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A theoretical calculation of the piezoresistivity and magnetoresistivity in p-type semiconducting diamond films

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Abstract

A theoretical study of the piezoresistivity and magnetoresistivity in p-type heteroepitaxial diamond films is presented, based on the Fuchs–Sondheimer thin-film theory and the valence band split-off model. The Boltzmann transport equation in the relaxation time approximation was solved and a mixed scattering by lattice vibrations, ionized impurities and surfaces was considered. The analytical expressions for the piezoresistive and magnetoresistive effects has been developed in a parallel-connection resistance model for the light-hole, the heavy-hole and the split-off bands. The calculated results are discussed and compared with experimental data. It is found that the self-spin interaction of the heavy holes could be related to stress. Moreover, a possible mechanism is presented to explain the fact that the magnetoresistivity of the p-type heteroepitaxial diamond films is greater than that of the diamond bulk.

1. Introduction

Diamond films are expected to become very important in applications for their outstanding mechanical, optical and thermal properties as semiconductors to a great variety of electronic devices [1, 2]. In the last decade, very important advances have been made in the research of diamond thin films prepared by chemical vapour deposition (CVD) methods. In 1993, heteroepitaxial diamond films were successfully grown on mirror-polished single-crystalline (001) silicon substrates by microwave plasma CVD using a bias-enhanced nucleation process [3, 4]. This method has produced diamond films superior in their structure and electric properties to those fabricated by the old CVD process. This is mainly because

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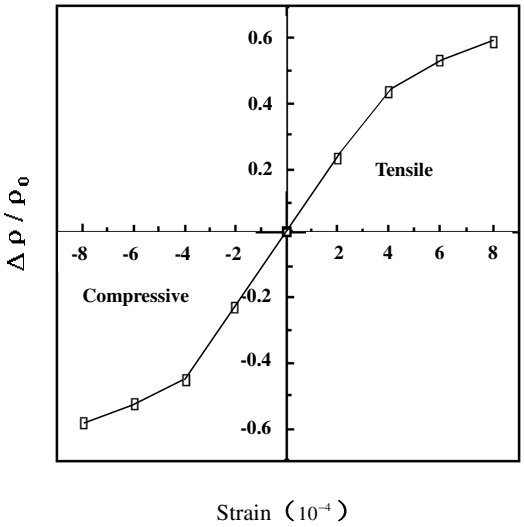


Figure 1. Variation of the piezoresistance as a function of the uniaxial stress in p-type heteroepitaxial diamond films (experimental results).

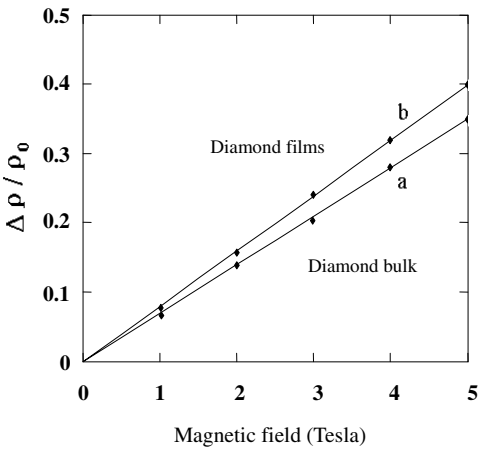
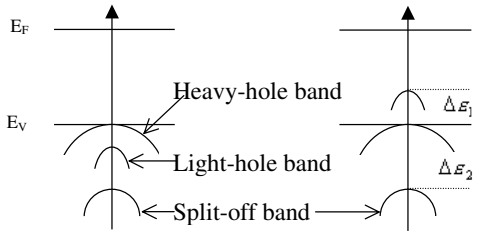


Figure 2. Variation of the magnetoresistance as a function of the magnetic field B ranging from 0 to 5 T for a strip sample (experimental results). (*a*) p-type heteroepitaxial diamond films, (*b*) diamond bulk.

