

# Thermoelectric power of supported thin polycrystalline films

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A general expression is proposed for the thermoelectric power of polycrystalline metal films attached on a substrate. The correcting terms due to thermal expansions of the film and its substrate are calculated, including the thermal strains. Comparison with experimental data related to noble metal films shows that the more important correction is due to thermal strains.

## 1. Introduction

Several papers have been recently published [1-5] concerning the difference between the temperature coefficient of resistivity (TCR) of supported and unsupported metal films in which three types of electronic scattering mechanisms are simultaneously operative, i.e. background, grain boundary and external surfaces scatterings.

The effect of thermal strains due to the difference in thermal expansion coefficients of the film and the substrate has been studied by several authors [6-11] independently from grain-boundary conduction in thin films.

Since the complete expression [12] for the TCR of polycrystalline metal films,  $\beta_{fp}$ , is somewhat sophisticated, an attempt has been made in this paper, to give a simple analytical expression for  $\beta_{fp}$ , starting from the Mayadas-Shatzkes model [13], and to derive the complete and linearized expressions for the polycrystalline film thermoelectric power,  $S_{fp}$ .

## 2. Theory

The TCR of a polycrystalline unsupported film,  $\beta_{fpu}$ , has been previously calculated, Equation 23 in [12]; an alternative expression has also been proposed [2, 14].

Neglecting the thermal variations in the electronic reflection coefficients at grain boundaries

and external surfaces,  $r$  [13] and  $p$  [15], respectively, gives:

$$\beta_{fpu}/\beta_0 = 1 + \frac{g(\alpha) - A + B + C}{f(\alpha) - A} + \frac{(D - A)\alpha_f}{(f(\alpha) - A)\beta_0} + \frac{(g(\alpha) + B + C - D)\alpha_g}{(f(\alpha) - A)\beta_0}, \quad (1)$$

where  $f(\alpha)$  is the Mayadas-Schatzkes function [13]

$$f(\alpha) = 1 - \frac{3}{2}\alpha + 3\alpha^2 - 3\alpha^3 \ln(1 + \alpha^{-1}) \quad (2)$$

with [13]

$$\alpha = \frac{l_0}{a_g} \frac{r}{1 - r}, \quad (3)$$

where  $l_0$  is the bulk mean free path and  $a_g$  is the constant average grain diameter (polycrystalline film) and [12]

$$A = \frac{6}{\pi k} (1 - p) \int_0^{\pi/2} d\phi \int_1^\infty \frac{\cos^2 \phi}{H^2(t, \phi)} \times \left( \frac{1}{t^3} - \frac{1}{t^5} \right) \frac{1 - \exp[-kt H(t, \phi)]}{1 - p \exp[-kt H(t, \phi)]} dt, \quad (4)$$

$$B = \frac{6}{\pi} (1 - p)^2 \int_0^{\pi/2} d\phi \int_1^\infty \frac{\cos^2 \phi}{H^2(t, \phi)} \times \left( \frac{1}{t^2} - \frac{1}{t^4} \right) \frac{\exp[-kt H(t, \phi)]}{\{1 - p \exp[-kt H(t, \phi)]\}^2} dt, \quad (5)$$

$$C = \frac{12\alpha}{\pi k} (1-p) \int_0^{\pi/2} d\phi \int_1^{\infty} \frac{\cos \phi}{H^3(t, \phi)} \times \left( \frac{1}{t^2} - \frac{1}{t^4} \right) \frac{1}{(t^2 - 1)^{1/2}} \times \frac{1 - \exp[-kt H(t, \phi)]}{1 - p \exp[-kt H(t, \phi)]} dt \quad (6)$$

$$D = \frac{6}{\pi} (1-p)^2 \int_0^{\pi/2} d\phi \int_1^{\infty} \frac{\cos^2 \phi}{H(t, \phi)} \times \left( \frac{1}{t^2} - \frac{1}{t^4} \right) \frac{\exp[-kt H(t, \phi)]}{\{1 - p \exp[-kt H(t, \phi)]\}^2} dt, \quad (7)$$

where  $k$  is the reduced thickness,

$$k = a \cdot l_0^{-1}, \quad (8)$$

$a$  is the film thickness,

$$g(\alpha) = \alpha \frac{df(\alpha)}{d\alpha}, \quad (9)$$

$$\alpha_f = \frac{dLna}{dT}, \quad (10)$$

$$\alpha_g = \frac{dLna_g}{dT}, \quad (11)$$

$T$  is the absolute temperature and  $\beta_0$  is the TCR of the bulk material.  $H$  is a function of the integration variables  $t$  and  $\phi$ .

