why temperatures of the circuit element should differ from that of the attached nanocontacts. In this paper, the proposed QED theory for the Ovshinskyeffect follows that [7,8] for memristors.Ironically, the backgrounds are quite similar. After Ovshinsky's published his paper [1] on reversible switching with GST films, Chua proposed [9] similar switching with memristors. Unlike Ovshinsky's actual working GST films, Chua's memristor was based on purely hypothetical arguments. Chu argued that the

common electronic circuit elements of resistor, capacitor and inductor lacked symmetry, and therefore a missing fourth element [10] called a memristorwas required for completeness. But Chua lacked a working prototype, and the memristor lay dormant until 2008 when a groupat Hewlett-Packard (HP) developed [11] a working TiO_2 memristor.

Both GST films and memristors are submicron, and therefore QM is expected in any explanation of attendant charging. Indeed, the applicability of QM to memristors [11] is supported by the fact that only at the nanoscale is the memristor behavior detectable. Supramicron memristors behave just like ordinary resistors, where resistance is equal to the voltage divided by the current. Similarly, QM is applicable to submicron GST filmswith supramicron films behaving like ordinary resistors.

V. Purpose

Propose the switching in PC-RAM devices is caused by the increased mobility from charge carriers in the form of excitons (holes and electrons) produced by the photoelectric effect from QED radiation created from the conservation of Joule heating that otherwise is conserved by an increase in temperature.

VI. Theory

QM precludes temperature increases in PC-RAM devices during heating provided the GST films are submicron and sandwiched between materials of a lower refractive index. Supramicron GST films that are macroscopic do not follow QMand do indeed increase in temperature during heating. Fig. 1 shows theGST filmof thickness d sandwiched between electrodes under heating power P by a current I or heat H pulse.

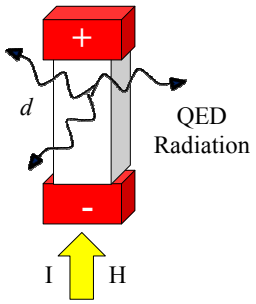


Fig. 1 GST filmunder Current I or Heat H Pulse

A. QM Restrictions

To understand how QED radiation is produced in GST films, consider the QM restriction on heat capacity in conserving heat by an increase in temperature. Unlike classical physics, theheat capacity of the atom by QM depends on its EM confinement. At 300 K, the Einstein-Hopf relation for the average Planck energy of the harmonic oscillator in terms of kT and thermal wavelength $\lambda_T=hc/kT$ is shown in Fig. 2.

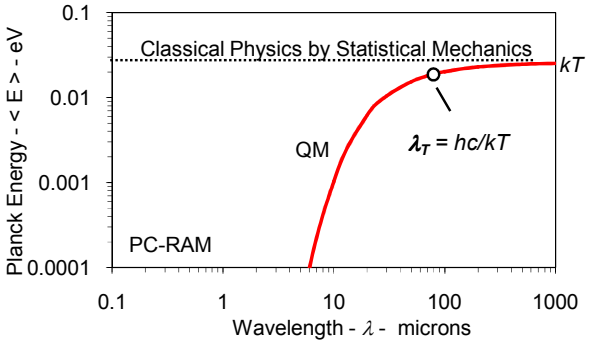


Fig. 2 Classical and QM Oscillators - Heat Capacity at 300 K

Unlike classical oscillators allowing the atom to have heat capacity at all wavelengths, QM oscillators only haveheat capacity for $\lambda>\lambda_T$and restrict heat capacity for$\lambda<\lambda_T$. At 300 K, λ_T= 50 microns. Fig. 2 shows the heat capacityis less than kT for$\lambda<\lambda_T$and is only available for $\lambda>\lambda_T$. For GST films having $\lambda<$ 1 micron, QM by requiring heat capacity to vanish precludes anyincrease in temperature upon heating.

A. QED Confinement

GST filmslack heat capacity and cannot conserve absorbed heat by an increase in temperature. Instead, conservation proceeds by the QED induced frequency up-conversion of the absorbed heat to the TIR confinement frequency of the GST film.Since GST films have high surface to volume ratios, the absorbed EM energy is confined by TIR almost entirely in the filmsurface. The TIR confinement is momentary and occurs only upon absorption of EM energy, and therefore the TIR confinement effectively sustains itself.

