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Characterization of the free-carrier concentrations in doped β-SiC crystals by Raman scattering

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LO phonon-overdamped plasmon coupled modes in *n*-type epitaxial films of β-SiC have been measured in the carrier concentration range from 6.9×10^{16} to 2×10^{18} cm^{-3}. The carrier concentrations and damping constants are determined by line-shape fitting of the coupled modes and compared with the values derived from Hall measurements. The concentrations obtained from the two methods agree fairly well. The Faust–Henry coefficient determined from the fitting is 0.35. The line-shape analysis of the coupled mode has shown that the dominant scattering mechanisms in β-SiC are deformation-potential and electro-optic mechanisms.

I. INTRODUCTION

Raman scattering from LO-phonon-plasmon coupled modes has been extensively studied in III-V semiconductors with high carrier mobilities.[1] From the analysis of the frequency and band shapes of the coupled modes the concentration and mobility of the carriers have been determined. On the other hand, plasmons are overdamped ($\omega_p\tau<1$) in SiC, II-VI compounds, and GaP because of large collision damping. For these crystals, the upper branch of LO-phonon-plasmon coupled modes shows only slight shifts to the high-frequency side accompanied by broadening of the bands as the carrier concentration is increased, and the lower branch becomes too broad to be observed. Recently, LO phonon-overdamped plasmon modes have been measured in GaP with various doping levels by Irmer *et al.*[2] They have shown that free-carrier concentration can be determined from the Raman scattering analysis of doped GaP . LO phonon-overdamped plasmon modes have been also measured in highly doped 6H-SiC by Klein *et al.*,[3] although the doping level of the sample studied was limited to high concentration ($n=10^{19}$ cm^{-3}). Recently, epitaxial films of β-SiC on Si substrates with good crystal quality have been grown by chemical vapor deposition.[4–8] The development in the growth technique of SiC crystals has enabled us to characterize doped β-SiC crystals by Raman spectroscopy.

In this work, peak frequencies and band shapes of the LO-phonon-plasmon modes have been measured for various samples with different carrier concentrations. Using the Raman cross section derived by Irmer,[2] and Hon and Faust,[3] we have made line-shape fitting to the observed spectra. Free-carrier concentrations obtained from this fitting agree well with those determined from Hall measurements.

II. EXPERIMENT

Samples used in this experiment were β-SiC crystalline films grown by chemical vapor deposition (CVD).[8] SiH_4 and C_3H_8 were used as source gases in a flow of H_2 carrier gas. A mirror-polished Si crystal of (100) face was placed on an rf-heated graphite susceptor. The Si substrate surface was etched with HCl gas and then carbonized with C_3H_8 gas prior to epitaxial growth. The β-SiC films were grown on the carbonized Si substrate at 1350 °C. The film thickness was about 10 μm. The *n*-type crystals were grown by doping nitrogen in the concentration range from 6.9×10^{15} to 2×10^{18} cm^{-3}. The doping levels of the samples were varied by changing flow rates of N_2 gas. The concentration and mobility of the free carriers were determined by Hall measurements.

Raman scattering spectra were measured at room temperature using the 4880-Å line of an Ar^+ ion laser. A quasi-back-scattering geometry was employed. Scattered light dispersed with a SPEX 1403 double monochromator was detected by a photomultiplier or an optical multichannel detector (Tracor-Northern TN-6133). The spectral slit width employed was 2 cm^{-1} for undoped samples and 4 cm^{-1} for doped samples.

III. RESULTS AND ANALYSIS

Raman spectra of TO- and LO-phonon bands have been measured for samples with different carrier concentrations. Figure 1 shows typical examples of the spectra. The intensity of the LO-phonon band is normalized to unity. Since the penetration depth of 4880-Å light is longer than the thickness of the SiC films, a signal from the Si substrate is always observed. The two-phonon Raman bands of the Si substrate are subtracted in this figure. The TO-phonon band is forbidden for an exact back-scattering geometry for a (100) surface. However, the TO band is observed in this experiment because the incident light is not exactly normal to the surface of the sample. As described later, the appearance of the TO and LO bands is useful for determining the normalized intensity of the LO band in doped samples. As seen in this figure, the LO band shifts toward the high-frequency side and broadens with the decrease of the peak intensity as the carrier concentration is increased. On the other hand, the frequency and half width of the TO band do not vary with the carrier concentration.

