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First- and second-order Raman scattering from semi-insulating 4H-SiC

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We have measured the first- and second-order Raman spectra from semi-insulating 4H-SiC at room temperature under nonresonant excitation. The results are compared with Raman spectra of n-type doped 4H- and 6H-SiC. The second-order spectra for both 4H- and 6H-SiC contain an acoustic branch and an optical branch, which is clearly dependent on SiC polytype. The measured two-phonon spectra are assigned by comparison with theoretical calculations. [S0163-1829(99)03211-7]

Silicon carbide (SiC) is currently being explored as a material for the next generation of high-power and high-temperature electronics. An important physical property of SiC is the occurrence of polytypes.[1] 4H- and 6H-SiC are of considerable technological interest due to their large band gaps and high electron mobilities.[1] Recently high quality 4H- and 6H-SiC wafers have been grown.[2,3]

Device isolation using insulating layers is critical to semiconductor electronics. Progress has been made recently in the production of semi-insulating SiC for this purpose,[4] but these samples have not yet been well studied. The characterization of semi-insulating SiC is essential for the development of the next generation of SiC materials and devices.

One-phonon Raman spectra are sensitive only to phonons at the Γ point ($k=0$) of the Brillouin zone. However, in SiC the polytype structure in the large zone allows us to see other phonons that have a pseudomomentum of zero in the Brillouin zone.[5] The polytype dependence of one-phonon Raman spectra for doped SiC has been extensively studied.[5–10] Second-order Raman spectra reflect the entire Brillouin zone because any two phonons with opposite wavevectors will have a total momentum of zero.[11] Two-phonon Raman spectra are a sensitive test of theoretical models of the lattice dynamics,[11–16] because typically they are continuous spectra with peaks corresponding to regions or points of the dispersion curve with zero gradient and hence maxima in the phonon density of states. The second-order Raman spectrum of 3C-SiC has previously been studied.[13,17]

We present here one- and two-phonon Raman spectra of semi-insulating 4H-SiC, and two-phonon Raman spectra for n-type doped 4H- and 6H-SiC. The optical branch of the second-order Raman spectra for SiC was found to be polytype dependent and much more complex than the (cubic) 3C-SiC polytype. These observations reflect clear changes in the phonon density of states with polytype, while the frequencies of the Γ point phonons vary by less than 5%. The identification of spectra was obtained by reference to experimental studies and theoretical calculations.

The Raman spectrometer used has been described in detail before.[18] An Ar/Kr laser and a triple spectrometer with a charge-coupled-detector were used. The polarization was unspecified both for incident and collected light. Collection geometry was in the near backscattered configuration perpendicular to the (0001) face of the sample. There are no selection rules for second-order Raman scattering for wurzitic materials.[19] The doped samples of 4H- and 6H-SiC used were typically 1 3/8 to 2 inch wafers from a variety of sources and were n-type nitrogen doped over a nominal range of 10^{18} to $10^{19}\,\mathrm{cm}^{-3}$. The semi-insulating sample was a 1 3/8 inch wafer with a resistance of greater than $10^5\,\Omega$ cm.

The one-phonon Raman spectrum for semi-insulating 4H-SiC is shown in Fig. 1. Calibration was performed with atomic emission lamps, so that the spectrum is accurate to approximately 0.5 cm^{-1}. The peaks visible are common to all of the 4H-SiC samples studied. A full assignment of the peaks can be found elsewhere.[5,9,18] The major peaks are

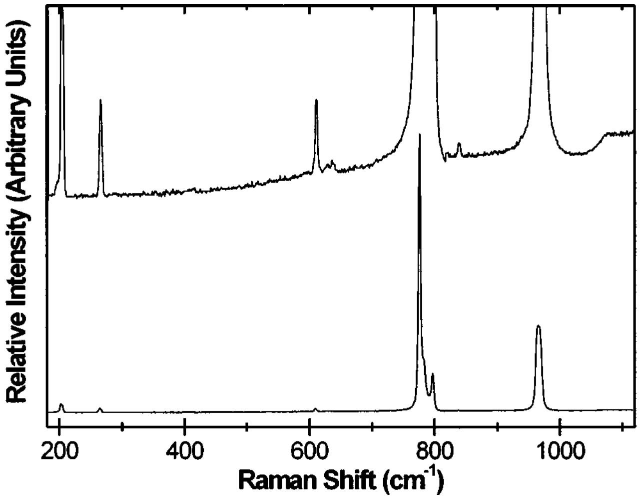

FIG. 1. Raman spectrum of semi-insulating 4H-SiC taken at room temperature with 514.5 nm excitation. The spectrum is also shown with an enlarged y scale to show detail.

