Modified equations for the evaluation of energy distribution of defects in asgrown thin films by Vand's theory

V. Damodara Das

Articles you may be interested in

Microstructure and defect investigations of the as-grown and annealed ZnO/Si thin films
J. Appl. Phys. **102**, 053521 (2007); 10.1063/1.2773633

Field emission from as-grown and surface modified BN and CN thin films
J. Vac. Sci. Technol. A **17**, 1191 (1999); 10.1116/1.581793

Asgrown superconducting thin films of Bi(Pb)SrCaCuO by magnetron sputtering
Appl. Phys. Lett. **57**, 925 (1990); 10.1063/1.103383

Asgrown YBaCuO thin films by reactive coevaporation with oxygen plasma cooling
J. Appl. Phys. **66**, 3907 (1989); 10.1063/1.344033

Asgrown superconducting BiSrCaCuO thin films by coevaporation
Appl. Phys. Lett. **55**, 702 (1989); 10.1063/1.101574

Modified equations for the evaluation of energy distribution of defects in as-grown thin films by Vand's theory

V. Damodara Das

Thin Film Laboratory, Department of Physics, Indian Institute of Technology, Madras 600 036, India

It is pointed out that the use of Vand's original equations for the evaluation of defect density distribution in energy in as-grown thin films lead to results which are in error by at least 6% in the case of thin films vacuum deposited at room temperature. Modified equations that can be applied to thin films formed at any arbitrary temperature T_0 K have been obtained. It is found that except for one equation, the remaining three equations are identical to those of Vand. It has also been shown that Vand's original equations can be applied in the case of thin films formed at an arbitrary temperature if the actual time t in the original equation is replaced by a time t_0 measured as if heating had started at 0 K. Experimental plots of decay energy distribution of defect cluster density [$F_0(E)$ vs E plots] obtained using the modified equations and Vand's original equations in the case of bismuth thin films deposited at different substrate temperatures (300–450 K) are also presented to show the extent of the errors and their substrate temperature dependence. These errors are also compared with the errors inherent in the theory and the approximations made in the derivation.

PACS numbers: 73.60.Dt, 68.55. + b, 61.70. − r, 81.40.Rs

INTRODUCTION

It is well known that thin films prepared by the vacuum deposition process contain a large number of lattice imperfections, owing to the very nature of the vacuum deposition process, which are far in excess of the equilibrium concentration. These defects contribute significantly to the electrical resistivity of a thin film. A majority of these defects can be removed by aging and annealing treatments and, consequently, the electrical resistivity of the film will decrease. By studying the nature of the variation of electrical resistivity during the annealing/aging process, information can be obtained about the defects being removed. Vand has developed a theory of resistivity changes associated with the annealing of defects specifically applicable to thin films[1-4] by making some assumptions. His theory has been applied by several workers[5-20] to study the defects in as-grown thin films, and a majority of workers have used the equations given in references.[2-4] However, these equations are valid only when the thin films are prepared at or close to 0 K and heat treated starting from that temperature. When the films are prepared at much higher temperatures near or above room temperature ($\sim$ 300 K), the above equations give results which are in error (by at least 5%) and give slightly distorted defect density distribution curves. The present paper arrives at modified equations which are applicable to any arbitrary, nonzero temperature of film deposition. The equations are identical to the original equations but for an extra term dependent on the temperature of the film deposition in one of the equations.

MODIFIED EQUATIONS

Following Vand[1] we make the following assumptions in arriving at the modified equations. In the fourth assumption below we take into account the fact that the thin films are prepared at any arbitrary temperature T_0 K and hence the heating also starts at T_0 K. Vand had assumed that the films are formed at 0 K and the heating also starts at 0 K. Also, we use the temperature of heating as the variable rather than the time of heating, as was done by Vand. This is convenient and simpler, as we shall see, to arrive at the equations.

