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Optical properties of amorphous multilayer structures

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The Tauc-law extrapolation has been recently applied to obtain the band gap of the hydrogenated amorphous silicon (a-Si:H) component of a-Si:H/a-SiN$_x$:H alternating layer structures. An increase in the deduced band gap of the a-Si:H layer as its thickness is reduced below 30 Å has been attributed to quantum confinement in the a-Si:H sublayers. The Tauc law has proven inadequate, however, in fitting optical absorption data of a-Si:H over a wide range of photon energy, and thus may introduce systematic errors in the gap determinations for the multilayers. In this paper, we describe the results of exact classical calculations of the transmission spectra of a series of a-Si:H/a-SiN$_x$:H alternating layer structures which are employed to obtain an estimate of the possible errors. We find a systematic increase in the a-Si:H band gap of about 150 meV as the thickness of the a-Si:H layer is reduced from 150 to 5 Å, attributable to the use of the constant-index-of-refraction Tauc-law formalism. Our calculations also suggest that interface roughness between the layers can enhance this effect in certain circumstances. As a result, we believe that the optical absorption data should be applied with care in the evaluation of quantum confinement effects.

I. INTRODUCTION

The results of optical absorption measurements on hydrogenated-amorphous-silicon- (a-Si:H) based multilayer structures have been used as evidence for the existence of bound electronic states in the potential wells established above the gap of the a-Si:H layer (confined by wide band-gap layers) as its thickness is reduced below 30 Å. The optical band gap, E_g, deduced for the a-Si:H layers exhibits a relatively sharp increase as the thickness of the confined layers is decreased below the 30-Å threshold, maintaining a fixed thickness for the confining layers.[1-3]

Ugur, Johanson, and Fritzsche[4] have established a technique to analyze the optical transmission spectrum of multilayer systems such as a-Si$_{1-x}$C$_x$:H/a-Si:H and a-SiN$_x$/a-Si:H, consisting of absorbing and nonabsorbing components. These authors have shown that it is appropriate to use the overall thickness of the structure and an effective-medium (EM) index of refraction n equal to the volume-fraction-weighted average of the indices of the two components. Then the absorption spectrum $\alpha(h\nu)$ deduced from the transmission data using these assumptions, is taken to be that of the absorbing component (and is used to obtain its band gap).

In Refs. 1-3, the band gap was determined from the deduced $\alpha(h\nu)$ data using the extrapolation of $(\alpha h\nu)^{1/2}$ vs $h\nu$ to zero ordinate [i.e., the constant-n form of the Tauc law, Eq. (2)]. It is well known,[5] however, that the constant-dipole-matrix-element expression:

$$(\alpha n/h\nu)^{1/2} = \text{const}\times(h\nu - E_g) \quad (1)$$

has been found to fit better the available data than the Tauc law:

$$(\alpha n h\nu)^{1/2} = \text{const}\times(h\nu - E_g) \ , \quad (2)$$

which uses the assumption of a constant momentum matrix element. A comparison of energy gaps of identical a-Si:H samples of different thickness reveals systematic errors introduced by using a constant-n Tauc law because of the upward curvature of the plotted data.[6] Similar errors are especially important in the comparison of the gaps of different multilayers where samples of widely different *optical* thickness may be compared. For multilayers with a fixed-thickness nonabsorbing component, this leads to an overestimate of the band gap of samples with thin absorbing layers relative to those with thick layers. In studies performed to date, no estimate of these errors has been undertaken.

In the present report, we apply experimental values for the index of refraction n and the extinction coefficient k as a function of photon energy, for the two-component materials in an exact calculation of the transmission spectra for a series of multilayer structures. As a result, a simulation of the experimental data is obtained (with no quantum effects included) which can be used to determine the magnitude of the systematic errors introduced by applying the constant n formulation of the Tauc law to the deduced absorption data for the absorbing sublayer.

