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On the origin of aluminum-related cathodoluminescence emissions from sublimation grown 4H-SiC(1 1 $\bar{2}$ 0)

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ABSTRACT

The spatial origins of emissions from homoepitaxial 4H-SiC(1 1 $\bar{2}$ 0) films have been investigated by cathodoluminescence, secondary ion mass spectrometry, and electron trajectory simulations. At 15 keV (300 K), the spectrum contained three peaks. The most intense peak corresponded (3.18 eV) to the nitrogen donor-to-valence band transition. The lesser two peaks at 2.94 eV and 2.75 eV involved aluminum and oxygen impurities, respectively; both impurities were determined to be in high concentrations in the film–substrate interfacial region. At 25 keV (300 K) the primary emission broadened into a band at ~3.10 eV. Deconvolution revealed three peaks; the most intense emission was again the nitrogen donor-to-valence band transition. The remaining two peaks at 3.02 eV and 2.90 eV were consistent with transitions involving aluminum impurities. The former peak was not observed in the spectra obtained at lower electron beam energies and was correlated with the conduction band-to-aluminum acceptor level transition. Monte-Carlo simulations showed the origin of the 25 keV (300 K) spectrum was the film–substrate interface. An analysis of the aluminum impurity concentration in this region revealed that the cause of the 3.02 eV emission was a dramatic increase in the concentration of aluminum (3×10^{16} cm^{-3} to 1×10^{18} cm^{-3}). The emissions comprising the 3.10 eV band were further investigated at 6 K and 25 keV. The difference in the intensity of the conduction band-to-aluminum acceptor level transition at 6 K and 300 K was attributed to thermal impurity ionization and the spike in the interfacial aluminum concentration previously described.

1. Introduction

4H-SiC continues to be the leading candidate material for high-power electronic applications due principally to its wide bandgap and large breakdown electric field [1]. Because the active region in SiC-based high-power devices can exceed 100 μm in thickness, considerable effort has led to the development of growth techniques capable of significant growth rates. To achieve the latter, SiC chemical vapor deposition is routinely performed at temperatures >1500 °C. At these extreme process conditions, the diluent gas can react with the graphite parts and/or the protective silicon carbide coating on the graphite. This reaction: (1) produces by-products that influence the C/Si ratio in the gas phase and can re-deposit on the substrate as a film and (2) releases impurity atoms into the vapor phase that incorporate into the growing film. In a prior study, we showed that (1) and (2) cause a significant concentration of aluminum impurities at the film–substrate interface [2]. Burk and Rowland [3] found that a similar spike in the aluminum concentration at the interface depleted the carrier concentration in capacitance-voltage measurements of SiC films; in some cases unintentional p–n junction behavior was observed.

Because cathodoluminescence (CL) can simultaneously obtain spectral and spatial information, this technique has been used by other investigators to study impurity-related emissions in 4H-SiC [4–11]. The research performed by Kakanakova-Georgieva and co-workers [5,7] and Díaz-Guerra and Piqueras [10] is the most pertinent to this work. Specifically, the former used CL to analyze

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the influence residual impurities have on emissions from 4H-SiC grown by sublimation epitaxy [5,7]. Díaz-Guerra and Piqueras [10] performed CL to characterize optical transitions involving deep levels in the band gap of 4H-SiC. It was speculated that the deep levels resulted from residual impurities based on deep level transient spectroscopy performed in another study [12]. The following is the first known published report in which CL, in tandem with secondary ion mass spectrometry (SIMS), has been used to spatially characterize how interfacial aluminum (and other) impurities influence the luminescence spectrum of 4H-SiC(1 1 $\bar{2}$ 0).

2. Experimental procedure

Commercially available 4H-SiC(1 1 $\bar{2}$ 0) wafers, diced from 4H-SiC boules grown in the [0 0 0 1] direction were used as substrates. The mechanically polished wafers were cleaned in a 10% HF solution to remove the native oxide prior to loading into the thin film growth chamber of a vertical, hot wall CVD system. The holder-sample assembly was radiantly heated using an inductively coupled susceptor. Prior to the introduction of process gases the growth chamber was evacuated to $\leq 2 \times 10^{-6}$ Torr. Hydrogen served as the diluent gas during heating, epitaxial growth, and cooling; the flow rate was 1.00 slm. The reactants were the Si- and C-containing by-products derived from the reactions between the hydrogen and the SiC coatings on the graphite susceptor and the holder-sample assembly [2]. The growth pressure and temperature were 20 Torr and 1450 °C, respectively. All films were grown to a thickness of ~1.5 μm. Intentional doping was not investigated.

