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Hall data analysis of heavily boron-doped CVD diamond films using a model considering an impurity band well separated from valence bands

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We have performed a detailed analysis of Hall data taken in a temperature (T) region of 100–700 K for heavily boron-doped diamond thin films homoepitaxially grown using high power-density microwave plasma CVD method. Their substrates were composed of a high-quality undoped homoepitaxial CVD layer grown similarly on vicinal (001) high-pressure/high-temperature-synthesized Ib diamond. The atomic ratio of boron to carbon in the source gas was 8000 ppm. Hall data taken from each specimen at various T's demonstrated (1) a metallic behavior in the low T region well below room temperature and (2) a clear peak of the T dependence of positive Hall coefficients around 350 K. The latter suggests the presence of multi groups of holes having substantially different mobilities and energies. In fact, calculated curves based upon a multi-type-carrier transportation model can well reproduce the corresponding experimental data. The T dependences were analyzed through a fitting procedure for the various important parameters employed such as the activation energies from the valence bands to the energy-fluctuated acceptor levels and carrier mobilities averaged over the concerned bands. The present analysis strongly suggests as follows. (1) Almost T-independent density of holes with the lowest average mobility in each heavily boron-doped diamond film move in an impurity band, (2) light holes and heavy holes whose densities increase exponentially with increasing T run in the valence bands in the vicinities of their maxima at substantially higher mobilities than that in the impurity band, and (3) the impurity band is well separated in energy from the valence bands.

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1. Introduction

Diamond is one of the attractive materials for various electrical, electronic and electrochemical applications due to its high carrier mobilities, extremely high breakdown electric fields, highest thermal conductivities, largest electrochemical potential windows, low thermal expansion coefficients near room temperature (RT) and so on [1]. Thus, diamond is expected as a potential material for high-performance electronic devices such as high power and high-speed devices [2,3], ultraviolet (UV) detectors [4] and UV light-emitting diodes [5]. Presently, the microwave plasma chemical–vapor-deposition (MWPCVD) method with high power densities is recognized as one of the most promising fabrication techniques for producing such high-quality diamond films at reasonably low costs. Recently, we have found that vicinal (001) substrates can effectively improve the crystalline quality of the homoepitaxial diamond films through significant (or almost complete) reductions of surface hillocks as well as simultaneous substantial increases in both the growth rate and the doping efficiency [6,7].

In the case of boron-doped p-type CVD diamond films, being indispensable to the device applications, however, there are some problems to be overcome. The main one is related to serious decreases in the carrier mobility with increases in the density of doped B atoms even in the medium carrier density region although the heavily doping process of B atoms is rather easily performed among the diamond CVD growth processes. In order to improve electrical properties of heavily B-doped p-type diamond films, therefore, one should reveal the reason why the observed larger decreases in the carrier mobility with increasing dopant (B) density occur in diamond, compared to the other conventional semiconductors. For very heavily B-doped diamond films, superconducting behaviors at ultra-low temperatures have been reported [8]. It was suggested for such samples that an impurity band originating from the doped B acceptors was substantially merged in energy to the valence bands [9].

In this paper, we report that heavily B-doped diamond films grown using the high power-density MWPCVD method (by which substantially high crystalline quality samples can be fabricated) have a clear and broad peak around RT in the temperature dependence of their Hall coefficients. This fact suggests the presence of multi groups of carriers having substantially different mobilities and energies. Thus, these Hall data are analyzed in detail, based upon a multi-type-carrier transportation model which considers both an impurity band and the valence bands composed of one light-hole band and two heavy-hole bands in diamond. The present analysis using a curve fitting procedure indicates that the model employed well reproduces

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the observed temperature dependences of the Hall data, suggesting that the impurity band is located in energy above the top of the valence bands and well separated from the valence bands.

