# Behavior of Oxygen in Plastically Deformed Silicon\*

S. LEDERHANDLER<sup>†</sup> AND J. R. PATEL

Research Division, Raytheon Manufacturing Company, Waltham, Massachusetts

(Received July 10, 1957)

The density of dislocations in silicon crystals is shown to have a marked effect on the annealing of the  $9 \mu$  infrared absorption band at 1000°C. (This absorption band had previously been shown to be due to oxygen and to be dependent on the amount of oxygen present.) The annealing behavior has been studied in crystals grown from quartz crucibles and in samples where dislocations have been introduced by plastic bending. For a deformed sample with a dislocation density of  $10^7/\text{cm}^2$ , the amplitude of the 9- $\mu$  band is reduced appreciably in 15 minutes at 1000°C, while the undeformed sample with a dislocation density of 10<sup>4</sup>/cm<sup>2</sup> requires about 12 hours. Preliminary light-scattering experiments in deformed and annealed samples show a definite anisotropy of the scattered intensity when the light vector is perpendicular or parallel to the dislocation lines.

#### INTRODUCTION

T has now been generally established<sup>1,2</sup> that oxygen is present in concentrations up to 10<sup>18</sup>/cm<sup>3</sup> in silicon crystals grown from quartz crucibles. The absorption band in the infrared spectrum of silicon which appears at 9  $\mu$  has been shown to be due to oxygen<sup>1,3</sup> and to be dependent on the amount of oxygen present.<sup>1</sup> By suitable heat treatment, at 1000°C, the amplitude of the 9- $\mu$  band can be decreased to a minimum value.<sup>4,5</sup> It has been shown that on subsequent heat treatment at 1300°C, the original amplitude of the band can be very nearly regained. Furthermore, this heat-treatment cycle may be continued with no apparent loss of oxygen from the crystal.<sup>4,6</sup> At the lower temperature of heat treatment, 1000°C, marked discrepancies in the time necessary to decrease the 9- $\mu$  band to its minimum value were observed. For example, in one of the crystals examined, the amplitude was reduced to its minimum value in about 10 hr, while for another crystal grown in apparently the same manner, annealing times up to 48 hr were insufficient. It was suspected that the annealing process, which probably involves the movement of oxygen from sites that are optically active at a wavelength of  $9 \mu$  to those that are inactive, might be structure-sensitive, and dependent on the imperfections present in the crystal. Inasmuch as the crystals all contained approximately the same detectable impurity concentration  $(5 \times 10^{14} / \text{cm}^3)$ , it was postulated that the different dislocation densities introduced in these crystals during growth may have a strong effect on the rate of annealing. Accordingly, the present experiments were undertaken with a view to studying the heat-treatment behavior of samples in which dislocations were deliberately introduced by plastic deformation.

### **Experimental Procedure**

Dislocations may be introduced into single crystals of silicon in a controlled manner by plastic bending at elevated temperatures. Single-crystal samples,  $5 \times 0.8$  $\times 0.3$  cm, were bent by a pure couple at the ends about the [211] axis. The orientation of the longitudinal axis of the single crystal was such that slip occurred primarily on the (111) plane. The samples were heated to approximately 950°C by passing a current through them and held at that temperature for approximately 90 seconds during deformation. The current was then switched off and the samples allowed to cool by radiation. Specimens were cut from the deformed sections for the absorption measurements. The densities of dislocations introduced by bending were obtained by a direct count of etch-pit densities on the (211) face.<sup>7</sup>

Infrared absorption measurements were made with a single-beam double-pass Perkin-Elmer spectrometer modified to accommodate a sample at the exit slit to minimize defocusing effects. The samples were heat treated in quartz tubes that had been evacuated prior to filling with helium. The short-time heat treatments were performed in a suitably programmed furnace with a thermocouple near the samples to record the temperature continuously. The samples attained their annealing temperature in times that were short compared to the annealing time.

## Annealing of Undeformed Single Crystals at 1000°C

Silicon crystals grown from quartz crucibles have been examined for a variety of growth conditions.<sup>4</sup> Under ordinary conditions of growth with rotation, the crystals exhibit a large absorption band at  $9\,\mu$ . The measured average value of the absorption coefficient  $\alpha$  is about

<sup>\*</sup> Supported in part by The Bureau of Ships.

<sup>†</sup> Now with Radio Corporation of America, Semiconductor Division, Somerville, New Jersey.

