A clarification of the index of refraction of beta-iron disilicide

M. C. Bost[a] and John E. Mahan
Department of Electrical Engineering, Colorado State University, Fort Collins, Colorado 80523

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Previously published values of the index of refraction of beta-iron disilicide are corrected. Based on improved measurements and analysis, the undispersed value of the refractive index is 5.6. The previously published analysis of the absorption coefficient showed that the material possesses a direct forbidden energy gap of approximately 0.87 eV. The type of the transition is unchanged, but the band-gap value is slightly shifted to 0.89 eV.

INTRODUCTION

Beta-iron disilicide and certain other transition-metal silicides have been shown to be semiconductors of potential technological importance. Several recent investigations of the basic properties of these materials,[1,2] and their growth as thin films,[3-7] have been conducted to explore their possible usage in optoelectronic devices. Of particular interest, when selecting a suitable material to realize an optoelectronic device, is the value and type of its energy gap and the values of its optical constants.

We recently published a study of this kind for beta-iron disilicide.[1] The values of the optical constants presented in that work were determined from measurements of the normal-incident transmittance and reflectance of thin films on silicon substrates. A model of the silicide-silicon optical system was developed which expressed the transmittance and reflectance in terms of the thicknesses and optical constants of the two materials. The equations in this model cannot be solved in closed form, thus, a damped-Newton fitting routine was used to find values of the silicide optical constants which were solutions to these equations. Further analysis of the data, on which our previous publication was based, has shown that the published values of the index of refraction for energies below 0.85 eV are in error.

ANALYSIS

The mathematical model of the thin-film/substrate optical system contains a number of transcendental functions.[8] Because of this, while the reflectance and the transmittance are single-valued functions of the index of refraction (n) and the extinction coefficient (k), n, and k are multivalued functions of the reflectance and the transmittance.[9,10] Thus, over a reasonable area of n-k space there will be a number of calculated (n,k) solutions for each measured reflectance-transmittance pair.

This can be demonstrated by referring the reader to the three-dimensional plot in Fig. 1. This figure is a representation of the error, as a function of n and k, between the calculated and the measured transmittance and reflectance near a wavelength of 2.25 μm for a representative sample. The error (E), is defined as the larger of the absolute values of the errors in either transmittance or reflectance for each n-k pair:

$$E = \text{the greater of} \begin{cases} |T_{\text{meas}} - T_{\text{calc}}| \\ \text{or} \\ |R_{\text{meas}} - R_{\text{calc}}|. \end{cases} \quad (1)$$

The minima in this plot are possible solutions, and thus possible true values of n and k, for the material at this wavelength. For this example, at least five minima exist, at approximately (6.5, 0.6), (7.3, 0.5), (8.1, 0.4), (8.8, 0.4), and (9.7, 0.3), in the region of n-k space under consideration. Only one of these solutions can be physically correct. It was one of the mathematically correct, but physically incorrect, solutions which we previously reported. It should be noted that it is primarily n that varies, with k showing only a small variation among the apparent solutions.

For an ideal optical sample and measurement system (perfectly planar interfaces, no measurement error, etc.), exactly one of these minima would have had precisely zero error. However, since we are working with real materials such conditions do not hold, and in fact, the amount of error associated with each of the minima is of the same order, about 1%. Because of this, based solely on the numerical solution of the equations representing the optical model, the solution which is physically correct cannot be determined.[10,11]

In order to determine the physically correct solution, an independent method of determining either n or k must be used over at least part of the wavelength range. The transmittance and reflectance data suggest such a method. In the data for thicker films, such as that presented in Fig. 2, a substantial number of interference fringes exist. The well-known source of these interference fringes is multiple reflections within the film.[12] When light is moving from a low refractive index material to a high refractive index material and is reflected at the interface, a phase shift of 180° occurs in the reflected light. Since, in the present case, the index of refraction of the silicide film is expected to be greater than the refractive indices of either the air or the silicon substrate, the initally reflected ray will undergo a 180° phase shift, but none of the internally reflected rays will undergo a phase shift due to reflection. Therefore, considering reflection from the film, if the path length difference between the light rays being reflected is a half number of wavelengths, they will combine constructively and a maximum will occur in the reflectance. The condition for this constructive interference is

[a] Present address: Intel Corporation, Hillsboro, Oregon 97124.

