Modifications of Richardson-Dushman Thermionic Emission Current Density Equation for Nano-Materials

Dilip K. De*

Department of Physics,
Covenant University, Canaan Land,
Ota, Nigeria.
dilip.de@covenantuniversity.edu.ng

Olawole C. Olukunle

Department of Physics,
Covenant University, Canaan Land,
Ota, Nigeria
olukunle.olawole@covenantuniversity.edu.ng

Abstract— **The noble prize winning Richardson-Dushman equation (RDE) had been found to be quite applicable for thermionic emission from metals as far as temperature variation is concerned except the fact that the thermionic emission constant vary from metal to metal contrary to the original equation. We have derived expression for the temperature (T) dependence of work function (W) of a material considering thermal expansion and variation of the chemical potential with temperature. We find that the calculated dW/dT as well as the effective thermionic emission constant, A_{eff} of metals are fairly in good agreement with experimental results of many metals. We then modify the RDE by using temperature dependent work function and report the excellent fitting of thermionic emission current density data from monolayer graphene with our modified equation. We discuss briefly the potential application of the modified Richardson Dushman equation for thermionic emission from nano-materials. The latter will appear in details in paper II.**

Keywords— *Work function, temperature dependent chemical potential, modification of Richardson Dushman equation, thermionic emission, thermal expansion coefficient, nano-materials, metals.*

I. Introduction

In a metal the valence electrons of the atoms gets detached from the parent atoms when the atoms form the metal. These valence electrons can move freely within the body of the metal but are held by an electrostatic barrier that prevents them from flying out of the metal under normal circumstances (i.e, at room temperature, no external electric field etc.). As a result of the barrier an electron must have a minimum energy W in order to be able to escape out of the metal. This is called the work function W. However, when a metal is heated to high temperature (>700 C) there is a significant number of electrons in the Fermi energy distribution with energy greater than W. Such electrons usually get out of the metal surface in the form of an electron current. This phenomenon, where electrons are emitted from a hot metal surface has been termed as thermionic emission by Owen William Richardson [1,2] who, for his work was awarded Nobel prize[3]. Richardson[3] in his Nobel lecture predicted the form of the dependence of thermionic emission current density J on temperature T, as:

$$J = A_0 T^2 e^{-W/k_B T} \qquad (1)$$

Where k_B is the Boltzmann constant. A_0 is a constant with same value for all metals. This equation later became known as Richardson-Dushman (RD) equation[4]. Sommerfield later derived the equation based on free electron theory of metals[4] and showed that A_0 is given by

$$A_0 = \frac{4\pi e m k_B^2}{h^3} = 1.2 \times 10^6 \ A/m^2 K^2 \qquad (2)$$

Even though the temperature (T) dependence on J in RD equation (1) was found to hold fairly well, the constant A_0 was found to vary from metal to metal [5, 6] and this variation has remained unexplained theoretically so far. Moreover, in Somerfield derivation as well as in the original work of Richardson, the work function W was assumed to be independent of temperature, contrary to experiments[7]. Metals have high number density of free electrons (n) and hence the Fermi energy at absolute zero temperature, (E_{F0}) is also high, usually of the order of a few eV [8a]. This can be understood from the relation

$$E_{F0} = \left[\frac{h^2}{8m}\right]\left(\frac{3n}{\pi}\right)^{\frac{2}{3}} = 3.65 \times 10^{-19} n^{2/3} \qquad (3)$$

In nano materials like graphene the surface density of free carriers has been estimated and experimentally determined to be within[8b,c] 10^{12} - 10^{13} /cm^2. Considering the diameter of carbon atom that makes graphene[9], this translates to a carrier density [10,11] of 1.6×10^{26} to 1.6×10^{27}/m^3. In the case of metals the free carrier density [8a] 1.15×10^{28} to 1.5×10^{29}/m^3. Free carrier density in carbon nano-tube[13] is 7×10^{24}/ m^3. Free carrier density [14a] in graphite is 7×10^{24}/ m^3. Maximum

carrier density in carbon nano tube is calculated[14a] to be $9.9 \times 10^{24}/ m^3$. Thus nano materials are expected to have much smaller (E_{F0}) than metals. As we shall see in later section the work function is expected to be temperature dependent in such materials. As a consequence the Richrdson-Dushman equation should break down in such materials as has been observed[14b]. Metals usually have a small temperature coefficient of work function which, as is shown later, nearly independent of temperature, due to high (E_{F0}). Where as in nano-materials dW/dT is expected to be temperature dependent as a result of low (E_{F0}). This calls for modification of Richardson-Dushman equation, specially, for thermionic emission from nano-materials.

