Electrically active point defects in *n*-type 4H–SiC

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An electrically active defect has been observed at a level position of $\sim$0.70 eV below the conduction band edge (E_c) with an extrapolated capture cross section of $\sim 5\times 10^{-14}$ cm^2 in epitaxial layers of 4H–SiC grown by vapor phase epitaxy with a concentration of approximately 1×10^{13} cm^{-3}. Secondary ion mass spectrometry revealed no evidence of the transition metals Ti, V, and Cr. Furthermore, after electron irradiation with 2 MeV electrons, the 0.70 eV level is not observed to increase in concentration although three new levels are observed at approximately 0.32, 0.62, and 0.68 eV below E_c with extrapolated capture cross sections of 4×10^{-14}, 4×10^{-14}, and 5×10^{-15} cm^2, respectively. However, the defects causing these levels are unstable and decay after a period of time at room temperature, resulting in the formation of the 0.70 eV level. Our results suggest strongly that the 0.70 eV level originates from a defect of intrinsic nature. The unstable behavior of the electron irradiation-induced defects at room temperature has not been observed in the 6H–SiC polytype. © *1998 American Institute of Physics.* [S0021-8979(98)02414-1]

INTRODUCTION

Silicon carbide continues to be actively investigated due to its potential use in high temperature, power, and frequency devices. To date the 4H polytype appears to be the material of choice for device applications (as compared to the 6H polytype) because of its substantially higher and more isotropic carrier mobility.[1] As in other semiconducting materials, the presence of deep levels in the energy band gap, the result of electrically active impurities, defects (e.g., vacancies), or some combination thereof, needs to be evaluated as device performance can be either enhanced or degraded depending on the position of the level in the electronic band gap as well as its charge carrier capture cross section and concentration. Transition metal impurities have attracted much attention recently as these are invariably found in bulk samples of SiC,[2–6] the result, apparently, of the mechanical process employed in the production of the SiC powders used in the sublimation growth. Additionally, these impurities have been suggested as carrier lifetime control centers. Identification of these low concentration impurities and their associated positions in the electronic band gap can be complicated by the high doping concentrations ($\geq 10^{18}$ cm^{-3}) typically found in bulk samples which make the formation of either a *p*-*n* or Schottky-type diode difficult. Recently, Jenny *et al.*[3,4] have reported the position of the vanadium acceptor level at $E_c - 0.80$ eV through the incorporation of the metallic impurity during sublimation growth while Achtziger *et al.* have reported on the Cr level at $E_c - 0.74$ eV through the use of ion-implanted radioactive isotopes.[7] The identification and characterization of intrinsic defects, however, have received less attention.[2,8] In addition, the use of ion implantation techniques for the introduction of impurity species as dopants may introduce lattice damage that might be difficult to remove through thermal annealing as has been reported in the 6H–SiC polytype.[9] In this letter, we report on our recent findings of deep level defects in as-grown and electron-irradiated 4H–SiC epitaxial layers.

EXPERIMENT

The *n*-type epitaxial layers were grown on 4H–SiC *n*-type substrates nitrogen doped with concentrations above 10^{18} cm^{-3} via a vapor phase epitaxial process that has been previously described.[10] The resulting layers were not intentionally doped resulting in *n*-type layers approximately 10 μm thick with a uniform carrier concentration as determined by capacitance–voltage (CV) profiling in the range from 5×10^{14} to 8×10^{15} cm^{-3}. Schottky barrier contacts were formed on the samples by electron beam evaporation of either 200 nm of Ni or Cu through a metal mask held in contact with the samples. The circular contacts had a diameter of 1 mm. Prior to the evaporation, the samples were solvent cleaned with trichloroethylene, acetone, and ethanol, and prior to insertion into the evaporation system, dipped into a 10% HF solution and pulled dry. The samples were held at room temperature during the metal deposition with the base pressure in the chamber less than 8×10^{-8} Torr.