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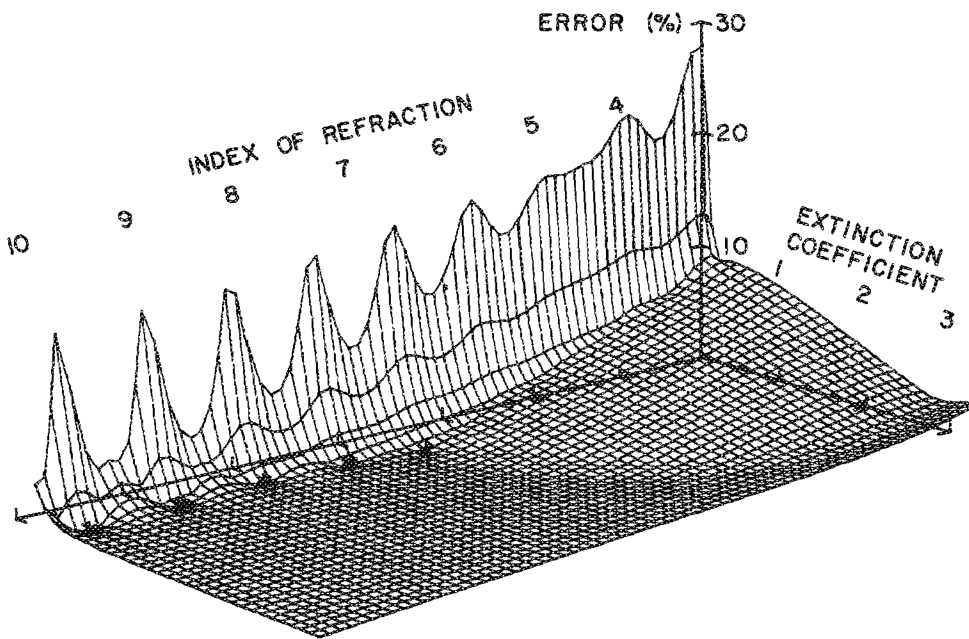

FIG. 1. A sample plot of the maximum error between the value calculated from the optical model and the measured values of the reflectance and transmittance near a wavelength of 2.25 μm. The minima, which represent possible solutions, are marked by an asterisk.

$$2nd = (m + \tfrac{1}{2})\lambda, \quad (2)$$

where d is the thickness of the silicide film, n is the silicide index of refraction, λ is the vacuum wavelength, and m is the order of the interference. Similar relations may be written for destructive interference in the reflectance and complementary ones for both constructive and destructive interference in the transmittance. In films in which either two maxima or two minima occur in either set of data, the orders of the interference can be determined and, thus, estimates can be made of the value of the index of refraction of the silicide film at the wavelengths of the extrema considered.

It should be pointed out that this analysis is appropriate only in regions of low absorption such as occurs at energies below 0.55 eV in Fig. 2. Due to the existence of nonzero absorption and various defects that cause scattering in the films, the index of refraction determined in this way will contain some error, as is apparent from the scatter in the data in Fig. 3. However, the accuracy of such a figure is usually sufficient for identifying the correct solution from a plot such as Fig. 1.

(n,k) values obtained with the aid of Fig. 3 are displayed in Fig. 4. This plot differs from the one previously published by us in several details. In addition to correcting our previous analysis of the data, we have added substantial amounts of new data to the curve. With improvements in the measurement apparatus, the mathematical smoothing which was previously used has been eliminated.

In evaluating the reliability of the index of refraction data, the type of samples used to produce the data must be

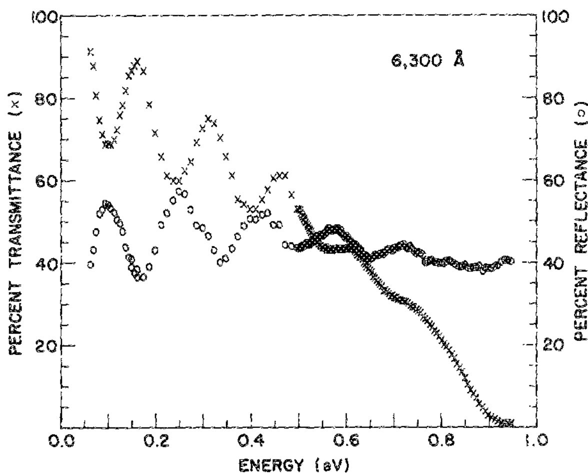

FIG. 2. The measured transmittance and reflectance as a function of wavelength for a 6300-Å-thick film.

