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Phenomenological description of piezoresistivity in semiconducting perovskite ferroelectrics

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An expression has been developed for the hydrostatic piezoresistive effect in semiconducting perovskite ferroelectrics. Numerical solutions are presented for a spectrum of surface-state densities in semiconducting barium titanate with a positive temperature coefficient of resistivity. The computations were carried out for some postulated pressure and temperature levels, above the ferroelectric-paraelectric anomaly temperature T_c. A comparison to experimental data is given.

INTRODUCTION

Semiconducting, donor-doped polycrystalline barium titanate exhibits an anomalous increase in resistivity (Fig. 1) known as the positive temperature coefficient of resistivity (PTCR) above the ferroelectric Curie temperature T_c.[1,2] Goodman[3] compared the temperature dependence of dc resistivity of semiconducting polycrystalline $BaTiO_3$ doped with 0.05 at. % 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 $BaTiO_3$.

PTCR materials are based on the crystalline solution $(A_yBa_{1-y-x}D_x)TiO_3$, where A may be the divalent Curie temperature shifters Sr^{2+} or Pb^{2+}, or grain growth inhibitors such as Ca^{2+} and D is a dopant ion. The Curie temperature of barium titanate decreases linearly with Sr^{2+} substitution for Ba^{2+}; the Curie temperature of $SrTiO_3$ is near 10 K. Complete solid solution occurs between $BaTiO_3$ and $PbTiO_3$, and substitution of Pb^{2+} for Ba^{2+} has the effect of raising the Curie temperature monotonically towards that of $PbTiO_3$ (763 K).

Semiconducting properties are produced by (i) doping with a trivalent element (e.g., La^{3+}, Y^{3+}, . . . , etc.) which substitutes for Ba^{2+} on the lattice site; or (ii) doping with a pentavalent element (e.g., Nb^{5+}, Sb^{5+}, . . . , etc.) which substitutes for titanium. In this manner free electrons are generated in the titanium $3d$ conduction band through the formation of a (Ti^{4+} Ti^{3+}) complex as follows, $(Ba_{1-x}{}^{2+}D_x{}^{3+})(Ti_{1-x}{}^{4+}Ti_x{}^{3+})O_3$. The dopant concentration x is usually within a few tenths of an atomic percent, depending upon the dopant type and the required electrical properties of the final composition. Development of large (6–8 orders of magnitude) PTC anomaly requires low level (approximately 500 ppm) acceptor doping with ions such as Mn.

The piezoresistive effect, i.e., the specific change of electrical resistivity of semiconductors with applied stress, is of interest from both the fundamental[4,5] and device technology viewpoints.[6] It is a linear coupling between mechanical stress and electrical resistivity, and is represented by a fourth rank polar tensor. Many pressure, vibration, and acceleration sensors which utilize this phenomenon are fabricated on a precisely micromachined and etched n-type silicon wafer. Four p-type resistors are etched in a definite pattern with respect to the crystallographic axes of the wafer (where piezocoefficients are maxima) and connected to form a Wheatstone bridge. Piezoresistive polycrystalline silicon sensors have also been considered.[7]

Semiconducting barium titanate compositions exhibit large piezoresistive coefficient.[8–14] For instance, the hydrostatic piezoresistive coefficient Π_h which is a linear combination of the longitudinal Π_{11} and transverse Π_{12} components ($\Pi_h = \Pi_{11} + 2\Pi_{12}$) is 2 orders of magnitude larger than that of silicon ($\sim 6 \times 10^{-11}$ m^2/N). A recent review of the experimental and theoretical developments of piezoresistivity in semiconducting ferroelectric perovskites is given in Ref. 15.

In this work we have developed an expression for the hydrostatic piezoresistive coefficient in semiconducting

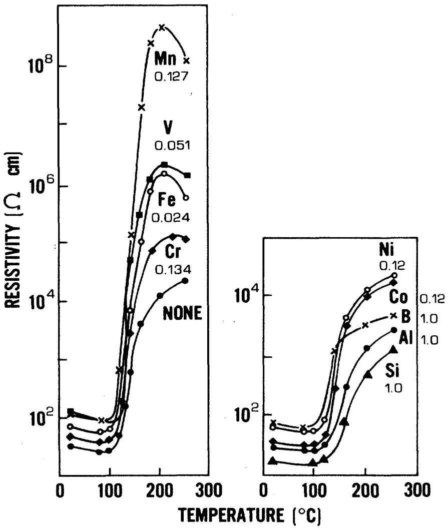

FIG. 1. Positive temperature coefficient of resistivity (PTC) in semiconducting ceramic barium titanate (Ref. 32).