Similar to creating QED photons of wavelength λ by supplying EM energy to a QM box with sides separated by$\lambda/2$, the absorbed EM energy is frequency up-converted to dimension d. The QED photon energy E and frequency f are:

$$E = hf, f = \frac{c}{\lambda},\ \lambda = 2nd \qquad (1)$$

where, h is Planck's constant, c the velocity of light, and $n$is the refractive index of the GST film.

C. Optical Properties of GST Films

In the amorphous state, the GST films require [1] the created QED photons to have Planck energy E exceeding the optical bandgap, $E_g$from 0.6 to 1.4 eV. For activation of electrical conduction, QED photon energies are required [1] to exceed 0.7 to 1.6 eV, although more recently [2.3] the activation of GST films$E_a$is given as ~ 0.3 eV.

Laser photons having $E>E_g$or $E_a$can always be selected to exceed the GST bandgap and activation energies. But lasers are not necessary. By QED theory, any formof EM energy, say a pulse of heat by a current I or heat H pulse,naturally creates QED photons. For GSTfilmhaving a refractive index n ~ 4.4, Planck energies $E$from 0.7 to 1.6 eVare created in GST film thicknesses $d<$235 and 88 nm, respectively.

D. QED Photons and Rate

Classical heat transfer conserves absorbed heat by an increase in temperature, but is not applicable to GST filmsbecause of QM restrictions on heat capacity. Instead, thepower P of the current I or heat H pulse is conserved by creating a number N_P of QED photons inside the GST film. The QED photon rate is,

$$\frac{dN_P}{dt} = \frac{\eta P}{E} \quad (2)$$

where, t is time. Only a fraction η of the power Pcreates excitons, the remainder (1-η) is lost to the surroundings as shown in Fig. 3. By the photoelectric effect, the rate dN_{ex}/dt of excitons created, each comprising an electron and hole is,

$$\frac{dN_{ex}}{dt} = Y\frac{dN_P}{dt} = \frac{\eta Y P}{E} \quad (3)$$

where,Y is the exciton yield.

E. QED Photons, Excitons, and Charge

The creation of charge carriers inthe GST film requires QED photons having Planck energy greater than the energy $E_g$of the band gap. The excitons comprising electron-hole pairsform as the QED photons produce an electron charge $Q_E$leavinga mobile positive charged hole having charge Q_H

The GST film resistance R depends on the conductivity $\sigma$and resistivity ρ given by the number density of electrons N_E and holes N_H,

$$\sigma = \frac{1}{\rho} = \mathrm{e}\left(N_E\mu_E + N_H\mu_H\right) \quad (4)$$

where, μ_E and μ_H are the electron and hole mobility.

However, electron-hole pairs may recombine to create another photon having lower energy than the QED photon. But this is unlikely in GST films because the electrons separate from the holes under the high field F across the film.

F.Conductivity and Mobility

The current I through the GST films [12] cannot be based on mobilityμ alone, but also depends on conductivityσ. Hence, the current I,

$$I = I_o \exp\left(\frac{\beta F^{\frac{1}{2}}}{kT}\right) \quad (5)$$

where, β is a constant for given material. Since current is proportional to both mobility and conductivity, mobility μat ambient temperature may be expressed [13] by,

$$\mu = \mu_o \exp\left(\alpha F^{1/2}\right) \quad (6)$$

where, $\mu_o$is the mobility at zero field. For example, organic light emitting tris-(8-hydroxyquinolate) aluminum (Alq3) filmis correlated by α = 9.22x10^{-3} (cm/V)$^{1/2}$and μ_o= 3.04x10^{-7} cm^2/V-s. In the literature, the GST mobility [2] isindependent of GST film thickness, i.e.,μ= 2x10^{-5} cm^2/V-s.

G. QM Charging

Excitons form in proportion to the fraction ηP of QED photons absorbed and the yield Y.The Q_H and Q_E are the number of created positive charged holes and negative charged electrons. Under the high electric field F, the charge carriers drift toward the opposite polarity terminals as shown in Fig. 3.