Introducing in Equation 1,  $X^*$  and  $Y^*$  defined by

$$X^* = (g(\alpha) - A + B + C) (f(\alpha) - A)^{-1} \quad (12)$$

and

$$Y^* = (D - A) (f(\alpha) - A)^{-1} \quad (13)$$

gives

$$\beta_{fpu}/\beta_0 = 1 + X^* + Y^* \alpha_f/\beta_0 + (X^* - Y^*) \alpha_g/\beta_0. \quad (14)$$

The effects of thermal strains on the TCR,  $\beta_{fpu}$ , can be calculated from the longitudinal and transverse strain coefficients of resistivity of unsupported films, respectively,  $\gamma_{plu}$  and  $\gamma_{ptu}$ , as recently shown [5]. The theoretical values of  $\gamma_{plu}$  and  $\gamma_{ptu}$  are easily deduced from the theoretical values related to supported films presented in a previous paper [16]:

$$\gamma_{plu} = \eta + 1 + X^*(\eta + 1) + Y^*(-1 - \mu) \quad (15)$$

and

$$\gamma_{ptu} = \eta + 1 + X^*(\eta - \mu), \quad (16)$$

where  $\mu$  is Poisson's ratio of the film and  $-\eta$  is the strain coefficient of the bulk mean free path.

Since the difference between the TCR of a supported and an unsupported film is given [5] by

$$\beta_f - \beta_{fu} = (\gamma_{lu} + \gamma_{tu}) \frac{\alpha_s - \alpha_f}{1 - \mu}, \quad (17)$$

where  $\alpha_s$  is the thermal expansion coefficient of the substrate, the general expression for the TCR,  $\beta_{fpu}$ , of polycrystalline supported films is then, by introducing Equations 14 to 16 in Equation 17:

$$\begin{aligned} \beta_{fpu}/\beta_0 = & 1 + X^* + Y^* \alpha_f/\beta_0 + (X^* - Y^*) \alpha_g/\beta_0 \\ & + [2(\eta + 1) + X^*(2\eta - \mu + 1) \\ & - Y^*(\mu + 1)] (\alpha_s - \alpha_f) (1 - \mu)^{-1} \beta_0^{-1}. \end{aligned} \quad (18)$$

Neglecting any dependence on Fermi energy in electrical parameters, except that of the mean free path, and defining

$$U = \left( \frac{dLn l_0}{dLn E} \right)_{E=E_F} \quad (19)$$

and

$$V = \left( \frac{dLn A}{dLn E} \right)_{E=E_F}, \quad (20)$$

where  $E$  is the electron energy,  $E_F$  is the Fermi energy and  $A$  is the area of the Fermi surface, the general expression for the thermoelectric power of supported polycrystalline films,  $S_{fpu}$ , is given by [17]

$$S_{fpu} = -\frac{\pi^2 k_0^2 T}{3eE_F} [V + U(1 + X^*)], \quad (21)$$

where  $e$  is the electronic charge and  $k_0$  is the Boltzmann constant. When interpreting experimental data, particularly at low temperatures, it must be remembered that Equation 21 is related to the thermoelectric power due to electronic transport only, and that it has been derived [17] from the free electron model under the assumption of spherical Fermi surfaces (which may only approximately be the case). However, such a description is in many cases convenient [18].