<sup>&</sup>lt;sup>1</sup> Kaiser, Keck, and Lange, Phys. Rev. **101**, 1264 (1956). <sup>2</sup> H. A. Papazian and S. P. Wolsky, J. Appl. Phys. **27**, 1561

<sup>(1956).</sup> 

<sup>&</sup>lt;sup>3</sup> H. J. Hrostwosky and R. H. Kaiser, Bull. Am. Phys. Soc. Ser. II, 1, 295 (1956).

<sup>&</sup>lt;sup>4</sup> S. Lederhandler, Bull. Am. Phys. Soc. Ser. II, 1, 381 (1956).
<sup>4</sup> S. Lederhandler, Bull. Am. Phys. Soc. Ser. II, 1, 381 (1956).
<sup>5</sup> W. Kaiser, Phys. Rev. 105, 1751 (1957).
<sup>6</sup> In a previous unpublished report by S. Lederhandler and H. Statz (referred to in reference 3) it is shown that an absorption band at  $19.5 \mu$  behaves, on heat treatment, in a manner similar to the 9- $\mu$  band.

<sup>&</sup>lt;sup>7</sup> J. R. Patel (to be published).



FIG. 1. Annealing of the  $9-\mu$  absorption band at 1000°C for silicon crystals grown from quartz crucibles.

5.6 cm<sup>-1</sup>. Since  $\alpha$  is related to the extinction coefficient by the relationship  $\alpha = 4\pi k/\lambda$ , where  $\lambda$  is the wavelength and k is the average value of the extinction coefficient, we find that k is  $4 \times 10^{-4}$ . On heat treatment at 900– 1100°C for periods up to 48 hours, the extinction coefficient usually decreases to a minimum value. For heat treatment at 1000°C, the minimum value of k appears to be about  $1.0 \times 10^{-4}$ . Absorption due to free carriers was not an important consideration in samples heat treated at 1000°C. The initial carrier concentration was approximately  $5 \times 10^{14}/\text{cm}^3$  and remained essentially unchanged after prolonged annealing at 1000°C.<sup>4</sup>

The decrease in the amplitude of the 9- $\mu$  band as a function of heating time at 1000°C has been investigated for a large number of samples from different crystals. Differences in the annealing rates of crystals grown under apparently identical conditions were observed. The time dependence of annealing at 1000°C of samples from 3 different crystals is shown in Fig. 1, where the extinction coefficients at time t=0 have been normalized to  $k = 3.5 \times 10^{-4}$ . The marked difference in the rate of anneal of crystals A and B is evident. After 10 hours at 1000°C, the extinction coefficient, k, of crystal B has reached its minimum value while k of crystal A is not very different from its initial value. Crystal C is intermediate between A and B. This difference in annealing behavior cannot be due to any detectable impurity effect since electrical measurements show that crystals A, B, and C had approximately the same concentration of carriers.

## Annealing Behavior of Deformed Silicon at 1000°C

The annealing behavior of heavily deformed and lightly deformed single crystals, as determined from

TABLE I. Treatment of specimens before annealing at 1000°C.

Specimen	Time at $T = 950^{\circ}$ C	Deformation	Etch pit counts (average)
C-1	90 sec	Light	3×10 <sup>6</sup> /cm <sup>2</sup>
C-2	90 sec	None	$2 \times 10^4$ /cm <sup>2</sup>
C-3	90 sec	Heavy	$2 \times 10^{7} / \text{cm}^{2}$
C-4	0 sec	None	$2 \times 10^{4}$ /cm <sup>2</sup>

changes in the  $9-\mu$  absorption band, was compared with the behavior of control samples cut from adjacent sections of the same crystal. The specimens used are identified in Table I, and the treatment accorded them before annealing at 1000°C is specified.

The density of dislocations, as stated before, was obtained by suitably etching the sample and counting the etch pits on the (211) face. It has been shown that these pits are due to edge dislocations.<sup>7</sup> Average densities only are quoted in Table I, since the densities in the bent samples varied from a maximum at the specimen edge to a minimum at the neutral axis of the specimen. In Fig. 2, the amplitude of the 9- $\mu$  band for the samples in Table I is plotted as a function of annealing time at 1000°C. The curves have been normalized at t=0 for  $k=3.5\times10^{-4}$ . The plot shows very clearly the differences in annealing behavior of samples with varying dislocation densities. The heavily deformed sample C-3 has reached its equilibrium value



FIG. 2. Extinction coefficient as a function of annealing time at 1000°C for plastically deformed silicon.

in about 3 hours, compared to the lightly deformed sample C-1 which takes about 6 hours and the control C-2 which requires about 48 hours.