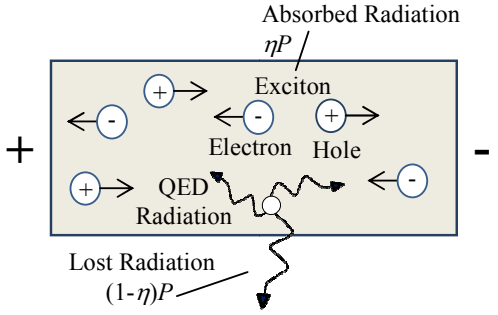


Fig. 3 GST Film–Exciton Charge Carriers

The rate $\eta YP/E$of excitonscreated is balanced by the electron$Q_E$and hole $Q_H$charges lost in moving toward opposite polarity terminalsby their respective $\mu_E$and $\mu_H$mobility in the electric field F.

$$\frac{dQ_E}{dt} = \frac{\eta Y P}{E} - Q_E\frac{\mu_E F}{d} \quad (7)$$

$$\frac{dQ_H}{dt} = \frac{\eta Y P}{E} - Q_H\frac{\mu_H F}{d} \quad (8)$$

Both exciton electron and hole equations are identical allowing the hole response to represent that of the electron for the same mobility. Taking $F = V/d$ and $V = Vo$gives,

$$\frac{dQ_H}{dt} = \frac{\eta Y P}{E} - \frac{\mu_H V_o}{d^2}Q_H \quad (9)$$

The hole Q_H solution is given by,

$$Q_H = \frac{d^2}{\mu_H V_o}\mathrm{x}$$
$$\left\{\frac{\eta Y P}{E}\left[1 - \exp\left(-\frac{\mu_H V_o}{d^2}t\right)\right] + \frac{\mu_H V_o}{d^2}\exp\left(-\frac{\mu_H V_o}{d^2}t\right)\right\} \quad (10)$$

The $Q_E$solution is the same.

On average, the holes and electrons are centered in the GST film d and need to move d/2 to reach the voltage terminals, the resistance R is,

$$R = \rho\frac{d}{2A} = \frac{d}{2A}\frac{1}{\mathrm{e}(\mu_E Q_{EO} + \mu_H Q_{HO})/Ad} \approx \frac{d^2}{4\mathrm{e}\mu_H Q_H} \quad (11)$$

The resistivity ρassumesμ_E=μ_H with the same number $Q_E$of electrons as theQ_H holes. Note ρrequires units of per unit volume, where volume is Ad and A is GST film area. Initial resistance $R_o$gives the Q_{HO}charge,

$$Q_{HO} = \frac{d^2}{4\mathrm{e}\mu_H R_O} \quad (12)$$

The current I is,

$$I = \frac{V_o}{R} \quad (13)$$

VII. SIMULATIONS

The QED theory is applied to threshold current in PC-RAM devices comprising GST films. A literature review showed the data in (Fig. 1 of [14]) to be representative of GST and a wide variety of chalcogenide alloys, and therefore was chosen as the Reference for verifying the correctness of QED theory. Of note, the Reference shows the DC threshold current is super linear with the GST film thickness from 10 to 10000 nm and with various contact materials. By QED theory, current is simulated using:

Alq3mobility depending on GST thickness,and Typicalmobility for all thicknesses.

Simulations were programmed in FORTRAN 95,a brief summary of which is as follows.

A. Alq3 Mobility

1. *QED Photons and GST Activation :* The QED photons have Planck energy $E = hc/2nd$. The refractive index n of amorphous GST is $n \sim 4.4$. For GST thickness $d < 100$ nm, the Planck energies E are > 1.4 eV, thereby allowing activation of GST film energies < 1.6 eV. For $d > 100$ nm, the QED photons have lower energy for GST activation.

2. *Heating Power :* The GST film is heated by a power Ppulse of current I or light HIn GST films, the rate of QED photons created is, $dN_p/dt = \eta YP/E$.Assuming QED radiation is completely absorbed, $\eta=1$. Alternatively, there is no QED radiation loss to the surroundings.Lacking yield data, a unity Y was assumed. For GST films having$d < 100$ nm, $E > 1.4$ eV. Assuming the pulse $P = 10$ mW, the rate of 1.4 eV QED photons created is, $dNp/dt < 3.9\text{x}10^{16}$ / s.

3. *Field and Mobility :* The Alq3 mobility [13] was used in the simulations. The electric field F assumed constant voltage V_o = 1 V that for GST film thickness from 10 to 10000 nm, correspond to $F = Vo / d$ of 10^6 to 10^3 V/cm. Equation (6) givesthe ALq3 mobility from $3.04\text{x}10^{-3}$ to $4.03\text{x}10^{-7}$ cm^2/V-s. In comparison, the Typicalmobility cited in the literature [2] for GST is $2\text{x}10^{-5}$ cm^2/V-s.

