

Numerical computation of the piezoresistivity matrix elements for semiconducting barium titanate

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The piezoresistivity matrix elements for semiconducting barium titanate that has a positive temperature coefficient of resistivity, have been derived from the stress dependence of a back-to-back Schottky-barrier model. Numerical computation of their magnitude as well as their temperature dependence will be presented for a spectrum of surface-state densities. A comparison to experimental data is given.

INTRODUCTION

Piezoresistivity, the change of electrical resistivity of semiconductors with stress, is of interest both from the fundamental- and device- (sensor) technology viewpoints. It provides valuable information concerning the conduction mechanisms in semiconductors, such as barrier tunneling, strain-induced carrier repopulation, and intervalley scattering.^{1,2}

The piezoresistance properties of silicon and germanium were originally investigated by Smith.³ Many pressure, torque, vibration, and acceleration sensors which utilize this phenomenon are commercially available. In addition to Si and Ge single crystals, there has been an increasing interest both at the fundamental- and device-technology levels in other materials which exhibit large piezoresistance effect, better temperature stability of the piezoresistance coefficients, or the deposition flexibility on different substrates. Polycrystalline semiconducting ferroelectric barium titanate,⁴⁻⁸ and polycrystalline Si and Ge thin films,⁹ thick-film resistors,¹⁰ and conductive particle-polymer heterostructures¹¹ are examples of such materials. Moreover, the analysis of the pressure effect on the electrical resistivity of this class of materials gives a deeper insight of the nature of conduction mechanisms.

Semiconducting, donor-doped polycrystalline barium titanate exhibits an anomalous increase in resistivity known as positive temperature coefficient of resistivity (PTCR) above the ferroelectric Curie temperature T_C .^{12,13} Goodman¹⁴ compared the temperature dependence of dc resistivity of semiconducting polycrystalline BaTiO₃ doped with 0.05% Sm to that of a single-crystal barium titanate of the same composition. No appreciable anomaly in resistivity above T_C was observed in single-crystal BaTiO₃. The anomalous increase in resistivity above the ferroelectric-paraelectric Curie temperature is explained by Heywang¹³ as being due to the rapid decrease in dielectric constant above T_C .

In Heywang's treatment the grain boundary is modeled as a strong-depletion-slight-inversion back-to-back Schottky barrier. To account for the lower and relatively constant resistivity observed in the ferroelectric state, Jonker¹⁵ has suggested that normal components of spon-

aneous polarization at the end of alternate 90° domains could effectively compensate the surface states present at the grain boundaries, therefore eliminating a potential barrier there.

In addition, the longitudinal Π_{11} and transverse Π_{12} piezoresistivity matrix elements of semiconducting BaTiO₃ are almost 2 orders of magnitude larger than those of silicon and germanium. In contrast to Si and Ge, the hydrostatic piezoresistivity coefficient (which is a linear combination of Π_{11} and Π_{12}) is very large.⁵ A recent review of the experimental and theoretical developments of piezoresistivity in semiconducting ferroelectric perovskites is given in Ref. 16.

To gain deeper insights about the origin of the observed large piezoresistivity in polycrystalline semiconducting perovskite barium titanate, and the sign of these coefficients, we have computed the two linearly independent piezoresistivity matrix elements, namely, Π_{11} and Π_{12} as well as their temperature dependence above the Curie temperature T_C . Computational results and a comparison to existing experimental data will be given.

SYMMETRY ASPECTS OF PIEZORESISTIVITY

The piezoresistive effect is a linear coupling between mechanical stress and electrical resistivity. Thus, it is represented by a fourth rank polar tensor Π_{ijkl} ($i, j, k, l = 1, 2, 3$). The phenomenological theory of piezoresistivity is conveniently formulated in the isothermal representation, however, the difference between the isothermal and adiabatic changes are very small and negligible.¹⁷ The equation of state of a crystal subjected to a stress X_{kl} and an electric field E_i is written as¹⁸

$$E_i = \sum_j \rho_{ij} I_j + \sum_j \sum_k \sum_l \Pi_{ijkl} X_{kl} I_j \quad (i, j, k, l = 1, 2, 3), \quad (1)$$

where ρ_{ij} is the resistivity tensor, and I_j is the current density. Taking the partial derivatives of Eq. (1) with respect to the current density I_j , and rearranging,

$$\partial E_i / \partial I_j = \rho_{ij}(X) - \rho_{ij} = \sum_k \sum_l \Pi_{ijkl} X_{kl}. \quad (2)$$