PTCR perovskites above the Curie temperature T_c. Phenomenological equations for the paraelectric state dielectric constant under hydrostatic pressure conditions have been used to formulate the stress and temperature dependence of the static quiescent condition barrier height, and the occupation probability of the surface acceptor states. The constitutive equations have been solved numerically for a range of surface acceptor states to yield the pressure and temperature dependence of barrier height, occupation probability of surface acceptor states, and the piezoresistivity coefficient for barium titanate.

Although in the present treatment the elastic boundary conditions are assumed to be uniform compressive hydrostatic stresses, other stress regimes could be similarly treated in a straightforward manner.

BARRIER LAYER MODEL

A plausible explanation of the PTC effect is given by Heywang[2] as being due to the rapid decrease in dielectric constant above the ferroelectric-paraelectric Curie temperature which leads to a sharp rise in the height of the grain boundary potential barrier. In Heywang's treatment the grain boundary is modeled as a strong depletion-slight inversion, back-to-back Schottky barrier (defined by the approximation $\rho = eN_d$ within the barrier, and $\rho = 0$ outside it; where ρ is the charge density). The expression for the static quiescent condition (zero current) barrier height ϕ is obtained by solving the one-dimensional Poisson's equation under the assumption that barium titanate is a linear and isotropic dielectric[2,16,17] (a valid approximation above T_C)

$$\phi = e^2 N_d d^2 / 2\epsilon\epsilon_0 , \tag{1}$$

where e is the electronic charge, N_d the donor concentration per unit volume, d the thickness of the depletion layer, ϵ the relative permittivity (dielectric constant) and ϵ_0 the free space permittivity.

The charge in the surface states must be equal in magnitude to the charge in the depletion region (charge neutrality)

$$n_s = 2N_d d , \tag{2}$$

$$n_s = n_{a,s} - n_{d,s} , \tag{3}$$

where n_s is the net concentration of ionized surface states, $n_{a,s}$ the total concentration of ionized surface acceptor states, and $n_{d,s}$ the concentration of surface donor states (considered negligible). Substituting from Eq. (2) in Eq. (1), the barrier height takes the form

$$\phi = e^2 n_s^2 / 8\epsilon\epsilon_0 N_d . \tag{4}$$

The nature of the surface acceptor states, the existence of which is assumed necessary for the formation of the grain boundary potential barriers, has been controversial. Chemisorbed oxygen molecules during sintering have been proposed by Jonker.[18] Daniels *et al.*[19] suggested that highly concentrated barium vacancies near the grain surface are responsible for the formation of acceptor states. Experimental work by Kuwabara,[20] however, supports the chemisorbed oxygen model near the grain boundary interface as the reason for the formation of surface states. The calculations of Lewis *et al.*[21,22] showed that transition-metal (e.g., Mn) rich skin in the form of a thin layer around the grain surface is likely to occur. Charge compensation of such acceptor dopant can occur via anion vacancies or holes. The transition-metal skin layer would also provide more favorable oxygen adsorption sites.

In Heywang's treatment the surface states are assumed to lie at one fixed energy level E_s, well below the Fermi level (fully occupied), and the donor levels are sufficiently close to the conduction band (fully ionized); n_s is given by

$$n_s = N_s / \{1 + \exp[(E_F + \phi - E_s)/kT]\} , \tag{5}$$

where N_s is the density of the surface acceptor states, the occupation probability F (Fermi Dirac) is

$$F = 1 / \{1 + \exp[(E_F + \phi - E_s)/kT]\} , \tag{6}$$

the resistivity ρ is given by

$$\rho = \rho_0 \exp(\phi / kT) , \tag{7}$$

where k is Boltzmann's constant, and ϕ is a mean barrier potential.

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

$$\epsilon = C / (T - T_0) \tag{8}$$

where T_0 is the extrapolated Curie-Weiss temperature (108 °C), and C the Curie constant (1.7×10^5 K). Therefore the rapid decrease in dielectric constant above the ferroelectric transition temperature T_C is responsible for the sharp rise in barrier height, hence the observed PTC anomaly.