II. RICHARDSON-DUSHMAN EQUATION (RDE) FOR THERMIONIC EMISSION FROM A METAL.

It is seen from Table 1 that the effective thermionic emission constant Ao ($=A_o \times b$ in Table 1) is quite less than the theoretical value of 1.20×10^6 Amp/m^{2}K^2 for most of the metals except cesium. In the derivation [4] of Eq. 2 it is assumed that the work function, W is independent of temperature, contrary to experimental observation[7,13]. In the next section we consider the temperature dependence of W and modify Eq.1.

III. VARIATION OF WORK FUNCTION (W) OF A METAL WITH TEMPERATURE

The relation of W with T of a pure metal depends primarily on the change of E_F with T and thermal expansion. To work out this change we rely on the fact that the total number of electrons N(T) in a given piece of metal at T = 0 K is the same as at T = T K. (It is assumed that during thermos electron emission in a thermionic energy converter (TEC), electrons will be replaced at the emitter through load current. The case where electron emission takes place without the electrons being replaced at the emitter will not be treated here). Now at

T = 0 K, $E_F = E_{F_0}$ and for E< E_{F_0} the Fermi function f(E) = 1 at

0 K.

Using the concept of density of state g(E)[8a] and E_{F_0}, the total number, N of free electrons in the metal are given by:

at temperature 0 K,

$$N(T = 0 (K)) = V_0 \int_0^{E_{Fo}} g(E) \, dE \qquad (5a)$$

at finite temperature T,

$$N(T) = V \int_0^{\infty} g(E)f(E)dE \qquad (5b)$$

Where

$$f(E) = \frac{1}{1+\exp(E - E_F(T))/k_B(T)} \qquad (5c)$$

is the well-known Fermi-function. In Eq.5a the upper limit is E_{Fo}, because at 0 K free electrons fills the energy levels up to E_{Fo}. In Eq. 5b the upper limit is ∞ because at any finite temperature above 0 K, there is a Fermi distribution with energy extending up to ∞.

Considering thermal expansion of the metal,

$$V = V_0(1 + 3\alpha T) \qquad (6)$$

Where α = Linear thermal expansion coefficient. Thermionic emission takes place at high temperature (>1000 K). Change of E_F with T will change the work function W with T [Eq. 4] and this in turn will affect the thermionic emission current density (J) from that given by RD Equation. This is going to play special role in nano-materials where E_F is much lower compared to metals [Eq.1], due to much lower concentration of carriers [see results and discussion] at ambient temperature. Our primary objective now is to obtain E_F and hence W, as a function of T from the equations (4) to (6) and compare with experimental results for metals (Paper I). The 2nd objective is to see how this affects the RD equation and how the modified RD equation fits the experimental results of graphene and carbon nano-tube and detailed comparison with regular (unmodified) RD equation (paper II).

Since N(T=0) = N(T) as discussed above, from eqns. 4 to 6

$$V_0 \int_0^{E_{Fo}} g(E) \, dE = V_0(1 + 3\alpha T) \int_0^{\infty} g(E)f(E)dE \qquad (7)$$

Now noting that $g(E) = 0$ for E< 0, the limits 0 to ∞ on the RHS of Eq.(7) can be replaced by $-\infty$ to ∞. Then following Sommerfield's expansion method as explained in Ref.8a, we get from Eq.7,

$$E_F = \frac{E_{F0}^{3/2}}{E_F^{1/2}} - 3\alpha T E_F - (1 + 3\alpha T)[\frac{\pi^2}{12} \frac{(k_B T)^2}{E_F} + \frac{7\pi^4}{960} \frac{(k_B T)^4}{E_F^3}] \qquad (8)$$

The numerical coefficients for successive terms in (8) get smaller and smaller with higher power of T. For temperature T such that $K_B T < E_{F0}$, terms up to the fourth power of T are sufficient.

