

Piezoresistivity in the Oxide Semiconductor Rutile ( $\text{TiO}_2$ )

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The piezoresistive effect in single crystals of the oxide semiconductor rutile ( $\text{TiO}_2$ ) has been studied. The fourth-rank piezoresistive tensor for the  $D_{4h}$  tetragonal symmetry of rutile may be expressed in terms of seven piezoresistive coefficients. Room-temperature values for these coefficients are presented for different resistivity material in the range from approximately 1000 to 0.1 ohm cm, resulting from various concentrations of oxygen deficiency in the nonstoichiometric  $\text{TiO}_2$  lattice. Some of these coefficients were also measured at 77° and 380°K. The measured piezoresistive coefficients are of the order of  $+10^{-11}$  cm<sup>2</sup>/dyne. The longitudinal piezoresistive coefficient measured along the "c" axis,  $\pi_{33}$ , diminishes with increasing oxygen deficiency, while that along the "a" axis,  $\pi_{11}$ , increases with oxygen deficiency. This trend is interpreted in terms of the impurity band conduction model proposed for rutile.

## INTRODUCTION

RUTILE, one of the three crystal modifications of titanium dioxide, is an oxide semiconductor whose electrical properties are dependent on the amount of oxygen deficiency in the  $\text{TiO}_2$  crystal lattice. A complete transition from a good insulator ( $10^{13}$  ohm cm) to a conductor ( $10^{-1}$  ohm cm) can be achieved by changing the stoichiometric composition of  $\text{TiO}_2$ . By hydrogen reduction, rutile samples from 0.15 to 1000 ohm cm can readily be prepared. The decomposition, or reduction, of titanium dioxide, and the resulting semiconductor properties, have been studied in detail.<sup>1-6</sup> Measurements by x-ray techniques indicate that the rutile structure is maintained for a weight loss of less than 2%.<sup>7</sup> The optical and photoconductive properties of rutile have been studied by Cronmeyer, who reports the energy gap to be 3.05 ev.<sup>8,9</sup> Breckenridge and Hosler have made measurements of the electrical resistivity and Hall coefficient of reduced rutile, both single crystal and ceramic.<sup>10</sup> Grant, in a recent review paper, summarizes the nature of the band structure of rutile.<sup>1</sup> In addition, he considers impurity band conduction in rutile, where it has been estimated that overlapping of the impurity wave functions is sufficiently large for the formation of impurity bands. Conduction in rutile exhibits large effective electron masses and low carrier mobility which is characteristic of impurity band conductivity.

Due to the very low electron mobility ( $\mu_{\text{Hall}}$  is the order of 0.1 to 1.0 cm<sup>2</sup>/volt-sec),<sup>10</sup> a characteristic of

the oxide semiconductors, Hall effect and magneto-resistance measurements are very difficult. It was hoped that a knowledge of the effects of strain on the conduction process in rutile would be helpful. To the authors' knowledge, they are the first to report piezoresistivity in materials of low carrier mobility or in crystals possessing a tetragonal symmetry.<sup>11,12</sup>

Rutile is the most stable modification of  $\text{TiO}_2$  and the only one that can exist at temperatures very much above 900°C. A unit cell is tetragonal with a  $D_{4h}$  symmetry. The lattice constants for rutile are  $a=4.594 \pm 0.003$  Å and  $c=2.959 \pm 0.002$  Å.<sup>13</sup> It has a density of 4.26 g/cm<sup>3</sup>. The static dielectric constant,  $k$ , in stoichiometric rutile in the "c" direction is 173 and in the "a" direction is 89.<sup>1</sup> The crystal lattice for the rutile modification of  $\text{TiO}_2$  is composed of somewhat distorted  $\text{TiO}_6$  octahedra.

For crystals with a center of symmetry, such as rutile, the electric field components may be expressed in a Maclaurin series as functions of the current density components,  $I_j$ , and stress components,  $T_{kl}$ ,<sup>14</sup> which reduces to:

$$E_i = \rho_{ij} I_j + \pi_{ijkl} I_j T_{kl}.$$

The piezoresistive coefficient,  $\pi_{ijkl}$ , is a fourth-rank tensor consisting of 81 components. It can be shown in general that

$$\pi_{ijkl} = \pi_{jikl} = \pi_{ijlk} = \pi_{jilk},$$

reducing the number of components to 36 forming a  $6 \times 6$  matrix. The number of components may be further reduced by considering the symmetry of the crystal. The resulting matrix arrangement of the fourth-rank piezoresistive tensor for tetragonal crystals with the Schöenflies symmetry  $D_{4h}$  is presented in Table I. For rutile there are two longitudinal coefficients  $\pi_{11}$  and  $\pi_{33}$ ; three transverse coefficients,  $\pi_{12}$ ,  $\pi_{13}$ , and  $\pi_{31}$ ;

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<sup>8</sup> D. Cronmeyer, Phys. Rev. **113**, 1222 (1959).