II. COMPUTATIONAL TECHNIQUE

Index-of-refraction (n) and extinction-coefficient (k) data over a wide spectral range were required for bulk films of a-Si:H and a-SiN$_x$:H in order to calculate the transmission spectra of the multilayers. As a result, for a-Si:H, we used the spectroscopic-ellipsometry-derived data of Bagley, Aspnes, Celler, and Adams[7] for n and k between 1.5 and 3.5 eV. These data were taken on a very-low-H-content sample prepared by low-pressure chemical vapor deposition. This does not influence the generality of our results, since the material revealed a Tauc gap of 1.85 eV, greater than or equal to that of higher-H-content

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glow-discharge a-Si:H. For the a-SiN_x:H, k values were determined from the photothermal deflection spectroscopy and transmission results of Roxlo, Tiedje, and Abeles.[8] The n values for a-SiN_x:H were established by our spectroscopic-ellipsometry measurements[9] on a film of band gap similar to that of Ref. 8.

The complex transmission and reflection coefficients of each multilayer structure were computed using the matrix multiplication technique described in detail elsewhere.[10] In generating the transmission data, enough layers were used to make the overall film thickness as close as possible to 6000 Å. We fixed the thicknesses of the a-SiN_x:H layers at 30 or 150 Å and varied the thickness of the a-Si:H layers. As a result, when the a-Si:H thicknesses were 5 and 100 Å for the 30-Å a-SiN_x:H structures, for example, the total numbers of layers were 342 and 92, respectively.

After generating the transmission spectra using this technique, they were analyzed by the procedure described in detail by Swanepoel.[11] With this procedure, the envelopes of fringe maxima and minima in the weakly absorbing range were used to determine a set of values for the thickness and the effective index of refraction at different wavelengths. The thickness values were averaged, and the effective indices were fit to a polynomial in energy which was extrapolated over the complete wavelength range. The thickness obtained using this procedure matched within about 2% of the film thickness used in the generation of the data. The thickness and index function were used to obtain $\alpha(h\nu)$. Finally, to be consistent with current analysis techniques (see, for example, Ref. 3), we applied the EM approximation described in Ref. 4 to adjust the effective absorption edges determined by this technique into absorption edges for the a-Si:H component. It should be noted that in our work the 10^{-4}–10^{-2} transmission region was employed for the extrapolation, corresponding to that region accessible experimentally. Thus, for the 5 Å/30 Å a-Si:H/a-SiN_x:H multilayer film, the energy range employed for the extrapolation was 2.65–3.0 eV. For the 20 Å/30 Å film, the corresponding range was 2.40–2.65 eV.

We also explored the effect of imperfect interfaces on the optical parameters. Spectroscopic ellipsometry measurements indicate that most amorphous semiconductor surfaces and interfaces exhibit some degree of roughness which is a remnant of the initial nucleation and growth process.[9,12] For the multilayers, such structure can be optically modeled using a layer interposed at each interface whose optical constants are determined by an effective-medium approximation. We chose the Bruggeman effective-medium approximation in our calculation of the optical constants of the interfacial regions.[13-15] The volume fractions were determined such that the total film volume fractions were the same for the structure with both perfect and imperfect interfaces. For example, for the case of a 10 Å/30 Å a-Si:H/a-SiN_x:H structure with 5-Å modulation, the a-Si:H layers are widened to 20 Å with a 0.5/0.5 volume fraction mixture of the two components. In the case where the interface thickness is 20 Å, the entire multilayer becomes a 0.25/0.75 a-Si:H/a-SiN_x:H effective-medium mixture.

III. RESULTS AND DISCUSSION

The final results, after conventional analysis by the constant n form of Eq. (2), are given in Fig. 1. Instead of remaining constant, as would be expected if this analysis was correct, the optical gap for the series of structures with a 30 Å a-SiN_x:H layer varies from 1.85 eV for a-Si:H layers greater than about 50 Å in thickness to 2.01 eV for the thinnest a-Si:H layers used, 5 Å. A similar effect is observed for the structures with 150 Å a-SiN_x:H layer thickness. In this case, however, the region of transition is between 100 and 250 Å. This behavior shows explicitly that the position at which the transition occurs is determined by the effective optical density of the samples.