(i) The defects which are annealed out at moderate temperatures of heating are of "combined type," that is, vacancies and interstitials in close proximity with each other, i.e., point defect clusters.

(ii) These point defect clusters require a characteristic decay energy E to get annealed out by small scale diffusion and the decay energy of the defects can vary from zero to the activation energy for self-diffusion depending upon the number and the configuration of point defects constituting a cluster.

(iii) A defect of decay energy, E contributes to the resistivity of the film an amount $\rho(E)$ and hence the contribution to resistivity by all the defects is

$$\rho_i = \int_0^\infty \rho(E)N(E)dE,$$

where $N(E)$ is the density of defects of energy E.

(iv) The film is formed at T_0 K and hence the heating during the annealing process starts from T_0 K. Also, the heating rate dT/dt is uniform and is a K/s.

The starting decay equation of Vand[1] giving the rate of change of defect density given by

$$\frac{dN(E, t)}{dt} = - CN(E, t)\exp^{(-E/kT)} \tag{1}$$

(where $C = 4\nu_{max} n$) can be written, by changing the variable from time (t) to temperature (T), as

$$a\frac{dN(E, T)}{dT} = - CN(E, T)\exp^{(-E/kT)}. \tag{2}$$

Separating the variables and integrating from the initial tem-

perature T_0 and defect density N_0 to T and N, we get

$$\int_{N_0}^{N} \frac{dN}{N} = \frac{-C}{a} \int_{T_0}^{T} \exp^{(-E/kT)} dT. \tag{3}$$

Following Vand, if we put $x = kT/E$, the equation becomes

$$\ln(N/N_0) = \frac{-CE}{ka} \int_{x_0}^{x} \exp^{(-1/x)} dx, \tag{4}$$

where $x_0 = kT_0/E$.

Using the approximation valid for small x (i.e., temperatures much lower than E/k, which is indeed the case because $E \sim 1$–2 eV), viz.,

$$\int_{x_0}^{x} \exp^{(-1/x)} dx = [x^2 \exp^{(-1/x)}]_{x_0}^{x}, \tag{5}$$

we get

$$\ln(N/N_0) = \frac{-CE}{ka} [x^2 \exp^{(-1/x)} - x_0^2 \exp^{(-1/x_0)}]. \tag{6}$$

The approximation made in the solution of the integral above amounts to about 2.5% at room temperature and about 4% at 500 K. The function $N(T)$ has an inflexion point and at the latter we have, again assuming $x \ll 1$ and neglecting x and x^2 in comparison to 1,

$$\exp^{(-1/x)} = \left(\frac{-ka}{CE}\right)\left(\frac{-1}{x^2}\right). \tag{7}$$

Using a new variable $u = 1/x$, we can write the above equation as

$$\exp^{(-u)} = \frac{au}{CT}, \tag{8}$$

where we used $E = kT/x = ukT$. Taking logarithms, we get

$$u + \ln u = \ln(CT/a). \tag{9}$$

Now, as $dT/dt = a$, we get

$$(T - T_0)/t = a. \tag{10}$$

Therefore, upon substitution of the value of a in Eq. (9), we get

$$u + \ln u = \ln \frac{CT}{(T - T_0)} t, \tag{11}$$

or

$$u + \ln u = \ln 4v_{max} nt + \ln [T/(T - T_0)], \tag{12}$$

where we substituted $C = 4v_{max} n$. We have

$$\rho_i(T) = \int_{0}^{\infty} \rho(E)N(E, T)dE = \int_{0}^{\infty} F(E, T) dE. \tag{13}$$

It can be shown, following Vand,[1] that the first derivative at the inflexion point of the function $N(T)$ is

$$\frac{dN}{dT} = \frac{-Nk}{E} \frac{1}{x^2} = \frac{-Nk}{E} u^2, \tag{14}$$

which is very large in magnitude. [For example, if $E = 1.5$ eV, and $u = 37$, N changes by 8% for a 1° change in temperature.] Therefore, the function $N(T)$ falls sharply at the inflexion temperature T_i. Hence, we can replace the function $N(E, T)$ in the integral for $\rho_i(T)$ by the function $N_0(E)$, the initial defect density for $T > T_i$ and, by $N = 0$ for $T < T_i$.

