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TECHNICAL NOTES

Temperature coefficient of the energy gap of β-silicon carbide

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FOR THE study by optical means of the temperature dependence of the energy gap of a semiconductor, the necessary data are absorption spectra as a function of temperature. Absorption coefficients are frequently computed from plots of optical transmission vs. wavelength, using either known values of the reflectivity R or by measuring the transmission T at several sample thicknesses. In this study, suitable transmission spectra of β-SiC as a function of temperature were available for only one sample thickness. These spectra were analyzed to determine the temperature coefficient of the energy gap.

The sample used was an n-type crystal of cubic silicon carbide grown by an extension of the method of KENDALL.[1] Powder pattern analysis of other crystals from the same lot indicated the presence of only the cubic structure. Laue back-reflection photographs of this sample showed sharp spots; however, the transmission of polarized visible light indicated several areas whose orientation or strain differed from that of the bulk of the sample. Spectrographic analysis of this lot of crystals indicated the presence of Al, B, Ca, Fe and Mg impurities to the extent of approximately 10^{17} cm^{-3}. After optical study, resistivity measurements[2] at two points on the sample gave values (at 500°K) of 0·1 Ω-cm and 0·3 Ω-cm. The sample was a plate approximately 2 mm dia. with a thickness of (0·0114 ± 0·0002) cm. The normal to the polished faces was at an angle of 17° to a (111) direction; the unpolarized incident light beam was perpendicular to these faces.

Transmission spectra were taken on a recording single beam spectrometer in which a tungsten lamp was the light source and the dispersing element was a Leiss double-prism monochromator using flint glass prisms. An RCA-7265 photomultiplier tube, powered by a Northeastern regulated power supply, was used as a detector. Chopped beam operation employing a Perkin-Elmer Model 107 thirteen-cycle amplifier was used. The average resolution was 0·005 eV over the spectral range studied. Wavelength markers, whose positions were calibrated with a mercury lamp, were put directly on the trace using standard circuitry. Transmission measurements were made using the sample-in, sample-out method employing a resistance-heated evacuated sample holder between the monochromator exit slit and the detector. A Wheelco Instrument 'Capacitrol' was

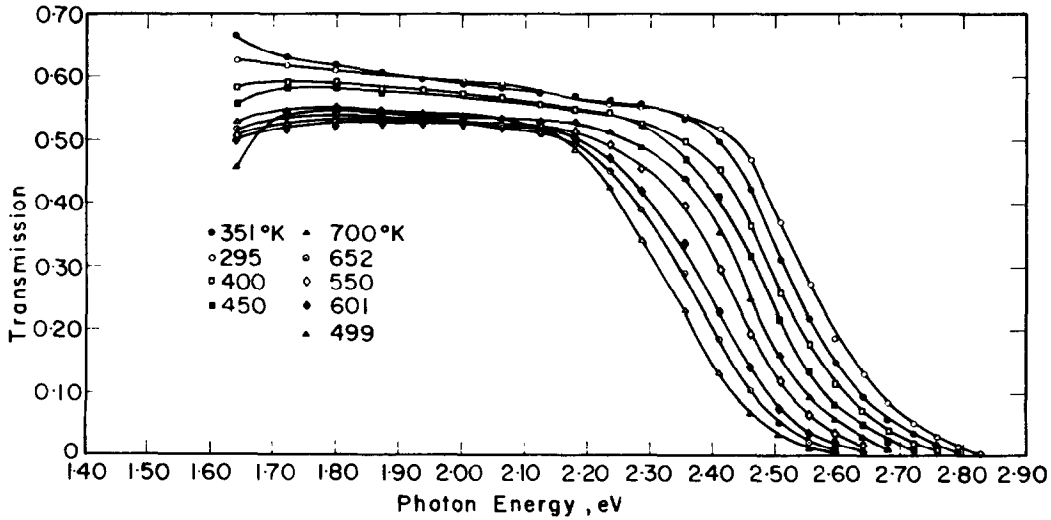

FIG. 1. Transmission vs. incident photon energy.

used for temperature regulation, and iron–constantan thermocouples were used for both measurement and control. The temperature during the recording of any spectrum varied by no more than ± 1°K, and the values quoted are estimated to be accurate to ± 2°K. The transmission was calculated at various wavelengths by linear interpolation between the wavelength markers, and an average value of the transmission was then calculated at each wavelength using the two spectra taken at each temperature.