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<sup>10</sup> R. G. Breckenridge and W. R. Hosler, Phys. Rev. **91**, 793 (1953).

TABLE I. The matrix arrangement of the fourth-rank piezoresistive tensor for the tetragonal crystals with the  $D_{4h}$  symmetry (longitudinal coefficients  $\pi_{11}$  and  $\pi_{33}$ ; transverse coefficients  $\pi_{12}$ ,  $\pi_{13}$ , and  $\pi_{31}$ ; shear coefficients  $\pi_{44}$  and  $\pi_{66}$ ).

$\pi_{11}$	$\pi_{12}$	$\pi_{13}$	0	0	0
$\pi_{12}$	$\pi_{11}$	$\pi_{13}$	0	0	0
$\pi_{31}$	$\pi_{31}$	$\pi_{33}$	0	0	0
0	0	0	$\pi_{44}$	0	0
0	0	0	0	$\pi_{44}$	0
0	0	0	0	0	$\pi_{66}$

and two shear coefficients  $\pi_{44}$  and  $\pi_{66}$ . These  $\pi$  coefficients have been divided by resistivity and are reported in this paper as  $\Delta\rho/\rho T$  in units of  $\text{cm}^2/\text{dyne}$ .

#### EXPERIMENTAL PROCEDURE

Single-crystal samples approximately  $2 \times 2 \times 15$  mm were cut from x ray oriented boules of stoichiometric rutile.<sup>15</sup> Spectrographic analysis indicated no detectable impurities in these crystals.<sup>16</sup> The maximum total error in the orientation of the cut samples was estimated at  $\pm 2^\circ$ .

The crystals were reduced or oxidized in a quartz-tube oven, by circulating either hydrogen or air at various temperatures from  $450^\circ$  to  $1100^\circ\text{C}$  for various time intervals. The oxidation-reduction process was completely reversible, and the measurements were repeatable within experimental error, even though the crystal in question might have been reduced and oxidized several times.

Considerable difficulty was encountered in securing good ohmic contacts to the reduced material. Best results were obtained by cleaning the samples in a solution of  $\text{H}_2\text{SO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  and then soldering with pure, clean indium metal. Mechanical clamps were attached to the soft indium current electrodes, which deformed when clamped, assuring a good mechanical and electrical contact to the soldered crystal. All the longitudinal measurements were made by the four-contact method; however, only two contacts were used for the transverse measurements.

The experimental procedure was similar to that previously described.<sup>17-21</sup> In order to obtain values for all seven of the coefficients for the  $D_{4h}$  symmetry, samples were cut in four crystal orientations as follows:  $[100]$ ,  $[001]$ ,  $[110]$ , and  $[111]$ . Seven configurations, four longitudinal and three transverse, were utilized. The crystal directions in which the current is measured and the stress is applied are tabulated in Table II for each of the seven measured  $\pi$  coefficients. A tensile load was applied in each case to the sample by means of a beam balance. The potential drop across the electrodes was measured with a Leeds & Northrup Type K

potentiometer. A constant current was maintained through the crystal by including a current-limiting resistor in the external circuit, very large with respect to the sample resistance. The procedure was to load the crystal, observe the change in voltage,  $\Delta V$ , then unload the crystal and again observe  $\Delta V$ . An average of about ten determinations was made for each datum point. A load of 800 to 900 grams was applied, giving stresses of about  $2.5 \times 10^7$  dyne/cm<sup>2</sup>. Values of  $\Delta V/V$ , which are equal to  $\Delta R/R$  for a constant current, were of the order of  $10^{-4}$ , where  $R$  is the measured sample resistance. The piezoresistive effect in rutile was linear over the measured range and exhibited a reversal in sign with a change in the direction of stress. No hysteresis was observed.

#### CORRECTIONS

The quantity  $\Delta R/RT$  must be corrected for the stress-induced dimensional changes in order to obtain  $\Delta\rho/\rho T$ . This longitudinal and transverse dimensional change per unit stress may be expressed in terms of the elastic compliances.<sup>22</sup> The corrections for the seven configurations employed are presented in Table II. Values for the six elastic moduli of rutile from which these compliances were calculated are also listed. These moduli were measured by the authors and reported elsewhere.<sup>23</sup> The difference between the elastic moduli for oxidized and reduced rutile were determined to be negligible for purposes of computing the corrections to the  $\pi$  coefficients.