Therefore, we can write the equation for $\rho_i(T)$ as

$$\rho_i(T) = \int_{E_i(T)}^{\infty} \rho(E)N_0(E) dE = \int_{E_i(T)}^{\infty} F_0(E) dE, \tag{15}$$

where E_i is the lowest energy of the defects which are still present in the film at temperature T_i.

This implies that at any temperature T there are two groups of defects, one with energies $E < E_i(T)$ and the other with $E > E_i(T)$ and only the latter group exists in the film at the temperature T (in the initial concentration) and hence contributes to resistivity. As temperature T increases, E_i the energy dividing the defects into two groups shifts to higher energies, thus decreasing $\rho_i(T)$.

Differentiating the above equation with respect to temperature, we get,

$$\frac{d\rho_i}{dT} = -F_0(E) \frac{dE_i}{dT}, \tag{16}$$

as, for $E = \infty$, $N_0 = 0$.

But, as we have seen, at the inflexion point of the function $N(T)$

$$\exp^{(-1/x)} = \frac{ka}{CE} \frac{1}{x^2}. \tag{17}$$

Substituting back $x = kT/E$, and differentiating with respect to temperature T, we get, after some manipulation

$$\frac{dE_i}{dT} = \frac{ku(u + 2)}{u + 1} = kU, \quad \text{where} \quad U = \frac{u(u + 2)}{u + 1}, \tag{18}$$

and we used $u = 1/x = E/kT$.

Substituting for dE_i/dT from Eq. (18) in Eq. (16), we get

$$F_0(E) = \frac{-d\rho_i/dT}{kU}. \tag{19}$$

The energy E is given from the relation

$$u = 1/x = E/kT \tag{20}$$

by

$$E = ukT.$$

Using Eq. (12), the value of u for a given temperature T (and time t) can be calculated and using this value of u, the value of U can be calculated at the same temperature T using Eq. (18). Using these values of u and U and knowing the rate of change of defect resistivity, $d\rho_i/dT$ at that temperature T experimentally, the function $F_0(E)$ and the decay energy E can be calculated using Eqs. (19) and (20), respectively. Repeating this proceedure at different temperatures, a plot of $F_0(E)$ vs E giving the defect density distribution in decay energy can be drawn for the film in question.

Comparing Eqs. (12), and (18)–(20) with the corresponding Vand's equations[1] we find that while Eqs. (18)–(20) are identical to those of Vand, Eq. (12) differs from the corresponding Vand's equation by an extra term on the right hand side, viz., $\ln [T/(T - T_0)]$ which is a function of the initial temperature T_0 and the temperature T. However, it should be noted that because u is evaluated from this equation and occurs in all the other three equations, the error occurring in u due to the deletion of the term $\ln [T/(T - T_0)]$ in Eq. (12) gives values of U, $F_0(E)$, and E [from Eqs. (18)–(20)] which

are in error. It should be further noted that in the equation for $F_0(E)$, u occurs in the form $U = u(u + 2)/u + 1$ in the denominator, while in the equation for E it occurs in the numerator as u. Therefore, the errors occurring in $F_0(E)$ and E are of opposite sign and also of slightly different magnitudes [error in $F_0(E)$ will be about 90% of that in E] and hence the defect density decay energy plots [$F_0(E)$ vs E plots] will be slightly distorted.

The above error can be eliminated by the simple means of measuring not the true time t, the time measured from the start of heating, but the time t_0 as if heating had started from 0 K at a uniform rate of a K/s. This can be seen as follows.

We can write

$$\ln [T/(T - T_0)] = \ln(T/at), \qquad (21)$$

because $T - T_0 = at$.

