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Variable angle of incidence spectroscopic ellipsometry was used to determine the optical constants near the band edge of boron carbide (B_5C) thin films deposited on glass and n-type Si(111) via plasma-enhanced chemical-vapor deposition. The index of refraction n, the extinction coefficient k, and the absorption coefficient are reported in the photon energy spectrum between 1.24 and 4 eV. Ellipsometry analysis of B_5C films on silicon indicates a graded material, while the optical constants of B_5C on glass are homogeneous. Line shape analyses of absorption data for the films on glass indicate an indirect transition at approximately 0.75 eV and a direct transition at about 1.5 eV.
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I. INTRODUCTION

The physical and electrical properties of boron carbide make it attractive for use in high-temperature thermoelectronic conversion and in microelectronic applications.[1] Many techniques have been used to fabricate boron carbide thin films.[1–4] However, the use of plasma-enhanced chemical-vapor deposition (PECVD) using a single source compound, closo-1, 2-dicarbadodecarborane ($C_2B_{10}H_{12}$), yields material whose resistivity is ten orders of magnitude greater than films deposited by other methods.[2] This allows the fabrication of heterojunction devices with good electrical characteristics.[2,4] As a means of further characterizing these films, we report the optical constants of high resistivity boron carbide (B_5C) thin films employed in heterojunctions with n-type silicon (111), and films deposited on glass substrates.

In this work the B_5C thin films have been optically characterized using two different techniques; spectroscopic ellipsometry and spectrophotometry. The samples deposited on glass were studied using both techniques because the substrate and the films were optically transparent in the range of interest. Transmission and reflection measurements were simultaneously analyzed to obtain the film absorption. The optical band gap and other information about the transition probabilities between the semiconductor bands were also extracted from these data. Variable angle spectroscopic ellipsometry (VASE) data, and normal incidence transmission data, were obtained for the samples on glass substrates. The transmission and VASE data were both necessary in order to find a unique solution for the optical constants and film thickness. The optical constants obtained for samples on glass substrates were then used as starting values in a model to solve for the optical constants of the samples on silicon.

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II. THEORY AND EXPERIMENTAL TECHNIQUE

Nondestructive VASE was applied to three samples of B_5C films on glass substrates and eight others on n-type Si(111) substrates. An independent VASE analysis was performed on the bare silicon and glass substrates to account for substrate effects.

The experimental data were taken at three different angles of incidence 65°, 70°, and 75°. A spectroscopic scan was performed between 1.24 and 2.5 eV for the Si substrate samples, and 1.24–4.0 eV for glass substrate samples. The ellipsometric parameters, psi (Ψ) and delta (Δ), were measured by the automated ellipsometer at each photon energy (in steps of 10 nm of wavelength). The measured quantities were expressed in terms of a complex number (ρ) containing values of tan(Ψ) and phase angle (Δ):[5]

$$\rho = \frac{R_p}{R_s} = \tan(\Psi)\exp(j\Delta), \tag{1}$$

where R_p and R_s are the complex reflection coefficients for the light polarized parallel (p) and perpendicular (s) to the plane of incidence, respectively. A regression analysis was performed to calculate Ψ and Δ based on an assumed model for the structure using Fresnel's equations for reflection of polarized light from planar media.[6,7] Model parameters included film thickness, film and substrate optical constants, and nonidealities such as film inhomogenity and nonuniform film thickness.

In analyzing the VASE data, the film thickness and other parameters of the model were varied according to the Levenberg–Marquardt algorithm[8] until the calculated ψ and Δ curves fit the measured curves as closely as possible. The error function to be minimized is:[9]

$$MSE=\frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\Psi_i^{\text{mod}}-\Psi_i^{\text{exp}}}{\sigma_{\Psi,i}^{\text{exp}}}\right)^2+\left(\frac{\Delta_i^{\text{mod}}-\Delta_i^{\text{exp}}}{\sigma_{\Delta,i}^{\text{exp}}}\right)^2\right], \tag{2}$$

where N is the number of measured (Ψ,Δ) pairs, and M is the number of variable parameters of the model. The standard deviations (σ_Ψ^{exp} and $\sigma_\Delta^{\text{exp}}$) of the measured Ψ and Δ are obtained using multiple revolutions of the rotating analyzer during data acquisition.[10]

