where g is the order of the group, and f_β is the dimension of the βth representation. This relation simplifies Eq. (C8).

$$\rho_\beta^{(0)}(\omega)=gf_\beta^{-1}\sum_{k\lambda}{}' f(k)^{-1}\sum_{s'}|\langle k\lambda|\beta_{s'}\rangle|^2. \quad \text{(C10)}$$

For the tetragonal configurations $|E_g\rangle$ and $|E_{g'}\rangle$ in a cubic crystal where $g=48$ and $f_\beta=2$, we would calculate ρ from

$$\rho_E^{(0)}(\omega)=24\sum_{k\lambda}{}' f(k)^{-1}[|\langle k\lambda|E_g\rangle|^2 + |\langle k\lambda|E_g'\rangle|^2]. \quad \text{(C11)}$$

The expression analagous to Eq. (42) for the other tetragonal configuration is

$$\langle E_g'|k\lambda\rangle=iN^{-1/2}[\epsilon_{k\lambda}{}^{y+}\sin k_ya-\epsilon_{k\lambda}{}^{z+}\sin k_za]. \quad \text{(C12)}$$

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Piezoresistive Properties of Reduced Strontium Titanate*

O. N. Tufte and E. L. Stelzer
Honeywell Research Center, Hopkins, Minnesota

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The piezoresistance effect has been investigated in reduced single-crystal strontium titanate in the temperature range from 4.2 to 296°K. At 296°K, the elastoresistance coefficients $(m_{11}-m_{12})$, m_{44}, and $(m_{11}+2m_{12})$ have been evaluated in samples having a wide range of electron concentrations. The piezoresistance results indicate that the conduction-band edge consists of two types of energy minima separated by several hundreths of an eV with the minimum at $k=0$ being the lowest in energy. Below approximately 110°K, the piezoresistance effect becomes very anisotropic and for certain crystallographic directions, a saturation of the piezoresistance is observed at stress values between 1×10^8 and 2×10^8 dyn/cm^2. The low-temperature piezoresistive properties appear to be a result of the cubic-to-tetragonal phase transition and it is postulated that these effects are due to a stress-induced alignment of the tetragonal domains.

I. INTRODUCTION

The recent discovery[1] of superconductivity in heavily doped semiconducting strontium titanate ($SrTiO_3$) has led to special interest in the energy-band structure of this material. The existence of superconductivity in heavily doped semiconductors was theoretically predicted by Cohen,[2] but a detailed comparison of the theory with experimental results depends on a knowledge of the energy-band structure of the material. Since superconductivity has not been observed in any of the more common semiconductors where the energy-band structures are known, it is important to investigate the energy-band structures of less-well-known materials in which superconductivity is observed. Also, $SrTiO_3$ is one of a relatively new class of semiconducting compounds having a cubic perovskite structure at higher temperatures and para-electric or ferroelectric properties at lower temperatures. It is therefore of interest to investigate the energy-band structure of these materials to aid in the interpretation of their electrical and optical properties.

The energy band structure of $SrTiO_3$ has been investigated theoretically by Kahn and Leyendecker.[3] For the conduction band, their results indicate that a set of minima along the ⟨100⟩ reciprocal axes is lowest in energy and that the minimum at the center of the Brillouin zone is only slightly higher in energy than the ⟨100⟩ minima. The energy surfaces associated with the ⟨100⟩ minima are predicted to be highly anisotropic ellipsoids with a large density-of-states effective mass. Measurements[4] of the electrical conductivity, Hall coefficient, and thermoelectric power tend to confirm the large density-of-states electron effective mass. However, the position of the lowest energy minima within the Brillouin zone has not been experimentally determined.

The piezoresistance effect is useful for investigating the symmetry of the points of minimum energy within the Brillouin zone. For cubic crystals, the relation between the piezoresistance coefficients and the various possible energy band structures has been calculated on the basis of the electron-transfer effect[5] and the results have been verified experimentally for several semiconductor materials.[6]

The purpose of the present work is to investigate the

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* A preliminary account of this work was presented at the American Physical Society Meeting at Kansas City, Missouri, 1965.