Cathodoluminescence (CL) measurements were performed using a CamScan MaXim 2040 S scanning electron microscope (SEM) equipped with an Oxford MonoCL system at 6 K and 300 K. The cold stage was manufactured by Camscan USA (now Tescan USA); in this configuration, the accuracy of the temperature was ±2 K. The electron beam energy varied between 10 keV and 25 keV. The spectral data was not corrected for system response (i.e., absorption in the optics that is not constant with wavelength). Cathodoluminescence spectra were fit with a Gaussian peak-type and linear background subtraction. The trajectories of the electrons within the epitaxial and the bulk SiC were simulated using a Monte-Carlo-based routine [13,14]. The simulations were performed as a function of energy from 10 keV to 25 keV to spatially estimate the source of the emissions observed in the CL spectra. Secondary ion mass spectrometry (SIMS) was employed to measure the atomic concentrations of select impurities as a function of depth. Aluminum and boron were determined using an O_2^+ beam; a Cs^+ beam was employed for the analysis of nitrogen and oxygen. Measurements were made using a CAMECA IMS-6F. The cesium analyses were typically achieved at 14.5 keV impact energy with 50 nA primary beam current into a 140 μm × 140 μm rastered area and detection of ions from a 30 μm diameter circle at the center of the raster. Analyses with an oxygen primary beam were made at 5.5 keV impact energy with a 100 nA primary beam current into a 160 μm × 160 μm rastered area with detection of ions from a 60 μm diameter circle at the center of the raster. Analysis of nitrogen at high sensitivity was achieved using established techniques [15].

3. Results

3.1. Cathodoluminescence spectra

Results from the electron trajectory simulations are plotted in Fig. 1 as the fraction of energy dissipated versus depth. For the purposes of this work, the energy dissipated was assumed to be proportional to the number of electron–hole pairs generated by the interaction between the electron beam and sample [16,17]. Thus, the data in this figure allow one to spatially estimate the source of emissions within our CL spectra for a particular energy of the electron beam.

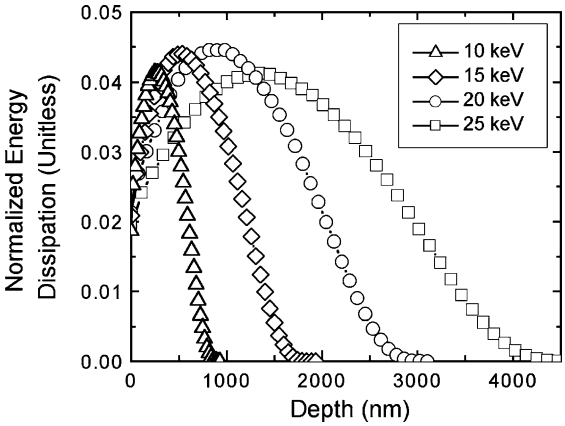

Fig. 1. Monte-Carlo simulations showing the depth distribution of electrons in 4H-SiC for electron beam energies of 10–25 keV. The energy dissipated was assumed to be proportional to the number of electron–hole pairs generated by the interaction between the electron beam and sample.

Fig. 2 shows the 300 K cathodoluminescence spectra acquired from the 1.5 μm 4H-SiC film at different electron beam energies. The 10 keV spectrum in Fig. 2(a) is dominated by a broad emission centered at 2.56 eV. This energy is similar to the nitrogen-to-boron donor–acceptor pair (NB-DAP) transition when the energy of the boron acceptor level is taken as ~0.65 eV above the valence band and the nitrogen level 0.06 eV below the conduction band [18]. At this energy the depth of the interaction volume is less than 1 μm; thus, the spectrum in Fig. 2(a) was generated from emissions originating solely within the epitaxial film. These results are similar to those obtained by Kakanakova-Georgieva et al. [7] at the same beam energy and temperature. A single broad peak was located at 2.38–2.43 eV in their spectra acquired between 1.75 and 3.25 eV. These authors also attributed this emission to transitions related to boron and its occupation of C sites in the SiC lattice [7]. All additional CL spectra acquired in the present research contained peaks at photon-energies <2.60 eV. Unless otherwise noted, a recombination process involving boron is assumed to be the origin of the peaks at these longer wavelengths, and there will be no further discussion of boron-related emission peaks in this wavelength regime. The reader is referred to Ref. [7] for an in-depth analysis of boron-related luminescence in 4H-SiC.

Additional peaks arise in the spectrum acquired using a 15 keV electron beam (Fig. 2(b)). The most intense emission has a peak at 3.18 eV and is associated with the nitrogen donor-to-valence band transition (N-DV) [18]; this peak was not observed at an electron beam energy of 10 keV. The emission at 2.94 eV is consistent with the nitrogen-to-aluminum donor-to-acceptor pair (NAl-DAP) transition [18]. The peak at 2.75 eV is also absent in the lower electron-energy spectrum; 2.75 eV is consistent with the location of an oxygen-related emission observed by Díaz-Guerra and Piqueras [10]. Because the distribution of electrons extends to a maximum depth of ~1.8 μm, the origin of the emissions in the 15 keV spectrum resides near the film–substrate interface. The correlation between the simulation results and the energy-dependent CL is addressed in more detail in Section 4.

Two bands located at ~3.10 eV and 2.37 eV are immediately apparent in the spectrum acquired at 25 keV (Fig. 2(c)). At this energy, the distribution of electrons reaches ~4.3 μm. The 3.10 eV band in Fig. 2(c) does not directly correspond with a major impurity-related emission for 4H-SiC, because the peak is located between reported energy values for transitions involving nitrogen