Figure 1 also shows the results of this calculation for the 10 Å/30 Å a-Si:H/a-SiN_x:H structure using imperfect interfaces with widths of 10 and 20 Å. It is found that the data for the 10 Å thick interface give a gap which is identical within error to that for the sharp interface. The 20 Å thick interface data give a significantly larger gap. This shows that under certain conditions, significantly different band-gap values can be obtained for structures accommodating the same volume fractions of the two components, depending on the form of the effective medium approximation.

Next, we will review in more detail why we observe an increase in the band gap of the a-Si:H with decreasing sublayer thickness. The effect is due to the use of a fixed transmission range for data analysis. A fixed transmission range (10^{-4}–10^{-2}) results in a variable energy range for the data analysis; i.e., the average energy at which the transmission data is analyzed for the 5-Å a-Si:H sublayer structure is significantly greater than that for the 50-Å

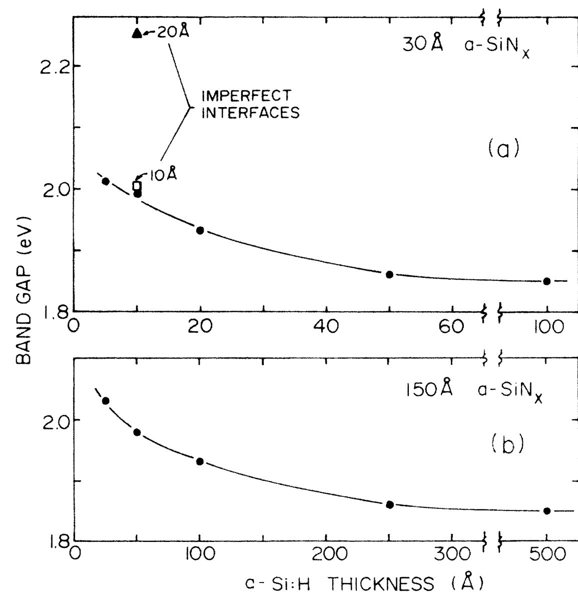

FIG. 1. Optical band gap vs a-Si:H layer thickness determined from model calculations of multilayer structures with a fixed a-SiN_x:H layer thickness of (a) 30 Å and (b) 150 Å. Also shown in (a) are two data points for structures for which the assumption of abrupt interfaces is relaxed.

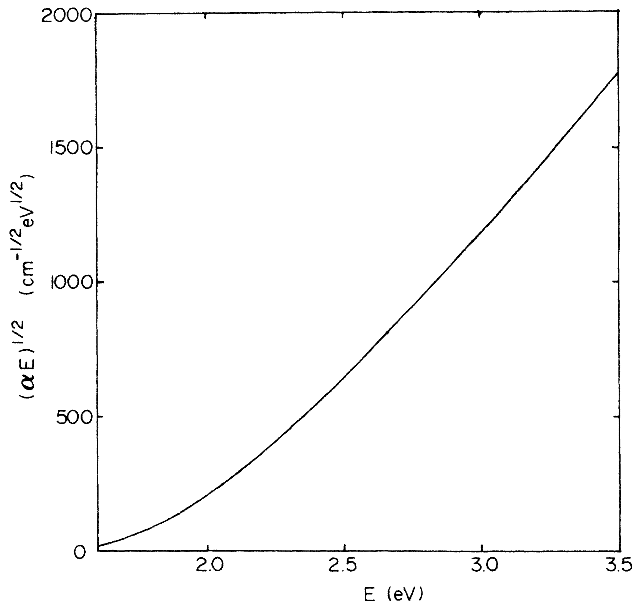

FIG. 2. Absorption data from Ref. 7 plotted using the constant n form of the Tauc relationship.