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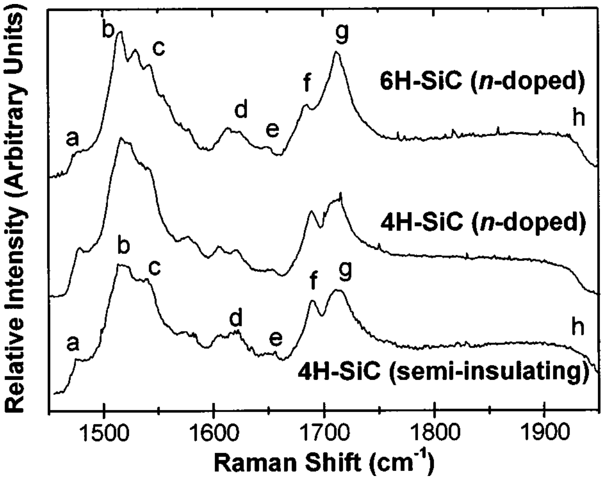

FIG. 2. Second-order Raman spectra of semi-insulating 4*H*-SiC and *n*-type doped 4*H*- and 6*H*-SiC, under the same conditions as Fig. 1. The nominal nitrogen concentration was $2.1\times10^{18}\,\mathrm{cm}^{-3}$ for both doped samples.

TABLE I. Peak frequencies for spectra in Fig. 2.

Peak frequency (cm^{-1})			Label
Semi-insulating 4*H*-SiC	*n*-type doped 4*H*-SiC	*n*-type doped 6*H*-SiC	
1475	1478	1476	a
1515	1515	1516	b
	1526		
		1532	
1542	1544	1542	c
1577	1576		
1606	1605		
		1614	
1622	1621	1626	d
1654	1655	1651	e
1689	1689	1686	f
1714	1713	1714	g
1925/1930	1925	1925/1930	h

203.5 cm^{-1} which is an E_2 planar or transverse acoustic mode. 610.5 cm^{-1} is A_1 axial or longitudinal acoustic (LA), 777.0 cm^{-1} E_2 planar optical, 797.5 cm^{-1} E_1, and 964.5 cm^{-1} is an A_1 longitudinal optical mode (LO).

We have previously noted[18] a feature in the Raman spectra which starts at around 500 cm^{-1} and extends past 1000 cm^{-1}. It is visible in the enlarged section of Fig. 1. By variation of the laser wavelength we have verified that this feature is due to Raman scattering and not luminescence. Its width (several hundred wavenumbers) and position suggests that it is the acoustic branch of the two-phonon Raman spectrum. This assignment is consistent with experimental studies of (cubic) 3*C*-SiC[13,17] and theoretical calculations.[20] Smaller peaks on top of this pedestal are of interest. Particularly pronounced in the semi-insulating 4*H*-SiC Raman spectrum is a low frequency shoulder in the 777 cm^{-1} peak, at a shift of around 740 cm^{-1}, and a peak at around 1100 cm^{-1}. Another Raman peak at about 633 cm^{-1}, which sometimes appears as a doublet, may also be part of the overtone spectrum. These peaks do not exhibit any change as nitrogen concentration is varied, thus we have not assigned these peaks to local modes of the nitrogen atoms.

The region of the spectrum between 1450 cm^{-1} and 1950 cm^{-1} in SiC is shown in Fig. 2, for semi-insulating and *n*-type doped 4*H*-SiC, and *n*-type doped 6*H*-SiC. The peak frequencies are listed in Table I. We have assigned these peaks to the optical branch of the second-order Raman spectrum. This part of both the 4*H*- and 6*H*-SiC spectra is much more complex than for the cubic (3*C*) polytype, as observed by Olego and Cardona,[17] and by Windl *et al.*[13] Figure 2 clearly demonstrates the differences in the two-phonon spectrum between polytypes. The smaller features visible are reproducible in samples of different origin.

There is no significant change in the spectra between the semi insulating and doped 4*H*-SiC, nor is there any variance with doping level. Therefore we have concluded that none of the observed peaks in this region are due to local mode vibrations of the nitrogen.

