The influence of impurities and planar defects on the infrared properties of silicon carbide films

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Two cubic, single crystal silicon carbide (3C-SiC) films with similar thickness are shown to exhibit significantly different optical properties at mid-infrared wavelengths. Depth profiling by time-of-flight secondary ion mass spectroscopy indicates that these two films have substantially different n-type impurity concentrations that are responsible for the observed differences in optical absorption. The influence of impurities manifests as substantially different planar defect morphologies. © 2011 American Institute of Physics. [doi:10.1063/1.3585098]

Since the discovery of extraordinary optical transmission1 there has been renewed interest in optical SiC films, specifically in the mid-infrared (IR) regime. Crystal-line SiC exhibits a frequency dependent permittivity \( \varepsilon_{\text{SiC}}(\omega) \) in the IR reststrahlen band, originating from the excitation of optical phonon modes. This has been shown to mediate hole-array transmission and absorption at tunable IR frequencies.2,3 At small scales, the ability to manipulate IR excitation of optical phonon modes. This has been shown to

In this work, we report on the relationships between film composition and defect structure and permittivity \( \varepsilon_{\text{SiC}}(\omega) \). \( \varepsilon_{\text{SiC}}(\omega) \) is given by the polaritonic function2 with an additional Drude term representing the response of free carriers, which result from impurities:

\[
\varepsilon(\omega) = \varepsilon_\infty \frac{\omega_p^2}{\omega^2 + i \gamma \omega} + \frac{\omega_p^2}{\omega(\omega + \Gamma)} ,
\]

where \( \varepsilon_\infty \) is the infinite-frequency permittivity, \( \omega_{\text{LO}} \) and \( \omega_{\text{TO}} \) are the longitudinal and transverse optical phonon modes, respectively. \( \gamma \) accounts for damping of optical phonons due to finite anharmonicity of vibrational modes.\( \omega_p \) the free-carrier plasma frequency, and \( \Gamma \) the carrier scattering frequency. While \( \omega_p \) depends on impurity concentration (discussed later), \( \Gamma \) is thought to be influenced by a number of factors, including grain size and crystal structure.

To isolate the dominant parameter \( \omega_p \) or \( \Gamma \) that influences \( \varepsilon_{\text{SiC}}(\omega) \), two 3C-SiC (100) oriented films of comparable thicknesses (F1 and F2) were examined. The films were grown in separate cold-wall atmospheric chemical vapor deposition (CVD) reactors. The film surfaces were cleaned under flowing hydrogen at 1000 °C. F1 was carburized using a propane/hydrogen gas mixture at 1150 °C for 600 s whereas F2 was carburized with a similar gas mixture at 1360 °C for a shorter duration of time of 90 s. The combination of a lower temperature and longer carburization duration (1150 °C, 600 s) or of a higher temperature and shorter carburization duration (1360 °C, 90 s) provides similar carburization characteristics. SiC was then grown on both films at approximately 1350–1360 °C by flowing a propane/silane gas mixture into the reactor. The difference between the two films is that F1 was produced in a load-locked reactor that was pumped prior to deposition, whereas F2 was not. The absence of a load-lock for F2 is likely to result in background contamination, such as N, that may not be removed during hydrogen etching. The films were sectioned into three parts: one was used to determine optical properties, another to analyze composition, and the third to study the microstructure.

Fils were fabricated into air-bridged membranes (300 \( \mu \text{m} \)) by KOH etching of the Si substrate.3 Transmittance \( (t) \) and absorbance \( (a) \) data from these membranes were collected using an IR microscope coupled to a Fourier Transform Infra-Red spectrometer. The incident angle was \( \theta=25^\circ \), and \( p \)-polarized radiation with a wavelength range from 5.6 \( \mu \text{m} \)–16.7 \( \mu \text{m} \) was used.

Point defect concentrations were measured using time-of-flight (tof) SIMS, performed with Cs and O sources that probed for n-type (N) and p-type (Al and B) impurities, respectively. For TEM analysis, plan-view and cross-sectional samples were observed under bright-field and dark-field conditions with a JEOL 2010F TEM to determine the structure, thickness, and defect characteristics.

Experimental transmittance and absorbance data for these films are shown in Fig. 1. F1 exhibits efficient transmittance with minimal absorption while F2 is significantly more absorptive. Furthermore, F1 exhibits a sharp resonance at approximately 10.2 \( \mu \text{m} \), which is completely damped in F2.

tof-SIMS analysis showed that F2 contained at least three orders of magnitude more N near the SiC/Si interface [Fig. 1(e)] compared to F1, and approximately two orders of

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magnitude more N away from the film interface. Quantification of the absolute N concentration is possible using tof-SIMS but requires preparation of reference standards that are beyond the scope of this work. Neither film was found to contain significant concentrations of p-type impurities. Extrinsic impurities, such as N, contribute free carriers that may quench optical resonance. Since these films were not intentionally doped, the presence of significant N at the film/Si interface for F2 is most likely due to the load-lock: once the wafer is loaded, the N source is cut off and its concentration in the film decreases as the film growth proceeds, which is consistent with what was observed in Fig. 1(c).