The constraints imposed by the internal symmetry of the piezoresistivity tensor ($\Pi_{ijkl} = \Pi_{ijlk} = \Pi_{jilk}$) reduce the number of independent tensor coefficients from 81 to 36. Furthermore, the point-group symmetry of the crystal imposes additional constraints on the remaining 36 components.¹⁹ In the reduced tensor notation Π_{ij} ($i, j = 1, 2, \dots, 6$) represents the piezoresistivity matrix. The piezoresistivity matrix elements can be written in terms of the specific change of resistivity, and we take the origin at the unstressed state as follows:

$$\Pi_{ij} = 1/\rho_0 (\partial \rho_i / \partial X_j) . \quad (3)$$

For silicon and germanium (point group $m\bar{3}m$), the nonvanishing piezoresistivity matrix elements are Π_{11} , Π_{12} , and Π_{44} . Polycrystalline materials, however, belong to the spherical symmetry group $\infty\infty mmm$, and Π_{44} is a linear combination of Π_{11} and Π_{12} (i.e., $\frac{1}{2}\Pi_{44} = \Pi_{11} - \Pi_{12}$). Two coefficients, namely, Π_{11} and Π_{12} are thus required to completely specify the piezoresistance properties of the polycrystalline state.

PIEZORESISTIVITY MATRIX ELEMENTS— CONSTITUTIVE EQUATIONS

The grain-boundary barrier of semiconducting polycrystalline (PTCR) BaTiO_3 is modeled as a strong-depletion–slight-inversion, back-to-back Schottky barrier. The expression for the static, quiescent-condition (zero current) Schottky-Heywang barrier height ϕ is given by¹³

$$\phi = e^2 n_s^2 / 8\epsilon\epsilon_0 N_d , \quad (4)$$

where e is the electronic charge, n_s the net concentration of ionized surface acceptor states, ϵ the dielectric constant, ϵ_0 the free-space permittivity (8.854×10^{-12} F/m), and N_d the donor concentration per unit volume.

Above the Curie temperature T_C , the Curie-Weiss law is obeyed; the dielectric constant for BaTiO_3 is given by

$$\epsilon = C / (T - T_0) , \quad (5)$$

where T_0 is the extrapolated Curie-Weiss temperature, and C the Curie constant.

According to the Landau-Ginzburg-Devonshire theory of a proper ferroelectric derived from a prototypic symmetry $Pm\bar{3}m$ (e.g., BaTiO_3), the single-domain paraelectric state dielectric reciprocal susceptibility χ^{-1} is given by

$$\chi^{-1} = 2\alpha_1 \epsilon_0 , \quad (6)$$

where α_1 is the tensor coefficient of the second-order polarization term in the free-energy density function.

For high-permittivity solids such as BaTiO_3 , it is valid to assume that $\chi \sim \epsilon$. Thus

$$\alpha_1 = (1/2\epsilon_0 C)(T - T_0) = \beta(T - T_0) , \quad (7)$$

where $\beta = 1/2\epsilon_0 C$. The expression for barrier height under zero-stress conditions is obtained by combining Eqs. (4)–(6) to yield

$$\phi = (\beta e^2 n_s^2 / 4N_d)(T - T_0) . \quad (8)$$

In earlier work,²⁰ the hydrostatic stress dependence of the grain-boundary barriers, and the occupation probability of the surface acceptor states above the ferroelectric-paraelectric Curie temperature T_C , have been modeled for perovskite PTCR materials using the Landau-Ginzburg-Devonshire formalism. This model does not take into account any bulk (grain) contribution to the piezoresistive effect. In other words, it assumes that piezoresistivity is wholly a barrier-layer effect. This is a reasonable assumption because, above T_C , the conduction mechanisms are dominated by the barrier layer.