the polycrystalline diamond films produced by the old method contain a larger number of grain boundaries and defects, which decreases the carrier mobility. During the past decade, many people studied experimentally the piezoresistive and magnetoresistive effects [5–11] of diamond films. Wang and Jiang *et al* reported remarkable piezoresistive [8, 9] and magnetoresistive effects [10, 11] in p-type heteroepitaxial diamond films (figures 1 and 2), which have many very interesting mechanical, magnetic and thermal properties. The gauge factor is greater than 1000 and changes with stress. The magnetoresistivity is strongly dependent on the concentration of boron doping atoms, the mobility of the carriers, the temperature, the magnetic field and the geometric form of the samples.



a) **Tensile stress** b) **Compressive stress**

Figure 3. The valence band split models of the diamond films under (*a*) tensile stress, (*b*) compressive stress.

Although there has been extensive experimental study of the diamond films, a theoretical model explaining their very interesting properties is lacking. This was the motivation of our work. We present, for the first time, a theoretical calculation of the piezoresistive and magnetoresistive effects in heteroepitaxial p-type semiconducting diamond films. Our theoretical model is based on the Fuchs–Sondheimer (FS) thin-film theory [12] and the valence band split-off model. By solving the Boltzmann equation we calculate the pure piezoresistivity (magnetic field equal to zero) and the pure magnetoresistivity (stress equal to zero) and finally we compare these results with experimental data.

2. Theoretical model

It is commonly believed that in diamond films piezoresistance is caused by valence band split-off (produced by stress), though magnetoresistance is attributed to the hole's deflection in a magnetic field. Although at first sight piezoresistance and magnetoresistance are two completely different phenomena, they have some important features in common. In thick films, in which the quantum size effect is negligible, the movement of the holes can be considered to follow the Boltzmann equation for piezoresistance, as well as for magnetoresistance. Therefore, based on the following valence band split-off model, we attempt to give a unified theory for the description of the two phenomena.

The proposed valence band split-off model in p-type diamond films is shown in figure 3. In this model the movement of the heavy-hole band is neglected, as the effective mass of the light holes is much smaller than that of the heavy ones. Moreover, we assume that the stress does not change the self-spin interaction of the heavy holes. Plot (*a*) in figure 3 shows the split-off of the valence band under uniaxial tensile stress (100), where the light-hole band shifts by $\Delta\varepsilon_1$ downwards in energy. Plot (*b*) in figure 3 shows the split-off of the valence band under uniaxial compressive stress (100), in which case the light-hole band shifts by $\Delta\varepsilon_1$ upwards.

In order to simplify the calculation, the influence of the grain boundaries is neglected. This is a good approximation for heteroepitaxial diamond films of good quality. Moreover, the changes of the hole density distribution caused by stress is considered, although the changes of the effective mass, the mobility and the Fermi energy of the holes are neglected.

From the valence band split-off model shown in figure 3, the ratios of change of the hole concentrations between light-hole, split-off and heavy-hole bands are expressed as

$$\text{Tensile}: p_{12}(\Delta\varepsilon) = \frac{p_1}{p_2} = \left(\frac{m_1^*}{m_2^*}\right)^{\frac{3}{2}} \exp\left(-\frac{\Delta\varepsilon_1}{kT}\right) \tag{1}$$

$$p_{32}(\Delta\varepsilon) = \frac{p_3}{p_2} = \left(\frac{m_3^*}{m_2^*}\right)^{\frac{3}{2}} \exp\left(-\frac{\Delta\varepsilon_2}{kT}\right) \tag{2}$$

$$\text{Compressive}: p_{12}(\Delta\varepsilon) = \frac{p_1}{p_2} = \left(\frac{m_1^*}{m_2^*}\right)^{\frac{3}{2}} \exp\left(\frac{\Delta\varepsilon_1}{kT}\right) \tag{3}$$

$$p_{32}(\Delta\varepsilon) = \frac{p_3}{p_2} = \left(\frac{m_3^*}{m_2^*}\right)^{\frac{3}{2}} \exp\left(-\frac{\Delta\varepsilon_2}{kT}\right) \tag{4}$$

in which p_i and m_i ($i = 1, 2, 3$) are the hole concentrations and the effective mass of the light-hole, heavy-hole and split-off bands respectively. $\Delta\varepsilon_2$ is the energy difference (0.006 eV) between the heavy-hole and the split-off bands.