Heywang's model, however, requires the assumption of a high effective dielectric constant $\epsilon_{(\mathrm{eff})}$ below the Curie temperature to account for the lower and relatively constant resistivity observed in the ferroelectric state. The value of $\epsilon_{(\mathrm{eff})}$ corresponds to that measured with large signal.[17] Jonker[23] has refined the model by suggesting that the normal components of spontaneous polarization (ΔP_n) at the end of alternate 90° domains could effectively compensate the surface states present at the grain boundaries, therefore eliminating a potential barrier there. Thus, for temperatures below T_C, an approximate expression for the barrier height can be written as

$$\phi = [e^2 n_s^2 - (\Delta P_n)^2] / 8\epsilon\epsilon_0 N_d . \tag{9}$$

PHENOMENOLOGICAL DESCRIPTION OF THE STRESS AND TEMPERATURE DEPENDENCE OF BARRIER HEIGHT

The ferroelectric nature of the grain boundary in semiconducting barium titanate suggests phenomenological theories. In many ferroelectric crystals, it has often proven useful to correlate the dielectric, piezoelectric, and elastic properties of paraelectric and ferroelectric phases by a phenomenological thermodynamic theory. Therefore the dielectric properties of the "insulating" grain boundary in semiconducting barium titanate could be analyzed under different thermal, elastic, and electric boundary conditions.

For many crystals this Landau-Ginzburg-Devonshire formalism gives an excellent semiquantitative description of the dielectric, elastic, piezoelectric, and electrothermal properties when only the lowest-order terms are linearly temperature dependent, higher-order terms temperature independent, and often for a very truncated series expansion.[24,25] For a more accurate description over a wider temperature range, additional higher-order terms, and/or temperature-dependent higher-order co-efficients can be included.[26,27]

Consider the free energy density function for a proper ferroelectric derived from a prototypic symmetry group $Pm3m$. For Brillouin-zone-center lattice modes, the Landau-Ginzburg-Devonshire free energy density may be written as a power series in dielectric polarization P_i $(i=1,2,3)$ as follows:

$$\begin{aligned}G=&\alpha_1(P_1^2+P_2^2+P_3^2)+\alpha_{11}(P_1^4+P_2^4+P_3^4)+\alpha_{12}(P_1^2P_2^2+P_2^2P_3^2+P_3^2P_1^2)+\alpha_{111}(P_1^6+P_2^6+P_3^6)\\&+\alpha_{112}[P_1^4(P_2^2+P_3^2)+P_2^4(P_3^2+P_1^2)+P_3^4(P_1^2+P_2^2)]+\alpha_{123}P_1^2P_2^2P_3^2-1/2s_{11}(X_1^2+X_2^2+X_3^2)\\&-s_{12}(X_1X_2+X_2X_3+X_3X_1)-1/2s_{44}(X_4^2+X_5^2+X_6^2)-Q_{11}(X_1P_1^2+X_2P_2^2+X_3P_3^2)\\&-Q_{12}[X_1(P_2^2+P_3^2)+X_2(P_3^2+P_1^2)+X_3(P_1^2+P_2^2)]-Q_{44}(X_4P_2P_3+X_5P_3P_1+X_6P_1P_2)\ ,\end{aligned}\tag{10}$$

where α_i, α_{ij}, α_{ijk} (in reduced tensor notation) are related to the dielectric reciprocal susceptibility (dielectric stiffness) and high-order reciprocal susceptibility coefficients at constant stress and Q_{11}, Q_{12}, Q_{44} are the electrostriction constants written in polarization notation. In Eq. (10) the tensile stresses are denoted by X_1, X_2, X_3, and the shear components by X_4, X_5, X_6, respectively. The expression is complete up to all six power terms in polarization, but contains only first-order terms in electrostrictive and elastic behavior.

The first partial derivatives of the free energy density with respect to the components of P_i, X_i, and T give the conjugate parameters, the electric field E_i, the negative of the strain $-x_{ij}$, and the entropy change $-S$, respectively,

$$(\partial G/\partial P_i)=E_i\ ,\tag{11}$$

$$(\partial G/\partial X_{ij})=-x_{ij}\ ,\tag{12}$$

$$(\partial G/\partial T)=-S\ .\tag{13}$$

The single-domain dielectric reciprocal susceptibilities are given by

$$(\partial^2 G/\partial P_i\partial P_j)=1/\chi_{ij}\tag{14}$$

and the elastic compliances s_{ijkl} and piezoelectric constants b_{ijk} are given by

$$(\partial^2 G/\partial X_{ij}\partial X_{kl})=-s_{ijkl}\ ,\tag{15}$$

$$(\partial^2 G/\partial p_i\partial X_{jk})=-b_{ijk}\ .\tag{16}$$

Equation (11) with $E_i=0$, and the condition that Eqs. (12) and (13) must have positive values, gives the stability conditions for the spontaneously polarized states. Under zero stresses [all X_i vanish in Eq. (10)], the solutions of Eq. (10) which are of interest include the paraelectric cubic ($Pm3m$) and ferroelectric tetragonal ($P4mm$) states:

(i) paraelectric state ($T>T_C$);

$$\begin{gathered}P_1^2=P_2^2=P_3^2=0;\quad G=0\ ,\\ \chi_{11}=\chi_{22}=\chi_{33}=\chi_p,\quad \chi_{12}=\chi_{23}=\chi_{31}=0\ ,\\ (1/\chi_p)=2\alpha_1\epsilon_0\ ,\end{gathered}\tag{17}$$

where $\alpha_1=(1/2\epsilon_0 C)(T-T_0)$;

(ii) ferroelectric state ($T<T_C$);

$$P_1^2=P_2^2=0\ ,$$

$$P_3^2=\frac{-\alpha_{11}+[(\alpha_{11})^2-3\alpha_1\alpha_{111}]^{0.5}}{3\alpha_{111}}\ ,\tag{18}$$

$$G=\alpha_1P_3^2+\alpha_{11}P_3^4+\alpha_{111}P_3^6\ ,\tag{19}$$

$$\chi_{11}=\chi_{22}\neq\chi_{33},\quad \chi_{12}=\chi_{23}=\chi_{31}=0\ ,$$

$$(1/\chi_{33})=(2\alpha_1+12\alpha_{11}P_3^2+30\alpha_{111}P_3^4)\epsilon_0\ ,\tag{20}$$

$$(1/\chi_{11})=(2\alpha_1+2\alpha_{12}P_3^2+2\alpha_{112}P_3^4)\epsilon_0\ ,\tag{21}$$

where $\epsilon_0(8.854\times10^{-12}\ \mathrm{F/m})$ is the free space permittivity.

In ferroelectric polycrystalline solids, a complete free energy function is particularly valuable, since often in a polycrystalline ensemble the elastic and electric boundary conditions upon the individual crystallites are uncertain. It is frequently not clear whether "unusual" properties are intrinsic and to be associated with these boundary conditions, or are extrinsic and associated with such phenomena as domain and phase boundary motion.

A properly developed free energy density function will permit the manner in which these parameters change under different elastic and electric boundary conditions to be evaluated.[28,29] It can be shown that for uniform tensile stresses, the α_1 coefficient in Eqs. (10), (11), (18), (19), and (20) can be written as

$$\alpha_1(X_1,X_2,X_3)=\alpha_1+[Q_{12}(X_1+X_2)+Q_{11}X_3]\ ,\tag{22}$$

where X_1, X_2, X_3 are the normal stress components. Therefore the manner in which the dielectric constant and other tensor properties change with some postulated elastic boundary conditions can be easily computed.

Under hydrostatic pressure conditions, $X_1=X_2=X_3=p$, $X_4=X_5=X_6=0$; substituting for these values of X in Eq. (22) the dielectric inverse susceptibility of the paraelectric state Eq. (17) becomes

$$\chi_p^{-1}=2(\alpha_1+Q_h p\epsilon_0^{-1})\epsilon_0 \tag{23}$$

$$=2\beta[T-(T_0-Q_h\beta^{-1}\epsilon_0^{-1}p)]\epsilon_0 , \tag{24}$$

where $Q_h(=Q_{11}+2Q_{12})$ is the hydrostatic electrostriction coefficient and $\beta=1/(2\epsilon_0 C)$ with C being the Curie-Weiss constant. Therefore, above T_C the inverse dielectric susceptibility follows a Curie-Weiss law with a pressure-dependent Curie-Weiss temperature

$$T_0(p)=T_0(0)-Q_h\beta^{-1}\epsilon_0^{-1}p \tag{25}$$

at constant temperature, the Curie-Weiss law can be expressed as follows:

$$\chi^{-1}=2Q_h(p-p_0) , \tag{26}$$

where $p_0=-\beta\epsilon_0(T-T_0)/Q_h$.