In Fig. 2 the peak frequencies of the LO plasmon and

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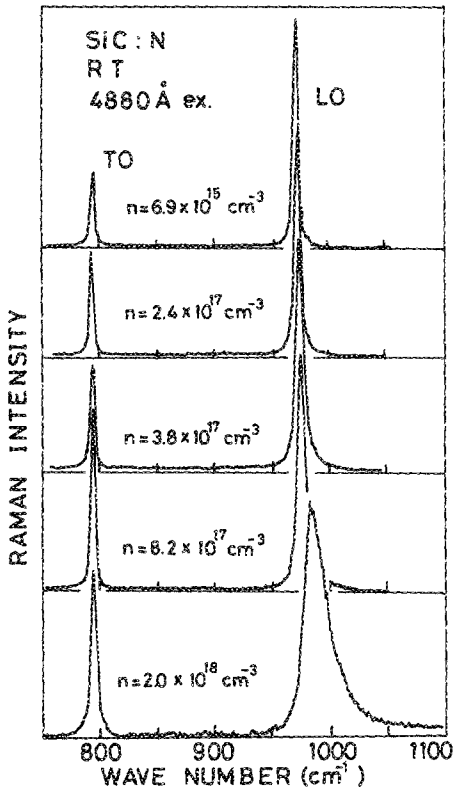

FIG. 1. Typical Raman spectra of β-SiC films at several doping levels. The carrier concentrations n shown in this figure are values obtained by Hall measurements. The peak intensities of the coupled modes in the respective spectra are made uniform height.

TO bands are plotted as a function of the carrier density. The peak frequencies of these Raman bands were calibrated by plasma lines of the Ar^+ laser. The frequency of the TO-phonon band in any samples lies at 795 ± 0.5 cm^{-1}, being independent of the carrier concentration. The frequency of the LO band increases slightly with increasing carrier concentration below 10^{17} cm^{-3}, and increases rapidly above 5×10^{17} cm^{-3}. The variation of the LO-phonon frequency with carrier concentration indicates that the LO-phonon band is coupled with the overdamped plasmon in doped β-SiC crystals.

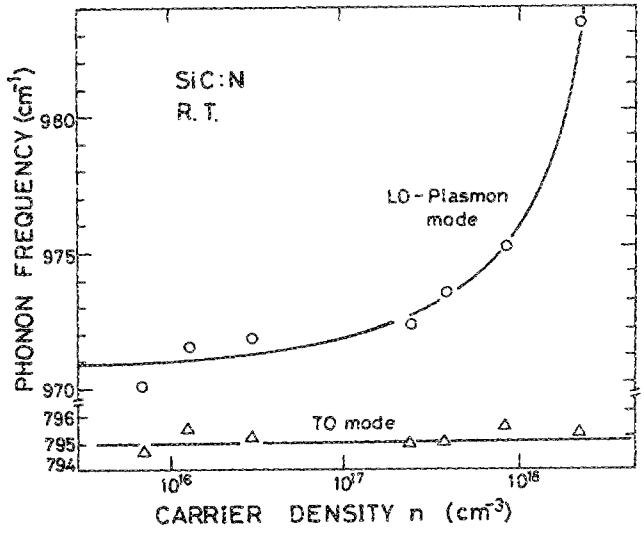

FIG. 2. The peak positions of the TO- and LO-plasmon modes are plotted as a function of the carrier concentration. The solid line is calculated using Eqs. (1) and (2).