If t_0 is the time taken to reach the temperature T from 0 K at a uniform rate of heating a K/s, then, $T = at_0$.

Therefore, we get

$$\ln [T/(T - T_0)] = \ln(t_0/t). \qquad (22)$$

Therefore, Eq. (12) becomes

$$u + \ln u = \ln Ct + \ln(t_0/t),$$

or $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (23)$

$$u + \ln u = \ln Ct_0.$$

This equation is similar to Vand's original equation $u + \ln u = \ln Ct$, but for the fact that the true time t required to reach the temperature T is replaced by the time t_0 measured as if the heating had started from 0 K itself at the same uniform rate of a K/s. Thus, in Vand's original equation if we use t_0 instead of t the error is eliminated and the value of u evaluated will be correct. Hence, the errors in U, E, and $F_0(E)$ will also be eliminated and so also the slight distortion in $F_0(E)$ vs E plots.

MAGNITUDES OF THE ERRORS INVOLVED

To estimate the magnitudes of the errors involved let us take the typical values of experimental parameters as

$T_0 = 300$ K, heating rate $a = 3$ K/min and maximum temperature of annealing 600 K. Then, $\ln [T/(T - T_0)]$ has values between 2.0 and 0.3 for temperatures T in the range 306–600 K. As for the heating rate of 3 K/min, u will have values around 37–38 for different temperatures, the error in the u value in the above temperature range will be between 6% and 1%. As U is very nearly equal to u the error in U will also be nearly the same, and so also are the errors in $F_0(E)$ and E. The $F_0(E)$ value decreases by about 5.5%–0.9% and the E value increases by 6%–1% for different temperatures in the above range. The errors are larger at lower temperatures (energies) and decrease as the temperature (energy) increases. It should also be noted that as the deposition temperature T_0 increases, the errors in the plots become increasingly larger as the term $\ln [T/(T - T_0)]$ becomes larger.

Another important point to be noted is that the use of the original equation for the evaluation of u leads to different values of u at a given temperature (for a given heating rate) for films deposited at different substrate temperatures and hence gives different values of the decay energy for a given temperature for the above films. This is basically wrong as the energy associated with a given temperature should be independent of the deposition temperature of the film. This error which amounts to at least 6% is also eliminated by using the modified equation because of the presence of the additional term dependent on the temperature of deposition in the equation.

COMPARISON OF CALCULATIONS FROM EXPERIMENTAL DATA

Figures 1–5 show the plots of decay energy distribution of defect cluster density [$F_0(E)$ vs E plots] obtained by applying modified equations and Vand's original equations to the experimental data on bismuth thin films vacuum deposited at substrate temperatures 30, 70, 95, 120 and 170 °C and heated up to about 200 °C at the rate of 3 K/min. It should be noted from the figures that the lowest energy of the defects whose information can be obtained is about 1.08 eV in the case of the film deposited at room temperature (30 °C). This
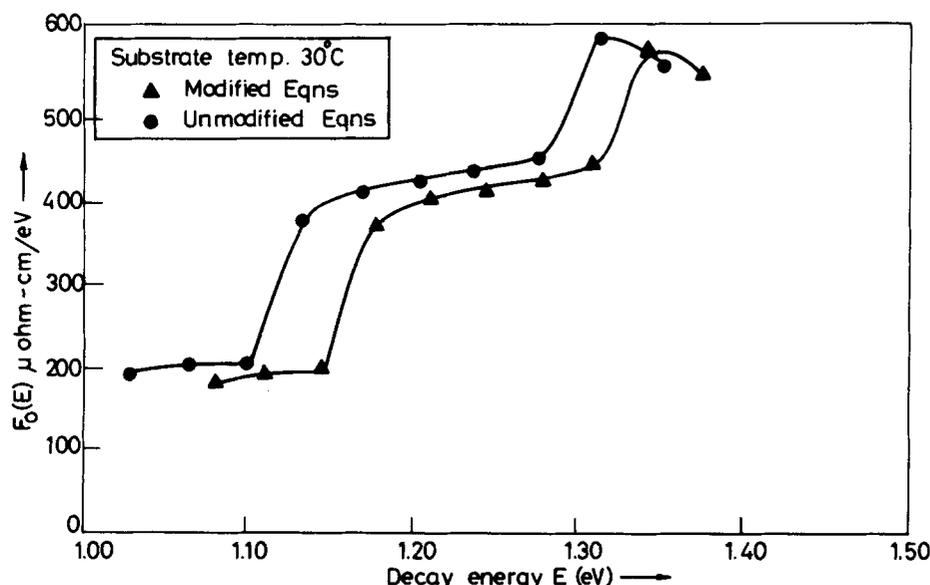