HYDROSTATIC PIEZORESISTIVITY COEFFICIENT

The expression for barrier height [Eq. (4)] and the paraelectric state dielectric inverse susceptibility [Eq. (24)] can be combined to yield

$$\phi(p,T)=\beta\epsilon_0(e^2 n_s^2)[T-(T_0-Q_h\beta^{-1}p)]/(4N_d) , \tag{27}$$

the occupation probability (Fermi Dirac) of the surface states [from Eq. (5)] takes the form

$$F(p,T)=n_s(p,T)/N_S$$

$$=1/(1+\exp\{[E_F+\phi(p,T)-E_s]/kT\}) , \tag{28}$$

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

$$E_F=kT\ln(N_c/N_d) , \tag{29a}$$

$$N_c=2(2\Pi m_e^* kT/h^2)^{3/2} , \tag{29b}$$

where N_d and m_e^* are the donor concentration and the electron effective mass, respectively, and h is Planck's constant. Equation (29a) is a valid approximation for $E_F<-kT$, i.e., for $N_d<2N_c$.

Under isothermal conditions, the resistivity expression [Eq. (7)] and the barrier height expression [Eq. (27)] can be differentiated with respect to pressure p to yield, respectively,

$$(1/\rho)(\partial\rho/\partial p)_T=(1/kT)(\partial\phi/\partial p)_T=\Pi_h \tag{30}$$

and

$$(\partial\phi/\partial p)_T=(e^2/4N_d)[n_s^2 Q_h+\beta(T-T_0)(\partial n_s^2/\partial p)_T] , \tag{31}$$

where Π_h is the hydrostatic piezoresistivity coefficient. Equations (28), (30), and (31) can be combined to yield the following expression for the hydrostatic piezoresistivity coefficient:

$$\Pi_h=(e^2N_s^2/4kTN_d)[F^2Q_h+\alpha_1(\partial F^2/\partial p)_T] . \tag{32}$$

COMPUTATION AND DISCUSSIONS

Numerical computations of the hydrostatic piezoresistivity coefficient and its temperature characteristics have been carried out for semiconducting barium titanate, since most of its physical constants are well documented in the literature.[30] Values for N_c, N_d, and E_s (the activation energy of the surface acceptor states) are taken to be $1.56\times10^{28}/\mathrm{m}^3$, $10^{25}/\mathrm{m}^3$, and 1.442×10^{-19} C V, respectively.[24] It was pointed out by Jonker[24] that values of N_s of several times $10^{18}/\mathrm{m}^2$ (i.e., 1, 1.4, 2, 2.8, 4) are needed in order to reach high barrier potential. The hydrostatic electrostriction coefficient Q_h, the Curie-Weiss constant C, and the extrapolated Curie-Weiss temperature T_0 for barium titanate were taken to be 0.024 $\mathrm{m}^4/\mathrm{C}^2$, 1.7×10^5 K, and 381 K, respectively.

By substituting for E_F from Eq. (29a) in Eq. (28), Eqs. (27) and (28) can be solved iteratively using the bisection method to yield ϕ (C V) and the occupation probability of the surface acceptor states as function of stress (MPa) and temperature (K). In this manner the isothermal resistance change with hydrostatic pressure and the hydrostatic piezoresistivity coefficient have been calculated for different temperature levels above the ferroelectric-paraelectric Curie temperature of barium titanate. The same procedure has been repeated for each level of surface acceptor state density.

Figure 2 shows the manner in which ϕ/kT varies with temperature under zero applied stress for different values of surface acceptor states N_s. The results are similar to those obtained earlier by Jonker.[23] The stress dependence of the occupation probability of surface acceptor states is depicted in Figs. 3(a)–4(b) for two temperature levels. The effect of hydrostatic pressure on the isothermal change of ϕ/kT is illustrated in Figs. 5(a) and 5(b) for different levels of N_s. In Fig. 6 the resistivity

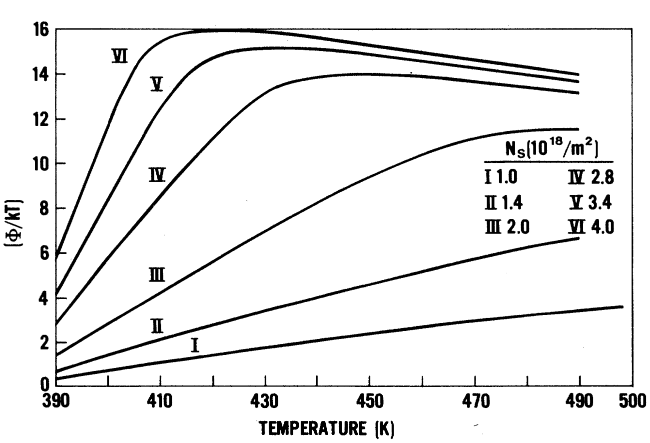

FIG. 2. Calculated ϕ/kT vs temperature for several levels of N_s.