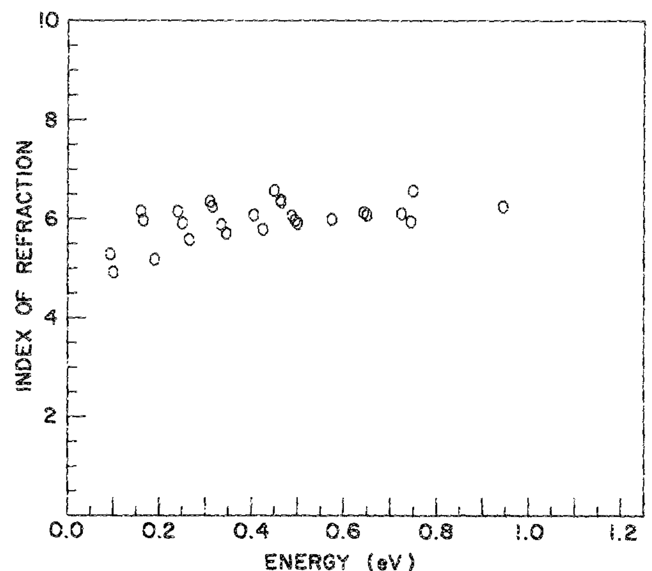

FIG. 3. The index of refraction as a function of wavelength as determined from the fringe spacings in the transmittance and reflectance data.

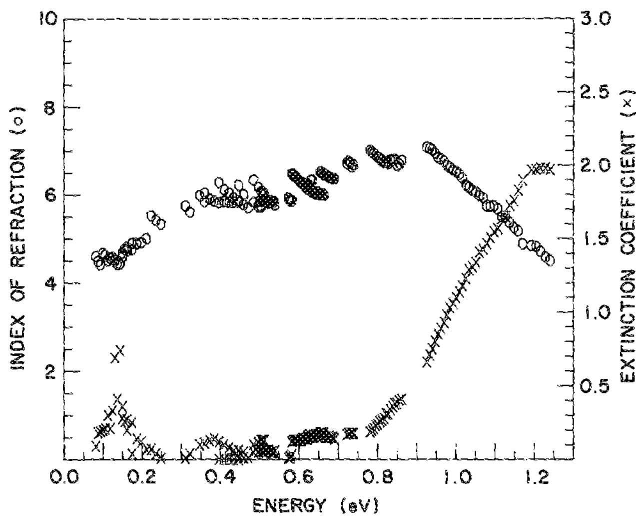

FIG. 4. The index of refraction and extinction coefficient as functions of wavelength as determined using the optical model.

considered. The index of refraction data has a standard deviation of only 0.01, however, there is a potential for a larger error in the data due to the polycrystalline nature of the samples. Considering the well-known difficulties and uncertainties[13,14] in determining the optical constants of a material from polycrystalline samples, we do not trust the index of refraction value beyond one decimal place.

The effect of the new analysis procedures on the extinction coefficient and the absorption coefficient is much less than on the index of refraction, as is demonstrated by Fig. 5. The absorption coefficient data have been plotted in a manner that would yield a linear plot for a single direct allowed transition, with the energy intercept in that instance being the minimum photon energy (E_G) required.[15] It is clear that the behavior is more complex than this simple case. The data on this plot may be better described by a function constructed to include two direct transitions:

$$K = \begin{cases} 0 & \text{for } h\nu < E_G \\ A(h\nu - E_G)^{1/2} & \text{for } E_G \leqslant h\nu \leqslant E_2 \\ A(h\nu - E_G)^{1/2} + B(h\nu - E_2)^{1/2} & \text{for } E_2 \leqslant h\nu, \end{cases} \tag{3}$$

where E_G is the value of the band gap, E_2 is the energy at which a second higher-energy direct transition occurs, h is Plank's constant, A and B are constants that depend on the details of the band structure, and ν is the frequency of the incident photon. Equation (3) is plotted as the solid line in Fig. 5, with E_G equal to 0.89 eV and E_2 equal to 1.01 eV. The interpretation suggested by this figure is that the material exhibits two direct transitions, one at 1.01 eV and another, corresponding to the forbidden energy gap, at 0.89 eV. Therefore, it may still be stated that beta-iron disilicide is a direct band-gap material, however, the value of the band gap is shifted slightly to approximately 0.89 eV.