### DISCUSSION

The results of the previous section show that the rate of annealing of the 9- $\mu$  band in silicon depends in a very sensitive fashion on the dislocation density of the material. The magnitude of this effect is evident from Fig. 2. For specimen C-3 with a dislocation density of  $10^{7}$ /cm<sup>2</sup>, the band has practically decreased to its minimum value after 15 minutes at 1000°C. The rate of annealing does decrease rapidly as the dislocation density decreases; however, the annealing effect will still be significant in crystals grown from the melt, where the dislocation density is high ( $10^{4}-10^{5}$ /cm<sup>2</sup>). Since the density of dislocations in crystals which have been grown under apparently identical conditions is seldom the same, the variability of the observed annealing behavior for the three different crystals is probably due in large measure to these differences in dislocation density. From the present data, it is not possible to draw any definite conclusions as to the actual mechanism of the annealing process. However, some general conclusions on the behavior of oxygen in crystals pulled from quartz crucibles may be drawn. Comparison with floating-zone crystals shows that oxygen must enter silicon from the silica crucibles used in growing crystals from the melt.<sup>1</sup> At temperatures close to the melting point,  $1300^{\circ}-1350^{\circ}$ C, the 9- $\mu$ absorption band is high<sup>4,5</sup> and does not decrease with prolonged heating, as it does at lower temperatures. It is reasonable, therefore, to assume that oxygen enters the crystal from the melt and is frozen into positions where it is optically active. Some annealing of the  $9-\mu$ band must take place as the crystal is cooled through the temperature at which the band decreases. Usually, however, for normal rates of growth and low dislocation densities, the crystal is never at these temperatures long enough for appreciable annealing to occur. If the samples are now held at 1000°C, the oxygen apparently prefers to be in optically inactive sites, as evidenced by the decrease in the 9- $\mu$  absorption band.

It appears that the role of dislocations is to aid the annealing processes by offering favorable sites at which oxygen can precipitate. In this connection, it may be pointed out that the dislocation density varies quite markedly across the cross section of silicon crystals. Therefore, the observed variation in the 9- $\mu$  band along the cross section of the crystal<sup>8</sup> may actually be due to some annealing of the band as the crystal is cooled during growth. The densities of dislocations, as shown by etch pits, may vary from  $10^2/\text{cm}^2$  at the center of the crystal to  $10^4/\text{cm}^2$  at the outer edge. Hence, the amplitude of the 9- $\mu$  band in crystals grown from the melt does not provide an unambiguous criterion for the oxygen content of the crystal.

Further evidence that dislocations play an important role in the annealing process is provided by some preliminary experiments on the angular dependence of scattered light by deformed crystals. It has previously been reported<sup>9</sup> that small inhomogeneities are present in silicon crystals grown from the melt and that the size of these inhomogeneities changes on heat treating at 1000°C. Preliminary light-scattering measurements on control and deformed samples after heating for 12 hr at 1000°C show that in the undeformed sample the scattered intensity is independent of sample orientation. For the heavily deformed sample with the light beam polarized first parallel and then perpendicular to the dislocation lines, a marked difference in the magnitude as well as the angular dependence of scattered intensity



FIG. 3. Etch pits on (211) face of silicon deformed by plastic bending, after annealing for 12 hours at 1000°C

was observed. The data were consistent with the scattering expected from inhomogeneities with the long dimension parallel to the dislocation lines.<sup>10</sup> Evidently, some changes occur during annealing since the anisotropy of scattering is not marked in deformed samples before heat treatment. All aspects of this problem are not clear yet and further work along these lines is being continued.

Attempts to observe oxygen precipitates along dislocation lines in silicon using an infrared microscope were unsuccessful. However, with the copper precipitation technique of Dash,<sup>11</sup> it has been shown that the dislocation lines in the deformed samples are generally oriented in one direction, as expected from the geometry of slip.<sup>7</sup> Furthermore, the copper precipitates themselves lie with their long dimension along the dislocation line. This appears to be consistent with the preliminary data of light-scattering experiments on deformed and annealed crystals.

As seen in Fig. 2, the control samples exhibit a curious behavior in the initial stages of heat treatment at 1000°C. It is noticed that for both the heated and unheated controls the extinction coefficient first increases and subsequently decreases for heating times less than 1 hour at 1000°C. It is difficult to understand why this should occur, since at 1000°C oxygen evidently prefers to be in optically inactive sites, as shown after heating for long times at 1000°C. The initial rise may be due to the arrangement of oxygen prior to precipitation. Further experiments are necessary to clarify this initial behavior of the  $9-\mu$  band.

Heating at 1000°C did not appear to result in any appreciable annealing of the dislocation configuration introduced during bending. Figure 3 shows a photomicrograph of etch pits on the (211) face of the heavily

<sup>&</sup>lt;sup>8</sup> W. Kaiser and P. H. Keck, J. Appl. Phys. 28, 882 (1957).