3. Theoretical calculation

Considering a strip of a diamond film with thickness d in an electric field $\vec{E}$, a magnetic field $\vec{B}$ and a uniaxial stress (100), the Boltzmann equation in the relaxation time approximation can be written as

$$\vec{v} \cdot \nabla f - \frac{e}{\hbar}(\vec{E} + \vec{v} \times \vec{B}) \cdot \nabla_{\vec{b}} f = -\frac{f - f_0}{\tau} \tag{5}$$

in which $f_0(\vec{v})$ denotes the equilibrium distribution function, $f(\vec{v}, \vec{r})$ is the distribution function, $\vec{v}$ is the velocity of the hole, $\vec{r}$ is the position vector of the hole, $\hbar$ is Planck's constant, τ is relaxation time and $\nabla_{\vec{b}}$ is the gradient of wavevector $\vec{b}$.

We assume the FS thin-film theory is valid for the diamond films in which an isotropic isothermal solid, the hole conduction from three uncoupled valence bands associated with spherical energy surfaces, and mixed scattering by lattice vibrations, ionized impurities and surfaces. The general solution of equation (5) can be written in the form

$$f = f_0 - \vec{v} \cdot \vec{D} \frac{\partial f_0}{\partial \varepsilon}[1 + F(\vec{v}) \exp(-z/\tau v_z)] \tag{6}$$

where $\vec{D}$ is a vector to be determined, ε is the hole energy and $F(\vec{v})$ is a function determined by boundary conditions. Assuming that the surface scattering is composed of diffuse scattering and mirror reflection, $F(\vec{v})$ can be defined to be $F^{\pm}(\vec{v})$ for $v_z > 0(+)$ and $v_z < 0(-)$ from Fuchs boundary conditions [13]:

$$F^{+}(\vec{v}) = -\frac{1 - s}{1 - s \exp(-d/\tau v_z)} \qquad v_z > 0 \tag{7}$$

$$F^{-}(\vec{v}) = -\frac{1 - s}{1 - s \exp(d/\tau v_z)} \exp(d/\tau v_z) \qquad v_z < 0 \tag{8}$$

where s is the coefficient of surface scattering, which expresses the fraction of holes specularly scattered at the external surfaces ($z = 0$ and d).

Substituting equation (6) into (5), we obtain $\vec{D}$ at an approximation in which we restrict the first-order terms to $\vec{E}$ and the second-order terms to $\vec{B}$:

$$\vec{D} = -\frac{e\tau\vec{E}A + e\tau^2\omega(\vec{B} \times \vec{E})A^2/B}{1 + \omega^2\tau^2A^2} \tag{9}$$

in which $A = 1 + F(v) \exp(-z/\tau v_z)$ and $\omega = eB/m^*$ (m^* is the effective mass of the hole).

For a single valence band, the Maxwell–Boltzmann statistics and spherical energy band surfaces are assumed. We then can obtain the conductivity components of the strip sample by

$$\sigma_{xx} = \frac{4e^2 p}{3m^*\sqrt{\pi}} \int_0^\infty \frac{\tau\varphi(\nu, s)}{1+\omega^2\tau^2} \alpha^{3/2} \mathrm{e}^{-\alpha}\, \mathrm{d}\alpha \tag{10}$$

$$\sigma_{xy} = -\frac{4e^2 p}{3m^*\sqrt{\pi}} \int_0^\infty \frac{\tau^2\omega\eta(\nu, s)}{1+\omega^2\tau^2} \alpha^{3/2} \mathrm{e}^{-\alpha}\, \mathrm{d}\alpha \tag{11}$$

in which $p = p(\Delta\varepsilon)$ is the hole density and $\alpha = (E_V - \varepsilon)/kT$.