Transmission spectra were taken at 295°K, 351°K, 400°K, 450°K, 499°K, 550°K, 601°K, 652°K and 700°K. Plots of transmission vs. incident photon energy at these temperatures covering the spectral range studied are shown in Fig. 1. The values of transmission T obtained are estimated to have an uncertainty of ± 3 per cent for values of $T \leqslant 0{\cdot}40$; the results for $T > 0{\cdot}40$ show some scatter and are considered less reliable. A similar plot for values of $T \leqslant 0{\cdot}40$ showing a larger number of calculated points, is shown in Fig. 2. Isotransmission plots, in which photon energy is plotted against temperature with transmission as a parameter, were used to obtain a value of the temperature coefficient of the energy gap E_G. If the reflectivity R in the spectral region of small intrinsic absorption does not vary greatly with temperature (as is the case for Ge and Si[3]), this method is essentially the same as making an isoabsorption plot in which the slope of the isoabsorption lines will approach (dE_G/dT) as the absorption coefficient $\alpha \to 0$. The value of (dE_G/dT) will be in error by a term of the order of the temperature variation of the energy of the phonon involved in the indirect transition. This error is believed to be less than the experimental error shown below. Since the transmission approaches $(1-R)/(1+R)$ as $\alpha \to 0$, the slope of the isotransmission lines approaches (dE_G/dT) as $T \to (1-R)/(1+R)$. Hence, for the optimum determination of (dE_G/dT) by this method, the transmission should be measured in the spectral region in which absorption due to intrinsic excitation is very small. However, only the data for $T \leqslant 0{\cdot}40$, which consist of a set of curves whose shape is not changing with temperature, were used. A series of isotransmission plots using these data is shown in Fig. 3. The isotransmission lines are parallel within ± 5 per cent, and the slopes show no trend as a function of transmission. The average slope of the isotransmission lines shown provides a value of the temperature coefficient of the band gap.

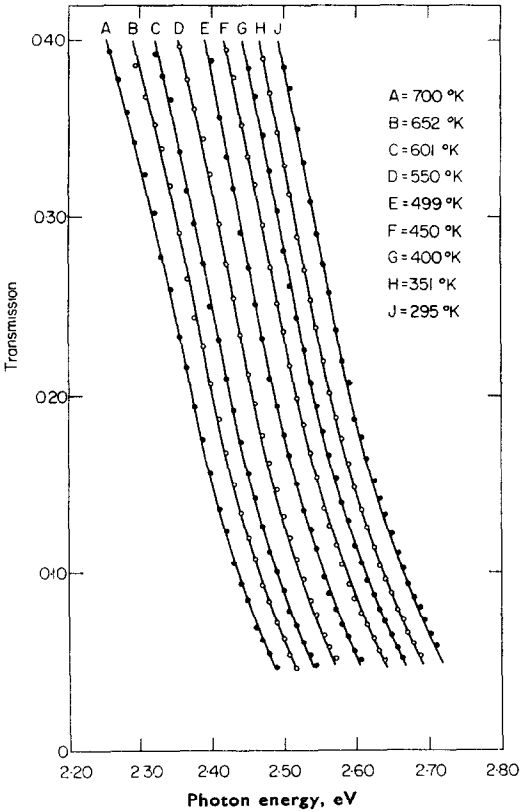

Fig. 2. Transmission vs. incident photon energy for $T \leqslant 0{\cdot}40$.