[1] J. F. Schooley, W. R. Hosler, and M. L. Cohen, Phys. Rev. Letters **12**, 474 (1964); J. F. Schooley, W. R. Hosler, E. Ambler, J. H. Becker, M. L. Cohen, and C. S. Koonce, Phys. Rev. Letters **14**, 305 (1965).

[2] M. L. Cohen, Phys. Rev. **134**, A511 (1964).

[3] A. H. Kahn and A. J. Leyendecker, Phys. Rev. **135**, A1321 (1964).

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[5] C. Herring, Bell System Tech. J. **34**, 237 (1955); C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).

[6] For a review see R. W. Keyes, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 11.

energy band structure of the conduction band of $SrTiO_3$ by means of the piezoresistance effect.

II. EXPERIMENTAL PROCEDURE

The $SrTiO_3$ single crystals were obtained from the National Lead Company. The crystals were oriented by means of x rays and sliced with a diamond abrasive saw. The slices were then reduced as described below to obtain the desired resistivity, and oriented samples in the form of rectangular parallelopipeds having dimensions of the order of $10\times1\times1$ mm were cut from the slices. The surfaces of the samples were lapped and mechanically polished. Electrical contacts were made by means of ultrasonically soldered indium metal.

The undoped crystals have a room temperature resistivity of the order of 10^{11} Ω cm. To obtain sample resistivities down to approximately 0.09 Ω cm, the slices were reduced by heating at 1150°C in vacuum using the methods described by Frederikse *et al.*[4] For lower resistivities, the samples were reduced by heating at 1150°C in purified hydrogen. One crystal was doped with 0.05% by weight of niobium when grown and samples from this crystal were used without reduction.

The piezoresistance effect was measured by means of compressive stress over the stress range from approximately 3×10^7 to 1×10^9 dyn/cm². Only the longitudinal piezoresistance effect was investigated. The method for stressing the sample is similar to the method described by Cuevas and Fritzsche.[7] A sketch of the sample holder is shown in Fig. 1. The sample holder is constructed entirely of brass. Uniaxial compression is obtained by pulling the lower end of the sample upwards against the top of the sample holder, which is held in place by the outside thin-wall stainless-steel tube. The inner rod is connected through an *O*-ring seal to a beam balance which is external to the cryostat. The *O*-ring seal is loosened while measurements are being made to reduce friction, and at low temperatures helium gas is introduced in the space between the inside rod and the outside tube to prevent the solidification of moisture and air in the system. The cryostat has a double-wall tube separating the sample holder from the cooling bath. The space between the walls may be evacuated or filled with helium to form an adjustable heat leak from the sample holder to the cooling bath so that measurements can be made as a function of temperature at temperatures above 4.2°K.

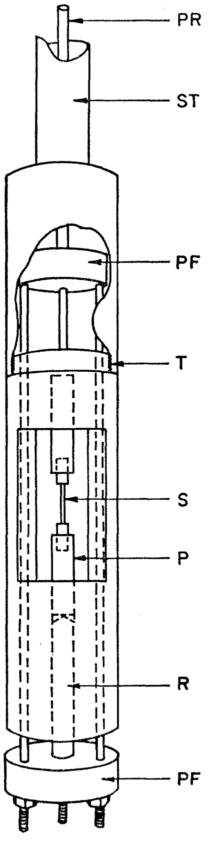

FIG. 1. Sample holder for the investigation of the piezoresistance effect by means of longitudinal compressive stress. PR–pulling rod; ST–thin-wall stainless-steel tubing; T–threaded joint; S–sample; P–movable piston for compressing sample; R–rod connecting pulling frame to movable piston; PF–pulling frame.