4. *Current and Resistance* : The current I response to 1000 ns is shown in Fig. 3.The 10 nm GST film has a peak I of about 2.8 mA while the 100 and 1000 nm films (not shown) have peak Iat 28 and 50 mA. The 10 nm GST film responds faster than the 100 and 1000 nm films.

The resistance R response is shown in Fig. 5. All GST film thicknesses were assumed to have an initial resistance $R_o = 1\text{x}10^6$ohms. The 10 nm GST film resistance R is reduced to 350 ohms while that of the 100 and 1000 nm films is reduced to 35 and 500 ohms, respectively.

5. *Comparisons with Reference :* Sampling the current response was continuous in time to allow comparison with the functional form of the Reference, i.e., $I = I_o d^m$, where I_o and $m$are the unknowns. At each instant of time, Solution A consists of writing two equations for the current I inthe 10 and 100 nm films and solving for m and I_o. Similarly, Solution B corresponds to the 100 and 1000 nm films.

Fig. 5 shows the Solution A and B transients for $m$up to 100 ns, the average of which is shownas the dotted line.The Reference has a slope m = -1.4 and is reasonable approximated by QED theory at $m \sim$ - 1.5.

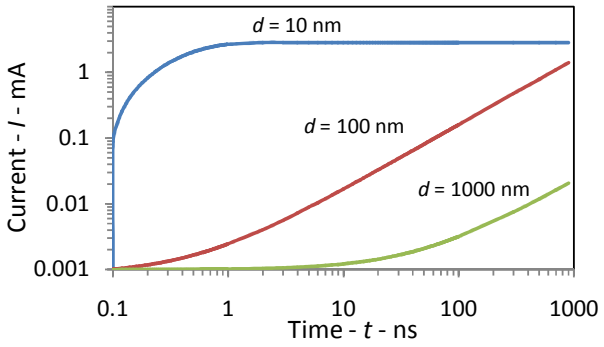


Fig. 4 Transient *I*–Alq3 Mobility

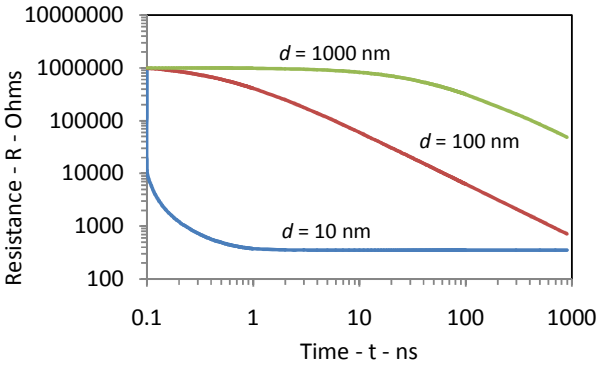
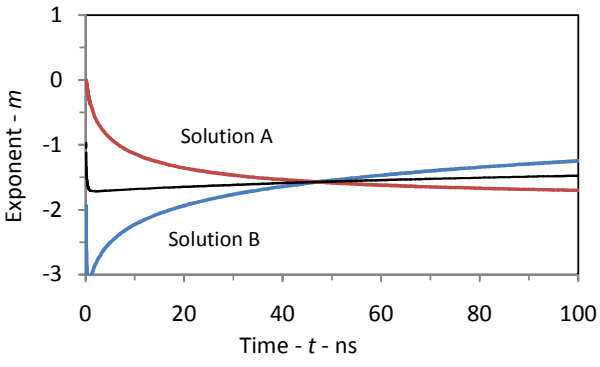


Fig. 5Transient Resistance *R* – Alq3 Mobility

(a)



(b)

Fig. 5 Transient Exponent*m* – Alq3 Mobility

B. Typical GST Mobility

The simulation of current in GST films having Typical mobility [2]of $\mu = 2\text{x}10^{-4}$ cm^2/V-s follows that described for the Alq3 mobility. Figs. 6 and 7 give the transient I and R response while Fig. 8 gives the Solution A and B for exponent$m$of QED theory to the Reference.