Substituting from Equation 18 into Equation 21 yields

$$S_{fp} = -\frac{\pi^2 k_0^2 T}{3e E_F} \left\{ V + \frac{U}{\beta_0} \left[ \beta_{fp} - Y^* \alpha_f - (X^* - Y^*) \alpha_g - [2(\eta + 1) + X^*(2\eta - \mu + 1) - Y^*(\mu + 1)] (\alpha_s - \alpha_f) (1 - \mu)^{-1} \right] \right\}. \quad (22)$$

For an infinitely-thick polycrystalline film, the thermoelectric power reduces to the grain-boundary thermoelectric power,  $S_g$ , the expression for which is derived from that of  $S_{fp}$  by taking  $p = 1$ , that is, by assuming that the scattering at external surfaces does not play any rôle, and, taking into account the limiting values of  $Y^*$  and  $X^*$ ,

$$\text{and } Y^*|_{k \rightarrow \infty} = Y^*|_{p \rightarrow 1} = 0 \quad (23)$$

$$X^*|_{k \rightarrow \infty} = X^*|_{p \rightarrow 1} = \frac{g(\alpha)}{f(\alpha)} \quad (24)$$

$$S_g = -\frac{\pi^2 k_0^2 T}{3e E_F} \left\{ V + \frac{U}{\beta_0} \left[ \beta_g - \frac{g(\alpha)}{f(\alpha)} \alpha_g - \left[ 2(\eta + 1) + \frac{g(\alpha)}{f(\alpha)} (2\eta - \mu + 1) \right] \times (\alpha_s - \alpha_f) (1 - \mu)^{-1} \right] \right\}. \quad (25)$$

It has been previously shown that the grain-boundary parameters were more convenient than the bulk parameters for studying size effects in resistivity and TCR [19, 20], thermoelectric power [21, 22] and strain coefficients [23, 24].

If it is assumed that thermal variations in electronic transport properties are, to a first approximation, only due to variations in the electronic mean free path, Equation 18 reduces to

$$\beta_{fp}^1 / \beta_0 = 1 + X^*, \quad (26)$$

where  $\beta_{fp}^1$  is the limiting expression for  $\beta_{fp}$ , and Equation 21 takes the form

$$S_{fp} = -\frac{\pi^2 k_0^2 T}{3e E_F} \left( V + U \frac{\beta_{fp}^1}{\beta_0} \right). \quad (27)$$

The validity of Equation 27 has been established in the Fuchs–Sondheimer [15] conduction model [25], in a general grain-boundary conduction model [21, 26], in the Mayadas–Shatzkes model [13] and, also, in the recent three-dimensional and two-dimensional models in which the effects of the arrays of scatterers are simultaneously

taken into account [27, 28] or not taken into account [29, 30].

If it is assumed that

$$\alpha_f = \alpha_g \quad (28)$$

and

$$\alpha_s = \alpha_f, \quad (29)$$

that is, the film is assumed to be unsupported, Equation 18 goes to the form

$$\beta_{fpu} / \beta_0 = 1 + X^* \left( 1 + \frac{\alpha_f}{\beta_0} \right) \quad (30)$$

and Equation 21 becomes

$$S_{fpu} = -\frac{\pi^2 k_0^2 T}{3e E_F} \left( V + U \frac{\beta_{fpu} + \alpha_f}{\beta_0 + \alpha_f} \right). \quad (31)$$

This equation has been proposed by Warkusz [14].

### 3. Approximate theoretical expressions for thermoelectric power

Several papers [19, 24, 31] have shown that the following linearized approximate expressions can be empirically derived from experimental data:

$$k\beta_{fp} / \beta_g \approx k - (1 - p)H(\alpha); \quad (32)$$

$$kX^* \approx k \frac{g(\alpha)}{f(\alpha)} - (1 - p) \left[ 1 + \frac{g(\alpha)}{f(\alpha)} \right] H(\alpha); \text{ and} \quad (33)$$

$$kY^* \approx -(1 - p)(C_1 + C_2\alpha)^{-1}, \quad (34)$$

where  $C_1$  and  $C_2$  are constants [24].