For most of the measurements, the sample ends were cast in epoxy cylinders which fit snugly into the end holes of the pistons of the compression frame. Special care is taken in casting the sample ends in epoxy to insure the accurate alignment of the sample with the pistons. For some of the measurements reported in this paper, the sample ends were not cast in epoxy but rather lapped flat and placed against a flat piston surface with a thin layer of Teflon between the sample and the piston for electrical insulation. Identical piezoresistance results were obtained with either method of mounting the samples. For extension measurements, each sample end and a hook were cast together in an epoxy cylinder, with the hook aligned to pull along the axis of the sample. These samples were then placed in another sample holder designed specifically for extension measurements.[8]

At room temperature the piezoresistance coefficients π_{11}, π_{12}, and π_{44} were obtained by a combination of longitudinal piezoresistance measurements on [100]- and [110]-oriented samples and hydrostatic-pressure measurements.[9] The hydrostatic-pressure measurements were made over the pressure range from 2×10^8 to 2×10^9 dyn/cm² with an apparatus that has previously been described by Long.[10] At lower temperatures, only piezoresistance measurements were made so that all three coefficients could not be uniquely determined. All of the results have been corrected for the change in the dimensions with stress. The piezoresistance coefficients are defined as positive if the sample resistivity decreases with applied compressive stress.[9]

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[7] M. Cuevas and H. Fritzsche, Phys. Rev. **137**, A1847 (1965).
[8] O. N. Tufte and E. L. Stelzer, Phys. Rev. **133**, A1705 (1964).
[9] C. S. Smith, Phys. Rev. **94**, 42 (1954).
[10] D. Long, Phys. Rev. **99**, 388 (1955).

TABLE I. The measured piezoresistance and elastoresistance coefficients in $SrTiO_3$ at 296°K.

ρ (Ω cm)	n_{RH} (cm^{-3})	$\pi_{11}\times10^{12}$	$\pi_{12}\times10^{12}$	$\pi_{44}\times10^{12}$	m_{11}	m_{12}	m_{44}	$m_{11}-m_{12}$	$m_{11}+2m_{12}$
0.029	3.7×10^{19}	3.7	6.1	−0.1	26	29	−0.1	−3	85
0.090	1.2×10^{19}	2.4	5.5	1.0	19	25	1.2	−6	69
0.16	6.5×10^{18}	2.3	6.5	−1.0	21	29	−1.3	−8	79
0.38	2.9×10^{18}	2.9	4.9	0.8	19	23	1.0	−4	67
2.8	3.7×10^{17}	−1.7	1.4	1.7	−1.1	5.5	2.1	−6.6	10
7.9	1.3×10^{17}								−130
0.11(Nb)	9.5×10^{18}	2.9	6.9	−3.8	23	32	−4.7	−9	87

III. RESULTS

At room temperature (296°K), the piezoresistance effect in $SrTiO_3$ varies linearly with the applied stress and the piezoresistive properties can be specified in terms of the coefficients π_{11}, π_{12}, and π_{44} which are the components of the piezoresistance tensor.[6] The room-temperature values of the piezoresistance coefficients for samples having a range of room-temperature resistivities are shown in Table I. For each resistivity value in this table, measurements were made on two or more samples having different crystallographic orientations but approximately the same resistivity, and the results were combined to obtain the piezoresistance coefficients. The carrier concentrations n_{RH} have been evaluated from the room-temperature Hall coefficients assuming $n=(R_{H}e)^{-1}$ where R_H is the Hall coefficient and e the electronic charge. The elastoresistance coefficients, m_{11}, m_{12}, and m_{44}, have been derived from the piezoresistance coefficients using the elastic-constant values of Bell and Rupprecht.[11] The hydrostatic-pressure coefficient, $(m_{11}+2m_{12})$ is large and positive in the low-resistivity samples and becomes large and negative in the highest resistivity sample. The decrease in magnitude and change in sign of the hydrostatic-pressure coefficient coincides approximately with the appearance of an impurity activation energy, as determined by the temperature dependence of the Hall coefficient. The magnitude of the elastoresistance coefficients m_{11} and m_{12} is determined to a large extent by the hydrostatic-pressure coefficient, i.e., $m_{11}\approx m_{12}\approx\frac{1}{3}(m_{11}+2m_{12})$. The elastoresistance shear coefficients m_{44} and $(m_{11}-m_{12})$ are small for all samples investigated. The room-temperature piezoresistance coefficients measured on niobium-doped samples are also shown in Table I and agree very well with the results obtained on reduced $SrTiO_3$ of a similar resistivity. This indicates that the piezoresistive properties are not sensitive to the type of donor impurity but are rather determined by the behavior of electrons in the conduction band.