The optical branch of the overtone spectrum begins at 1476.0 cm^{-1} for both 4*H*- and 6*H*-SiC. This peak is labeled ''*a*'' in the figures and in Table I. The sharp edge of the overtone spectrum is due to a gap in the phonon density of states. Theoretical calculations of the phonon dispersion curve have shown that the lowest point in the optical phonon branch is the *K* point phonon.[20] The frequency of the *K* point phonon has been measured for 2*H*-SiC as 737 cm^{-1}.[21] We expect this value should be very similar for both 4*H*- and 6*H*-SiC. Our experimental value of 738 cm^{-1}, calculated from the second-order Raman spectra, confirms this hypothesis.

The high frequency tail of the overtone spectra is at approximately 1930 cm^{-1} (peak *h*). A similar tail is observed in the experimental data for 3*C*-SiC.[13] This feature is due to the overtone of the Γ point A_1(LO) phonon at 965 cm^{-1}. This is the highest point in the three dimensional vibrational band structure. This feature is well predicted by theoretical calculations.[20]

The region between 1514 cm^{-1} and 1580 cm^{-1} is the most prominent region in both the 4*H*- and 6*H*-SiC second-order Raman spectra. There is a clear dependence of the second-order Raman spectra on polytype. The most recent data on 3*C*-SiC showed one near featureless peak in this region.[13] The peak observed in 3*C*-SiC at 1519 cm^{-1} or 1520 cm^{-1} has been assigned[17] as the overtone of the TO(*X*) phonon at 761 cm^{-1}. This is consistent with theoretical phonon dispersion curves for 3*C*-SiC which predict a high density of states in this region.[20] Bechstedt *et al.*[16] have recently calculated the high symmetry point phonon frequencies for both 4*H*- and 6*H*-SiC. We observe that the frequency of the peak labeled ''*b*'' in Fig. 2 is consistent with possible values for an overtone of the *L* point phonon. Likewise, the 1542 cm^{-1} peak (*c*) which is present in both the 4*H*- and 6*H*-SiC polytypes is possibly due to an overtone of the *M* symmetry phonon at 771 cm^{-1}. The additional peak at 1526 cm^{-1} in the 6*H*-SiC spectrum is analogously due to a phonon from another point on the *L*-*M* branch, such as the *U* point. Calculations of the phonon dispersion curves[20] clearly show the optical *L*-*M* branch to be quite flat, indicating a high density of states.

The peak observed at 1714 cm^{-1} (*g*) in 6*H*-SiC and a broader peak at the same location in $4H$-SiC is the same as the high frequency peak reported in investigations of cubic SiC at approximately 1712 cm^{-1}. Olego and Cardona have pointed out that this frequency does not correspond to either 2LO(Γ) (1946 cm^{-1}), 2LO(X) (1658 cm^{-1}), or 2LO(L) (1676 cm^{-1}).[17] The authors hypothesized that this peak is due to an overtone of an M point phonon, which had not been directly measured by Raman or IR. Absorption measurements, which are not as accurate as Raman, have placed this M point phonon in $6H$-SiC to be at 863 cm^{-1}.[22] This is close to the value we obtain (857 cm^{-1}) by using Olego and Cardona's hypothesis with our two-phonon Raman measurements. A similar analysis can be used for the peak at 1688 cm^{-1} (f), which would attribute this peak to the overtone of an M point phonon previously measured to be 840 cm^{-1} by analysis of the exciton absorption phonon sidebands.[22]

Because of the gap in the phonon density of states, the numerous peaks that occur in the region between 1600 cm^{-1} and 1670 cm^{-1} for both $4H$- and $6H$-SiC must be combination bands, by analogy to the observations of Karch *et al.*[14] and Windl *et al.*[13] in $3C$-SiC. We note that these peaks appear to be more intense than those observed in $3C$-SiC and are seen here to be polytype dependent.

In summary, we have measured the first and second order Raman spectra of semi-insulating $4H$-SiC. The second-order Raman spectra of n-type doped and semi-insulating $4H$-SiC were found to be quite similar. The optical branches of the second order Raman spectra for $4H$- and $6H$-SiC were found to be polytype dependent and much more complicated than the two-phonon Raman spectra for cubic $3C$-SiC. Precise values for high symmetry point phonons in SiC have been obtained by the analysis of the second-order Raman spectra. Our experimental measurements are consistent with calculations of the phonon dispersion and calculated phonon frequencies for the L-M branch.[14–16,20] Both overtones and combination bands are observed in the second-order Raman spectra of $4H$- and $6H$-SiC.

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