Hence, from Equations 15 and 16

$$\begin{aligned} \gamma_{p1u} + \gamma_{p1u} &\approx (1 + \eta) \left( 2 + \frac{g(\alpha)}{f(\alpha)} \right) + \frac{g(\alpha)}{f(\alpha)} (\eta - \mu) \\ &- \frac{1 - p}{k} \left\{ H(\alpha) \left[ 1 + \frac{g(\alpha)}{f(\alpha)} \right] (1 + 2\eta - \mu) \right. \\ &\left. - (1 + \mu)(C_1 + C_2\alpha)^{-1} \right\}. \end{aligned} \quad (35)$$

A further simplification can be introduced: in the Mayadas–Shatzkes conduction model [13], the grain diameter  $a_g$  represents the average spacing between the scatterers perpendicular to the electric field and plays the rôle of a longitudinal geometrical parameter; in the case of isotropic thermal expansion of the film the behaviour of  $a_g$  is that of any geometrical parameter of the film. It can therefore be assumed that Equation 28 holds.

Introducing Equations 28 and 32 to 34 in Equation 22 yields

$$\begin{aligned}
S_{\text{fp}} \approx & -\frac{\pi^2 k_0^2 T}{3e E_{\text{F}}} \left[ V + \frac{U}{\beta_0} \left( \beta_{\text{g}} - \beta_{\text{g}} \frac{1-p}{k} H(\alpha) \right. \right. \\
& + \alpha_{\text{f}} \left. \left. \left[ -\frac{g(\alpha)}{f(\alpha)} + \frac{1-p}{k} H(\alpha) \left[ 1 + \frac{g(\alpha)}{f(\alpha)} \right] \right] \right) \right. \\
& - (\alpha_{\text{s}} - \alpha_{\text{f}}) (1-\mu)^{-1} \left( (1+\eta) \left( 2 + \frac{g(\alpha)}{f(\alpha)} \right) \right. \\
& + \left. \left. \frac{g(\alpha)}{f(\alpha)} (\eta - \mu) \right. \right. \\
& - \left. \left. \frac{1-p}{k} \left[ H(\alpha) \left[ 1 + \frac{g(\alpha)}{f(\alpha)} \right] (1+2\eta - \mu) \right. \right. \right. \\
& \left. \left. \left. - (1+\mu) (C_1 + C_2 \alpha)^{-1} \right] \right) \right]. \quad (36)
\end{aligned}$$

Defining the difference,  $\Delta S_{\text{fp}}$ , in thermoelectric power of polycrystalline films by the relation

$$\Delta S_{\text{fp}} = S_{\text{fp}} - S_{\text{g}} \quad (37)$$

gives, from Equations 25 and 36

$$\begin{aligned}
\Delta S_{\text{fp}} \approx & -\frac{\pi^2 k_0^2 T}{3e E_{\text{F}}} \cdot \frac{U}{\beta_0} \frac{1-p}{k} \left( -\beta_{\text{g}} H(\alpha) \right. \\
& + \alpha_{\text{f}} H(\alpha) \left( 1 + \frac{g(\alpha)}{f(\alpha)} \right) \\
& + \left[ H(\alpha) \left[ 1 + \frac{g(\alpha)}{f(\alpha)} \right] (1+2\eta - \mu) \right. \\
& \left. \left. - (1+\mu) (C_1 + C_2 \alpha)^{-1} \right] (\alpha_{\text{s}} - \alpha_{\text{f}}) (1-\mu)^{-1} \right). \quad (38)
\end{aligned}$$

Introducing the relation of  $\beta_{\text{g}}$  with  $\beta_0$  [12, 13]

$$\beta_{\text{g}}^1 = \beta_0 \left[ 1 + \frac{g(\alpha)}{f(\alpha)} \right], \quad (39)$$