Between 296 and 115°K, the longitudinal piezoresistance varies linearly with stress, and the temperature dependence of the longitudinal piezoresistance effect for two sample orientations is shown in Fig. 2. For both orientations, only a small variation with temperature is found in this temperature range and similar dependences were observed on all samples investigated.

At approximately 110°K, which is the temperature at which the crystal structure of $SrTiO_3$ undergoes a cubic-to-tetragonal phase transition,[11–13] the piezoresistive properties show an abrupt change in behavior as indicated in Fig. 2. Two distinct types of behavior are found below 110°K, depending on whether the stress is applied along the [100] or the [111] axis of the cubic phase. If stress is applied along the [100] axis, the piezoresistance effect is negative (the resistivity increases for a compressive stress) and large in all samples and tends toward saturation at low stress levels as shown for several samples at 77°K in Fig. 3 and for two samples at 4.2°K in Fig. 4. The results in Figs. 3 and 4 are very reproducible on a given sample and no hysteresis effects in the piezoresistance were observed at any tempera-

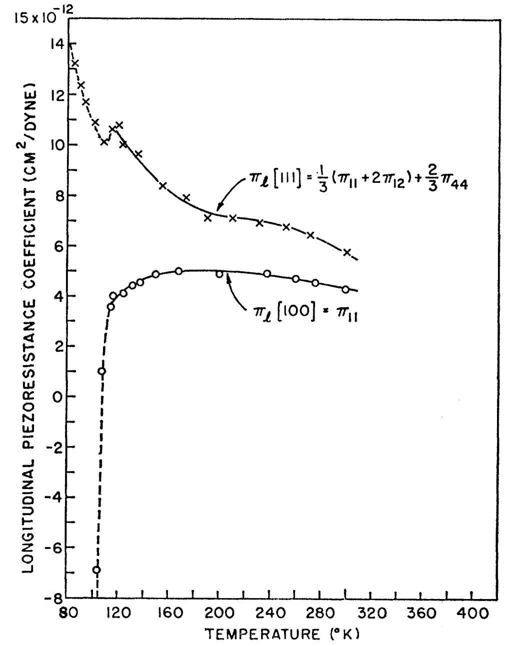

FIG. 2. The temperature dependence of the longitudinal piezoresistance for [100]- and [111]-oriented samples having a room-temperature resistivity of 0.029 Ω cm. The behavior below 110°K is indicated by a dashed line since the piezoresistance no longer varies linearly with stress. The points on the figure below 110°K are linear approximations of the actual behavior and are included only to show the abrupt change in magnitude in the [100]-oriented sample.

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[12] K. A. Müller, Helv. Phys. Acta **31**, 173 (1958).

[13] L. Rimai and G. A. deMars, Phys. Rev. **127**, 702 (1962).

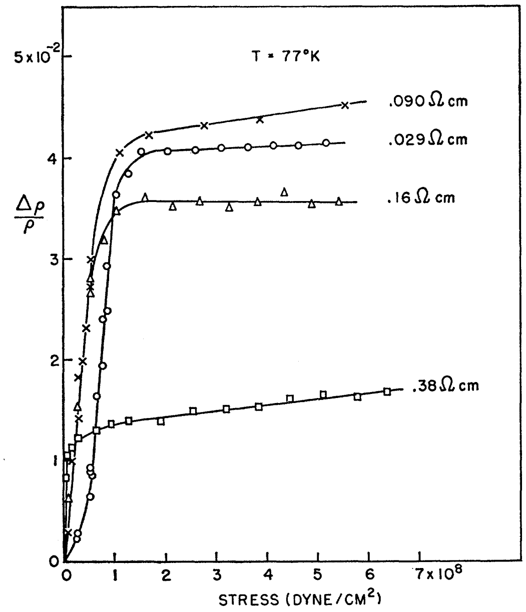

FIG. 3. Dependence of the longitudinal piezoresistance on stress at 77°K when stress is applied along the [100] axis. The resistivity values refer to room temperature (296°K).

ture. All of the [100]-oriented samples investigated have the general feature of a saturation of the piezoresistance effect at low stress values. However, on the basis of our results at 77°K, where the most extensive measurements were made, there does not appear to be any direct relation between the saturation value of the piezoresistance or the stress required for saturation and the room-temperature resistivity of the sample. The piezoresistance effect was measured on one sample using both compressive and tensile stress. For tensile stress, a low-stress saturation of the piezoresistance effect was again observed and the sign of the effect was opposite to that found for compressive stress. However, the saturation value of the piezoresistance as well as the stress required for saturation were not the same as for the compressive case. It is therefore concluded that while the results in Figs. 3 and 4 are useful in defining the qualitative behavior of the piezoresistance effect at low temperatures, the quantitative results may be dependent on factors not controlled in the present experiments.