2. Experimental

Two mechanically-polished high-pressure/high-temperature-synthesized (HPHT) Ib diamond substrates with a vicinal (001) surface were used in the present study. The one (called hereafter as Sample #1) had an off-angle of 4° along <100> direction whereas the other one (Sample #2) had an off-angle of 5° along <110> direction. The approximate size of these substrates was $3.0\times3.0\times0.5$ mm^3. By using the high power density MWPCVD method, undoped and heavily B-doped diamond layers were homoepitaxially grown in this order on each vicinal (001) substrate [10]. It should be noted that using the same MWPCVD method high-quality diamond layers can be grown on such vicinal substrates in the case of undoped and lightly-B-doped specimens [7]. The source gas used was CH_4 diluted with H_2. The experimental conditions employed for the undoped diamond growth in a stainless chamber were the MW power of 3.8–4.2 kW, total gas pressure of 120–130 Torr, substrate temperature of 1020 °C and CH_4/H_2 ratio of 4.0% while those for the heavily B-doped diamond growth in a quartz-tube-type chamber were the MW power of 300 W, total gas pressure of 75 Torr, substrate temperature of 1170 °C, and CH_4/H_2 (molecular) ratio of 4.0%. The dopant gas used was tri-methyl boron gas diluted with hydrogen gas. The B/C (atomic) ratio in the source gas was 8000 ppm. After these CVD growths, the homoepitaxial samples were chemically treated in a heated solution composed of H_2SO_4, HNO_3 and $HClO_4$ with their ratios of 3:4:1 to remove the specific surface conducting layer. Triple-layer ohmic electrodes composed of Ti (20 nm in thickness), Pt (10 nm) and Au (20 nm) were formed near the four corners of each sample by means of three successive electron-beam evaporations and subsequent vacuum annealing. The surface morphology of these specimens was characterized using a Nomarski-type optical microscope (OM), an atomic force microscope (AFM) and a scanning electron microscope. Steady-state cathodoluminescence (CL) spectra were measured at RT to obtain electronic information on the crystalline quality of undoped and heavily B-doped diamond layers. Hall data were obtained through AC Hall effect measurements based on the van der Pauw method [11] with the maximum magnetic field of 0.38 T in the temperature region of 100 K to 673 K.

3. Multi-type-carrier transportation model proposed for heavily B-doped CVD diamond

For a heavily B-doped diamond, we consider two or three groups of carriers which have substantially different mobilities and potential energies. Fig. 1 shows a schematic energy band diagram of our model. It is assumed that the mobile holes of the sheet density, p_i, in an impurity band which originates from incorporated boron acceptors with a substantially high volume density of N_A, have an averaged mobility, μ_i, while p_i is considerably less than the sheet density of the B atoms since only a part of the acceptors uncompensated by unintendedly incorporated donors should supply mobile holes to the impurity band due to a substantial fluctuation in energy and location. On the other hand, the holes of the sheet density, p_v, are assumed to run in the valence bands at an effective mobility, μ_v, which should be averaged for holes in the light-hole and heavy-hole valence bands whose highest energies are the same at the Γ point in the Brillouin zone. In the case of diamond, however, we should consider an additional factor reflecting the energy band structure: the valence bands near the valence band maximum at the Γ point are composed of three bands where the remaining lower-lying band has a heavy-hole feature and is separated by only 6 meV from the other two bands due to a relatively weak spin–orbit interaction [13–16]. Thus, in case of the Hall data analysis, the diamond valence bands even near the valence band maximum should be treated