The coupled modes of LO-phonon and overdamped plasmon have been studied in 6H-SiC,[3] GaP,[2,9] and ZnO.[10] The line shape of the coupled mode has been analyzed by the model developed by Hon and Faust,[9] Klein *et al.*,[3] and Irmer *et al.*[2] Klein *et al.* have indicated that in SiC and GaP the deformation-potential mechanism and electro-optic mechanism are dominant compared with the density-fluctuation mechanism.[1] Irmer *et al.* have extended the treatment by Klein *et al.* to include the effect of phonon damping in the Raman cross section. The Raman efficiency given by Irmer *et al.* consists of A and B terms which arise from the deformation-potential and electro-optic mechanisms and the charge-density fluctuation mechanism, respectively. The A term in the cross section derived by Irmer *et al.* coincides with that obtained by Hon and Faust who have calculated the Raman line shape of LO-phonon-plasmon modes regarding the crystal as a dielectric continuum. We have found that the $\omega^2\Gamma\omega_p^2$ term in Eq. (13) in Ref. 2 is missing. The corrected Raman cross section due to the deformation-potential and electro-optic mechanisms (A term) is expressed by[2]

$$I_A = \left.\frac{d^2S}{d\omega\, d\Omega}\right|_A = \frac{16\pi^4 n_2}{V_0^2 n_1}\frac{\omega_2^4}{C^4}\left(\frac{d\alpha}{dE}\right)^2 \times (n_\omega + 1) A\,\mathrm{Im}(-1/\epsilon)\,, \tag{1}$$

$$A = 1 + 2C\frac{\omega_t^2}{\Delta}\left[\omega_p^2\gamma(\omega_t^2-\omega^2) - \omega^2\Gamma(\omega^2+\gamma^2-\omega_p^2)\right] + C^2\left[\omega_t^4/\Delta(\omega_l^2-\omega_t^2)\right]\left[\omega_p^2(\gamma(\omega_l^2-\omega_t^2) + \Gamma(\omega_p^2-2\omega^2) + \omega^2\Gamma(\omega^2+\gamma^2)\right], \tag{2}$$

$$\Delta = \omega_p^2\gamma\left[(\omega_t^2-\omega^2)^2 + (\omega\Gamma)^2\right] + \omega^2\Gamma(\omega_l^2-\omega_t^2)(\omega^2+\gamma^2)\,. \tag{3}$$

Here, C is the so-called Faust–Henry coefficient[11] which is determined by the intensity ratio of LO- and TO-phonon bands in an undoped crystal,

$$\frac{I_{LO}}{I_{TO}} = \left(\frac{\omega_1+\omega_l}{\omega_1+\omega_t}\right)^4\frac{\omega_t}{\omega_l}\left(1+\frac{\omega_t^2-\omega_l^2}{C\omega_t^2}\right)^2. \tag{4}$$

The dielectric function ϵ is given by a sum of the contribution from phonons and plasmons

$$\epsilon = \epsilon_\infty\left(1 + \frac{\omega_l^2-\omega_t^2}{\omega_t^2-\omega^2-i\omega\Gamma} - \frac{\omega_p^2}{\omega(\omega+i\gamma)}\right), \tag{5}$$

where ω_p is the plasmon frequency

$$\omega_p^2 = 4\pi n e^2/\epsilon_\infty m^*\,, \tag{6}$$

and ω_t and ω_l are the frequencies of TO and LO phonons, respectively, γ is the plasmon damping constant, Γ is the phonon damping constant, n is the free-carrier concentration $\omega_{1,2}$ are the incident and scattered photon frequencies, V_0 is the volume of the unit cell, $n_{1,2}$ are the refractive indexes at $\omega_{1,2}$, and n_ω is the Bose-Einstein factor. The charge-density fluctuation also contributes to the Raman cross section. We include the contribution of this scattering

mechanism to the Raman efficiencies in performing the line-shape fitting of the coupled modes. However, as described later, it is shown that this contribution is quite small compared with two other mechanisms in β-SiC.

Recently, a cyclotron resonance of electrons in thin films of β-SiC has been observed by Kaplan *et al.*[12] The transverse and longitudinal masses of electrons determined from their experiment are $m_t = 0.247m_e$ and $m_l = 0.677m_e$. The effective mass is given

$$\frac{1}{m^*} = \frac{1}{3}\left(\frac{2}{m_t} + \frac{1}{m_l}\right) = (0.313m_e)^{-1}. \tag{7}$$

Taking ω_p, γ, Γ, and C in Eq. (1) as adjustable parameters, we have tried to fit the calculated line shape to observed LO-phonon-plasmon band. In this fitting, we have assumed that the intensity of the TO-phonon band is not affected by the free carriers. The couped mode in each crystal is normalized with the peak intensity of the TO band in order to estimate the relative intensity of the coupled mode. The measured intensity of this mode relative to the TO-phonon mode is also used in the fitting procedure.