Equation 38 becomes

$$\begin{aligned}
\Delta S_{\text{fp}} = & -\frac{\pi^2 k_0^2 T}{3e E_{\text{F}}} \frac{U}{\beta_0} \frac{1-p}{k} \left\{ \left( \frac{\alpha_{\text{f}}}{\beta_0} - 1 \right) \beta_{\text{g}}^1 H(\alpha) \right. \\
& + \left[ H(\alpha) \frac{\beta_{\text{g}}^1}{\beta_0} (1+2\eta - \mu) \right. \\
& \left. \left. - (1+\mu) (C_1 + C_2 \alpha)^{-1} \right] \right. \\
& \left. \times (\alpha_{\text{s}} - \alpha_{\text{f}}) (1-\mu)^{-1} \right\}. \quad (40)
\end{aligned}$$

When only the thermal variations in  $l_0$  are retained, Equations 32 and 40 reduce to

$$k \beta_{\text{fp}}^1 / \beta_{\text{g}} = k - (1-p) H(\alpha) \quad (41)$$

and

$$\Delta S_{\text{fp}}^1 = \frac{\pi^2 k_0^2 T}{3e E_{\text{F}}} U \frac{\beta_{\text{g}}^1}{\beta_0} \frac{1-p}{k} H(\alpha), \quad (42)$$

where  $\Delta S_{\text{fp}}^1$  is the limiting form for  $\Delta S_{\text{fp}}$ .

Introducing Equation 41 in Equation 42 gives

$$\Delta S_{\text{fp}}^1 = \frac{\pi^2 k_0^2 T}{3e E_{\text{F}}} U \frac{(\beta_{\text{g}}^1 - \beta_{\text{fp}}^1)}{\beta_0}. \quad (43)$$

Equation 43 can be directly derived from the general relation between thermoelectric power and the temperature coefficient of resistivity of unsupported films (neglecting thermal variations in geometrical parameters) [20, 21] by introducing an effective mean free path,  $l_{\text{g}}$ , [19] as recently shown (see Equation 12 in [22] and [15]).

#### 4. Comparison with experiments

In the practical case of Zn- and Al-sputtered films, the published values [32, 33] for  $\alpha$  and  $\beta_{\text{g}}$  agree with the following

$$\beta_{\text{g}} / \beta_0 < 0.5;$$

$$\alpha \geq 0.7; \text{ and}$$

$$0.5 > H(\alpha) > 0.35.$$

It may be noted that the usual Fuchs-Sondheimer asymptotic equation [15, 18] leads to  $H(\alpha) = 0.375$ . From the value of  $\alpha$  it is derived that  $(C_1 + C_2 \alpha)^{-1} > 3$ . Taking typical values:

$$\eta = 1.15, \quad \mu = 0.38, \quad \alpha_{\text{f}} = 20.10^{-6} \text{ } ^\circ\text{C}^{-1},$$

$$\alpha_{\text{s}} = 5.10^{-6} \text{ } ^\circ\text{C}^{-1} \text{ yields:}$$

$$\alpha_{\text{f}} \ll \beta_{\text{g}} < \beta_0;$$

$$|\alpha_{\text{s}} - \alpha_{\text{f}}| \ll \beta_{\text{g}}; \text{ and}$$

$$H(\alpha) \frac{\beta_{\text{g}}}{\beta_0} (1+2\eta - \mu) < (1+\mu) (C_1 + C_2 \alpha)^{-1}$$

and

$$H(\alpha) \ll (1+\mu) (C_1 + C_2 \alpha)^{-1} (1-\mu)^{-1}.$$

Hence, a rough approximation for Equation 40 could be derived from Equation 42:

$$\begin{aligned}
\Delta S_{\text{fp}}|_{\text{approx.}} = & \Delta S_{\text{fp}}^1 + \frac{\pi^2 k_0^2 T}{3e E_{\text{F}}} \frac{U}{\beta_0} \frac{1-p}{k} \left( \frac{1+\mu}{1-\mu} \right) \\
& \times (C_1 + C_2 \alpha)^{-1} (\alpha_{\text{s}} - \alpha_{\text{f}}). \quad (44)
\end{aligned}$$

The calculated values of  $C_1$  and  $C_2$ , respectively, are [24]

$$C_1 = 3 \quad \text{and} \quad C_2 = 3.8.$$

Equation 44 shows that the difference in thermoelectric power of polycrystalline noble metal films can be derived from the over-simplified Equation 42 corrected only for the effect of thermal strains.