The Cauchy dispersion model, which is usually best suited to model transparent dielectric layers, was used to model the B_5C layers in all our analyses. The optical constants of the Cauchy layer are defined by the following formulas:

$$n(\lambda)=A_n+\frac{B_n}{\lambda^2}+\frac{C_n}{\lambda^4}, \tag{3}$$

where n is the index of refraction, λ is the photon wavelength given in microns, A_n, B_n, and C_n are fitting variables, and

$$k(\lambda)=A_k\times\exp\left(B_k\left[\frac{12400}{\lambda}-\frac{12400}{C_k}\right]\right), \tag{4}$$

where k is the extinction coefficient, λ is in Å and A_k, B_k, and C_k (the band edge) are fitting variables.

The absorption coefficient (α) is related to the extinction coefficient (k) by

$$\alpha=\frac{4\pi k}{\lambda}. \tag{5}$$

The dielectric function $(\epsilon=\epsilon_1+i\epsilon_2)$ is given by

$$\epsilon=(n+ik)^2. \tag{6}$$

The connection between the microstructure of a thin film and its macroscopic dielectric response can be approximately modeled by the Bruggeman effective-medium approximation theory (EMA).[11–19] In this case, the effective dielectric function ϵ of a material consisting of a microscopic mixture of several components is given by the solution of

$$\sum_i f_i\frac{\epsilon_i-\epsilon}{\epsilon_i+2\epsilon}=0, \tag{7}$$

where ϵ_i are the dielectric functions of the individual constituents, and f_i are their volume fractions. This form of EMA assumes spherical microstructure, in which grain sizes are less than one quarter of the wavelength of the incident light.

A double-beam spectrophotometer (Perkin–Elmer Lambda-9 series) was used to measure the transmission and reflection of the glass and glass-substrate samples. The range of the photon energy spectrum used for this purpose was between 0.5 and 5.0 eV. The absorption of the boron carbide films was extracted from the transmission and reflection curves using:[20]

$$A=1-T-R, \tag{8}$$

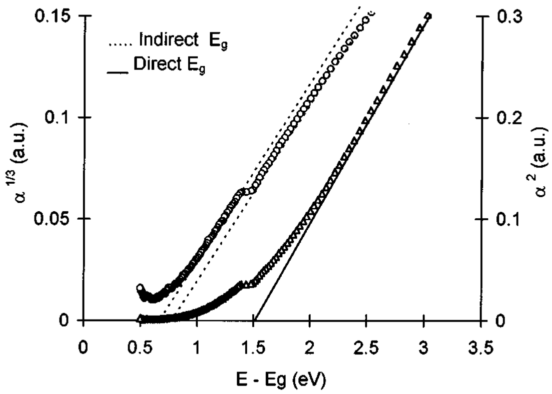

FIG. 1. An indirect transition at about $E_g=0.75$ eV and a direct transition at about $E_g=1.5$ eV based on McLean model approximation.

where A, T, and R are the absorption, transmission, and reflection, respectively. Although the absorption of the glass substrate is very weak in the spectral range of interest, it has been subtracted from the film-substrate data.

The samples were fabricated by PECVD from a single source compound closo-1,2-dicarbadodecaborane in a 13.6 MHz reactor described in detail elsewhere.[2]

III. RESULTS AND DISCUSSION

A. Spectrophotometry of B_5C on glass

The absorption coefficient (α) of the films was assumed to be proportional to the absorption (A) determined from the reflection (R) and the transmission (T) measurements according to Eq. (8).

The McLean method can be used to approximate the interband transition probabilities for various types of optical transitions in semiconductors:[21–23]

$$\alpha^N=C(h\nu-E_g), \tag{9}$$

where $N=2,\ \frac{2}{3},\ \frac{1}{2},\ \frac{1}{3}$ for allowed direct, forbidden direct, allowed indirect, and forbidden indirect transitions, respectively, and C is a constant.