FIG. 1. $F_0(E)$ vs E plots obtained by applying (a) modified equations (▲) and (b) original equations (●) to the experimental data during annealing of a bismuth thin film deposited at substrate temperature of 30 °C. (See text.)
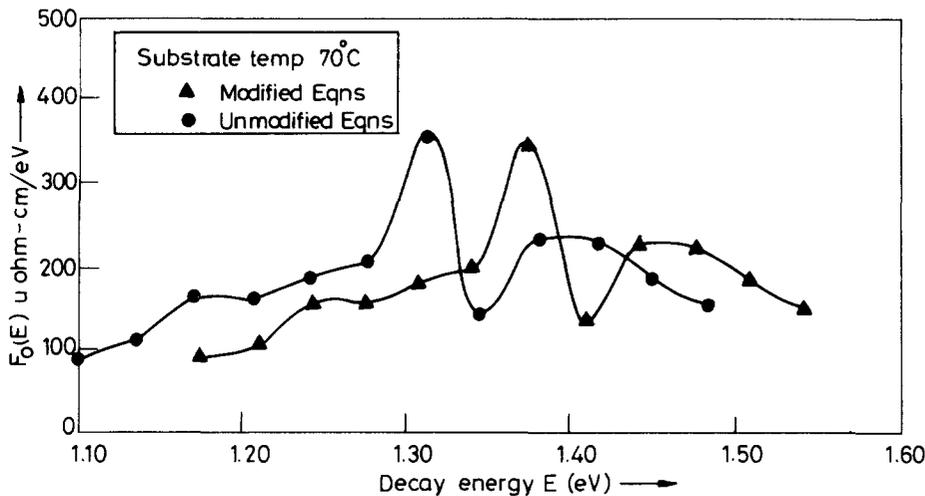
1025   J. Appl. Phys., Vol. 55, No. 4, 15 February 1984

V. Damodara Das   1025

FIG. 2. $F_0(E)$ vs E plots obtained by applying (a) modified equations (▲) and (b) original equations (●) to the experimental data during annealing of a bismuth thin film deposited at substrate temperature of 70 °C. (See text.)

is so because at this temperature the defect clusters of decay energy less than about 1 eV are already self-annealed before the experimental measurements can be started and hence no information about them can be got from the measurements. As we go to higher substrate temperature of film deposition, this lowest energy of defects whose information can be obtained shifts to higher energies. [For example, for the film deposited at 170 °C, this energy increases to 1.47 eV.] This is understandable as the defects of still higher energies are self-annealed at this temperature.

An examination of the two curves in each of the figures shows that the curves calculated from the modified equations shift to higher energies and to lower $F_0(E)$ values compared to those calculated from the original equations. This observation is in accordance with the discussion on the magnitudes of the errors involved.

Further, a careful examination of the plots shows the following.

(i) The plots obtained by the modified equations shift by larger and larger amounts from lower to higher decay energies from the plots obtained by the original equations as the substrate temperature of deposition increases. [For example, the shift at the lowest energy point for the deposition temperature of 30 °C is 0.05 eV while for 170 °C it is 0.15 eV.]