$$\varphi(\nu, s) = 1 + \frac{3\tau\nu}{4d} \int_0^{\frac{\pi}{2}} \sin^3\theta \cos\theta \left\{ \ln \frac{1+\omega^2\tau^2(1+F^+\mathrm{e}^{-d/\tau\nu\cos\theta})^2}{1+\omega^2\tau^2(1+F^+)^2} + \frac{2}{\omega\tau} \mathrm{tg}^{-1} \frac{\omega\tau F^+(1-\mathrm{e}^{-d/\tau\nu\cos\theta})}{1+\omega^2\tau^2[1+F^++F^+(1+F^+)\mathrm{e}^{-d/\tau\nu\cos\theta}]} \right\} \mathrm{d}\theta \tag{12}$$

and

$$\eta(\nu, s) = 1 + \frac{3\tau\nu}{4d\omega\tau} \int_0^{\frac{\pi}{2}} \sin^3\theta \cos\theta \left\{ -\frac{1}{\omega\tau} \ln \frac{1+\omega^2\tau^2(1+F^+\mathrm{e}^{-d/\tau\nu\cos\theta})^2}{1+\omega^2\tau^2(1+F^+)^2} + 2\mathrm{tg}^{-1} \frac{\omega\tau F^+(1-\mathrm{e}^{-d/\tau\nu\cos\theta})}{1+\omega^2\tau^2[1+F^++F^+(1+F^+)\mathrm{e}^{-d/\tau\nu\cos\theta}]} \right\} \mathrm{d}\theta. \tag{13}$$

We can restrict the $\varphi(\nu, s)$ and $\eta(\nu, s)$ to first-order terms: $\varphi(\nu, s) = \varphi(\nu_0, s)$, $\eta(\nu, s) = \eta(\nu_0, s)$ ($\frac{1}{2}m^*\nu_0^2$ is the kinetic energy of holes at the top of the valence band). With the conditions of thick films and weak magnetic field, equations (12) and (13) can be written as

$$\varphi(\kappa, s) = 1 - \frac{3}{8\kappa}(1-s) \tag{14}$$

$$\eta(\kappa, s) = 1 - \frac{9}{16\kappa}(1-s)\left(1+\frac{s}{3}\right) \tag{15}$$

in which $\kappa = d/\lambda$, $\lambda = \tau\nu_0$ (λ is the mean free path). Then we can write σ_{xx} and σ_{xy} as

$$\sigma_{xx} = \frac{4e^2 p\varphi(\kappa, s)}{3m^*\sqrt{\pi}} \int_0^\infty \frac{\tau}{1+\omega^2\tau^2} \alpha^{3/2} \mathrm{e}^{-\alpha}\, \mathrm{d}\alpha \tag{16}$$

$$\sigma_{xy} = -\frac{4e^2 p\eta(\kappa, s)}{3m^*\sqrt{\pi}} \int_0^\infty \frac{\tau^2\omega}{1+\omega^2\tau^2} \alpha^{3/2} \mathrm{e}^{-\alpha}\, \mathrm{d}\alpha. \tag{17}$$

For the mixed scattering by lattice vibration and ionized impurities, the relaxation time can be written as [14].

$$\tau = \frac{3\sqrt{\pi}m^*\mu_L}{4e} \frac{\alpha^{3/2}}{\beta+\alpha^2} \tag{18}$$

where μ_L is the hole mobility and β is a slowly varying function of the energy with a measure of impurity scattering (pure lattice scattering $\beta = 0$). In this case, the conductivity components σ_{xx} and σ_{xy} can be rewritten as functions of the magnetic field B and the energy split-off $\Delta\varepsilon_1$ of the valence band caused by uniaxial stress:

$$\sigma_{xx}(\gamma, \Delta\varepsilon_1) = e\mu_L p(\Delta\varepsilon_1)\varphi(\kappa, s)K(\gamma) \tag{19}$$

$$\sigma_{xy}(\gamma, \Delta\varepsilon_1) = -\tfrac{1}{2}\sqrt{\pi}e\mu_L\gamma^{1/2} p(\Delta\varepsilon_1)\eta(\kappa, s)L(\gamma) \tag{20}$$