The average value of the slopes of the isotransmission lines in Fig. 3 is $(-5{\cdot}8 \pm 0{\cdot}3) \times 10^{-4}$ eV/°K; a linear variation of the energy gap of $-5{\cdot}8 \times 10^{-4}$ eV/°K is therefore suggested for the temperature range 295°K to 700°K. This value is similar to the temperature coefficient of the band gap of other semiconductors. In particular, it may be compared with the value of $(dE_G/dT) = -3{\cdot}3 \times 10^{-4}$ eV/°K reported[4] for hexagonal (polytype 6H) silicon carbide for the temperature range 300°K to 700°K. The temperature dependence of the exciton energy gap in polytype 15R SiC has recently been reported.[5] In the temperature range from 300°K to 650°K, the variation is

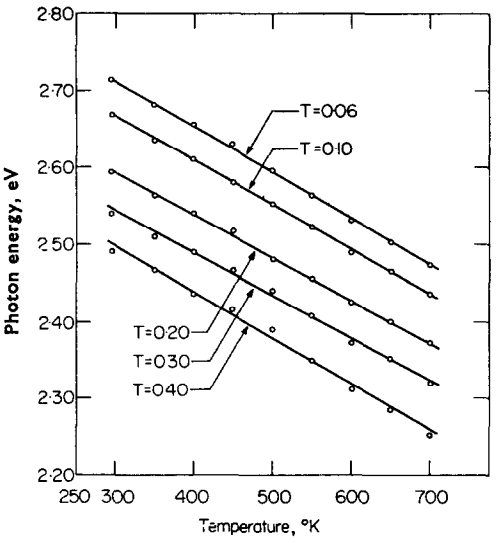

FIG. 3. Isotransmission plots for $T \leqslant 0{\cdot}40$.

essentially linear with a slope of approximately $-3{\cdot}3 \times 10^{-4}$ eV/°K. Additional data are required to utilize the deformation potential approach to estimation of the dilatation and electron-lattice interaction contributions[6] to (dE_G/dT). Unfortunately, these necessary data are not available for β-SiC.

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* This work was done while the author was with Raytheon Company.

L'interpretation du spectre optique des systemes d^1

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O'CONNOR ET CHEN ont publié dans ce Journal[1] un excellent travail experimental sur le spectre optique des systemes d^1. Cette lettre vient pour exposer la base theorique de leurs resultats experimentaux.

Les cations étudies ont été Ti(IV), Sc(III), Y(III), La(III) dans la forme d'impuretés dans des cristaux de fluorure alcalino-terreus (CaF_2). Dans ces conditions, le numéro de coordination de ces cations est six,[2,3,4] mais les compensations de charge produisent une compression axiale qui s'exprime par une distortion tétragonale de l'octaèdre. Pour ces cations la constante de couplage spin-orbite est très petite[5] (pour Ti(IV) $\lambda_{s0} = 154\ cm^{-1}$ et pour Y(III)$\lambda_{s0} = 290\ cm^{-1}$).

Le spectre optique de ces cations peut être interprète en considerant la distortion tétragonale comme le facteur primaire, et le couplage spin-orbite comme perturbation secondaire. Une distortion tétragonale prononcée se traduit par l'élévation des niveaux $e(t_{2g})$ au dessus du niveau $b_1(e_g)$.

Dans la symétrie D_{4h} les transitions dipolaires électriques sont toutes interdites à l'ordre zéro. Les transitions observées peuvent être soit dipolaires magnétiques soit assistées par des vibrations. La transition $a_1 \rightarrow b_2$ est interdite à l'ordre zéro même si on a affaire avec une transition dipolaire magnétique. Le couplage spin-orbite lève cette interdiction, mais la raie correspondante doit être nettement moins intense. Si les transitions sont assistées par des vibrations, on doit se rappeler[6] qu'en réalite CaF_2 ne comprend des phonons impaires que des types A_{2u} et E_u. Ainsi dans la symétrie D_{4h}, grâce au mécanisme vibronique, on doit avoir trois raies permises au même ordre.

Le spin appartenant à la représentation E_2[7,8] les niveaux qui resultent du couplage spin-orbite seront obtenus en calculant le produit direct de E_2 par chaque niveau du group D_{4h}. Le resultat pratique de la perturbation spin-orbite sera la disparition de la dégénérescence dans les niveaux