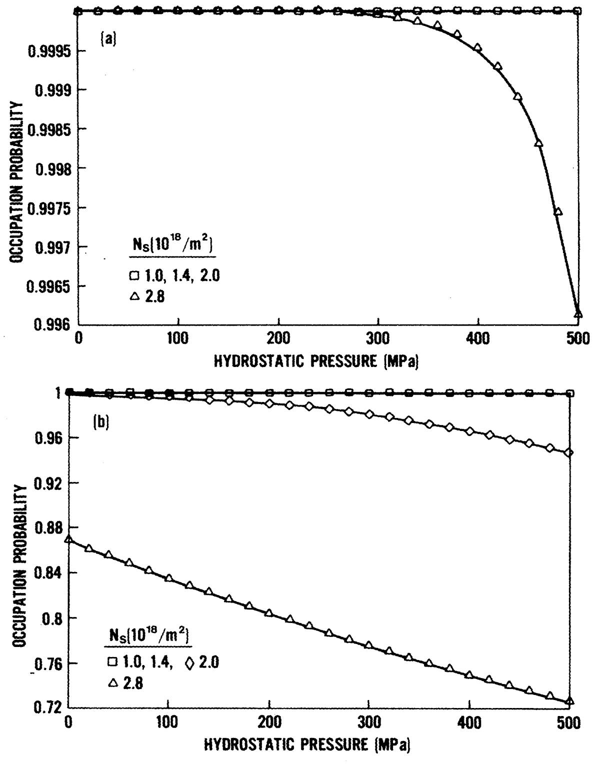

FIG. 3. Occupation probability of surface acceptor states (for $N_s = 1.0$, 1.4, 2.0, and $2.8 \times 10^{18}/\mathrm{m}^2$) vs hydrostatic pressure. (a) $T = 390$ K and (b) $T = 450$ K.

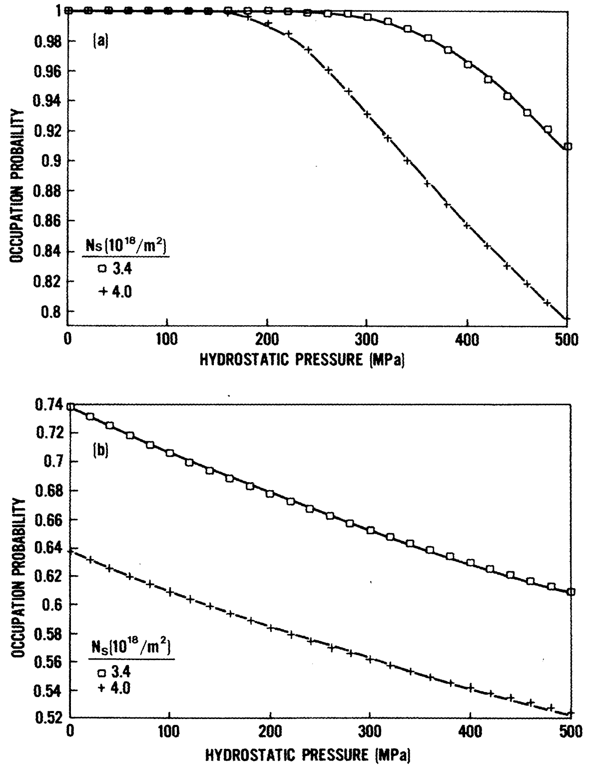

FIG. 4. Occupation probability of surface acceptor states (for $N_s = 3.4$ and $4.0 \times 10^{18}/\mathrm{m}^2$) vs hydrostatic prssure. (a) $T = 390$ K and (b) $T = 450$ K.