A plot of $\alpha^{\frac{1}{3}}$vs $h\nu$, as shown in Fig. 1, indicates the existence of an indirect band-to-band transition in the boron carbide (B_5C) semiconductor with band gap (E_g) between 0.7 and 0.8 eV. The uncertainty is caused by the anomalous, instrument-induced discontinuity at 1.4 eV. X-ray diffraction patterns for this material indicate that it is polycrystalline,[4] which is consistent with the assignment of direct and indirect optical transitions.[21,23–25] In addition, plotting α^2 against $h\nu$ in the higher energy range, above the indirect band gap, gives a straight line. Therefore, the allowed direct transition [with $N=2$ in Eq. (9)] is also observed, as shown in Fig. 1, with direct band gap $E_g=1.5$ eV. This result is comparable to the indirect band gap reported for mono-crystalline boron (beta-rhombohedral)[26–28] and is also consistent with the indirect band gap found for pure boron prepared in our system. The observed relation between the indirect band gap of pure boron (mono-crystalline) and the allowed direct band gap of boron carbide at 1.5 eV needs further investigation.

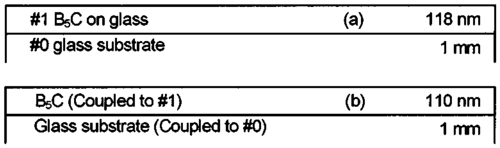

FIG. 2. A simple model used to simultaneously fit (a) the ellipsometric reflection data and (b) ellipsometric transmission data.

B. Ellipsometric analysis

1. Boron carbide (B_5C) on glass

Multiple-data type analysis[29] was used to model the samples on glass. Ellipsometric data and transmission data, both taken by the same instrument, were fit simultaneously while solving for the model parameters. The transmission and ellipsometric data taken together contain enough information to obtain unique optical constants and thickness solutions. The film thickness was also independently measured using a mechanical stylus. This measurement was used initially in the optical analysis to reduce the parameter correlation while solving for the optical constants. Later, solving for thickness as an independent parameter yielded a close agreement (5%–10%) with the film thickness measured by the mechanical stylus.

The procedure for analyzing the samples on glass was based on the model shown in Fig. 2. The glass substrate alone was first measured and fit by a Cauchy model in an independent analysis. The substrate Cauchy parameters were then fixed throughout the boron carbide film analysis. The boron carbide overlayer was also modeled by a Cauchy material (with different parameters). The best-fit Cauchy parameters and film thicknesses are shown in Table I. The difference in the boron carbide film thickness in the model used for ellipsometric data [see Fig. 2(a)] and the transmission data [see Fig. 2(b)] is due to the fact that two different locations on the film were measured in each approach. The best fit in this model gives a value of MSE=4.3.

The experimental and generated data of psi, delta, and the transmission are shown in Figs. 3(a) and 3(b), respectively. The Cauchy model index of refraction (n) and the extinction coefficient (k) are shown in Fig. 4. The real and the imaginary parts of the dielectric functions (ϵ_1,ϵ_2) may be evaluated according to Eq. (6).

TABLE I. The values of the Cauchy layer parameters for the measured psi and delta curves for B_5C thin films deposited on glass. The 90% confidence limits are given following the value of each parameter.

Parameter	Value ±90% confidence
VASE thickness	118±8 (nm)
Transmission thickness	110±8 (nm)
A_n	1.695±0.028
B_n	0.0523±0.0012
C_n	−0.0028±.0004
A_k	0.000 13±.00001
B_k	2.55±.02
C_k	8276±108

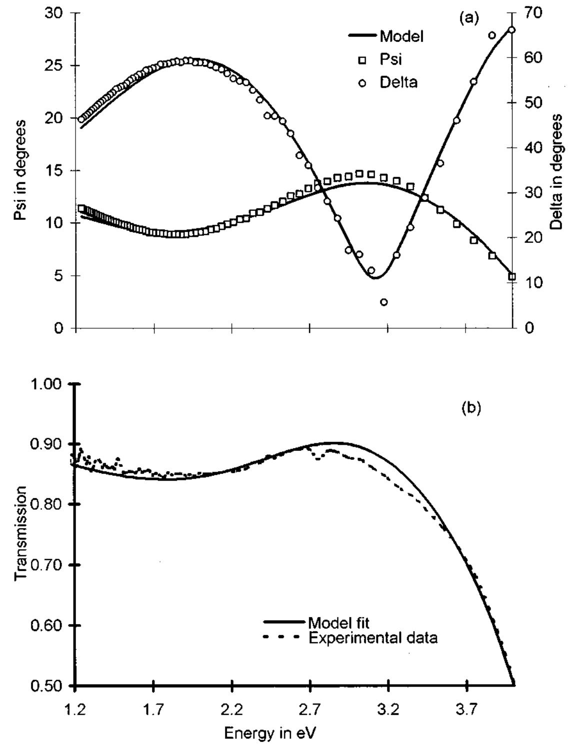

FIG. 3. The generated and experimental curves of (a) psi and delta (at 65° angle of incidence) and (b) the transmission at normal angle of incidence for B_5C film deposited on glass.