The transverse coefficients,  $\pi_{12}$ ,  $\pi_{13}$ , and  $\pi_{31}$ , have not been corrected for nonuniform current distribution at the electrodes.<sup>17</sup> The transverse electrodes were approximately 2 mm long and 2 mm wide.

#### ACCURACY OF MEASUREMENT

Considerable care was exercised to obtain samples which were uniform in oxygen deficiency throughout

TABLE II. A tabulation of the directions in which the current is measured and the stress is applied.

Piezoresistive coefficient	Crystal direction Current	Stress	Correction <sup>a</sup>	Magnitude of correction in $\text{cm}^2/\text{dyne}$
$\pi_{11}$	$[100]$	$[100]$	$-S_{11}+S_{12}+S_{13}$	$-1.6 \times 10^{-12}$
$\pi_{12}$	$[100]$	$[010]$	$S_{11}-S_{12}+S_{13}$	+1.4
$\pi_{31}$	$[001]$	$[100]$	$S_{11}+S_{12}-S_{13}$	+0.4
$\pi_{33}$	$[001]$	$[001]$	$-S_{33}+2S_{13}$	-0.5
$\pi_{13}$	$[100]$	$[001]$	$S_{33}$	+0.3
$\pi_{l[110]}$	$[110]$	$[110]$	$-S_{11[110]}+S_{12[110]}+S_{13[110]}$	-0.5
$\pi_{l[111]}$	$[111]$	$[111]$	$-S_{11[111]}+S_{12[111]}+S_{13[111]}$	-0.2

<sup>a</sup> Elastic moduli for rutile expressed in  $10^{12}$  dynes/cm<sup>2</sup> ( $C_{11}=2.8$ ,  $C_{33}=4.6$ ,  $C_{12}=1.8$ ,  $C_{13}=1.4$ ,  $C_{44}=1.3$ ,  $C_{66}=1.8$ ). Elastic compliances for rutile calculated from the above moduli expressed in  $10^{-12}$  cm<sup>2</sup>/dyne ( $S_{11}=0.9$ ,  $S_{33}=0.3$ ,  $S_{12}=-0.6$ ,  $S_{13}=-0.1$ ,  $S_{44}=0.8$ ,  $S_{66}=0.6$ ).  
G. Vick, L. Hollander, and A. Brown, Bull. Am. Phys. Soc. 4, 463 (1959).

<sup>22</sup> R. F. S. Hearmon, Suppl. Phil. Mag. 5, 323 (1956).

<sup>23</sup> Measurements were made by determining the velocity of 10-Mc/sec acoustic waves.

<sup>15</sup> Obtained from Linde Air Products.

<sup>16</sup> Detectable level in the order of 0.005%.

<sup>17</sup> C. S. Smith, Phys. Rev. 94, 1, 42 (1954).

<sup>18</sup> R. F. Potter, Phys. Rev. 108, 652 (1957).

<sup>19</sup> M. Pollack, Rev. Sci. Instr. 29, 42 (1954).

<sup>20</sup> A. J. Tuzzolino, Phys. Rev. 109, 1980 (1958).

<sup>21</sup> F. Burns and A. Fleischer, Phys. Rev. 107, 5, 1281 (1957).

TABLE III. Piezoresistive coefficients in partially reduced rutile. Both  $\pi$  and  $\rho$  were measured at indicated temperatures.<sup>a</sup>

Temp. °K	$\pi_{11}^b$	$\rho_a$	$\pi_{12}$	$\rho_a$	$\pi_{13}$	$\rho_a$	$\pi_{33}$	$\rho_c$	$\pi_{31}$	$\rho_c$	$\pi_{l[110]}$	$\rho_{[110]}$	$\pi_{l[111]}$	$\rho_{[111]}$
295	(d) 10.2	0.28	(d) 12	0.28	(g) -2.5	0.4	(g) 0.7	0.17	...	...	(g) 9.4	0.5	(r) 5.8	0.3
295	(b) 4.7	1.3	(b) 13	1.3	(f) -0.7	...	(f) 3.9	0.46	(b) 3.1	...	(i) 6.8	2	(m) 4.7	1.1
295	(n) 4.2	2.2	...	...	...	...	...	...	(b) 5.2	...	...	...	(l) 4.6	1.5
295	(a) 3.1	45.7	(a) 7	45.7	(h) 3.7	40	(h) 7.9	65	(a) 5.2	48	(k) 4.9	42	(s) 2.4	81
295	(c) 0.6	930	...	...	...	...	...	...	...	...	(j) 5.2	563	...	...
77	(b) 13.0	0.5	(b) 14	0.5	(o) -12	...	...	...	(b) 11	...	(i) 24	0.56	(l) 19	0.64
77	...	...	...	...	...	...	...	...	...	...	...	...	(m) 20	0.54
380	(b) 4.0	1.2	(b) 10	1.2	...	...	(f) 5	0.5	(b) 3	...	(i) 5	1.4	(t) 2	...
380	...	...	...	...	...	...	...	...	...	...	(k) 4.5	40	...	...
380	(c) 1.4	420	...	...	...	...	...	...	...	...	(j) 4	390	...	...