For the normal stress components X_3 and X_1 , the tensor coefficient α_1 takes the form

$$\alpha_1(X_1, X_3) = \alpha_1 + (Q_{12}X_1 + Q_{11}X_3) , \quad (9)$$

where Q_{11} and Q_{12} are the electrostriction tensor coefficients in polarization notation. Therefore, the mean barrier height ϕ and the occupation probability of surface acceptor states F (Fermi-Dirac) can be written for the stress component X_3 as

$$\phi(X_3, T) = (\beta e^2 n_s^2 / 4N_d)[T - (T_0 - Q_{11}\beta^{-1}X_3)] , \quad (10)$$

$$F(X_3, T) = 1 / (1 + \exp\{[E_f + \phi(X_3, T) - E_s] / kT\}) . \quad (11)$$

Similarly, for the stress component X_1 , we can write

$$\phi(X_1, T) = (\beta e^2 n_s^2 / 4N_d)[T - (T_0 - Q_{12}\beta^{-1}X_1)] , \quad (12)$$

$$F(X_1, T) = 1 / (1 + \exp\{[E_f + \phi(X_1, T) - E_s] / kT\}) , \quad (13)$$

where k is Boltzmann's constant and E_f the Fermi level.

The Fermi level E_f and the effective density of states of the conduction band N_c are given by

$$E_f = kT \ln(N_c / N_d) , \quad (14)$$

$$N_c = 2(2\Pi m_e^* kT / h^2)^{3/2} , \quad (15)$$

where m_e^* is the electron effective mass, and h is Planck's constant. Equation (14) is a valid approximation for $E_f < -kT$, i.e., for $N_d < 2N_c$.

The grain-boundary resistivity ρ is given by

$$\rho_i = \rho_0 \exp(\phi / kT) ; \quad (16)$$

under isothermal conditions, the resistivity expression can be differentiated with respect to stress X_j to yield

$$1/\rho_i (\partial \rho_i / \partial X_j)_T = 1/kT (\partial \phi / \partial X_j)_T = \Pi_{ij} . \quad (17)$$

The partial derivatives of the mean barrier potential with respect to the stress components X_3 and X_1 are

$$(\partial \phi / \partial X_3)_T = (e^2 / 4N_d) \{ n_s^2 Q_{11} + [\beta(T - T_0) + Q_{11}X_3] \times (\partial n_s^2 / \partial X_3)_T \} , \quad (18)$$

$$(\partial \phi / \partial X_1)_T = (e^2 / 4N_d) \{ n_s^2 Q_{12} + [\beta(T - T_0) + Q_{12}X_1] \times (\partial n_s^2 / \partial X_1)_T \} . \quad (19)$$

The expressions for the longitudinal Π_{11} and the transverse Π_{12} piezoresistivity matrix elements take the following forms:

$$\Pi_{11} = (e^2 N_s^2 / 4kTN_d) \times [F^2 Q_{11} + (\alpha_1 + Q_{11} X_3) (\partial F^2 / \partial X_3)_T], \quad (20)$$

$$\Pi_{12} = (e^2 N_s^2 / 4kTN_d) \times [F^2 Q_{12} + (\alpha_1 + Q_{12} X_1) (\partial F^2 / \partial X_1)_T]. \quad (21)$$

COMPUTATION AND RESULTS

Numerical computation of the barrier height, the occupation probability of surface acceptor states, and the isothermal piezoresistivity matrix elements has been carried out for semiconducting barium titanate, since most of its physical constants are well documented in the literature.²¹ Values for N_c , N_d , and E_s (the activation energy of the surface acceptor states) are taken to be $1.56 \times 10^{28} \text{ m}^{-3}$, 10^{25} m^{-3} , and $1.442 \times 10^{-19} \text{ C V}$, respectively.¹⁵ It was pointed out by Jonker¹⁵ that values of N_s of several times 10^{18} m^{-2} (i.e., 1,1.4,2,2.8,4) are needed in order to reach a high barrier potential. The electrostriction coefficients Q_{11} and Q_{12} , the Curie-Weiss constant C , and the extrapolated Curie-Weiss temperature T_0 for barium titanate were taken to be $0.1107 \text{ m}^4/\text{C}^2$, $-0.0432 \text{ m}^4/\text{C}^2$, $1.7 \times 10^5 \text{ K}$, and 381 K , respectively.