<sup>&</sup>lt;sup>9</sup> P. P. Debye and S. Lederhandler, Bull. Am. Phys. Soc. Ser. II, **2**, 66 (1957).

 <sup>&</sup>lt;sup>10</sup> O. Guentert (private communication).
 <sup>11</sup> W. C. Dash, J. Appl. Phys. 27, 1193 (1956).

deformed sample C-3 after annealing for 12 hours at 1000°C. The etch pits where the dislocation lines intersect the surface are still lined up predominantly on the primary slip planes. It has been shown elsewhere<sup>7</sup> that prolonged heating at 1300°C is necessary before any appreciable annealing of the dislocations is observed.

#### ACKNOWLEDGMENTS

The authors wish to thank E. Barton and J. Beauchemin for their assistance with the measurements. They are particularly grateful to various members of the Research staff for stimulating discussions of the results.

PHYSICAL REVIEW

#### VOLUME 108, NUMBER 2

OCTOBER 15, 1957

# Domain Conversion of Multidomain Barium-Titanate Single Crystals\*

P. H. FANG, S. MARZULLO, AND W. S. BROWER National Bureau of Standards, Washington, D. C. (Received July 19, 1957)

It is found that complete domain conversion of single crystal BaTiO<sub>3</sub> can be achieved by passing the crystal through the orthorhombic-tetragonal transition under an applied dc field. By using this process either complete a or c domain crystals can be prepared.

IRGIN BaTiO<sub>3</sub> single crystals grown by Remeika's method<sup>1</sup> usually are multidomain, i.e., several a and c domains occur in the same crystal. The method of converting these crystals into single c domain form (similar to the piezoelectric poling process) has been used often in ferroelectric studies. On the other hand, methods for converting multidomain crystals into a domain form are not known and measurements of a domain characteristics have been confined to crystals of small size. In this note, a method of converting multidomain single crystals into completely a domain form will be given.

In the usual method for c domain conversion, the multidomain crystal is first etched briefly in hot phosphoric acid at about 140°C (i.e., well above the Curie temperature of BaTiO<sub>3</sub>), and then the crystal is cleaned by water and immersed in glycerol between two plate electrodes. After the system is heated above the 120°C transition temperature, a dc voltage is applied and maintained while the temperature is brought down below the Curie point. Subsequently, the applied field is removed, and the resulting crystal in most cases is completely c domain.

In this study it has been found that domain conversion can also be accomplished if, instead of being heated above the 120° transition temperature, the crystal is cooled below 0°C and the temperature permitted to rise through the orthorhombic-tetragonal transition point. Furthermore, depending on the liquid medium used, either a complete c or a domain can be obtained. The resulting domains are identified by use of the polarizing microscope.

Table I lists three types of liquids and their dielectric

constants. Using the liquids in the first column, completely c domain crystals are obtained. The liquids in the second column result in completely a domain crystals. With the liquids in the third column, the domains are sometimes changed but remain mixed.

Inspection of this table shows a correlation between the dielectric constants of the liquids used and the type of domain conversion achieved. Using plate electrodes, complete c domain conversion is achieved with liquids of large dielectric constant (about 40), and a domain conversion with liquids of small dielectric constant (less than 10). Using liquids of intermediate dielectric constant (around 20) results in mixed domains.

No correlation was found between the chemical nature or the electrical conductivity of these liquids and the domain conversion.

It seems that the influence of the dielectric constant of the liquid medium on the domain conversion can be explained by the effect of the direction of the displacement vector D in the BaTiO<sub>3</sub> crystal due to the applied field. Denote by r the ratio of the dielectric constant of  $BaTiO_3$  to that of the liquid. For a small angle of D in the liquid medium with respect to the normal to the crystal surface, when r is small, then by the law of refraction, the direction of D in the crystal will be practically parallel to that of the c axis, and the converted crystal will become c domain. On the other hand, if r is very large, a large deviation of the direction of Din the crystal from the c axis will result; in the extreme case, a completely *a* domain crystal will be obtained.

The above consideration is confirmed by the following experiment: instead of using plate electrodes, if point electrodes are used, a large deviation of D in the liquid medium can be obtained such that the deviation with respect to the normal in the crystal is also very large in spite of a small r. In this case a completely a domain

<sup>\*</sup> Research supported by the U. S. Atomic Energy Commission. <sup>1</sup> J. P. Remeika, J. Am. Chem. Soc. **76**, 940 (1954).



FIG. 3. Etch pits on (211) face of silicon deformed by plastic bending, after annealing for 12 hours at 1000°C.