structure. This will have two effects: (1) As described in the introduction, the a-Si:H data used to generate the transmission spectra do not follow the Tauc law (see Fig. 2; higher-energy data extrapolate to a larger gap than do lower-energy data). This will result in a dependence of the derived gaps on thickness as in Fig. 1. (2) The use of a wavelength-independent-n formalism in both the EM approximation of Ref. 4 and in Eq. (2) contributes to such an effect as well, especially as the wavelength range of analysis extends into the ultraviolet. The data for the multilayer with 20-Å interface layers also appear to fit into this scheme since the energy range corresponding to the fixed transmission range of data analysis was significantly higher than for any of the other multilayers.

In an attempt to separate the two effects, we have performed Tauc-law analyses on the a-Si:H optical constants from Ref. 7 using different energy ranges for the extrapolation to determine the band gap. Figure 2 shows these data plotted as $(\alpha h\nu)^{1/2}$ vs $h\nu$. Table I lists the results using the same sets of energy ranges which were employed to obtain the band gaps of selected 30-Å a-SiN_x:H multilayers. Table I shows that as the energy range of analysis is shifted from a center value of 2.5 to 2.8 eV, a 50 meV increase in the extrapolated gap is observed for the reference a-Si:H. Thus, included in the 80-meV increase in the deduced gaps for the 30-Å a-SiN_x:H multilayers of a-Si:H thickness between 5 and 20 Å seen in Fig. 1, about 50 meV can be attributed to effect (1) in the previous paragraph. The remainder of the increase, we believe, is attributable to effect (2). Results of the analysis of 5 Å/30 Å and 20 Å/30 Å a-Si:H/a-SiN_x:H band gaps using energy independent n values of 3.4 and 1.95 for a-Si:H and a-SiN_x:H in the computer generation of the transmission data are presented in Table I also. The increase in band gap is now 40 meV, attributable solely to effect (1), showing explicitly that an increase in band gap of 30–40 meV with decreasing a-Si:H sublayer thickness between 5 and 20 Å is a result of using photon-energy-independent n formalisms.

IV. CONCLUSIONS

Despite evidence that the experimental absorption spectrum of hydrogenated amorphous silicon (a-Si:H) does not closely follow a constant index of refraction Tauc-law formalism, such analysis is conventionally applied to compare the band gaps of a-Si:H-based multilayer structures versus a-Si:H sublayer thicknesses. The observed increase in the gap with decreasing a-Si:H sublayer thickness has been interpreted as solely due to quantum confinement effects without any consideration to the possible artifacts due to the use of the Tauc law. In the worst-case situation, where the wider band-gap material is of fixed thickness, our classical multilayer simulations suggest that a signifi-

TABLE I. Tauc-law gaps determined from calculated data for selected model structures with 30 Å a-SiN_x sublayers (col. 2). Also included are the energy ranges over which the Tauc-law extrapolations were performed (col. 3) and the Tauc-law gap from the a-Si:H data of Ref. 7, using the given energy range.

a-Si:H/ a-SiN_x layer thicknesses (Å)	Tauc-law gap for model data (eV)	Energy range used to determine col. 2 value (eV)	Band gap from Ref. 7 expt. data for a-Si:H using this range (eV)
Photon-energy-dependent index of refraction (data of Refs. 7–9) assumed for a-Si:H and a-SiN_x:H component materials			
5/30	2.01	2.65–3.00	1.90
10/30	1.99	2.45–2.80	1.88
20/30	1.93	2.40–2.65	1.85
50/30	1.86	2.25–2.50	1.81
100/30	1.85	2.20–2.45	1.80
Constant index of refraction assumed for a-Si:H and a-SiN_x:H components			
5/30	1.94	2.70–3.10	1.92
20/30	1.90	2.40–2.85	1.89

cant fraction of the gap increase could be due to the artifact. For instance, in Ref. 2, the observed increase in the gap for 35 Å thick a-SiN$_x$:H multilayers was ~350 meV as the thickness of the a-Si:H layers decreased to 10 Å. This should be compared with our calculated value of 140 meV for the Tauc plot artifact over the same a-Si:H thickness range using sharp interfaces.