Secondary ion mass spectrometry (SIMS) measurements were conducted utilizing a Cameca IMS 4f microanalyzer

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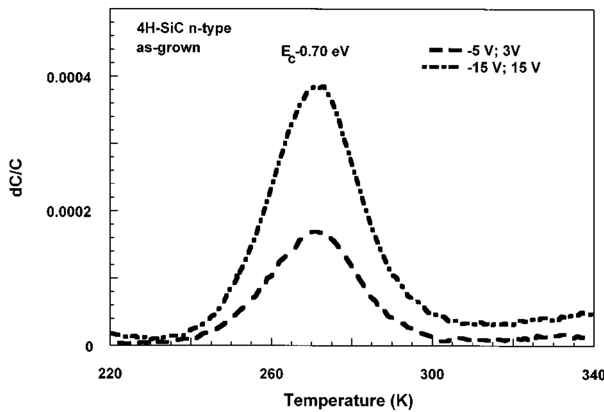

FIG. 1. DLTS spectra of as-grown n-type 4H–SiC with different reverse bias voltages and filling pulse voltages. The rate window for the spectra is $(3.20\ \mathrm{s})^{-1}$.

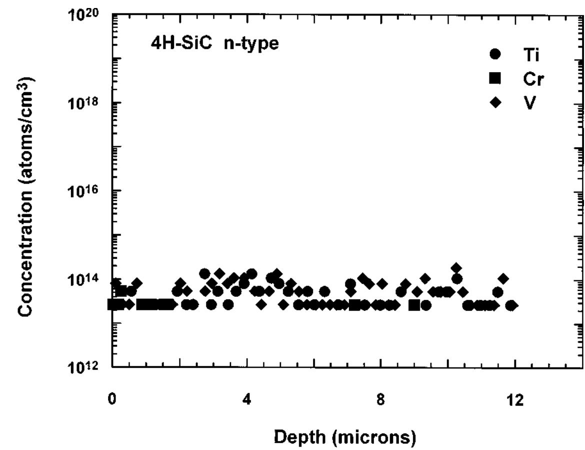

FIG. 3. SIMS profile of the V, Cr, and Ti concentration using O_2^+ ion sputtering.

using an O_2^+ primary ion beam having a net impact energy of 8.0 keV. The beam current was typically 1 μA and the O_2^+ ions were rastered over a surface area of $200\times200\ \mu\mathrm{m}^2$. Positive secondary ions ($^{48}Ti^+$) were recorded from the central part of this area ($\sim60\ \mu$m in diameter). The sputtered crater was measured using a Tencor 200A stylus profileometer allowing for conversion of the data to a concentration versus depth profile. Ion-implanted samples were used as standards.

Deep level transient spectroscopy (DLTS) was carried out in the temperature range of 77–365 K with rate windows varying from $(100\ \mathrm{ms})^{-1}$ to $(3.20\ \mathrm{s})^{-1}$. The DLTS setup is described in detail elsewhere.[11] A portion of the samples was then irradiated with 2 MeV electrons with a dose of $1\times10^{15}\ \mathrm{cm}^{-2}$ and then remeasured. The samples were attached to a water cooled stage during the irradiation and the sample temperature did not exceed 30 °C.

Depth profiling to obtain the concentration of a deep level as a function of depth was performed by choosing a rate window and holding the temperature at the maximum position of the peak observed in the DLTS spectrum. The steady state reverse bias is kept at a fixed potential while the majority carrier pulse is increased in a step-wise fashion. The concentration versus depth is then determined from the dependence of the DLTS signal on the pulse amplitude.

RESULSTS AND DISCUSSION

As shown in Fig. 1, only one peak is observed in the as-grown sample. The level is found to be 0.70 eV below the conduction band edge (E_c) with an extrapolated capture cross section of $5\times10^{-14}\ \mathrm{cm}^2$ as determined from an Arrhenius-type plot of the peak positions in the DLTS spectra. In the plot correction was made for the temperature dependence of the average thermal electron velocity and the density of states in the conduction band. Note as well that the lack of a Poole–Frenkel shift in temperature with increased electric field indicates that the level is acceptor-like.[12,13] Depth profiling revealed a uniform defect concentration profile (as a function of depth) as shown in Fig. 2.

In Fig. 3, SIMS analysis revealed that the concentration of Ti, V, and Cr was below the detectability limit for the system which was determined to be $\leqslant10^{13}\ \mathrm{cm}^{-3}$ for Cr and $<10^{14}\ \mathrm{cm}^{-3}$ for V and Ti.