Substituting E_F from Eq. (14) into Eqs. (11) and (13), Eqs. (10)–(13) were thus solved iteratively using the bisection method to yield ϕ (C V) and the occupation probability of the surface acceptor states as a function of the stress components X_1 and X_3 and temperature (K). In this manner, the change of ϕ/kT (which is proportional to the change of the logarithm of barrier resistivity normalized by that of the grain) with temperature, and the piezoresistivity matrix elements Π_{11} , and Π_{12} , were

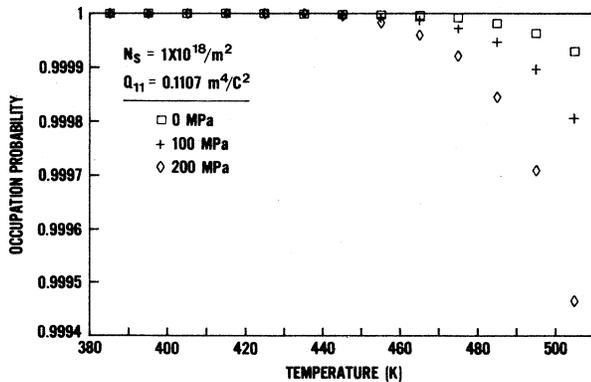


FIG. 1. Occupation probability of surface acceptor states (for $N_s = 1.0 \times 10^{18} \text{ m}^{-2}$ and $Q_{11} = 0.1107 \text{ m}^4/\text{C}^2$) vs temperature at different stress levels.

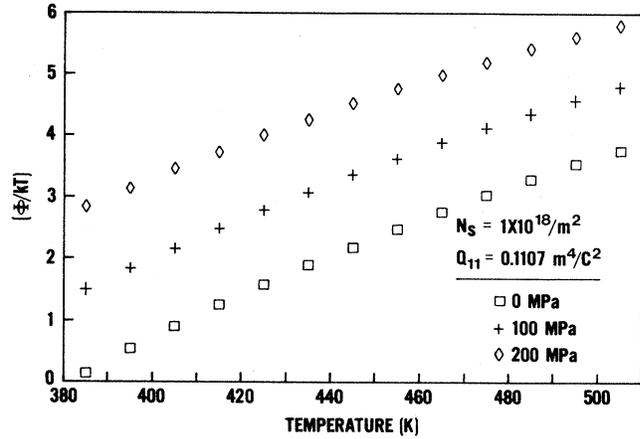


FIG. 2. Calculated ϕ/kT vs temperature at different stress levels.

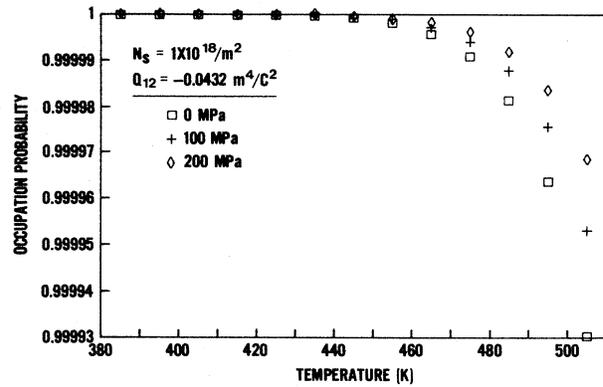


FIG. 3. Occupation probability of surface acceptor states (for $N_s = 1.0 \times 10^{18} \text{ m}^{-2}$ and $Q_{12} = -0.0432 \text{ m}^4/\text{C}^2$) vs temperature at different stress levels.