Figure 3 shows the Raman spectra of the LO-phonon-plasmon coupled mode for typical carrier concentrations. The solid curves represent the experimental traces . The theoretical fit is shown by the broken lines. A finite value of the Faust–Henry coefficient gives an asymmetric band shape. A rise of the low-frequency side of the coupled mode is sensitive to the parameter C. In this fitting a fixed value of the parameter C is used for all measured samples. As shown in Fig. 3, the agreement between the observed and calculated line shapes of the coupled mode is fairly good. The best fit is given in this figure.

It is to be noted that if we include the density fluctuation mechanism the band shape becomes too asymmetric and the fit of the high-frequency side of the coupled mode becomes worse. Further, the calculated intensity of the coupled mode relative to the TO band cannot be fitted to the observed one. The values of the ω_p and γ increase with increasing the carrier concentration. All samples satisfy the condition $\omega_p < \gamma$. This result indicates that the plasmon in β-SiC crystals has large damping rates and the LO phonon is coupled with the overdamped plasmon.

Using Eq. (6), we determine the free-carrier concentration n from the value of the plasma frequency obtained from the line-shape fitting, where we use $\epsilon_\infty = 6.57$ and $m^* = 0.313$. In Fig. 4 the values of n obtained from the Raman measurements are plotted against the carrier concentration deduced from the Hall measurements. The result in this figure reveals that the carrier concentration deduced from two methods agrees well.

As shown in Fig. 3, the damping constant of the carriers determined from the fitting increases with increasing concentration of the carriers. The value of γ is plotted in Fig. 5 as a function of that deduced from the Hall measurement. In the calculation we used the relation

$$\gamma_H = (3\pi/8)(e/m^*\mu_H), \tag{8}$$

where γ_H and μ_H are the damping constant and Hall mobility deduced from the Hall measurement, respectively. At low carrier concentration, γ and γ_H coincide with each other. As the carrier concentration is increased, the values of γ are larger than γ_H.

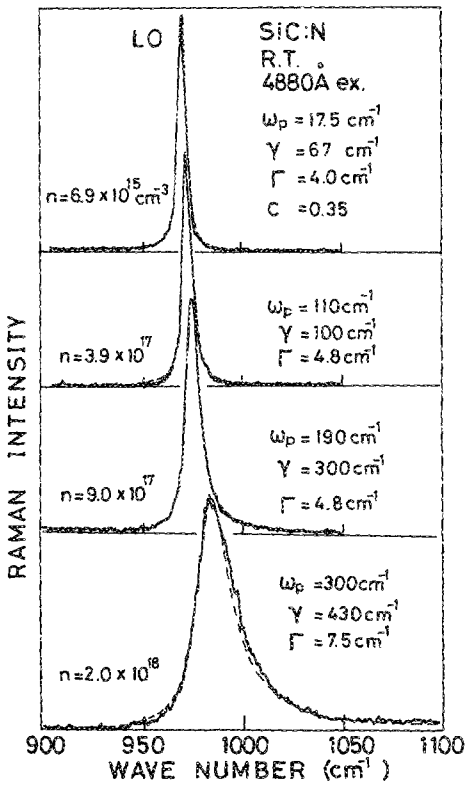

FIG. 3. Comparison of the experimental and calculated band shapes of the LO-plasmon coupled mode. The broken lines are theoretical fits using parameters shown in this figure. The carrier concentrations n are calculated from experimental plasma frequency using Eq. (6).