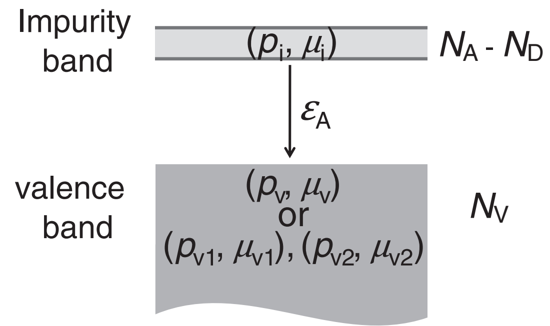

Fig. 1. Schematic energy band diagram for heavily boron-doped diamond and a related multi-type carrier model considering an impurity band which is completely separated in energy by an energy of ε_A on average from the top of the valence bands. It is assumed that the mobile holes with the density of p_i and with the mobility of μ_i exist in the impurity band which originates from the boron acceptors with the density of N_A. The valence bands with the effective density-of-states of N_V are composed of one light-hole band and two heavy-hole bands, and are separated by the spin-orbit interaction to two bands with a slightly different potential energy which has respective holes with the densities of p_{v1} and p_{v2}, and with their averaged mobilities of μ_{v1} and μ_{v2} in the three-type-carrier transportation model. The sum of the hole densities ($p_v = p_{v1} + p_{v2}$) and the hole mobility (μ_v) averaged over the valence bands are treated in the three-type-carrier transportation model.

as the two bands separated by the energy difference, $\Delta\varepsilon_{SO}$, of 6 meV due to substantial differences in the carrier mobilities and their scattering probabilities. Let p_{v1} and p_{v2} denote the sheet densities of the upper hole bands (called as the band "v1") with an average mobility of μ_{v1} and the lower hole band (called as the band "v2") with that of μ_{v2}, respectively. Then, one may adopt a three-type-carrier transportation model, where the sheet Hall coefficient, R_H, may be represented by the following equation with the elementary charge, e [12,13].

$$R_H = \gamma \frac{p_i\mu_i^2 + p_{\mathbf{v1}}\mu_{\mathbf{v1}}^2 + p_{\mathbf{v2}}\mu_{\mathbf{v2}}^2}{e(p_i\mu_i + p_{\mathbf{v1}}\mu_{\mathbf{v1}} + p_{\mathbf{v2}}\mu_{\mathbf{v2}})^2}. \tag{1}$$

By using the masses of the light and heavy holes in the band "v1", m_{lh} and m_{hh}, respectively, the temperature-dependent occupation factor, n_{h2}, and the mass for the band "v2", m_{h2} (where $m_{h2}\approx m_{hh}$), the following relations may be employed.

$$\left.\begin{aligned} p_{v1} &= p_v\left(m_{lh}^{3/2} + m_{hh}^{3/2}\right)/\left(m_{lh}^{3/2} + m_{hh}^{3/2} + m_{h2}^{3/2}\right) \\ p_{v2} &= p_v n_{h2} m_{h2}^{3/2}/\left(m_{lh}^{3/2} + m_{hh}^{3/2} + m_{h2}^{3/2}\right) \\ N_V &= \frac{2\left(m_{lh}^{3/2} + m_{hh}^{3/2} + m_{h2}^{3/2}\right)\left(2\pi k_B T\right)^{3/2}}{h^3} \end{aligned}\right\}, \tag{2}$$

where p_v is the total sheet density of holes in the valence bands, k_B Boltzmann's constant and T the absolute temperature. In the present case, the degeneracy factor, g_A, is 6, and it is supposed that $m_{lh} = 0.3\ m_0$ and $m_{lh} = 1.1\ m_0$, where m_0 is the electron rest mass [1]. For simplicity, the ratio of the Hall mobility to the conductivity mobility, γ, which is dependent on the scattering mechanism and ranges from 1.18 to 1.93 [13], was set to be unity in the present work.

Furthermore, for a partially compensated p-type diamond layer with a thickness of d, the following equation can be applicable to p_v.

$$\frac{p_v(p_v + dN_D)}{d(N_A - N_D) - p_v} = \frac{dN_V}{g_A}\exp\left(-\frac{\varepsilon_A}{k_B T}\right), \tag{3}$$

where N_D is the volume density of donors unintendedly created in the specimen, and ε_A is the averaged energy for holes to be excited from

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