in which

$$K(\gamma) = \int_0^\infty \frac{\alpha^3 e^{-\alpha}(\alpha^2+\beta)}{(\alpha^2+\beta)^2+\gamma\alpha^3}\,d\alpha \tag{21}$$

$$L(\gamma) = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\alpha^{9/2}e^{-\alpha}}{(\alpha^2+\beta^2)+\gamma\alpha^3}\,d\alpha \tag{22}$$

$$\gamma = \frac{9\pi}{16}(\mu_L B)^2. \tag{23}$$

Considering a parallel connection model for the light-hole, heavy-hole and split-off bands, the conductivity components may be expressed as

$$S_{xx}(\gamma, \Delta\varepsilon) = \sum_{i=1}^{3}\sigma_{xx}(i) \tag{24}$$

$$S_{xy}(\gamma, \Delta\varepsilon) = \sum_{i=1}^{3}\sigma_{xy}(i). \tag{25}$$

The expressions $\sigma_{xx}(i)$ and $\sigma_{xy}(i)$ are given by equations (19) and (20) while $i = 1, 2, 3$ designates the light-hole, heavy-hole and split-off bands respectively. Then the resistivity of the diamond films is expressed as

$$\rho(\gamma, \Delta\varepsilon_1) = \frac{S_{xx}(\gamma, \Delta\varepsilon_1)}{S_{xx}^2(\gamma, \Delta\varepsilon_1) + S_{xy}^2(\gamma, \Delta\varepsilon_1)}. \tag{26}$$

Accordingly, the piezoresistive and magnetoresistive effects can be derived respectively from equation (26):

$$\frac{\Delta\rho(\gamma, \Delta\varepsilon_1)}{\rho(\gamma, 0)} = \frac{A(\gamma, \Delta\varepsilon_1)}{A(\gamma, 0)}\frac{A^2(\gamma, 0) + \pi\gamma_2 B^2(\gamma, 0)/4}{A^2(\gamma, \Delta\varepsilon_1) + \pi\gamma_2 B^2(\gamma, \Delta\varepsilon_1)/4} - 1 \tag{27}$$

$$\frac{\Delta\rho(\gamma, \Delta\varepsilon_1)}{\rho(0, \Delta\varepsilon_1)} = \frac{A(\gamma, \Delta\varepsilon_1)A(0, \Delta\varepsilon_1)}{A^2(\gamma, \Delta\varepsilon_1) + \pi\gamma_2 B^2(\gamma, \Delta\varepsilon_1)/4} - 1 \tag{28}$$

in which

$$A(\gamma, \Delta\varepsilon_1) = \sum_{i=1}^{3} p_{i2}(\Delta\varepsilon_1)\mu_{i2}\varphi(\kappa_i, s)K(\gamma_i) \tag{29}$$

and

$$B(\gamma, \Delta\varepsilon_1) = \sum_{i=1}^{3} p_{i2}(\Delta\varepsilon_1)\mu_{i2}^2\eta(\kappa_i, s)L(\gamma_i) \tag{30}$$

where $p_{i2}(\Delta\varepsilon_1) = p_i/p_2$ and $\mu_{i2} = \mu_{Li}/\mu_{L2}$.

4. Numerical calculation and discussion

Equations (27) and (28) express the principal theoretical results for the piezoresistive and magnetoresistive effects in p-type heteroepitaxial diamond films. In order to compare the theoretical results with the experimental data, we calculate the pure piezoresistive and magnetoresistive effects derived from equations (27) and (28) respectively:

$$\frac{\Delta\rho(0, \Delta\varepsilon_1)}{\rho(0, 0)} = \frac{A(0, 0)}{A(0, \Delta\varepsilon_1)} - 1 \tag{31}$$

$$\frac{\Delta\rho(\gamma, 0)}{\rho(0, 0)} = \frac{A(\gamma, 0)A(0, 0)}{A^2(\gamma, 0) + \pi\gamma_2 B^2(\gamma, 0)/4} - 1. \tag{32}$$