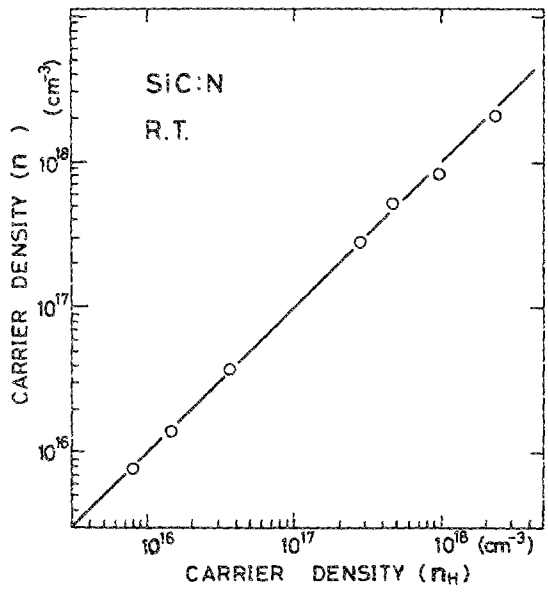

FIG. 4. The carrier concentrations n calculated from the Raman data vs those obtained from the Hall measurements n_H. The solid line represents a slope of 1.

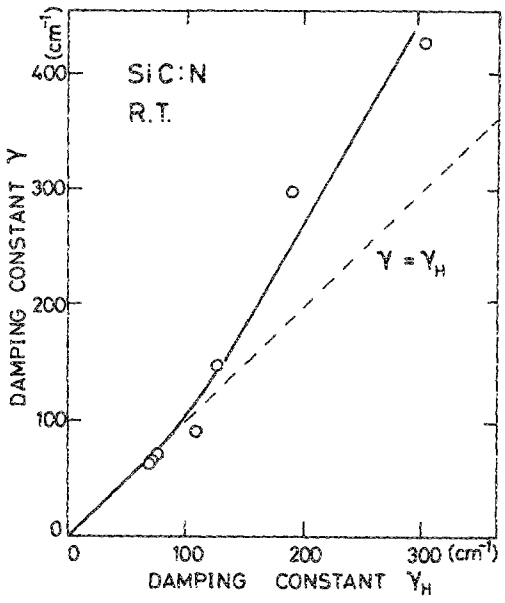

FIG. 5. The damping constants γ obtained from the Raman measurements vs those from the Hall measurements γ_H. The broken line represents the relation $\gamma_H = \gamma$.

IV. DISCUSSION

A. Evaluation of the carrier concentration and damping constant

The carrier concentrations derived from the Raman measurements agree well with those determined from the Hall measurements. This fact indicates that the Raman scattering technique can be used to determine the carrier concentration in β-SiC with high accuracy. The solid line in Fig. 2 is the peak position of the coupled mode obtained from the theoretical line-shape fitting. Using this figure, the carrier concentration of a sample can be easily evaluated from observed peak frequency of the coupled mode without the line-shape fitting procedure. Since the frequency of the coupled mode increases rapidly with carrier concentrations above 5×10^{17} cm^{-3}, the carrier concentration can be estimated with high accuracy for $n > 10^{16}$ cm^{-3}.

The carrier damping constants deduced from the Raman measurements γ and from the Hall measurements γ_H agree with each other at low carrier concentrations ($n < 10^{17}$ cm^{-1}), while the former becomes larger than the latter at the higher concentration. Previously, the carrier damping constants obtained by Raman measurements have been compared with those obtained by Hall measurements in GaAlAs,[13] ZnO,[10] and GaP.[2] In these samples, the carrier damping constants deduced from Raman measurements are equal to or larger than those from Hall measurements.

Bairamov *et al.*[10] observed that the line shape of the coupled mode in ZnO crystals depended on the laser power at 77 K. They suggested that the creation of nonequilibrium carriers by the laser radiation is responsible for the difference between the values of damping constants deduced from Raman measurements and those from Hall measurement. In our study, excitation power dependence has not been observed under Ar^+ laser excitation. Abstreiter *et al.*[13] reported that the observed linewidth of the upper branch of coupled modes in GaAlAs crystals was always larger than expected. In contrast to the present study, they found that the difference of the carrier damping obtained by Raman measurements and by Hall measurements decreases as the carrier concentration is increased. They considered a scattering process of the carriers at the interface between the depletion layer and the bulk, because the penetration depth of the laser light exceeds the depletion layer slightly for their samples. Since the absorption coefficient of β-SiC at 4880 Å is small (55 cm^{-1}), we observe Raman signals arising from not only the surface region of the crystal but also the bulk region. Therefore, it is not likely that the surface scattering plays an important role for the carrier scattering in β-SiC films. Irmer *et al.*[2] reported that the carrier damping constants obtained by Raman measurements did not coincide with the ones obtained by Hall measurements. They explained their results in terms of broadening effect of the LO-phonon band width by doping in addition to that of plasmon-LO-phonon coupling. We have observed no evidence of the additional influence of doping in the present study.