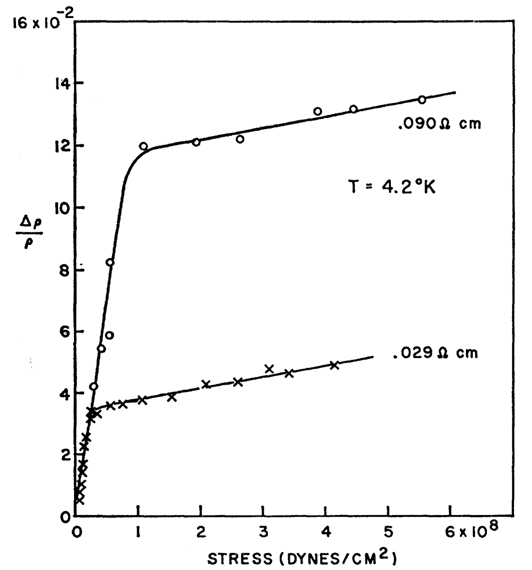

FIG. 4. Dependence of the longitudinal piezoresistance on stress at 4.2°K when stress is applied along the [100] axis. The resistivity values refer to room temperature (296°K).

If stress is applied along the [111] cubic axis, the sign of the piezoresistance effect remains the same as at higher temperatures and a nearly linear dependence on stress is found over the entire temperature range as shown in Fig. 5. The 4.2°K measurements were extended to a stress of 2×10^9 dyn/cm^2 and a linear continuation of the curve in Fig. 5 was found. The magnitude of the piezoresistance effect increases with decreasing temperature and this can be interpreted as an increase in the hydrostatic pressure coefficient, if we assume π_{44} remains small at all temperatures. The origin of the slight nonlinearity in the piezoresistance effect, that begins at approximately 110°K, is not understood.

If stress is applied along the [110] axis of the cubic phase, the results are intermediate between the [100] and [111] results. The stress dependence of the piezoresistance for several [110]-oriented samples is shown

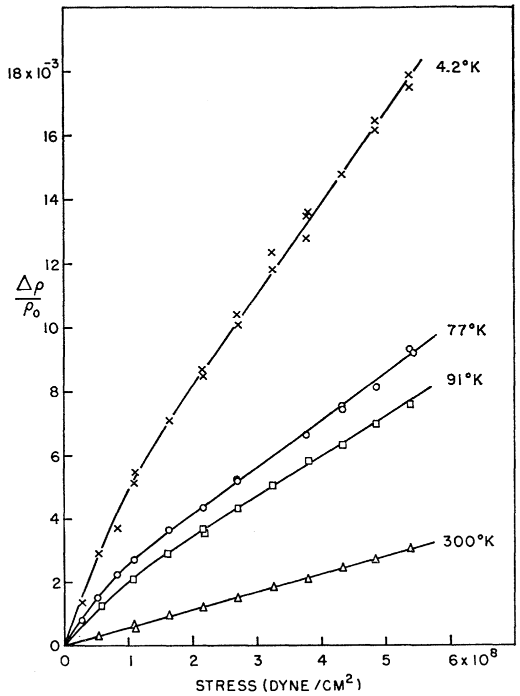

FIG. 5. Dependence of the longitudinal piezoresistance on stress and temperature when stress is applied along the [111] axis. This sample has a room-temperature resistivity of 0.029 Ω cm.