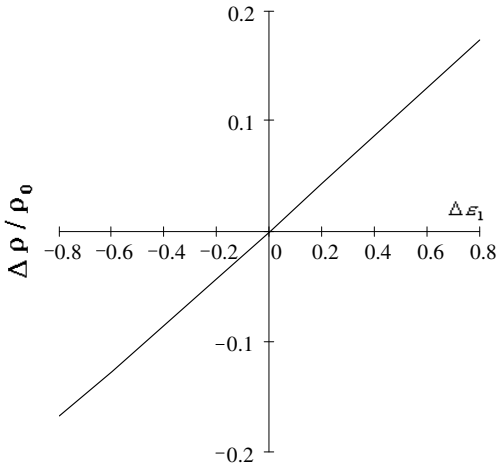


Figure 4. The piezoresistive effects under a weak stress (tensile and compressive) in p-type heteroepitaxial diamond films (theoretical results).

Table 1. The ratio of hole concentration.

Source	p_1/p_2	p_3/p_2
Theoretical value	0.19	0.28

Table 2. Values of μ_L, β, κ, m^*.

Parameter	Light-hole band	Heavy-hole band	Split-off band
μ_L (cm^2 V^{-1} s^{-1})	3900	195	1365
β	0.001	0.0001	0.0003
κ	9.2	60.7	17.3
m^*	$0.7m_0$	$2.12m_0$	$1.06m_0$

When surface scattering coefficient s changes from 0 to 1, numerical calculations show that the changes of the piezoresistance and magnetoresistance is only about 0.02 on the condition of weak stress and magnetic field. In order to simplify the calculation, we suppose the surface scattering coefficient (s) to be zero in the following calculation. The values of the calculated parameters are listed in tables 1 and 2.

4.1. The numerical calculation of the piezoresistive effect

Figure 4 shows the results of the numerical calculation of the piezoresistivity in heteroepitaxial diamond films with the strip structure under a weak uniaxial stress that leads to a small energy split-off $\Delta\varepsilon_1$ between light-hole and heavy-hole bands. When $|\Delta\varepsilon_1|$ is equal to 0.8×10^{-2} eV, the piezoresistance values are 0.174 for tensile stress and 0.168 for compressive stress respectively. It can be seen that the results are in good agreement with the experimental data in the following three aspects:

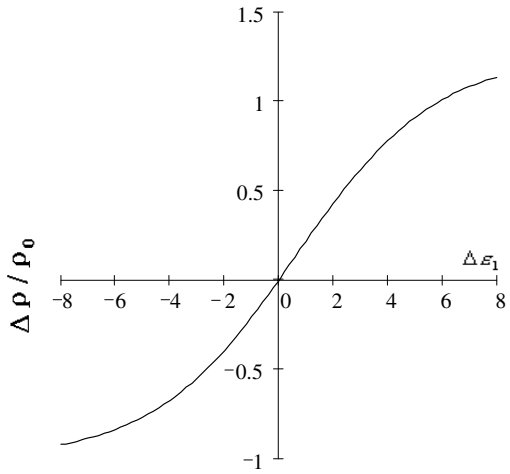


Figure 5. The piezoresistive effects at large stress (tensile and compressive) in p-type heteroepitaxial diamond films (theoretical results).

(i) the piezoresistive effect is positive under tensile stress and negative under compressive stress;
(ii) there is a linear relation between the piezoresistive effect and the energy level split-off $\Delta\varepsilon_1$;
(iii) the piezoresistive effect is symmetrical around the zero point.

Figure 5 shows that the piezoresistive effect tends to saturation for $\Delta\varepsilon_1$ values greater than 8×10^{-2} eV. As the gauge factor is given by the slope of the curve, piezoresistivity versus $\Delta\varepsilon_1$, the saturation of the piezoresistance implies that the gauge factor will decrease with increasing stress. This is in agreement with the experimental results [5–12]. However, there are two differences between the numerical calculation results on the one hand and the experimental data on the other. The first is that the symmetry of the saturated piezoresistance deteriorates with the increase of stress. It is 1.14 for tensile stress and 0.92 for compressive stress when $|\Delta\varepsilon_1|$ is equal to 8×10^{-2} eV. Using the method of extrapolation, the experimental values of saturated piezoresistance are about 0.7 and are symmetrical for tensile and compressive stress. The second difference is that the theoretical results of saturated piezoresistance (1.14 for tensile and 0.92 for compressive stress) are greater than the experimental result (0.7). For the first difference we can provide a possible explanation, that the self-spin interaction of the heavy holes could relate with tensile and the compressive stress which could have a different influence on the energy level split-off $\Delta\varepsilon_1$ between the heavy-hole band and the split-off band. Therefore, it could destroy the symmetry of the saturated piezoresistance. The second difference can be easily explained, as the influences of the grain boundaries are not considered here in the theoretical calculation.