(ii) Similar dependence of the magnitude of the shift is also observed in the case of $F_0(E)$ values which decrease by increasing amounts as the deposition temperature is increased. [Because of the small scale on the vertical axis, this is not readily apparent, but it is so.]

(iii) In a given figure, the magnitude of the shift due to the modified equations [both in the decay energy and the $F_0(E)$ values] is larger at the lowest energy point of the plots and smaller at the highest energy point. [For example, in Fig. 1 (substrate temperature 30 °C) the shifts in energies at the two points are 0.05 and 0.02 eV while in Fig. 5 (substrate temperature 170 °C) they are, respectively, 0.15 and 0.08 eV.]

All the above observations made from the plots obtained from the experimental data are in agreement with the discussion on the magnitudes of the errors involved in the use of the original equations.

COMPARISON OF THE ERRORS WITH THE APPROXIMATIONS IN THE THEORY

It is interesting to compare the magnitudes of the errors involved due to the deletion of the extra term in Eq. (12) with those inherent in the approximations made in the derivation
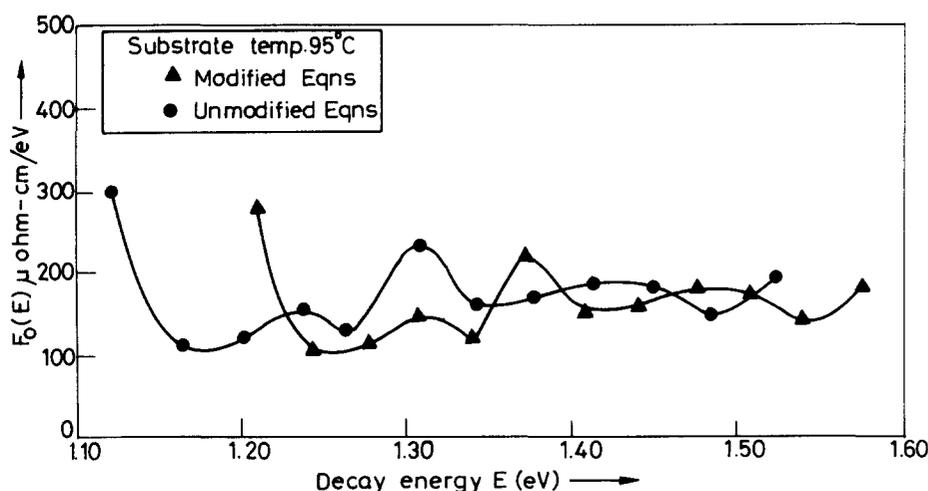

FIG. 3. $F_0(E)$ vs E plots obtained by applying (a) modified equations (▲) and (b) original equations (●) to the experimental data during annealing of a bismuth thin film deposited at substrate temperature of 95 °C. (See text.)

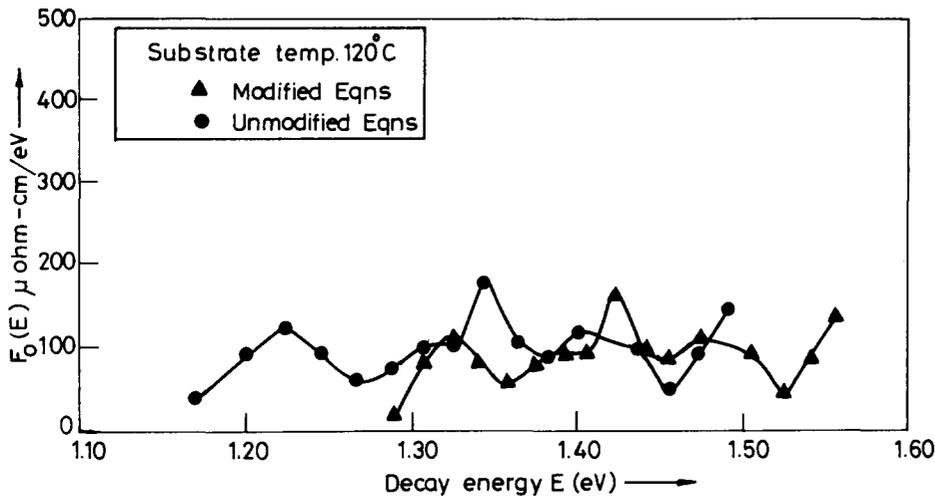FIG. 4. $F_0(E)$ vs E plots obtained by applying (a) modified equations (▲) and (b) original equations (●) to the experimental data during annealing of a bismuth thin film deposited at a substrate temperature 120 °C. (See text.)