After electron beam irradiation, as shown in Fig. 4, we find three electrically active deep levels assigned to positions

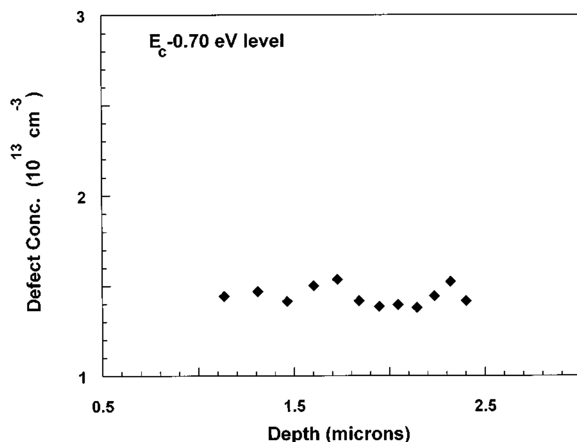

FIG. 2. Concentration vs depth profile of the 0.70 eV level below E_c.

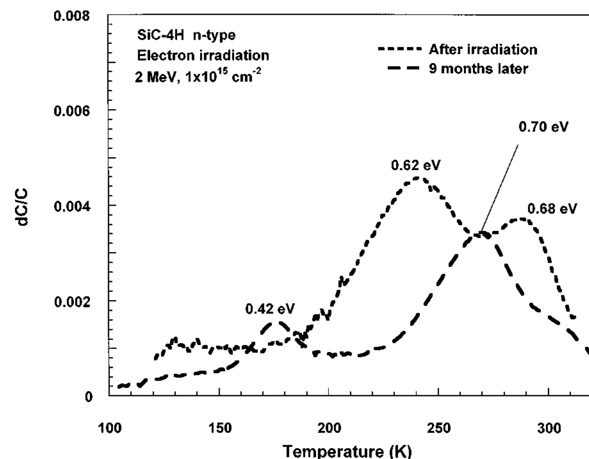

FIG. 4. DLTS spectra after electron irradiation. The rate window is $(3.20\ \mathrm{s})^{-1}$.

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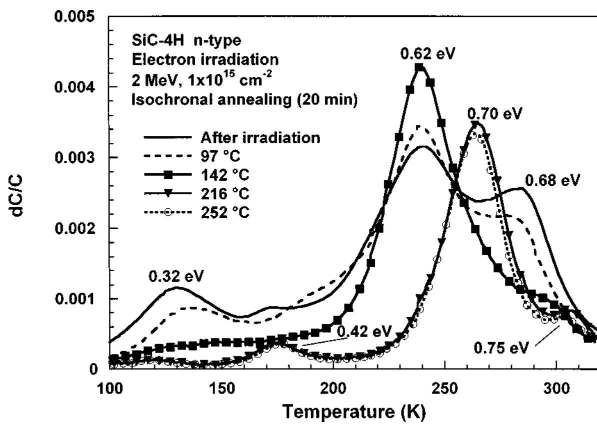

FIG. 5. DLTS spectra after electron irradiation. The annealing time at each temperature is 20 min. The rate window is $(3.20\ \mathrm{s})^{-1}$.

0.32, 0.62, and 0.68 eV below E_c which display extrapolated capture cross sections of 4×10^{-14}, 4×10^{-14}, and $5\times10^{-15}\ \mathrm{cm}^2$, respectively. These levels are only observed after irradiation. The position of the 0.62 and 0.68 eV levels in the electronic band gap along with the capture cross sections are consistent with the levels previously reported in as-grown epitaxial layers of 4H–SiC by Kimoto *et al.*[2] Interestingly, as shown in the same figure, after nine months at room temperature, the 0.62 and 0.68 eV levels are found to diminish significantly with the appearance of the 0.70 eV level and a previously unseen level at approximately $E_c-0.42$ eV with an extrapolated capture cross section of $6\times10^{-15}\ \mathrm{cm}^2$. All levels displayed acceptorlike behavior with no evidence of a Poole–Frenkel shift as a function of increasing electric field. It should be noted that modeling of the spectra incorporating the levels at 0.62, 0.68, and 0.70 eV seems to eliminate a high concentration of the 0.70 eV level immediately after electron irradiation as it was not possible to obtain a good fit when it was included. It should also be mentioned that the observed instability of the 4H–SiC defects is in contrast to that for 6H–SiC where the electron irradiation-induced defects were observed to be stable after a comparable period of time, an indication of the influence of the crystal structure on the stability of the defects.[14]