<sup>a</sup> Alphabetical indicators denote a series of measurements on a specific sample at a specific state of reduction.<sup>b</sup>  $\pi$  coefficients have been divided by resistivity and are reported as  $\Delta\rho/\rho T$  in units of cm<sup>2</sup>/dyne.

their volume. All samples were left in an inert atmosphere at a temperature slightly above the reaction temperature for some time after the crystal was oxidized or reduced. Some of these samples were cut, polished, and visually inspected to assure uniformity.

The effect of misalignment of the clamps, resulting in nonuniform stress distribution, was minimized by clamping to the soft indium soldered to the crystal. The markedly anisotropic resistivity exhibited by rutile makes correlation between the coefficients at various oxygen deficiency levels difficult. The resistivity values associated with  $\pi_{13}$  and  $\pi_{31}$  are only approximations, since no four-contact measurements were made along the pertinent crystal axes of the specific samples. However, the resistivity,  $\rho_{11}$ , associated with the  $\pi_{12}$  coefficient, was measured by the four-contact method. The longitudinal resistivity values were all determined by the four-contact method and are believed to be within  $\pm 5\%$ .

Measurements performed at 77°K and 380°K were, in general, subject to a greater limit of error than the room-temperature-values, due to increased drift, noise, and difficulty in measurement.

The total estimated error of the room-temperature longitudinal piezoresistive coefficients is of the order of  $\pm 1 \times 10^{-12}$  cm<sup>2</sup>/dyne. Since no four-contact measurements were made for the transverse coefficients, it is difficult to assign a confidence level for these values. Strain at the contact, contact resistance, and non-uniform current distribution at the contact must all be considered. To evaluate the magnitude of these effects, the hydrostatic coefficient was determined in both the "c" and the "a" crystal directions. These values indicate that the corrected transverse coefficients should in general be larger than those reported in Table III. These corrections should not exceed  $10^{-11}$  cm<sup>2</sup>/dyne.

### EXPERIMENTAL RESULTS

The longitudinal piezoresistive coefficients along the "a" axis,  $\pi_{11}$ , and along the "c" axis,  $\pi_{33}$ , are presented in Figs. 1 and 2, respectively, as a function of the appropriate resistivity at room temperature. These figures show that, as the density of oxygen vacancies is

decreased (that is, as resistivity is increased), the piezoresistive coefficient in the "a" direction,  $\pi_{11}$ , diminishes, while the coefficient along the "c" direction,  $\pi_{33}$ , becomes larger. Measurements at 77° and 380° K indicate that  $\pi_{11}$  is approximately proportional to the reciprocal of the absolute temperature, whereas this effect was not noted for  $\pi_{33}$ . The transverse coefficients involving the "c" axis,  $\pi_{13}$  and  $\pi_{31}$ , are small, while the  $\pi_{12}$  coefficient is considerably larger. All the measured piezoresistive coefficients are summarized in Table III.

Longitudinal measurements of  $\Delta R/RT$  were made on samples oriented in the [110] and the [111] crystal directions. These values are included in Table III. The shear coefficients may be obtained from these by the following relations

$$\pi_{l[110]} = \frac{1}{2}(\pi_{11} + \pi_{12} + \pi_{66})$$

and

$$\pi_{l[111]} = (l_1^4 + m_1^4)\pi_{11} + n_1^4\pi_{33} + 2l_1^2m_1^2(\pi_{12} + \pi_{66}) + (m_1^2n_1^2 + l_1^2n_1^2)(\pi_{13} + \pi_{31} + 2\pi_{44}).$$

The direction cosines for the [111] direction in Rutile are, in the notation of Mason and Thurston<sup>14</sup>:

$$l_1 = m_1 = 0.62, \quad n_1 = -0.48.$$

In order to select the correct values of the piezoresistive coefficients to insert into these equations, it is necessary