Preliminary calculations using the Bruggeman effective-medium approximation to simulate the optical constants of interfacial layers due to roughness show that such layers can also lead to an overestimate of the band-gap increase attributable to quantum confinement. Thus, roughness and intermediate alloying, not considered here, could possibly account for all of the observed shifts in the band gap, regardless of the $\alpha(h\nu)$ analysis technique.

By restricting optical studies to a series of multilayers with sublayer thicknesses which decrease together to maintain a fixed optical density, the analysis artifacts could be minimized. Our results in Fig. 1 for the 150-Å thick a-SiN$_x$:H multilayers suggest another way out of the dilemma of properly interpreting these data without applying the constant dipole-matrix-element formalism. If two sets of layers were prepared with the dimensions similar to the ones shown in Fig. 1, then the band-gap widening observed in the samples with the thick a-SiN$_x$:H sublayers between 50–250-Å a-Si:H sublayer thickness can provide an estimate of the effect of the different energy ranges of analysis since quantum confinement is not expected on this scale. For the samples with the thin a-SiN$_x$:H sublayers, any band-gap widening in excess of this "artifact" may be attributed to quantum-confinement effects. To our knowledge these considerations have not been applied to existing experimental data.

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[1]J. Kakalios, H. Fritzsche, N. Ibaraki, and S. R. Ovshinsky, J. Non-Cryst. Solids **66**, 339 (1984).

[2]T. Tiedje, B. Abeles, P. D. Persans, B. G. Brooks, and G. D. Cody, J. Non-Cryst. Solids **66**, 345 (1984).

[3]N. Ibaraki and H. Fritzsche, Phys. Rev. B **30**, 5791 (1984).

[4]H. Ugur, R. Johanson, and H. Fritzsche, in *Tetrahedrally-Bonded Amorphous Semiconductors,* edited by D. Adler and H. Fritzsche (Plenum, New York, 1985), p. 431.

[5]For a review, see A. Frova, in *Tetrahedrally-Bonded Amorphous Semiconductors,* edited by D. Adler and H. Fritzsche (Plenum, New York, 1985), p. 271. See also W. B. Jackson, S. M. Kelso, C. C. Tsai, J. W. Allen, and S.-J. Oh, Phys. Rev. B **31**, 5187 (1985).

[6]R. H. Klazes, M. H. L. M. van den Broek, J. Bezemer, and S. Radelaar, Philos. Mag. **45**, 377 (1982).

[7]B. G. Bagley, D. E. Aspnes, G. K. Celler, and A. C. Adams, in *Laser and Electron Beam Interactions with Solids,* edited by B. R. Appleton and G. K. Celler (Elsevier, Amsterdam, 1982), p. 483.

[8]C. B. Roxlo, T. Tiedje, and B. Abeles in *Optical Effects in Amorphous Semiconductors,* Snowbird, UT, edited by P. C. Taylor and S. G. Bishop, American Institute of Physics Conference Proceedings No. 120 (AIP, New York, 1984), p. 433.

[9]R. W. Collins and S. Guha, J. Non-Cryst. Solids **77&78**, 1003 (1985).

[10]R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1977), p. 332.

[11]R. Swanepoel, J. Phys. E **16**, 1214 (1983).

[12]D. E. Aspnes, A. A. Studna, and E. Kinsbron, Phys. Rev. B **29**, 768 (1984).

[13]For a discussion of effective medium approximations, see D. E. Aspnes, Thin Solid Films **89**, 249 (1982).

[14]D. E. Aspnes, J. B. Theeten, and F. Hottier, Phys. Rev. B **20**, 3292 (1979).

[15]R. W. Collins, W. J. Biter, H. Windischmann, and A. H. Clark, Thin Solid Films **129**, 127 (1985).