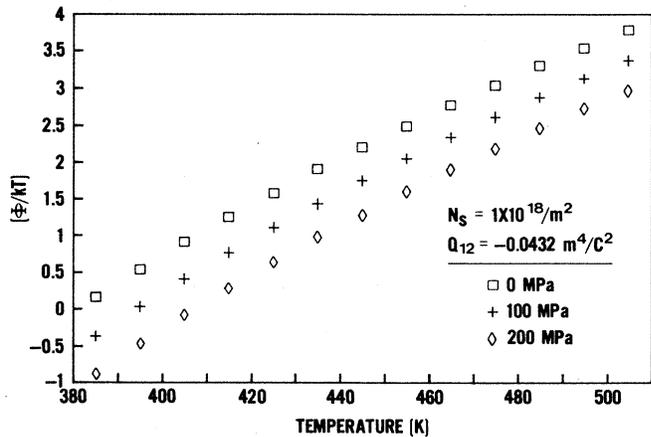


FIG. 4. Calculated ϕ/kT vs temperature at different stress levels.

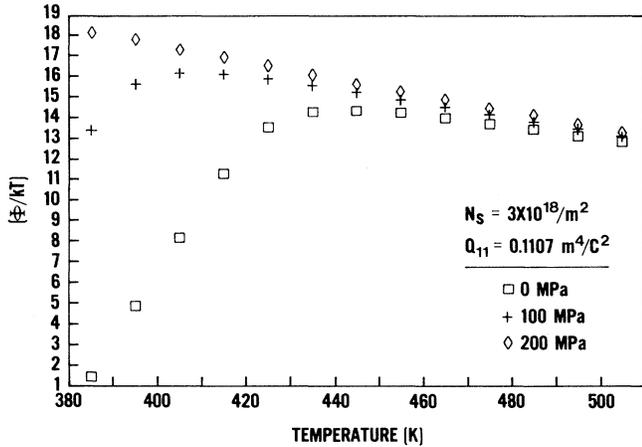
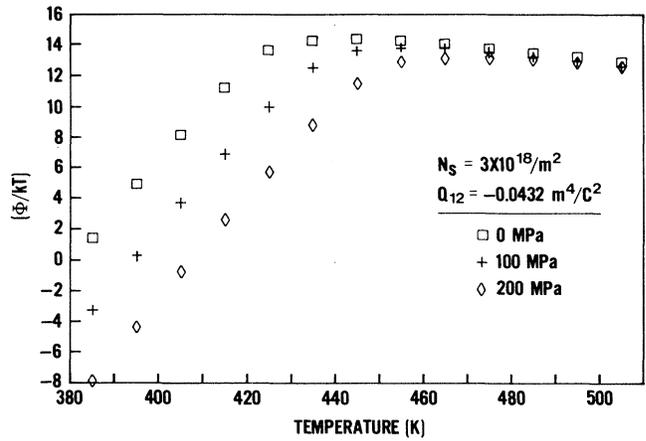
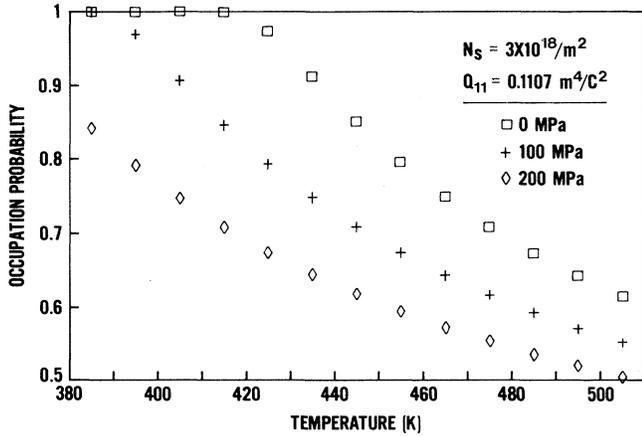


FIG. 6. Calculated ϕ/kT vs temperature at different stress levels.