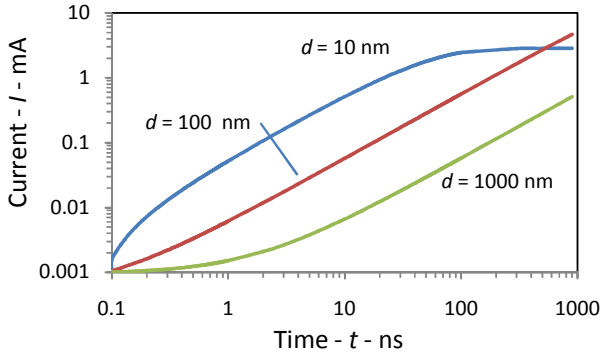


Fig. 6 Transient *I*– Typical Mobility

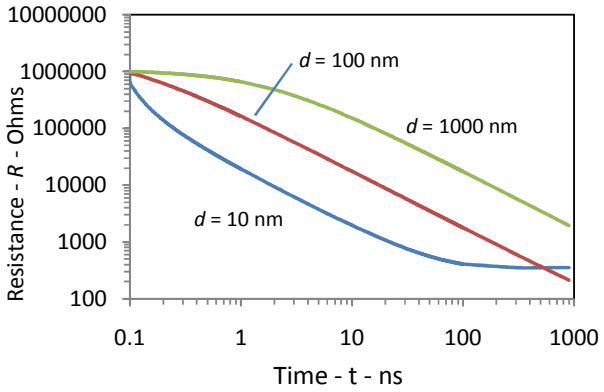


Fig. 7 Transient *R*– Typical Mobility

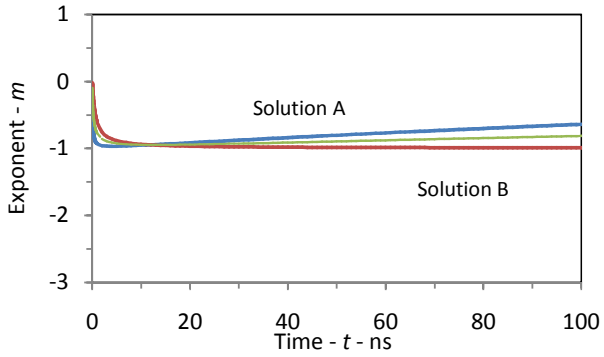


Fig. 8Transient Exponent *m*–Typical Mobility

For Typical mobility, Fig. 8 shows the exponent*m*~ -1. Comparison with Fig. 5 showing Alq3has *m* ~ -1.5 suggests that the Reference m = -1.4 follows the Alq3 relation. Otherwise, the Alq3 mobility provides a faster response than Typical as shown in the rise time ofcurrent *I* in Figs. 3 and6.

Alternatively, Figs. 5 and 7 show the time for the Alq3 10 nm GST film resistance to reduce from 1 Meg-ohm to 350 ohms is about 100X faster than for the Typical mobility. However,this is to be expected as the Alq3 correlation at $F = 1\text{x}10^{6}$ V/cm for the d = 10 nm GST film gives the mobility$\mu = 3\text{x}10^{-3}$ cm^2/V-s which is 100X higher than that of the Typical mobility of $2\text{x}10^{-5}$ cm^2/V-s.

VIII. DISCUSSION

A. QED Photons or Melting? Melting of GST films between heated plates is commonly assumed to occur without the temperatures ever being measured. Indeed, resistance measurements [15] of GST films from 3 to 30 nm sandwiched between 50 nm ZnS-SiO2 films at temperatures from ambient to 400 C did not measure the temperature of the GST film itself, but rather ASSUMED the GST film followed that of the sandwich surface. Although understandable, this assumption is contrary to QM.

Clearly, heat was transferred to the GST film, but QM precludes any temperature increase. Simply put, QM requires the GST film to remain at ambient temperature, and therefore melting does not occur. What is actually being measured is the reduced GST resistance from the increased mobility of charge carriers created from QED photons by the photoelectric effect.

We could resolve this problem by measurement of the GST temperature, but such measurements are difficult as found in many areas [6-8] of nanoscale heat transfer. Many researchers have been stymied by this problem, but by assuming the GST film melts, we have been led into a blind alley on PC-RAM research. Unfortunately, GST resistance is not caused by melting, and therefore the reduced resistance has nothing to do with crystallization kinetics and attendant Avrami coefficients.