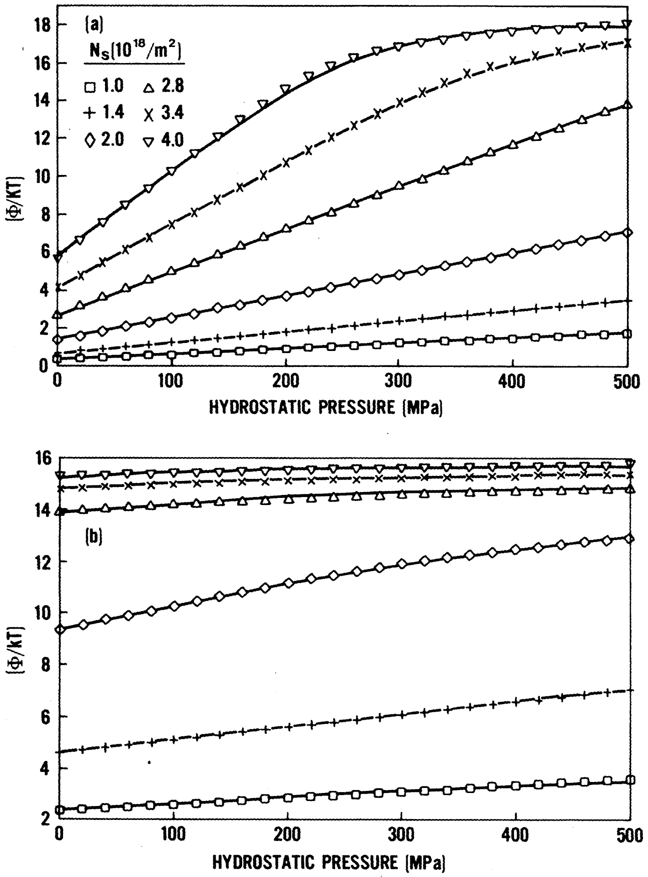

FIG. 5. Calculated ϕ/kT vs hydrostatic pressure for several levels of N_s. (a) $T = 390$ K and (b) $T = 450$ K.

versus temperature curves are plotted for different levels of hydrostatic pressure.

It is interesting to note that semiquantitatively the isothermal change of ϕ/kT with hydrostatic pressure for lower values of N_s [Figs. 5(a) and 5(b)] and the resistivity versus temperature behavior under hydrostatic pressure (Fig. 6) are similar to those observed experimentally by Janega[31] for semiconducting barium strontium titanate. The temperature dependence of the hydrostatic piezoresistivity coefficient is displayed in Figs. 7 and 8 for different values of surface acceptor states. The effect of variations in dopant concentration N_d on ϕ/kT is displayed in Fig. 9 as a function of stress and temperature. Similar computations were carried out to show the effect of activation energy variations on ϕ/kT; the results are depicted in Fig. 10.

The piezoresistive effect in semiconducting barium strontium titanate compositions has received considerable attention in recent years.[8-14] The published values of the hydrostatic piezoresistivity coefficient in the neighborhood of Curie temperature for these compositions are 0.7 to 3×10^{-8} m^2/N. The only measurements for barium titanate above and below T_C are those of Saburi[10] for the longitudinal Π_{11} and the transverse Π_{12} components. Based on these coefficients a calculated value of Π_h at

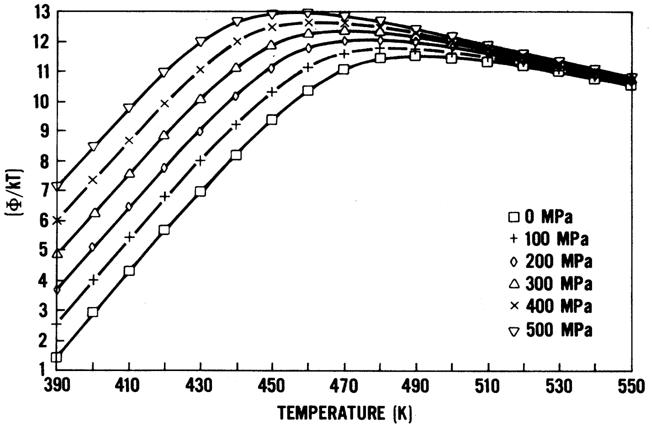

FIG. 6. Calculated ϕ/kT vs temperature for different levels of hydrostatic pressure bias ($N_s = 2.0\times10^{18}/\text{m}^2$).

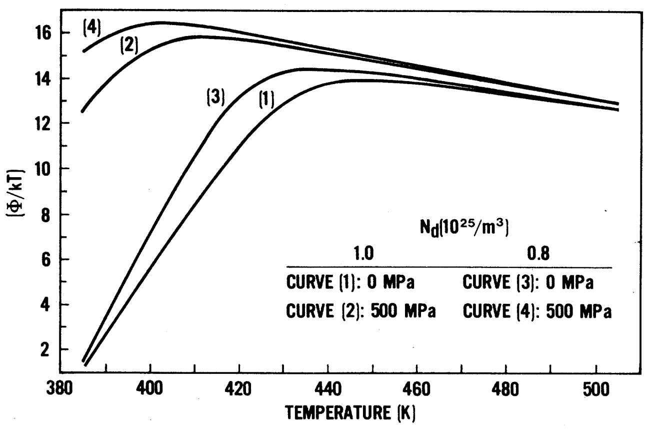

FIG. 9. The effect of variations of N_d on ϕ/kT as a function of temperature and pressure.