All these results have been derived from the Mayadas–Shatzkes model [13] but their validity is not altered when other grain-boundary conduction models for polycrystalline films are used since analogous linearized forms are obtained, for instance [34], from three-dimensional model [27] and, clearly, from the effective Fuchs–Sondheimer model [19].

## 5. Discussion

Equation 22 does not agree with an equation recently proposed (see Equation 8, [4]) but comments have been made [35] on this paper which suggest that a term has been partially omitted, since the effect of thermal strains on the mean free path did not appear; further details can be found in the Appendix.

An objection could be raised against Equation 28, since the average grain diameter  $a_g$  does not clearly have a physical existence [27] but is a geometrical tool for representing the effects of grain-boundary scatterings in the electric field direction; however, recent calculations relating to polycrystalline films exhibiting cubic grains [29] have shown that  $a_g$  could effectively represent the effects of three arrays of scatterers. This suggestion sustains the validity of Equation 28.

Starting from the Mayadas–Shatzkes conduction model new general theoretical forms for the TCR and the thermo-power of supported films have been obtained (Equations 18 and 27).

Linearized analytical expressions are derived which easily show the weights of the correcting terms (Equations 40 and 44); in the case of noble metals the correcting term due to thermal strains is not always negligible but the correcting terms due to the thermal expansion of geometrical parameters are negligible.

## Appendix

In a recent paper [4] an expression for the thermoelectric power of supported films (see Equation 8,

[4]) was derived from the Mayadas–Shatzkes [13] conduction model and used for calculating the thermoelectric power of unsupported films. In our opinion, a term has been omitted from this expression since the thermal strains (due to mismatch in the expansion coefficients of film and substrate [6]) have no effect on the electronic mean free path,  $l$ , (the strain coefficient of  $l$  does not appear in Equation 7 of [4]).

Verma and Jain [36] have previously proposed a theoretical expression for the difference between the TCR of thin supported and unsupported films, respectively,  $\beta_f$  and  $\beta_{fu}$ :

$$\beta_f - \beta_{fu} = [\gamma_1 + \gamma_2 - 2\mu_f(1 - \mu_f)^{-1}\gamma_3](\alpha_s - \alpha_f), \quad (\text{A1})$$

where  $\mu_f$  is Poisson's ratio of the film,  $\alpha_s$  and  $\alpha_f$  are, respectively, the coefficient of linear thermal expansion of the substrate and the film and

$$\gamma_i = \frac{1}{\rho_f} \left( \frac{\partial \rho_f}{\partial \epsilon_i} \right)_{\epsilon_j, \epsilon_k} \quad (\text{A2})$$

$$\text{for } i \neq j \neq k \quad \text{with } i, j, k = 1, 2, 3,$$

where  $\rho_f$  is the film resistivity and the index  $i$  is successively related to the film length, width and thickness and  $\epsilon_i$  is the strain in the  $i$ -direction.

According to Equation A2, the quantity  $\gamma_i$  is not a strain coefficient of resistivity, since a strain  $\epsilon_i$  does not induce correlated strains in the other directions. Introducing the longitudinal and transverse strain coefficient of resistivity of unsupported films, respectively,  $\gamma_{1u}$  and  $\gamma_{tu}$ , given by [8]

$$\gamma_{1u} = \gamma_1 - \mu_f \gamma_2 - \mu_f \gamma_3 \quad (\text{A3})$$

and

$$\gamma_{tu} = -\mu_f \gamma_1 + \gamma_2 - \mu_f \gamma_3 \quad (\text{A4})$$

Equation A1 takes the form

$$\beta_f - \beta_{fu} = (\gamma_{1u} + \gamma_{tu})(1 - \mu_f)^{-1}(\alpha_s - \alpha_f). \quad (\text{A5})$$

The physical significance of the above expressions has been recently presented elsewhere [5].