In the calculation of the Hall mobility we have assumed that the scattering by acoustic phonons is dominant and then the Hall factor is equal to $3\pi/8$. Under this assumption, the damping constant γ_H obtained from Hall measurement for the sample with $n = 2\times10^{18}$ cm^{-3} is 310 cm^{-1}, being smaller than the value of γ (420 cm^{-1}) estimated from the Raman measurement. When both acoustic-phonon scattering and ionized-impurity scattering mechanisms contribute to the Hall mobility, the resultant damping constant γ_H is given by the following equation:

$$m^*\gamma_H = \frac{3\pi}{8}\frac{e}{\mu_{ac}} + \frac{315\pi}{512}\frac{e}{\mu_i}, \tag{9}$$

where μ_{ac} and μ_i represent the Hall mobilities for acoustic-phonon and ionized-impurity scattering processes, respectively, when each mechanism is present alone. If we assume that the impurity scattering is dominant and the acoustic phonon scattering can be neglected, Eq. (9) gives the damping constant of $\gamma_H = 509$ cm^{-1} for this sample.

The above discussion suggests that both scattering mechanisms contribute to the carrier scattering in β-SiC samples with high carrier concentrations.

B. Raman scattering mechanisms and the Faust–Henry coefficient

In polar semiconductors, the Raman scattering from the plasmon-LO-phonon coupled modes takes place by the deformation-potential mechanism, electro-optic mechanism and the charge-density mechanism.[1] The line-shape analysis of the coupled mode has revealed that the Raman scattering from the coupled modes in β-SiC occurs mainly by the deformation-potential and electro-optic mechanisms. This conclusion is consistent with the result which was reported by Klein *et al.* for 6H-SiC.[3] Further, our conclusion is consistent with the large LO-TO splitting in β-SiC.

The line-shape calculation of the coupled modes using Eqs. (1) and (2) predicts the existence of a broad band due to the lower branch of the coupled modes. However, this

band is not observed in the present measurements. The reasons for this disagreement is not clear at present.

The Faust–Henry coefficient (C value)[11] is used as a fitting parameter in the line-shape fitting of the coupled mode. The best fit values are $C = +0.35$ for β-SiC films. This C value is close to the value reported for 6H-SiC ($C = +0.39$).[3] In order to evaluate the C value determined in this study, we have measured Raman spectra from (111) surface of SiC with an exact back scattering geometry. Small single crystals with a natural (111) face which were grown by silicon melt growth[14] were used for the Raman scattering measurement. The crystals grown on Si substrates by chemical vapor deposition method are thin films which have a (100) surface and it is difficult to choose a scattering geometry which allows observation of both TO and LO bands. It is found that the integral intensity ratio of LO and TO bands I_{LO}/I_{TO} is 0.68 ± 0.07. Using this value and Eq. (4), we get $C = 0.25 \pm 0.02$. This C value is nearly the same in sign and magnitude as determined in the line-shape fitting of the coupled mode in β-SiC. Another possible solution of Eq. (4) is $C = 3.0$. Using this C value, we cannot fit the calculated line shape to the observed LO-plasmon band. This value, then, is discarded from the present analysis of the coupled mode.

V. CONCLUSION

We have observed the LO-phonon-plasmon coupled mode in β-SiC crystals with various carrier concentrations. It is demonstrated that the Raman measurement is a suitable technique to determine the free-carrier concentrations and the damping constants in β-SiC. The line-shape fitting of the coupled mode reveals that the Raman scattering is driven mainly by the deformation-potential and electro-optic mechanisms. It is determined that the Faust–Henry coefficient is $+0.35$.

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