B. Optimum PC-RAM Material Amorphous GST having a refractive index of 4.4 is an optimum material for PC-RAM devices because TIR confinement of QED photons is assured as C and Mo contact materials that sandwich the GST film have lower indices. By QED theory, other high refractive index materials may be used, i.e., gallium and indium antimonide.

Consistent with QED theory, the Reference [14] for threshold currents showed independence of GST film response to contact materials: C, TiN, Pt-Ir, and Mo.

C. Simulations Numerical simulations of electrical, thermal, and phase change dynamics in PC-RAM devices [16] based on classical Fourier heat conduction and finite heat capacity lack the QM constraints that negate temperature increase in nanostructures.

It is far simpler and more meaningful to obviate Fourier's law altogether and simulate only the effects of QED radiation on exciton production. This paper is no exception as many assumptions were made for convenience, i.e., the power P of electrical heating, the yield Y of converting QED photons to excitons, the fraction η of QED radiation loss to the surroundings, and the simulation of GST film mobility by the Alq3 correlation. All need further work.

D.Other Nanostructures

1. Nanocars :Nanocars including molecular motors convert absorbed EM energy into mechanical motion. Molecular dynamics (MD) simulations of heat transfer in nanostructures is commonly used to understand how temperatures cause the observed motions.However, MD simulations based on classical physics by statistical mechanics falsely allow the atom to have

heat capacity. Because of this, the MD simulations [5] show the nanocarsdistort without moving as the goldsurface temperature is increased.

By classical physics, the nanocars should not move by heating the surface, as we know when we park our macroscopiccar in a lot with a flat surface on a hot summer day. If heating would produce charge, our car could move by electrostatic interaction with other charged cars in the lot. Nanocars are no different. Fig. 2 shows classical physics allows the atoms in our macroscopic cars to have the same kT energy as the atoms in the molecular prototype, and therefore nanocars like our macroscopic car do not move by heating.

However, QM differs in that the atom lacking heat capacity at the nanoscaleconserves the heat from the hot surface by the creationof QED photons that charge the cars by the photoelectric effect, the consequence of which is evidenced by the fact nanocars move by electrostatic interactions.

2. Ballistic Heat Transfer Diffusive heat transport occurs when the device size is far larger than the mean free path of phonons which for most materials is less than about 100 nm. For contact lengths< 100 nm, a heat transportrelation is not yet available because of the difficulty in measuring temperature at the nanoscale.

Nevertheless, temperature is claimed [6] measured inside nanoscale contacts using the magnetic ordering temperature as an embedded thermometer. A single ferromagnetic CoS_2 crystal was used as the sample to which the nanocontacts were made. By assuming the temperature inside the nanocontacts was that of the CoS_2 crystal. magnetometer and resistance measurements clearly showed the temperatureT_m of the crystal to increase above ambient and follow the relation $V^2 = C(T_m\text{-}T)$ where C is a material constant.

However, the temperature inside the contact itself was not measured, but rather that of the temperature in the CoS_2 crystal having a macroscopic size of millimeters. Hence, the contacts were a part of a macroscopic solid, and therefore the temperatures measured are those of the $CoS_2$and notthe nanocontact. Experiments to measure temperatures inside submicron fragments of the CoS_2crystal would establish once-and-for-allwhether ballistic heat transport or QED heat transfer is operating at the nanoscale.

IX. Summary and conclusions

1. QM precludes increases in temperature of GST films. Applying heat to the film creates QED photons that by the photoelectric effect produce the exciton charge carriers that under high electric fields reduce the GST film resistance.
2. The GST films do not melt and change phase from amorphous to crystalline state. The crystalline state is inconsequential to PC-RAM.
3. The Alq3 correlation shows reasonable agreement with the Reference slope of the threshold current vs. thickness. The Typical mobility does not.
4. Reductions in GST film resistance need not be limited to the usual electrical pulse heating, but anytime EM energy is absorbed, e.g., laser irradiation.
5. The Ovshinsky Effect is a QM size effect only occurring in submicron GST films depending on the mobility of charge carriers as first envisioned by Ovshinsky..
6. QM vindicates Ovshinsky's long-standing explanation that the reduced resistance of GST films is caused by the redistribution of charge carriers - not by melting.
7. The notion that melting occurs in supramicron GST film and not in submicron film may sound strange to many, but many things in QM are strange. It is time now to allow QM to assert itself in PC-RAM research

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