Eq.(8) is difficult to solve for E_F. As an approximation by replacing E_F by E_{Fo} [assumption valid $K_B T < E_F, E_{F0}$] on the RHS of Eq. (8) we get Eq.(9)

$$E_F = -E_{F0} = -3\alpha T E_{F0} - (1 + 3\alpha T)[\frac{\pi^2}{12} \frac{(k_B T)^2}{E_{F0}} + \frac{7\pi^4}{960} \frac{(k_B T)^4}{E_{F0}^3}] \qquad (9)$$

Using Eq.(4) we then obtain

$$W(T) = W_0 + 3\alpha T E_{F0} + (1 + 3\alpha T)[\frac{\pi^2}{12} \frac{(k_B T)^2}{E_{F0}} + \frac{7\pi^4}{960} \frac{(k_B T)^4}{E_{F0}^3}] \qquad (10)$$

W_0 is the work function of the material at T = 0 K. Eq. (10) gives us the temperature dependence of the work function of a metal. It is interesting to note that $W(T)$ for a given E_{F0} increases with T and one shall be able to tune $W(T)$ by tuning the carrier density in nano-materials, as E_{F0} depends on carrier density[Eq.1]. It also predicts that in materials with zero E_{Fo} ,

i.e., in insulator materials, W(T) is infinite, meaning that thermoelectron emission is not possible in insulators. This is in line with experiment. Because of the quantities, α and E_{F0}, this dependence on T is metal specific. The positive temperature coefficients of W(T) from Eq.(10) is consistent with that of many metals [7,13]. We shall examine this in some details in latter section. For temperatures T<E_{F0}/k but well below the melting point of the metal, the term with fourth power of T is sufficient. In general the relative contributions of the second, third and fourth terms depend on T and E_{F0} .

Eq.(10) is particularly important for estimation of J in materials like graphene, carbon nanotubes etc. with low E_{fo}(0 – 0.3 eV). This should also be important for computation of energy distribution[15] of emitted electrons from nano-materials. For metals where E_{FO}> a few eVs, the work function, dW(T)/dT in [Eq. 10] is practically temperature independent for T~2000 K which means metals have almost a linear variation of W with T. In such cases the second term in Eq.10 dominates the third and the fourth terms. For greater accuracy in computation of W the eq. 7 needs to be solved numerically, which is quite tedious and not easily applicable for computation of thermionic emission current density.

IV. NEW MODIFIED RICHARDSON DUSHMAN EQUATION (MRDE)

Richardson Dushman equation for thermoelectron current density (emitted along z direction) is given by:

$$J = \int dn e v_z = \iiint_{v_z=v_{z0}; v_y=0; v_x=0;}^{v_z=\infty; v_y=\infty; v_x=\infty;} \left[2e v_z \left(\frac{m}{h}\right)^3 \exp\left(\frac{E_F}{k_B T}\right)\right]$$

$$\times \exp\left(-\frac{(m(v_x^2+v_y^2+v_z^2)}{2k_B T}\right) dv_x dv_y dv_z \qquad (11)$$

where v_{z0} is the minimum velocity required for electron to get out of the metal in the z direction (direction of electron emission) and is given by:

$$v_{z0} = \sqrt{2\,(E_F + W(T))/m} \qquad (12)$$

From Eqs. (10) - (12) we finally get the modified Richardson-Dushman thermoelectronic emission equation (MRDE) for J as

$$J = A_0 T^2 exp(-[W_0 + 3\alpha T E_{F0} + (1 + 3\alpha T)[\frac{\pi^2}{12}\frac{(k_B T)^2}{E_{F0}} + \frac{7\pi^4}{960}\frac{(k_B T)^4}{E_{F0}^3}]]/k_B T) \qquad (13)$$

Eq. 13 gives us new modified thermionic emission equation that must be applied for materials like graphene, carbon nanotubes which have low E_{Fo} and at temperatures comparable to E_{Fo}/k_B. For E_{Fo} of the order of 0.3 eV and for T within 2500 K, terms up to fourth order in Eq.13 is sufficient, since the contribution of the sixth power of T will be negligible. For metals with high E_{Fo} (a few eVs), at temperatures $k_B T$< E_{Fo}, Eq. 13 approximately gives the ordinary RD temperature dependence with an effective thermionic emission constant A_{eff} (Eq.14).