2. Boron carbide (B_5C) on n-type Si(111)

The samples on glass substrates were analyzed with a simple model using multiple-data type analysis, hence their optical constants are used as starting values to model the samples on silicon. Neither the method of multiple-data type analysis, nor the method of multi-sample data analysis[30] could be used to analyze the films deposited on silicon substrates. This is because silicon is not transparent and the degree of thickness nonuniformity was different for all of the boron carbide films on silicon.

We show a complete analysis for a selected sample of B_5C on n-type Si(111), which has been prepared simultaneously with a previously analyzed sample on glass. In this

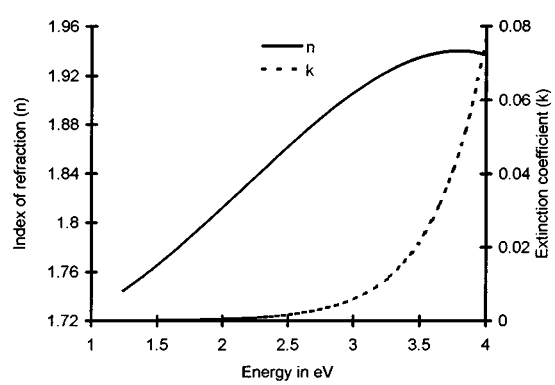

FIG. 4. The optical constants represented by the index of refraction (n) and the extinction coefficient (k).

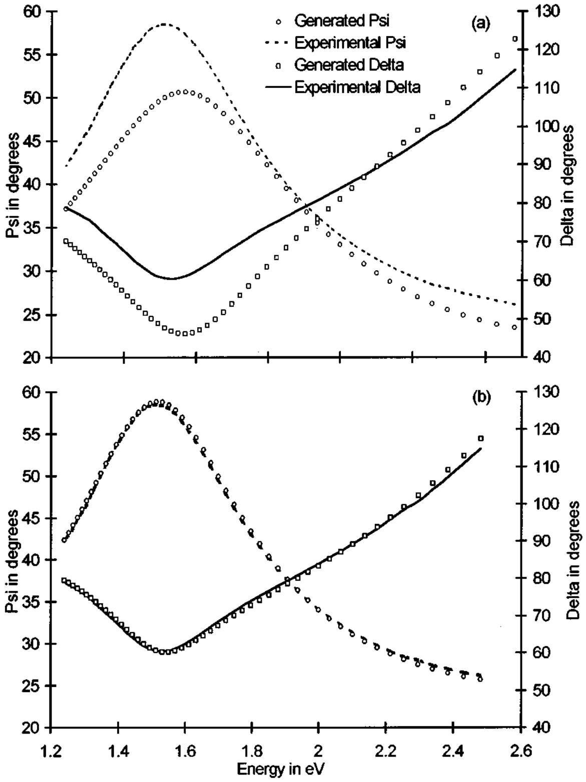

FIG. 5. (a) Experimental and generated data of psi (Ψ) and delta (Δ), at 65° angle of incidence, for a B_5C/Si sample, using homogeneous optical constants of B_5C deposited on glass and a nonuniform thickness in the model. (b) the best fit achieved using a nonuniformly thick, graded layer which contains void and the optical constants of B_5C deposited on glass.