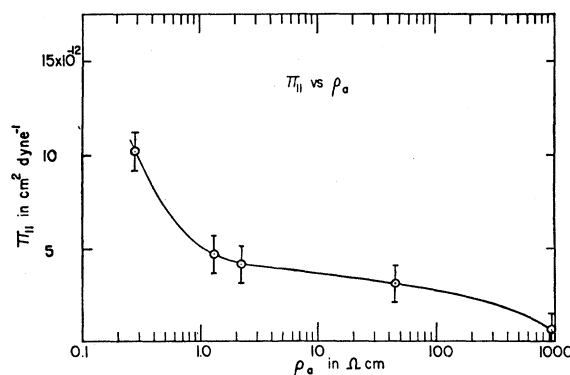


FIG. 1. Room-temperature longitudinal piezoresistivity along the "a" axis,  $\pi_{11}$ , as a function of resistivity.

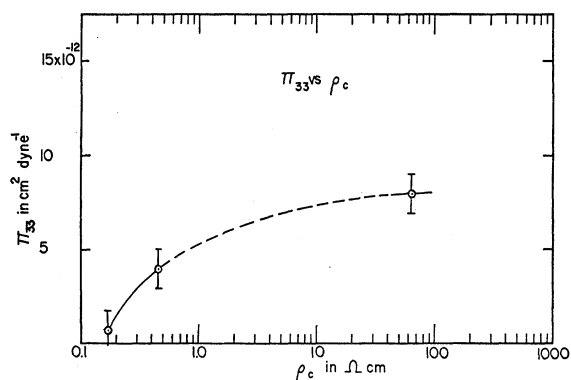


FIG. 2. Room-temperature longitudinal piezoresistivity along the "c" axis,  $\pi_{33}$ , as a function of resistivity.

to know, in considerable detail, the degree of anisotropy of resistivity as a function of oxygen deficiency. There are at present no such resistivity data available. The selection of reasonable resistivity values indicates that the shear coefficients do not differ greatly in magnitude from the values of the longitudinal and transverse coefficients.

Measurements of the hydrostatic coefficients were made at pressures up to 200 atmospheres. In the "c" direction,

$$\pi_{H[001]} = \pi_{33} + 2\pi_{31},$$

and was determined to be  $+(18 \pm 3) \times 10^{-12}$  cm<sup>2</sup>/dyne for a resistivity,  $\rho_c$ , equal to 0.17 ohm cm. In the "a" direction,

$$\pi_{H[100]} = \pi_{11} + \pi_{12} + \pi_{13},$$

and was determined to be  $+(32 \pm 5) \times 10^{-12}$  cm<sup>2</sup>/dyne for a resistivity,  $\rho_a$ , equal to 0.28 ohm cm. Both measurements were made by the four-contact method.

### DISCUSSION

The observed longitudinal piezoresistive measurement in rutile seems in reasonable agreement with a simple impurity band conduction model. The lack of good data on the dielectric constant, and the anisotropy of resistivity in partially reduced rutile, greatly inhibits a careful analysis of the piezoresistive effect. Assuming the dielectric constant is not significantly altered in reduced material, and considering the longitudinal  $\pi$  coefficients along the "c" axis of rutile, Fig. 2, where  $k_c=173$ , there appears to be considerable orbital

overlap even in 1000 ohm cm material, giving rise to a positive piezoresistive coefficient which diminishes with increasing oxygen vacancy density. Along the "a" axis, where  $k_a=89$ , the orbital overlap seems weak in the high resistivity range and only becomes significant in the fully-reduced samples. The positive sign of the transverse coefficients is difficult to explain with this simple orbital concept.

Another explanation for the observed piezoresistive effect in rutile could be based on the migration of defects in the lattice. This migration would be characterized by a relaxation time which should be long compared with that for the electronic process, and should therefore be experimentally observable.

### CONCLUSIONS

The piezoresistive effect in rutile has been studied in the resistivity range from  $10^{-1}$  to  $10^3$  ohm cm. The results indicate that there is a strong overlapping of the impurity wave functions in the "c" direction and very little in the "a" direction. More detailed information of the dielectric properties and the resistivity-temperature dependence of partially reduced rutile is necessary for a better understanding of this conduction process. The fourth-rank piezoresistive tensor has been analyzed for a  $D_{4h}$  symmetry with anisotropic resistivity. It appears that considerable information could be obtained from a study of piezoresistivity in the oxide semiconductors, and in other materials where the conduction process is characterized by low carrier mobility. Also, piezoresistivity studies at very low temperatures may yield valuable information on impurity band conduction mechanisms in the higher mobility semiconductor materials.

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