Eq. 13 gives us the modified thermionic emission equation with the constant Ao changed to a new constant Aeff

$$A_{eff} = A_0 \exp\left(-\frac{3\alpha E_{F0}}{k_B}\right) \qquad (14)$$

Now in Eq. (14) the term E_{Fo}/k_B is a constant of a given metal and is metal specific. E_{Fo} is given by Eq.3. The number density n can be calculated from, n = zNA ρ/M. z = valency; ρ = density; M = atomic mass. NA = Avogadro number. n can also be calculated from the following relation: n = xz/a3. Where x = number of atoms per unit cell of the metal crystal. z = valency of the metal. a = lattice constant of the metal. n of some metals calculated from the second relation is given in Table 1. E_{Fo} is then computed from Eq.(3). The nearly temperature independence of the thermal expansion coefficient α can be understood from the following considerations:

$$\alpha = \frac{\gamma(C_v^{ion}+C_v^{el})}{3B} \qquad (15)$$

Where γ is the overall Gruneisen parameter of the metal; this is primarily of the order of unity and temperature independent. B the bulk modulus. At temperatures above 300 K, C_v^{ion} assumes the value of 3R. C_v^{el} is usually much smaller than C_v^{ion}. The electronic contribution C_v^{el} is very negligible at high temperature. Thus α can be assumed to be fairly independent of temperature in a metal. For greater accuracy temperature dependence of α can be inserted in Eqs.7,10 & 13.

This new thermionic constant[14] A_{eff} is dependent on two quantities: α and E_{F0} which are both metal specific. It is to be noted that the Schottky effect (lowering of work function by the presence of electric field, E on to the metal surface) modification of the thermionic emission equation that is well-known is not added to eq.13. With Schottky- effect Wo is lowered to $W_0^/$ (Eq.16).

$$W_0^/ = W_0 - e\left(\frac{eE}{4\pi\epsilon_0}\right)^{0.5} \qquad (16)$$

The final modified equation for thermionic equation is given by:

$$J = A_0 T^2 exp(-[W_0^/ + 3\alpha T E_{F0} + (1 + 3\alpha T)[\frac{\pi^2}{12}\frac{(k_B T)^2}{E_{F0}} + \frac{7\pi^4}{960}\frac{(k_B T)^4}{E_{F0}^3}]]/k_B T) \qquad (17)$$

Eq. (17) can be said to be the final modified RD equation that takes care of Schottky effect, thermal expansion and change of chemical potential with temperature.

Because Fermi surface of a metal is not spherical in k-space. E_{F0} can depend on crystallographic orientation of the metal plates from which thermionic emission takes place and hence Aeff. In Eq. 10, for metals with E_{F0} of a few eVs, at temperatures up to 2500 K, dW/dT is primarily due to thermal expansion of metals. Since deviation of A_{eff} [Eq.14] from Ao is primarily due to thermal expansion of materials, A_{eff} and dW(T)/dT of a given metal can also depend on whether thermionic emission measurement is carried out on (i) thin wire; (ii) plate surface; (iii) spherical surface or cubical surfaces of the metal. At thermionic emission temperature of 900 K the de Broglie wavelength of electron is 41 Angstrom and it decreases with higher temperature. As long as the two dimensional plate thickness or the diameter of a long wire is significantly greater than 41 angstrom, three dimensional density of states and hence Eqs. (8 -14) will be valid for thermionic emission from plate surface and the cylindrical

surface of a wire. However, the effect of thermal expansion for three dimensional, two-dimensional (thin plate) and one dimensional (thin wire) emitters can be accounted by replacing 3α in Eqs. 10,13 and 17 by $r\alpha$ where r=1,2 and 3 for thermos electronic emitters in the shape of thin wire, a thin plate and a bulk cube or sphere..

III.3. Rate of change of work function and effective thermionic constants of metals:

With this idea A_{eff} and dW/dT for electron emissions from metal at temperatures $k_BT << E_{F0}$ can be given by:

$$A_{eff} = A_0 \exp\left(-r\alpha \frac{r\alpha E_{F0}}{k_B}\right) \qquad (18)$$

$$\frac{dW(T)}{dT} = r\alpha E_{F0} \qquad (19)$$

where r=1,2 and 3 for thermos electronic emitters in the shape of thin wire, a thin plate and a bulk cube or sphere respectively. Eq.(19) is valid for most metals as $E_{F0} > 2$ eVs.

$$a = \left(\frac{dW}{dT}\right)_{exp} \times 10^{-4} eV/K, \quad b = \left(\frac{dW}{dT}\right)_{th} \times 10^{-4} eV/K$$

TABLE I.   WORK FUNCTIONS AND RICHARDSON'S CONSTANTS FOR VARIOUS MATERIALS IN UNITS OF $A\ \mathbf{CM^{-2}\ K^{-2}}$ OR 10^4 [5,6]

Metal	W (eV)	$A\times b (Acm^{-2}K^{-2})$ B is material correction factor
Molybdenum	4.15	55
Nickel	4.61	30
Tantalum	4.12	60
Tungsten	4.54	60
Barium	2.11	60
Cesium	1.81	160
Iridum	5.40	170
Platinum	5.32	32
Rhenium	4.85	100
Thorium	3.38	70
Ba on W	1.56	1.5
Cs on W	1.36	3.2
Th on W	2.63	3.0
Thoria	2.54	3.0
BaO + SrO	0.95	~10^{-2}
Cs-oxide	0.75	~10^{-2}
TaC	3.14	0.3
LAB$_6$	2.70	29
Theoretical		120.2 (b=1)

TABLE II.   TEMPERATURE COEFFICIENT OF WORK FUNCTION FOR SOLID P-BAND METALS [7].