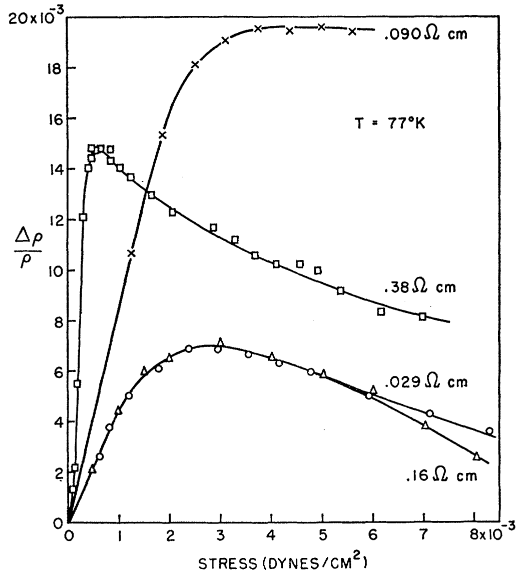

FIG. 6. Dependence of the longitudinal piezoresistance on stress at 77°K when stress is applied along the [110] axis. The resistivity values refer to room temperature (296°K).

in Fig. 6. The magnitude of the piezoresistance effect is much smaller than for [100]-oriented samples and appears to be made up of two components having opposite signs. One component saturates with increasing stress and the other component varies approximately linearly with stress. Here again, as for the [100]-oriented samples, the piezoresistance results do not seem to be directly related to the resistivity of the sample.

IV. DISCUSSION

The most striking feature of the room-temperature piezoresistance results is the large magnitude of the hydrostatic-pressure coefficient, $(m_{11}+2m_{12})$. The large negative value of the hydrostatic pressure coefficient in the most nearly pure samples is attributed to an increase in the impurity activation energy with pressure in a manner similar to the behavior reported by Sladek[14] in n-type GaAs. However, for all of the samples having electron concentrations greater than 1×10^{18} cm^{-3}, the impurity activation energy is zero, i.e., the Hall coefficient does not indicate any carrier freeze out down to 1.5°K. The large positive pressure coefficient in these samples suggests conduction by electrons in two different sets of conduction-band minima having different mobilities and separated by an energy comparable to kT at room temperature. If the energy separation between these minima is changed by the application of hydrostatic pressure, as in the group-IV and -III-V compound semiconductors,[15] electrons will transfer from one set to another with a resulting change in mobility and resistivity. The presence of two types of minima at the conduction-band edge has been predicted by Kahn and Leyendecker[3] whose calculations indicate that an energy minimum at the center of the Brillouin zone and a set of minima along the $\langle100\rangle$ reciprocal axes of the zone should be separated by an energy difference of a few hundredths of an eV with the $\langle100\rangle$ minima being the lower in energy. If the $\langle100\rangle$ minima were lower in energy, the coefficient $(m_{11}-m_{12})$ would be expected to be large, and $m_{12}=-\frac{1}{2}m_{11}$. The small magnitude of the coefficients $(m_{11}-m_{12})$ and m_{44} suggests that the minimum at $k=0$ is the lowest in energy and that the energy surfaces associated with this minimum are spherical. If the $\langle100\rangle$ minima were lower in energy than the [000] minimum by an energy comparable to kT at room temperature so that a significant fraction of the electrons would still be in states in the [000] minimum, and if electrons in these states had a much higher mobility, the coefficient $(m_{11}-m_{12})$ could be small, since a large fraction of the sample current would be carried by electrons in the [000] minimum. However, in this case, π_{11} should become smaller and perhaps negative with decreasing temperature since the number of carriers in the higher energy minimum will be reduced. Experimentally, π_{11} is very nearly independent of temperature down to approximately 130°K where effects of the phase transition begin to dominate. The lack of any dependence of the coefficient $(m_{11}-m_{12})$ on electron concentration is probably not significant since in the concentration range investigated none of the samples are statistically degenerate at room temperature because of the large density-of-states effective mass.[4] It is therefore concluded on the basis of the piezoresistive properties that the lowest lying minimum in the conduction band of SrTiO$_3$ in the cubic phase is at $k=0$ and the energy surfaces associated with this minimum are spherical. Also, the large value of the hydrostatic pressure coefficient indicates the presence of a second extremum, presumably in the [100] direction, separated in energy from the minimum at $k=0$ by approximately 0.02–0.04 eV.