The theoretical expressions for  $\gamma_{1u}$  and  $\gamma_{tu}$  are easily derived from previous calculations [16, 24] of the strain coefficients of supported films, using the Mayadas–Shatzkes conduction model [13], by substituting the Poisson's ratio of the film into that of the substrate giving [16, 24]

$$\gamma_{1u} = \eta + 1 + (f(\alpha) - A)^{-1} \{X(\eta + 1) + Y(-1 - \mu_f)\} \quad (\text{A6})$$

and

$$\gamma_{tu} = \eta + 1 + (f(\alpha) - A)^{-1} \{X(\eta - \mu_f)\} \quad (\text{A7})$$

Hence,

$$\gamma_{1u} + \gamma_{tu} = 2(\eta + 1) + (f(\alpha) - A)^{-1} \times [X(2\eta + 1 - \mu_f) + Y(-1 - \mu_f)], \quad (\text{A8})$$

where  $f(\alpha)$  is the Mayadas–Shatzkes function [13],  $A$  is the usual size effect function [15],  $X$  and  $Y$  have been previously defined by the product of  $[f(\alpha) - A]$  with  $X^*$  and  $Y^*$  respectively [16, 24] and  $-\eta$  is the strain coefficient of the bulk mean free path [37, 38].

Equations A6 and A7 have been derived [16] from the Mayadas–Shatzkes model [13] using the assumption [16] that the variation of the bulk conductivity and mean free path with strain may be entirely attributed to the change in amplitude of the thermal vibrations of atoms. Introducing Gruneisen's constant,  $G$ ,  $\eta$  can be expressed by [10, 39]

$$\eta = 2G(1 - 2\mu_f). \quad (\text{A9})$$

Equations A6 and A7 have been previously used [40] for obtaining analytical expressions which have been easily computed [40].

Using the same notations, the expression of the film TCR for the unsupported film is [41], when neglecting the thermal variation in electronic reflection coefficients,

$$\beta_{fu}/\beta_0 = 1 + (f(\alpha) - A)^{-1} \times \left( X + Y \frac{\gamma_a}{\beta_0} + (X - Y) \frac{\gamma_g}{\beta_0} \right), \quad (\text{A10})$$

where  $\gamma_a$  is the temperature coefficient of film of thickness  $a$ , that is:

$$\gamma_a = \frac{da}{a dT}, \quad (\text{A11})$$

and  $\gamma_g$  is the temperature coefficient of the average gain diameter  $a_g$ , that is:

$$\gamma_g = \frac{da_g}{a_g dT}. \quad (\text{A12})$$

If it is assumed that

$$\gamma_g = \gamma_a = \alpha_f \quad (\text{A13})$$

Equation A10 takes the form

$$\beta_{fu}/\beta_0 = 1 + (f(\alpha) - A)^{-1} X \left( 1 + \frac{\alpha_f}{\beta_0} \right) + \{2(\eta + 1) + (f(\alpha) - A)^{-1} \times [X(2\eta + 1 - \mu_f) + Y(-1 - \mu_f)]\} \times (1 - \mu_f)^{-1} \frac{(\alpha_s - \alpha_f)}{\beta_0}. \quad (\text{A14})$$

An alternative expression for this equation has been proposed by Warkusz (Equation 6 of [14]).

From Equations A5, A8 and A14, the general expression for  $\beta_f$  is derived

$$\beta_f/\beta_0 = 1 + (f(\alpha) - A)^{-1} X \left( 1 + \frac{\alpha_f}{\beta_0} \right) + \{2(\eta + 1) + (f(\alpha) - A)^{-1} \times [X(2\eta + 1 - \mu_f) + Y(-1 - \mu_f)]\} \times (1 - \mu_f)^{-1} \frac{(\alpha_s - \alpha_f)}{\beta_0}. \quad (\text{A15})$$

This expression cannot reduce to the equation which has been recently given (Equation 7 of [4]) but whose physical basis has not yet been published.

The derived expressions for the thermoelectric power and its difference (see Equations 8 and 9 of [4]) then seems questionable. The complete expressions derived from the general relation between the TCR and thermo-power [26] are complicated and an attempt will be made in future work by the present authors to derive simpler expressions.

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