Metal	W	a	b	Tm (K)	E_{Fo} (eV) $*$	$\alpha \times 10^{-6}$ /K
Ga	4.07	7.40	7.3[!!!]	303	10.4	23.5
In	3.90	4.3	4.36[!!]	429	8.63	25.3 [a]
Sn	4.18	2.20	2.41[!]	505	10.3	23.4
Bi	4.35	2.00	1.29[!]	544	9.90	13
Tl	3.69	1.20	2.45[!]	577	8.15	30
Pb	4.06	1.40	2.65[!]	606.6	9.47	28

TABLE III.   COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES* OF THERMIONIC EMISSION CONSTANT A$^{'}$

$$C = \mathbf{A}_{eff(th)} \times 10^4 (Acm^{-2}K^{-2}) \text{ AND } \mathbf{d} = \mathbf{A}_{eff(exp)} \times 10^4 (Acm^{-2}K^{-2})$$

Metal	$\alpha \times 10^{-6}/C$		$n(10^{28}/m^3)$	E_{F0}(eV)	c		d	
					r=1	r=2		
Ca	22.5	[28]	4.60	4.69	35.3		60	[30]
Cr	6.2	[28]	8.37	7.05	72.3	43.5	48	[30]
Cs	97	[28]	0.90	1.59	20		162	[30]
Iron	11.7	[28]	16.92	11.2	26.3		26	[30]
Ta	6.5	[28]	11.03	8.38	63.8		60	[30]

CONCLUSION

Original Richardson-Dushman thermionic emission equation is based on temperature independent work function W which gives thermionic emission equation with emission constant A same for all metals. Experiments confirm that A varies from metal to metal and W varies with temperature. We have considered temperature variation of work function of metals taking into account thermal expansion and temperature variation of chemical potential to obtain theoretical expression for temperature dependent work function (Eq.10) and modified Richardson-Dushman equation (Eq. 13 or17). We have seen fairly good agreements for several metals on dW/dT and A_{eff} with not so good agreement for alkali metals. To our knowledge there is no unified single theory that explains the experimental observations of A_{eff} and dW/dT for all metals and the thermionic emission from nano-materials. This modified equation does not affect the temperature dependence of thermionic emission current density much from the original RD law for metals because metals have high E_{Fo} compared to k_BT. It will however, significantly alter the temperature dependence for nano-materials which have low E_{Fo}. It is reported that the ordinary RD law cannot explain the experimental thermionic emission current data for graphene [22] and carbon nanotubes [14b]. We have verified that our model fits the data excellently well. We have seen that the values of thermal expansion coefficient and the carrier density derived from the fitting agree very well with independent experimental measurements. The excellent agreement of thermionic emission current density of monolayer graphene with our theory provides further validity of our theory-this aspect will be detailed in subsequent publications along with the detailed applications of the modified RD equation to nano-materials. The equation is expected to be important also in the studies of the energy distribution of thermally electrons from nano-materials [15] and for correct evaluation of performance of the energy converter for solar thermionic power conversion using nano materials.

REFERENCES

[1] O. W. Richardson,"The emission of electrons from tungsten at high temperatures: an experimental proof that the electric current in metals is carried by electrons", Science ,Vol. 38, pp. 57–61, July, 1913.

[2] O. W. Richardson, "On the negative radiation from hot platinum,"*Philosophical of the Cambridge Society"*, vol. 11, pp. 286-295, 1901.

[3] O. W. RICHARDSON "Thermionic phenomena and the laws which govern them. Nob

el Lecture", December , 1928.

[4] D. Manura, " Scientific instrument services Inc." 2008 http://simion.com/definition/richardson_dushman.html

[5] B. Wolf. "Handbook of ion sources. CRC Press", 1995.

[6] C. J. Smithells, "Metals Reference Book", Butterworths, London, vol 3, 1967.