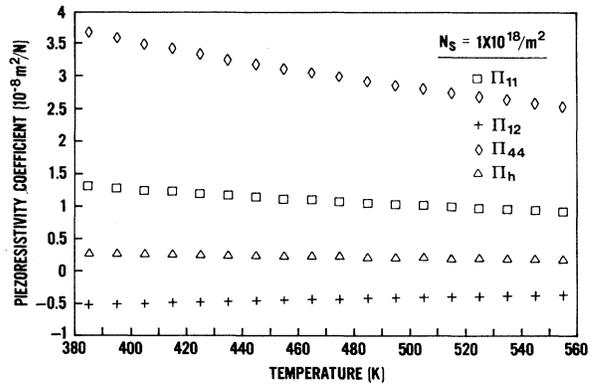


FIG. 9. Piezoresistivity coefficient vs temperature for $N_s = 1.0 \times 10^{18} \text{ m}^{-2}$.

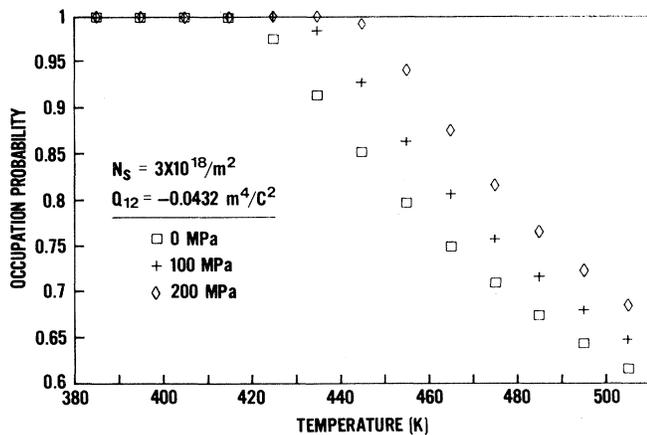


FIG. 7. Occupation probability of surface acceptor states ($N_s = 3.0 \times 10^{18} \text{ m}^{-2}$ and $Q_{12} = -0.0432 \text{ m}^4/\text{C}^2$) vs temperature at different stress levels.

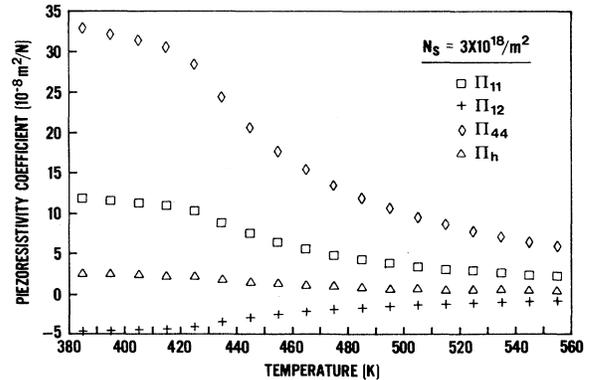


FIG. 10. Piezoresistivity coefficient vs temperature for $N_s = 3.0 \times 10^{18} \text{ m}^{-2}$.

calculated for different stress levels above the ferroelectric-paraelectric Curie temperature of barium titanate. The same procedure has been repeated for each level of surface-acceptor-state density.

The occupation probability of the surface acceptor states for $N_s = 1.0 \times 10^{18} \text{ m}^{-2}$ and $Q_{11} = 0.1107 \text{ m}^4/C^2$ versus temperature is depicted in Fig. 1 for three stress levels. Intermediate stress levels were omitted from the graph for clarity. Figure 2 shows the manner in which ϕ/kT varies with temperature for the same stress values. Figures 3 and 4 show a similar set of computations for the transverse stress component X_1 . The effect of stress components on the occupation probability of the surface acceptor states and ϕ/kT versus temperature for a higher value of N_s are illustrated in Figs. 5–8. The temperature dependence of the longitudinal Π_{11} , transverse Π_{12} , shear Π_{44} , and hydrostatic Π_h piezoresistivity coefficients is shown in Figs. 9 and 10 for the two values of surface-state densities.