It should also be noted that in Fig. 4 the absorption coefficient data have been extended to lower energies, and shows the existence of two extrinsic absorption peaks. Their approximate positions are 0.38 and 0.14 eV.

The revision of the index of refraction data allows a correct determination of the undispersed refractive index, n_0. This exercise is important secondarily because it demonstrates that the wavelength dependence of the index of refraction is physically reasonable. n_0 is most easily found[15] by plotting $[1/(n^2 - 1)]$ vs $(1/\lambda^2)$ as is done in Fig. 6. The relationship displayed by this plot is meaningful only at wavelengths where no absorption occurs. The value of n_0 given by the intercept at $(1/\lambda^2) = 0$ is 5.6. In a previously published determination of n_0[16] by others, a value of 5.25 was quoted. This former value was determined by extrapolating index of refraction measurements made at very long wavelengths back towards shorter wavelengths. The two

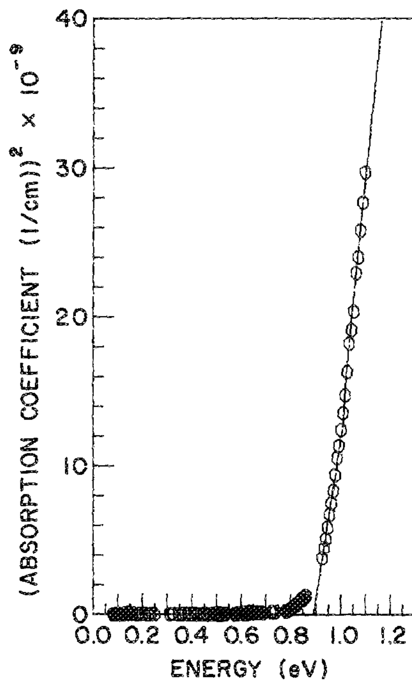

FIG. 5. A plot of the absorption coefficient squared vs energy. The solid line is a model based on the occurrence of direct transitions at 0.89 and 1.01 eV.

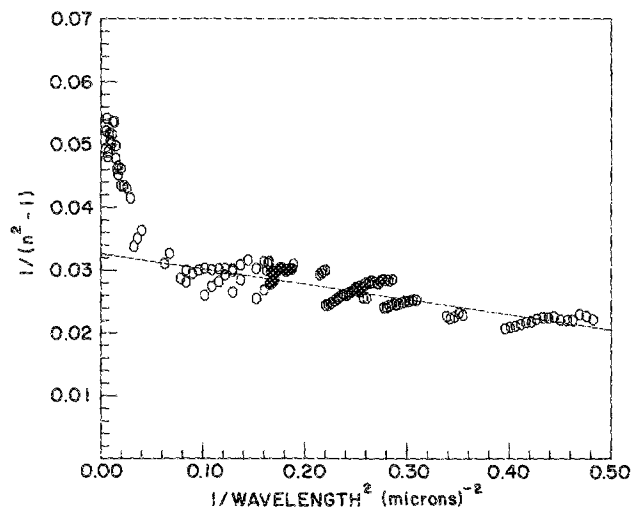

FIG. 6. A demonstration of how the value of the undispersed index of refraction was determined.

values are in reasonable agreement, considering that they were determined by very different methods and that both determinations were based on polycrystalline samples. Both of these values are high compared to those of the more common semiconductors; however, they are comparable to values published for the semiconducting lead salts.[17,18]

CONCLUSIONS

An independent measurement of the index of refraction is needed to correctly obtain the optical constants of thin films from reflectance and transmittance data. As a result, previously published values of index of refraction versus wavelength for beta-$FeSi_2$ have been corrected. A value of 5.6 was obtained for the undispersed value of the refractive index. The changes in the values of the refractive index have only a small effect on the previously determined values of the absorption coefficient. Beta-iron disilicide is still believed to be a direct band-gap material, however, the band-gap value is slightly shifted to 0.89 eV.

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