4.2. The numerical calculation of the magnetoresistive effect

Figure 6 shows a comparison of the numerical calculation results and experimental data of the magnetoresistive effect in heteroepitaxial diamond films with strip structure. It can be seen that the theoretical results are in agreement with the experimental data for diamond films. For

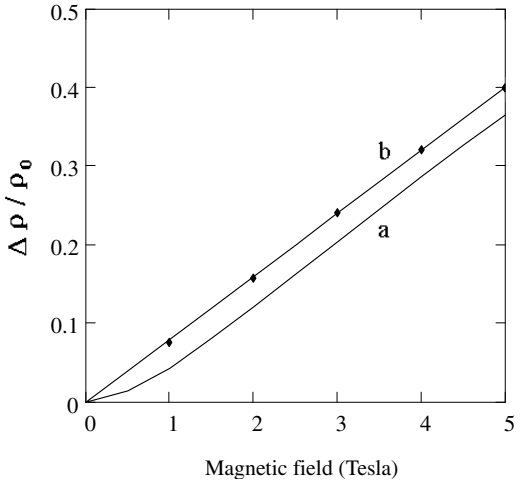


Figure 6. Comparison of the magnetoresistances between experimental data and theoretical calculation results in p-type heteroepitaxial diamond films with strip structure. (*a*) Experimental results, (*b*) theoretical results.

magnetic fields equal to 5 T, the theoretical and the experimental values for diamond films are 0.37 and 0.4 respectively, which are greater than that for diamond bulk (0.35). The difference between theoretical results and experimental data for diamond films is only about 5%. However, there are two questions arising from these results. The first is, why are the experimental values of the magnetoresistance in diamond films greater than the theoretical ones? The second is, why is the magnetoresistance of diamond films greater than that of diamond bulk? It is obvious, though, that the experimental values should be greater than the theoretical ones, as the effect of the grain boundaries was neglected. On the other hand, the magnetoresistance of diamond bulk should be greater than that of diamond films, in which surface scattering will decrease the magnetoresistance, opposite to the results mentioned above.

A plausible explanation of these problems is the following: the substrate stress, the surfaces and the boron doping can cause remarkable crystal lattice deformations in diamond films, changing considerably the energy band structure, the mobility of the holes, their effective mass and concentration distribution. Therefore, the magnetoresistance of the diamond films can be considerably changed, leading to the results mentioned above. It is very difficult to expound clearly the change of the magnetoresistive effect caused by these factors. We intend to study these questions extensively and publish the results in forthcoming papers.

5. Conclusions

A theoretical calculation of the piezoresistance and magnetoresistance in p-type heteroepitaxial diamond films is presented for the first time, based on the FS thin-film theory. This calculation was done by solving the Boltzmann transport equation in the relaxation time approximation, in which a mixed scattering by lattice vibrations, ionized impurities and surfaces was considered. It was found that the theoretical results of piezoresistive effects are in a good agreement with experimental data under a weak uniaxial stress, tensile or compressive. The discrepancy caused by the saturation exhibited by the piezoresistive effect under a high stress, tensile or compressive, can be attributed to the grain boundaries. The self-spin interaction of the heavy holes could be related to stress. We have also discussed the deviation of the magnetoresistive

effect between theoretical and experimental data. A possible explanation of this deviation was suggested based on the crystal lattice deformation caused in p-type heteroepitaxial diamond films by the substrate stress, the surfaces and the doping boron atoms.

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