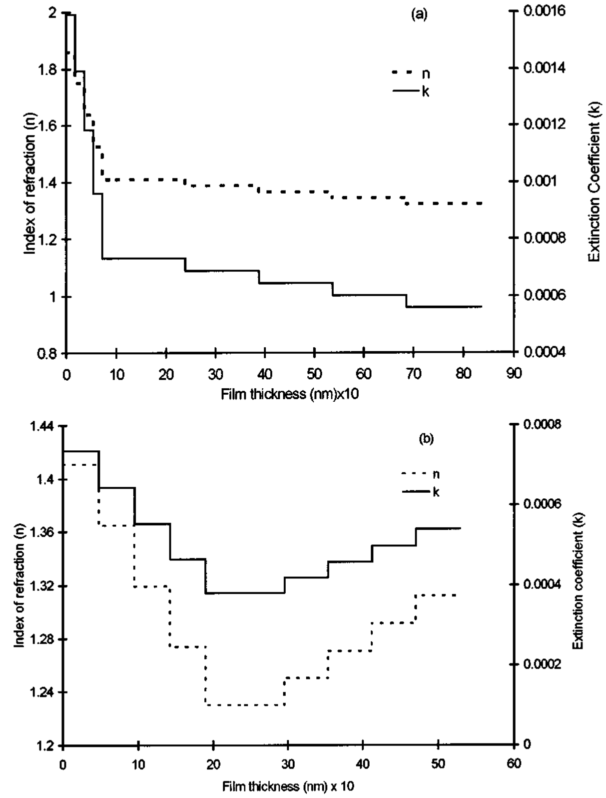

FIG. 6. Depth profile of the index of refraction (n) and the extinction coefficient (k) at 2.48 eV for a nonuniform graded material representing two observed types, (a) and (b), of B_5C films.

section, we limit the spectral range to 1.4–2.5 eV since the focus was on the optical properties of the films near the optical band edge.

An attempt was made to model the boron carbide film on silicon by using the optical constants of boron carbide deposited on glass (as described in Sec. I) based on the assumption that both structures are similar. Fitting only for a uniform film thickness yielded a qualitative fit to psi (Ψ) and delta (Δ) with the interference oscillation peaks at the right positions. However, the interference oscillation peaks were much sharper in the generated curves, indicating nonuniformity in the film thickness. Nonuniformity of the layer thickness (over the area of the ellipsometer probe beam, $\approx 1\times 3$ mm) was therefore included in the model as a fitting parameter, expressed as a percentage of the average film thickness.[31] A best-fit value of 18% nonuniformity smoothed the sharp peaks at the interface oscillation, as shown in Fig. 5(a), and significantly improved the MSE to 80.2.

In order to further improve the fit, roughness and interface layers, modeled by the EMA,[11,12] were considered in addition to thickness nonuniformity (kept at 18%), but no significant improvement was achieved. Next the Cauchy layer parameters [as given in Eqs. (3) and (4)] were again made variable, considering the boron carbide as a new material. A significant difference in the measured and calculated psi (Ψ) and delta (Δ) curves was still observed at high-energy values in the spectrum. The MSE dropped to 13.3, but substantial improvement was still needed. Again adding roughness and interface layers did not improve the quality of the fit.

The B_5C on silicon was next modeled as a graded layer containing an EMA mixture of B_5C (with optical constants from the films on glass) and void.[11–14,18] The film was divided into three regions and each region was divided evenly into five slices. The total film thickness and the nonuniformity (18%) were kept fixed while fitting for the void volume and the region's thickness. This procedure yielded the best fit between the experimental and generated data as shown in Fig. 5(b). The MSE is reduced to 6.

The results in Fig. 5(b) indicate a good agreement between the model and the actual material. However, it should be noted that the percentage of void in the model is not necessarily a physical constituent (though it could be), rather it is an indication of the difference in the mass density and the optical constants of B_5C films on silicon and glass.

Figure 6 shows the calculated index of refraction (n) and extinction coefficient (k) at photon energy of 2.48 eV as a function of position from the Si/B_5C interface for two different types of observed B_5C films. The depth profile for the optical constants of the film seen in Fig. 6(a) shows a rapid decrease in n and k from the interface into the film, and then a much slower decrease to the film surface. On the other hand, the depth profile of the film in Fig. 6(b) shows a much slower decrease in n and k from the interface into the film, where minimum values are obtained near the film center.

This is followed by an increase in *n* and *k* to the film surface. In spite of these variations in optical properties, all these B_5C/Si structures exhibit diode characteristics.[4]

IV. SUMMARY

The optical constants of PECVD B_5C on glass were determined by spectroscopic ellipsometry and spectrophotometry. The results indicated that the material deposited on glass is optically homogeneous. An indirect band gap (obtained by spectrophotometry) of ≈0.75 eV and a direct band gap of ≈1.5 eV were found.

The B_5C deposited on silicon appeared to have graded optical constants, as well as a nonuniform layer thickness. We observed two general types of graded structure. In one, a rapid decrease of the optical constants from the interface into the film occurred, and in the other a much more general decrease occurred. All the samples, regardless of the profile of their optical constants, exhibited heterojunction diode characteristics.

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