and the assumptions of the theory.

(i) In the solution of the integral in Eq. (5) the approximation made amounts to about 2.5% at room temperature and about 4% at 500 K.

(ii) The error in finding the inflexion point of the curve $N(T)$ vs T is also a function of temperature and is about 5% at room temperature and increases with temperature to about 7.5% at 500 K.

(iii) The approximation of the function $N(E)$ to a step function in arriving at Eq. (15) leads to an error which is also temperature dependent and increases from about 1.5% at room temperature to 2.5% at 500 K.

(iv) A nearly constant value of $n = 10$ assumed for the defects of all energies does not lead to a significant error in the calculation, for in the term $\ln Ct_0 = \ln 4\nu_{max} n t_0$, t_0 is of the order of 5000–10 000 s and n is of the order of 10, so that the former is 2–3 orders of magnitude larger than the latter [ν_{max} is $\sim 10^{12}/s$]. Hence, the error due to this assumption is less than 1% of the present error.

(v) The experimental limitation of measurement and the delay time involved in heating after the film is formed only limits the lowest energy of the defects whose information can be got by the experiments as detailed earlier and does not contribute to any error in the calculations.

A comparison of the errors in (i), (ii), and (iii) above with the error involved due to the deletion of the term in Eq. (12) in the case of the film deposited at room temperature shows that the error in (i) is about 1/2 and 2.5 times, in (ii) is 1 and 5 times, and in (iii) is 1/4 and 1.5 times the error involved in the deletion of the term, at temperatures 300 (lowest energy) and 500 K (highest energy), respectively.

In the case of films deposited at higher temperatures, the error involved due to the deletion of the term in Eq. (12) is much larger than the errors in (i), (ii), and (iii) for all temperatures (energies). For example, the former error in the case of the film deposited at 170 °C is, respectively 6, 3, and 10 times larger at low energies (300 K) and 2, 1, and 3 times larger at higher energies (500 K) compared to the errors in (i), (ii), and (iii), respectively.

CONCLUSIONS

It is pointed out that the use of Vand's equations for the evaluation of energy distribution of defects for the films
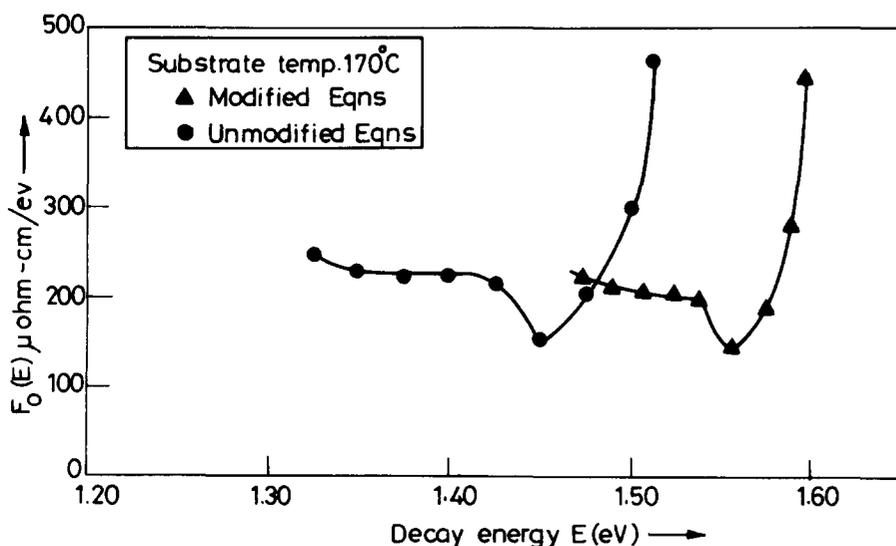