Figure 5 shows the effect of an isochronal annealing of an electron-irradiated sample. The annealing time at each temperature is 20 min. The 0.32 eV and the 0.68 eV levels start to decrease at ~90 °C which is followed by a simultaneous growth of the 0.62 eV level. The decay and growth of the peak amplitudes show an almost one-to-one correlation. The very similar decay of the 0.32 eV level and the 0.68 eV level indicates that they might correspond to different charge states of the same defect. At ~200 °C the growth of the 0.62 eV level is followed by a transition to the 0.70 eV level, which then stays constant at higher temperatures. As the peaks become more well defined for the higher annealing temperatures the 0.42 eV level and a peak at ~0.75 eV are revealed, i.e., they might be present immediately after irradiation.

The fact that the 0.70 eV level is observed in the as-grown sample as well as after the annealing of the 0.32, 0.62, and 0.68 eV levels (produced by electron irradiation) is consistent with a level having relatively high thermal stability as it is present after the growth temperature at 1550 °C. The observed decay and transition of the 0.32, 0.62, and 0.68 eV levels indicate either a high mobility or a disassociation of the responsible species at relatively low temperatures, although the exact mechanism is unclear at the present time. However, in silicon, the interaction of carbon interstitials with electron- or ion-induced defects can occur at room temperature resulting in the formation and increase in concentration of new electrically active defects correlated with the decay of others.[15] Similar effects may be occurring in the present case as the samples in this study are grown with a C/Si ratio of 1.2 or greater which may result in an incorporation of excess carbon in the epitaxial layer. Isothermal annealing studies are currently in progress to clarify the kinetics of this behavior.

Initially, Cr and V were considered strong candidates for the origin of these levels as they have been reported at 0.74 and 0.80 eV below E_c, respectively, and also have displayed high thermal stability as the incorporation of the impurity takes place either during the sublimation growth[3] or through ion implantation and postannealing at temperatures above 1300 °C.[7] SIMS analysis coupled with the electrical depth profiling reveals that there is insufficient Cr in our samples to account for this level, which reaches concentrations $\geqslant 2\times10^{14}\ \mathrm{cm}^{-3}$ after annealing of samples irradiated with electron doses $\geqslant 1\times10^{15}\ \mathrm{cm}^{-2}$. Additionally, Ti and V are ruled out as possible candidates since both species are below the detectability limit of our instrument and cannot be responsible for the concentration of the 0.70 eV level in annealed electron-irradiated samples. MeV electron irradiation produces mainly ''simple'' defects (e.g., vacancies and interstititials) which normally anneal at relatively low temperatures, thus, it is highly unlikely that the 0.70 eV level is such a defect as an isolated vacancy or interstitial since it would increase in concentration following irradiation and dominate the DLTS spectra. This is clearly not observed. Additionally the 0.70 eV level is probably not divacancy related as such defects should also dominate in samples directly following irradiation as has been observed in silicon.[16,17]

Two possible origins for this level are the antisites (Si_C or C_{Si}) or complexes involving impurities and vacancies, interstitials, or antisites. It should be noted that in the 3C–SiC polytype, the antisite defects are thought to be electrically inactive,[18] but to date there are no experimental or theoretical studies in the 4H–SiC polytype, that we are aware of, which preclude the antisites' electrical activity. SIMS analysis reveals that the impurities are not Ti, V, and Cr but may involve species such as nitrogen, hydrogen, or oxygen; however, low concentrations ($<10^{17}\ \mathrm{cm}^{-3}$) of hydrogen and oxygen are difficult to quantify due to the high background concentration in the SIMS instrument.

CONCLUSION

In conclusion, we report that a level at 0.70 eV below the edge of the conduction band is observed both in as-grown epitaxial layers of 4H–SiC and following electron irradiation after a period of time at room temperature

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(∼ nine months) or 20 min at ∼200 °C. The level is not related to the metallic impurities associated with Ti, V, or Cr and is most likely of intrinsic origin. Following electron irradiation, the decay of the 0.32, and 0.68 eV levels, which presumably correspond to different charge states of the same defect center, is accompanied by a growth of the 0.62 eV level and a transition to the 0.70 eV level. The decay may be the result of dissociation or migration and complexing of the defects. Apparently the room temperature instability of the defects is a characteristic of the 4H–SiC polytype as no such behavior has been observed in 6H–SiC.

ACKNOWLEDGMENTS

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