DISCUSSIONS

The piezoresistive effect in semiconducting barium strontium titanate compositions has been studied by several workers.^{4–8} The T_C of BaTiO_3 (130°C) decreases nearly linearly with Sr^{2+} substitution for Ba^{2+} . Thus, addition of Sr^{2+} , among other things, facilitates piezoresistance measurements over a wider temperature range on both sides of T_C . The only set of Π_{11} and Π_{12} measurements for pure BaTiO_3 above and below T_C is that of Saburi.⁴ The reported values for the paraelectric state piezoresistivity matrix elements in the vicinity of the Curie temperature are $-1.4 \times 10^{-8} \text{ m}^2/\text{N}$ and $-1.0 \times 10^{-8} \text{ m}^2/\text{N}$ for Π_{11} and Π_{12} , respectively, which are in a good agreement with theoretical predictions (Fig. 9), except for the sign of Π_{11} . This will be discussed later. The calculated values of ϕ/kT under zero stresses versus temperature (Figs. 2, 4, and 6) are similar to those obtained earlier by Jonker.¹⁵

The early work by Sauer *et al.*⁵ and Saburi⁴ resulted in a sign controversy for the piezoresistivity coefficient. A positive sign for the hydrostatic piezoresistivity coefficient was reported by Sauer and co-workers. Saburi, however, noted that far below the Curie temperature, both Π_{11} and Π_{12} were small and showed a negative peak around the Curie temperature, which depended upon Sr content. Above the Curie temperature, the piezoresistivity coefficient decreased rapidly, changed sign, and tended to a positive value asymptotically depending upon the Sr content.

Heywang *et al.*⁶ later showed that near the Curie temperature the piezoresistivity coefficient Π_{11} becomes more negative with increasing dc stress bias. However, with no bias, the piezoresistivity coefficient remained positive below and above the Curie temperature. Therefore, the manner in which the piezoresistivity coefficients vary with temperature depends to a large extent on the elastic boundary conditions which exist at or near the grain-boundary layer.

It is interesting to note that above T_C , model calculations presented earlier show that Π_{11} is positive, in agreement with Heywang's *et al.*⁶ measurements. On the other hand, Π_{12} is negative above T_C and remains negative over an extended temperature range (Fig. 9). However, for a higher density of surface states, Π_{12} changed sign and tended to a positive value asymptotically (Fig. 10) as observed by Saburi for Sr-modified BaTiO_3 .

Experimental and theoretical studies are required to analyze the nature of surface acceptor states and their energy distribution on the piezoresistive properties of BaTiO_3 . Experiments must be designed to accurately measure the two linearly independent piezoresistance matrix elements over a wide temperature range. The manner in which the piezoresistance coefficients and, hence, electrical resistivity vary with stress and temperature depends to a large extent on the stress pattern which exists at the grain boundaries.⁶

Unfortunately, in a polycrystalline ensemble, the elastic boundary conditions upon the individual crystallite are often uncertain. Useful information regarding the manner in which the internal stress pattern evolves with temperature can be obtained using Fourier- and convolution-analysis techniques. This is accomplished by increasing the sample's temperature to the paraelectric state and then monitoring the x-ray diffraction profiles of first- and second-order Bragg reflections that remain invariant in the paraelectric and ferroelectric states as the sample cools isothermally to the ferroelectric state.²²

Modeling of the piezoresistive effect below T_C (i.e., in the ferroelectric state) would be of interest. However, this task is further complicated by the existence of ferroelectric domains and the complex phenomena of domain wall motion at high pressures. In addition, if the barriers are completely compensated or "quenched" in the ferroelectric state,¹⁵ the piezoresistive effect below T_C is that of the bulk "semiconducting grains," without grain-boundary contribution. On the other hand, if the barriers are partially compensated, both the bulk and grain boundary will contribute to the observed piezoresistive effect.

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