FIG. 5. $F_0(E)$ vs E plots obtained by applying (a) modified equations (▲) and (b) original equations (●) to the experimental data during annealing of a bismuth thin film deposited at substrate temperature of 170 °C. (See text.)

grown near or above room temperature using the annealing method leads to errors of at least 6% and slightly distorted energy distribution plots. Modified equations that can be used for the films deposited at temperatures other than 0 K have been obtained. It has been shown that Vand's original equation can be used without error by simply replacing the true time t by a time t_0 measured as if heating starts from 0 K at the same rate of heating. The calculations on experimental data of bismuth films deposited at different substrate temperatures confirm the extent and the nature of the errors involved. It is also found that these errors are much larger than those inherent in the theory and the approximations made, especially for films deposited at higher substrate temperatures.

ACKNOWLEDGMENTS

[1] V. Vand, Proc. Phys. Soc. London 55, 222 (1943).
[2] L. I. Maissel, in Hand Book of Thin Film Technology, edited by L. I., Maissel and R. Glang (McGraw-Hill, New York, 1970), p. 13–26.
[3] T. J. Coutts, Electrical Conduction in Thin Metal Films (Elsevier, Amsterdam, 1974), p. 174.
[4] T. J. Coutts, in Active and Passive Thin film Devices, edited by T. J. Coutts (Academic, London, 1978), p. 77.
[5] P. G. Wilkinson and L. S. Birks, J. Appl. Phys. 20, 1168 (1949).
[6] P. G. Wilkinson, J. Appl. Phys. 22, 419 (1951).
[7] H. Tryoyoda and M. Nagashima, J. Phys. Soc. Jpn. 14, 274 (1959).
[8] V. V. Shah and Y. G. Naik, Ind. J. Pure. Appl. Phys. 3, 20 (1965).
[9] V. Damodara Das and M. S. Jagadeesh, Thin Solid Films 24, 203 (1974).
[10] V. Damodara Das and M. S. Jagadeesh, J. Phys. Chem. Solids 38, 167 (1977).
[11] M. S. Jagadeesh and V. Damodara Das, 7th IVC and 3rd ICSS Vienna 1977, p. 1935.
[12] V. Damodara Das and H. Udaya Kumar, 7th IVC and 3rd ICSS Vienna 1977, p. 1675.
[13] V. Damodara Das and Anand S. Talwai, Thin Solid Films 81, 25 (1981).
[14] L. Olumekor and J. Beynon, Thin Solid Films 53, L13 (1978).
[15] Samar K. Saha and P. C. Mahanta Ind. J. Pure Appl. Phys., 18, 159 (1980).
[16] Samar K. Saha and P. C. Mahanta, Ind. J. Pure Appl. Phys. 19, 2 (1981).
[17] K. Narayanadas, M. Radhakrishna, and C. Balasubramanian, Phys. Status Solidi A 48, K71 (1978).
[18] K. Narayanadas, M. Radhakrishnan, and C. Balasubramanian, Phys. Status Solidi A 56, 195 (1979).
[19] K. Narayanadas, M. Radhakrishnan, and C. Balasubramanian, Thin Solid Films 67, 357 (1980).
[20] A. R. Patel, N. C. Pandya, N. C. Chourasia, and G. K. Shiva Kumar, Phys. Status Solid A 71, 323 (1982).