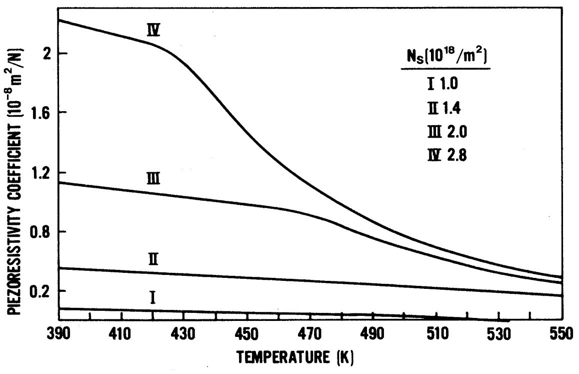

FIG. 7. Hydrostatic piezoresistivity coefficient vs temperature ($N_s = 1.0$, 1.4, 2.0, and $2.8\times10^{18}/\text{m}^2$).

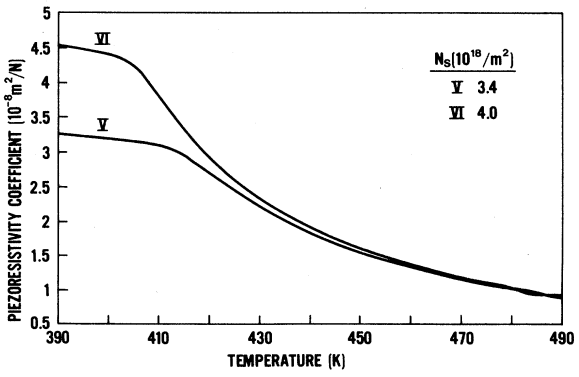

FIG. 8. Hydrostatic piezoresistivity coefficient vs temperature ($N_s = 3.4$ and $4.0\times10^{18}/\text{m}^2$).

400 K of -2.3×10^{-8} m²/N is obtained. Depending upon the surface acceptor state density, theoretical values of Π_h for barium titanate (Figs. 7 and 8) in the Curie temperature range are 0.3 to 4.5×10^{-8} m²/N.

The early work by Sauer *et al.*[9] and Saburi[10] 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 contents. Above the Curie temperature, the piezoresistivity coefficient decreased rapidly, changed sign, and tended to a positive value asymptotically.

Heywang and Guntersdorfer[8] later showed that near the Curie temperature the piezoresistivity coefficient becomes more negative with increasing dc stress bias. However, with no bias, the piezoresistivity coefficient remained positive below and above the Curie tempera-

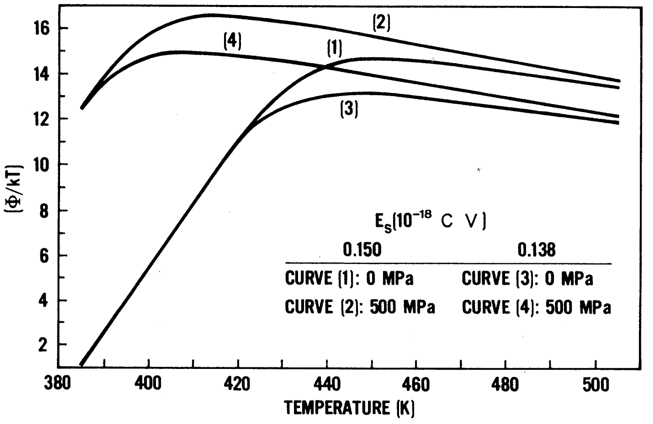

FIG. 10. The effect of variations of E_s on ϕ/kT as a function of temperature and stress.

ture. 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.

In a future work we intend to measure the hydrostatic piezoresistivity coefficient above the Curie temperature T_C and its temperature characteristics for a series of semiconducting compositions in the $BaTiO_3$:$SrTiO_3$ system and compare results to theoretical predictions. In the present treatment no grain (bulk) contribution to the piezoresistive effect was assumed. In other words, piezoresistivity is considered wholly a barrier layer effect. The dominant mechanism for the piezoresistive effect is the change of occupation probability of the surface acceptor states. Hence barrier height is a function of applied stress. The presence of ferroelectric domains below T_C, and the uncertain nature of the elastic boundary conditions which exist at the grain boundaries, renders it difficult to model the piezoresistive effect in the ferroelectric state. In addition, the behavior of domain walls and phase boundary motion at high pressures is a very complex phenomenon.

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