An estimate of the impurity concentration in F2 was obtained by fitting the experimental data to theoretical equations3 using a least-squared minimization to obtain the parameters \( \omega_p \) and \( \Gamma \). For this analysis, \( \epsilon_{\infty} = 6.7, \gamma = 4.75 \text{ cm}^{-1}, \omega_{TO} = 970 \text{ cm}^{-1}, \) and \( \omega_{LO} = 794 \text{ cm}^{-1} \) (Ref. 12) were assumed. This results in \( \omega_p = 2255 \text{ cm}^{-1} \) and \( \Gamma = 1669 \text{ cm}^{-1} \) for F2. F1 yielded identical fits with and without impurities confirmed by the corresponding spot-diffraction patterns of plan-view images confirm that the SiC films yield an electron mobility \( \mu_p = 9.1 \times 10^{13} \text{ cm}^2/\text{V s} \) (according to the relationship \( \mu_p = e/m^*_p \Gamma \)), which agrees well with experimental work.

Bright-field cross-sectional TEM images [Figs. 2(a) and 2(b)] indicate that both films are between 520–530 nm thick, cubic with a lattice parameter \( a_{\text{SiC}} \approx 4.3 \text{ Å} \), and single crystals confirmed by the corresponding spot-diffraction patterns [insets, Figs. 2(a) and 2(b)]. The Si/SiC interface in both films contain significant defect densities, most likely dislocations, due to the lattice mismatch between the substrate \( a_{\text{Si}} \approx 5.4 \text{ Å} \) and SiC. The absence of satellite spots in the SiC spot-patterns indicates that twins are not present but edge-on faults are visible on the \{111\} planes of both films. More importantly, since both films are cubic single crystals, the differences in optical properties cannot be attributed to variations in grain size or crystal structure.

The \{200\} superlattice reflections visible in the diffractation patterns of plan-view images confirm that the SiC films have an ordered, zinc blende structure [Figs. 2(c) and 2(d)]. F1 exhibits sharp features that appear to be planar defects [Fig. 2(e)], while F2 exhibits a dense network of dislocations and planar defects indicative of a higher defect density [Fig. 2(d)]. A more detailed analysis of F2, obtained by tilting the film with respect to the electron beam, reveals that the network of dislocations are subboundaries [Fig. 3(a)], which typically form by coalescence of dislocations. Tilting also reveals the presence of a few nanoscale grains that are not easily detected by selected area diffraction. These grains are a consequence of dislocation rearrangement within the sub-boundaries, thereby producing nanocrystalline regions with different orientations from the surrounding film [Fig. 3(b)]. The high defect density in F2 relative to F1 is consistent with previous work in hexagonal SiC,16 where impurity concentration and defect density were found to be correlated.

Planar defects are visible in both films, but are more prevalent in F1. In SiC, two types of planar defects are possible: (i) antiphase boundaries (APBs) with a \((1/4)(111)\) displacement vector and (ii) stacking faults (SFs) bound by Shockley partial dislocations of the type \((1/6)(211)\) due to the low SF energy of SiC (~15 mJ/m²) (Ref. 18). The
fringe contrast from APBs with a displacement vector \( \mathbf{R} = (1/4)(111) \) is visible by tilting from a zone-axis condition [Fig. 4(a)] to a two-beam condition with \( \mathbf{g} = [200] \) superlattice reflection [Fig. 4(b)]. The APB fringes disappear when the sample is tilted to a two-beam condition where \( \mathbf{g} = [220] \) and \( \mathbf{g} = [220] \) because \( 2\pi \mathbf{R} \mathbf{g} = 0 \), or \( \pm 2\pi \).

Under the same \( \mathbf{g} = [220] \) and \( \mathbf{g} = [220] \) two-beam condition, SF fringes become visible [Figs. 4(c) and 4(d)]. In fact, when a \( \mathbf{g} = [220] \) fundamental reflection is excited, the SF fringes perpendicular to \( \mathbf{g} = [220] \) bounded by a pair of partial dislocations \( b_{p,1} = (1/6)[211] \) and \( b_{p,2} = (1/6)[121] \) [Fig. 4(c)] become visible, while for the two-beam condition with a \( \mathbf{g} = [220] \) fundamental reflection, SF fringes bound by separate partial dislocations \( b_{p,1} = (1/6)[221] \) and \( b_{p,2} = (1/6)[121] \) are now visible [Fig. 4(d)]. From these images, the thicknesses of both APB and SF fringes are determined to be in the range 70–100 nm and, therefore, are likely too small to significantly influence optical performance in the mid-IR regime.

These results indicate that planar defects are not likely to significantly influence the optical performance, as evidenced by the excellent properties of F1. In contrast, the presence of higher N concentration in F2, directly and indirectly (through the formation of subboundary networks) affects electron scattering and ultimately its optical properties.

In conclusion, two 3C–SiC films with comparable thicknesses were studied and found to have different optical properties. The lossier film (F2) contained about three orders of magnitude higher N concentration compared to the better film (F1). Calculations confirm that F2 is moderately doped. Higher impurity concentration in F2 is indirectly manifested as higher defect density and a complex defect structure, as confirmed by TEM observations. The planar defects in the superior film (F1) do not influence the optical performance due to their small scale relative to the IR wavelength. The results suggest the optical properties in the mid-IR strongly depend on film composition and that SiC films with good optical properties, can be produced when the concentration of impurities and dislocations are minimized.

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