[7] Kh. I. Ibragimov and V. A. Korol'kov – "Temperature dependence of the work function of metals and Binary Alloys" Inorganic materials, vol. 37, pp 567-672., 2001.

[8a] M. H. Reinhert and Winston, W. N.Ashcroft and N. David "Solid State Physics"vol 2, pp.38, 1976. (1976).

[8a] S. Jang, M. Xiao, Ishigami, and M. S.Fuhrer, "Intrinsic and extrinsic performance limits of graphene devices on SiO2". Nature Nanotechnology, vol. 3 pp. 206 – 209, 2008. https://en.wikipedia.org/wiki/Graphene.

[9] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Electric field effect in atomically thin carbon films", Nature. 306, pp. 666, 2004.

[10] C. Riedl, C. Coletti, T. Iwasaki, A. A. Zakharov, and U. Starke, "Quasi-free-standing epitaxial graphene on sic obtained by hydrogen intercalation" Phys. Rev. Lett. vol. 103, pp. 246804, December, 2009.

[1] [11] M. Winters et al., Mater. Sci. Forum. vol. 129, pp.740, 2013.

[12] G. Comsa, Adrian Gelberg, and Beatrice Iosifescu, "Temperature Dependence of the Work Function of Metals" Phys. Rev. vol. 122, pp. 1091, May 1961.

[13] F. Kreupl and A. G. Qimonda "Carbon Nanotubes in Microelectronic Applications", Technology Innovations, Neubiberg, Germany, 2011.

[14a] H. Usmani 1R. Singh2 , N. Gupta3 "Calculation of carrier density and effective mass of Carbon nanotube", International Journal of Advanced Research in Electronics and Communication Engineering (IJARECE) Volume 1, Issue 6, December 2012,

[14b] X. Wei, S. Wang, Q. Chen, and L. Peng, "Breakdown of Richardson's Law in Electron Emission from Individual Self-Joule-Heated Carbon Nanotubes", Scientific Reports **4**, pp.5102, 2014.

[15] T. P. McCarthy, G. R. Reifenberger, and T. S. Fisher**,** "Thermionic and photo-excited electron emission for energy-conversion processes, Frontiers in Energy Research. vol. 2, pp. 54 2014.

[16] https://en.wikipedia.org/wiki/Molybdenum

[17] http://www.webelements.com/molybdenum/crystal_structure.html.

[18] P. Hidnert and W. B. Gero. "Thermal expansion of molybdenum", 1924.

[19] http://www.webelements.com/tungsten/crystal_structure.html

[20] D. Berger,. "Why does Tungsten not 'Kick' up an electron from the s sublevel". Bluffton College, USA.2009.

[21] G. J. Caravelli,"The Hall Effect in Silver and Tungsten"Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, October, 2006.

[22] S. J. Liang and L. K.Ang, "Electron thermionic emission from graphene and a thermionic energyconverter" Phys. Rev. Appl. vol. 3, 2015.

[23] J. G. Potter, "Temperature dependence of the work function of tungsten from measurement of contact potentials by the kelvin method, Phys. Rev. vol. 58, pp. 623, October, 1940.

[24] P. Hidnert and M. G. Blair, "Thermal expansivity and density of indium" Journal of Research of the National Bureau of Standards, vol. 30, pp. 427, June, 1943.

[25] C. Herring, M.H. Nichols, "Thermionic Emission" Rev. Mod. Phys.vol. 21, pp. 187 1949.

[2] [26] B. Lagel, "The application of the Kelvin Probe in materials science" Ph.D Thesis Robert Gordon University,2000A. http://openair.rgu.ac.uk

[27] https://en.wikipedia.org/wiki/Gallium

[28] ASM International, Materials Park, Ohio, USA, 2002. http://www.owlnet.rice.edu/~msci301/ThermalExpansion.pdf

[29] D. W. Koon, "Room temperature Hall coefficient and resistivity for selected chemical elements", Centro de Investigaciones en Ciencia e Ingeniería de Materiales,2000. http://it.stlawu.edu/~koon/HallTable.html.

[30] S. O. Pillai, Solid State Physics, 6th, ed., New Age International Publishers 2006, pp. 236.

[31] D. Yoon,W. Y. Son, and H. Cheong "Negative Thermal Expansion Coefficient of Graphene Measured by Raman Spectroscopy", Nano Lett., vol. 11, pp. 3227–3231, 2011.

[32] https://en.wikipedia.org/wiki/Graphene.