The effective mass of electrons in SrTiO$_3$ has been found to be dependent on temperature in a manner consistent with the proposed model of the conduction band. Frederikse *et al.*[4] report that the density-of-states effective mass decreases by a factor of 2 to 4 between 300 and 78°K. Barker[16] reports that the electric-susceptibility effective mass decreases by a factor of 4 between 300 and 90°K. These rather large changes in the effective-mass values would indicate a decrease in the number of electrons occupying states in the upper set of energy minima at the lower temperatures.

The large piezoresistance effects in SrTiO$_3$ at low temperatures appear to be a result of the cubic to tetragonal phase transition since the temperature at

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[14] R. J. Sladek, *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie, Paris, 1964), p. 545.

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[16] A. S. Barker, Jr., Bull. Am. Phys. Soc. **10**, 369 (1965).

which these effects begin to appear is approximately equal to the transition temperature (108°K).[11–13] Two possible sources of the piezoresistance effect in the tetragonal phase are a change in the energy-band structure caused by the phase transition, and a stress-induced change in the orientation of the tetragonal domains.

The low temperature piezoresistance effect is anisotropic and obeys approximately the symmetry properties required for many-valley-type band structure having minima along the $\langle 100\rangle$ reciprocal axes.[5] Also, the saturation of the piezoresistance effect with increasing stress is a characteristic of a many-valley-type band structure at low temperatures.[17] However, the stress required for saturation of the piezoresistance effect at 77°K is much too small to explain the piezoresistive properties on the basis of a many-valley-type energy-band structure unless the deformation potential constant is of the order of several hundred eV/strain. Also, a systematic dependence of the piezoresistive properties on the resistivity and electron concentration would be expected from the electron transfer effect. It is therefore concluded that the low-temperature piezoresistive properties are not a direct result of any abrupt change in the energy-band structure in going from the cubic to the tetragonal phase.

In the tetragonal phase, a $SrTiO_3$ crystal is made up of a large number of small tetragonal domains in which the tetragonal axis of the domain is aligned along one of the original cubic axes.[12] The tetragonal phase represents only a small displacement from cubic symmetry, so that the application of an external stress along one of the cubic axes might be expected to produce a realignment of the tetragonal domains. If the resistivity is anisotropic in the tetragonal phase, this mechanism could give rise to piezoresistance effects of the type found in the present experiments. The saturation of the piezoresistance effect would then indicate complete alignment of the domains with respect to the stress direction. If stress is applied along the [111] crystallographic direction, domain realignment will not occur and large piezoresistance effects would not be expected.

The large room-temperature piezoresistance effect in reduced $BaTiO_3$ has been attributed to domain alignment by Mattes.[18] In the case of $BaTiO_3$, a very nonlinear stress-strain relationship was also observed in the tetragonal phase. Such nonlinearities may also be present in $SrTiO_3$ below 110°K. In view of the many uncertainties in the present low-temperature results, a quantitative analysis is not warranted. The present results serve only to point out the existence of large nonlinear piezoresistive properties in $SrTiO_3$ below 110°K and suggest that the origin of these effects may be caused by the change in domain alignment with stress as in $BaTiO_3$.

V. CONCLUSIONS

The elastoresistance coefficients $(m_{11}-m_{12})$ and m_{44} are both less than 10, and the hydrostatic-pressure coefficient $(m_{11}+2m_{12})$ is approximately 80 at room temperature in heavily doped reduced $SrTiO_3$. These results, along with the temperature dependence of the longitudinal piezoresistance, suggest that the conduction-band edge in $SrTiO_3$ consists of two types of energy minima separated by an energy of several hundredths of an eV, with the minimum at $k=0$ being the lower in energy. At approximately 110°K, an abrupt change in the piezoresistive properties occurs because of the cubic-to-tetragonal phase transition. The origin of the piezoresistance effect in the tetragonal phase is postulated to be caused by a stress-induced realignment of the tetragonal domains.

ACKNOWLEDGMENTS

The authors wish to acknowledge helpful discussions with Dr. D. Long and Dr. J. D. Zook during the course of this work.

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[17] For typical results see Ref. 7.

[18] B. L. Mattes, J. Appl. Phys. 34, 682 (1963).