An unusual absorption “band” with a giant half-width has been detected in the infrared absorption spectra of silicon obtained by zone melting and subjected to cyclic heat treatment at 1250 °C with rapid cooling after each anneal and with partial removal of the thermal oxide in each cycle. A model explaining the observed features of the spectrum in terms of the transformation, occurring during heat treatment of impurity nanoprecipitates contained in the initial silicon and in terms of the microblock structure of the material is proposed. © 1997 American Institute of Physics.

The technological process of fabricating silicon semiconductor devices ordinarily includes a series of high-temperature heat treatments (HT) with partial removal of the thermal oxide after each treatment. To model this process approximately and to study the effect of such HTs on internal oxidation and other processes in silicon, which are important for device quality, the following experiment was performed. Plane-parallel plates, each about 1 mm thick and several centimeters long, were cut in the axial direction from the 26-mm-diameter silicon ingot obtained by zone melting. Each plate was polished on both sides using the factory technology. Two plates were annealed for 4 h in an oxygen stream at 1250 °C. Next, a boat with one of the plates was removed as quickly as possible from the furnace into air, and the second plate was cooled together with the furnace. Oxide was removed from part of the surface on both sides of each plate and an infrared (IR) transmission spectrum of the transmission in the range 2–25 μm was recorded in this section. The transmission was measured using a comparison sample, consisting of an unannealed plate of the same thickness from the same ingot. The absorption coefficient α(λ) was calculated from the transmission for each wavelength λ. Next, the annealing was repeated, but the oxide was removed from a larger area of the surface than the first time, after which the transmission spectra were recorded in the same sections of the plates as after the first anneal and in the newly exposed sections. These operations were repeated. Figure 1 illustrates the topography of the sample surface and the sequence of operations.

An unusual absorption band was observed in the spectra of all sections (zones I–VI in Fig. 1) of a plate which was quenched after each anneal (Fig. 2). The band is so wide that without a substantial compression of the λ scale it could be completely missed. A peak near 9 μm due to interstitial oxygen is seen against the background of this band. It was found that as silicon is gradually removed from the surface of the sample, the intensity of this peak decreases, i.e., the oxygen responsible for the peak is concentrated in the surface regions of the plates. In the process of annealing, oxygen penetrates into the sample from the surrounding atmosphere and diffuses into the volume of the silicon. The diffusion coefficient (D) in the near-surface layer containing an elevated (relative to the volume of the sample) amount of interstitial oxygen after heat treatment was estimated to be 1.1×10⁻⁹ cm²/s, which agrees well with the value 0.9×10⁻⁹ cm²/s obtained from the temperature dependence of D presented in...
Ref. 1. This is apparently the most accurate dependence, since in Ref. 1 agreement between the data obtained by different authors was also achieved in different temperature intervals with $D$ varying over eleven orders of magnitude.

The absorption band with a giant half-width is a volume effect. The absolute absorption at the maximum apparently depends primarily on the postanneal cooling rate and increases with this rate. No appreciable variation of the intensity of this absorption as a function of the number of anneals is observed — for curves 3 and 4 in Fig. 2, except for the maximum of the peak near 9 $\mu$m, the experimental points obtained in the first six anneals are essentially indistinguishable. The differences in the curves 3 and 6, which refer to the same zone but with different anneals, are most likely due to an intermediate anneal with slow cooling and (or) higher quench rate after the eighth anneal. The observed effect is easily reversible. For example, after the seventh anneal, which is accompanied by slow cooling (the first six anneals were accompanied by quenching), the intensity of the band decreases almost to zero (curve 2), but the next anneal with quenching restores the magnitude of this absorption (curve 6).

As one can see from Fig. 2, the shape of the band and the position of the maximum are different in different zones of the working plate which has undergone quenching. For example, as the light probe is moved along the axis of the ingot (from zone I to zone VI), the band transforms into a superposition of strongly overlapping components (curves 3–5). This change in the shape of the band is especially clearly seen after an intermediate anneal with slow cooling. In this case, as a result of the next anneal with quenching, two maxima appear in the spectrum from the section of the plate (zone I) where one maximum was observed after the first six anneals with quenching (compare curves 3 and 6). In the spectrum where such a splitting is most clearly observed, these maxima lie near 8 and 12 $\mu$m.

All observations presented above, taken collectively, suggest that the appearance of an absorption band with a giant half-width in the IR spectrum is most likely due to the presence of nanoprecipitates of silicon oxide and carbide (or, possibly, nitride), which are optically inactive before heat treatment, in the initial silicon and (or) their transformation during treatment. We are not dealing here with the precipitation of particles of a second phase, as often is the case with silicon during heat treatment — in that case the absorption bands have a much smaller half-width than the band studied here. Moreover, such formations in silicon have a tendency to dissipate at temperatures of the order of 1250 °C and higher. The situation at hand most likely concerns weakly ordered and very small clusters of Si–O and Si–C (or Si–N) bonds with an unusually wide variance in the bond angles and, possibly, bond lengths. Only in this case could the superposition of a set of narrower bands with maxima in a wide range of $\lambda$, which correspond to different variants of the incorporation of these bonds into the silicon matrix, give a result similar to the observed effect. X-Ray diffractionmetry of the silicon investigated apparently supports this assumption. The rocking curve for this material was found to be broadened compared with the standard curve for the silicon employed in semiconductor technology, suggesting a possible microblock structure in the experimental material. In this case the interval of $\lambda$ where the absorption peaks of built-in impurity formations are distributed can indeed be very wide. If the assumptions made above are correct, then the ease with which the band with the giant half-width, which accompanies the alternation of anneals with fast and slow cooling (Fig. 2, curves 2 and 6), appears and disappears, could indicate that these formations are extremely small. Unfortunately, I have no information about the origin and past history of the plates employed in the experiments; such information undoubtedly would be helpful for the present discussion.

The fact that one of the maxima lies near 8 $\mu$m makes it possible to attribute the shorter wavelength component of the band to absorption on Si–O bonds. The absorption band with a maximum at 1230 $\text{cm}^{-1}$, which is most often observed in the spectra of silicon after heat treatment and is due to SiO$_2$ precipitates, lies in this region (see, for example, Ref. 2). It should be noted that in studying the state of oxygen in silicon with different heat treatments, the base of the interstitial oxygen peak at 9 $\mu$m in many spectra contains additional absorption extending over a long distance on both sides in $\lambda$ (see, for example, Ref. 3). This additional absorption has not yet been explained. It has not been ruled out that it could be due to processes which are similar to those which led in our investigations to the appearance of an absorption band with a giant half-width.

The longer wavelength component with a maximum near 12 $\mu$m is very likely due to clusters of Si–C bonds.¹ The change in the ratio of these components in the spectra from different zones of a quenched plate could then reflect a difference in the content and (or) state of O and C in different parts of the ingot. The increase in the long-wavelength component after an intermediate anneal with slow cooling could be due to the formation of nuclei, in the process of such cooling, for more intense subsequent formation of clusters of Si–C bonds, which are observed after annealing with quenching. The simultaneous formation of Si–O and Si–C clusters is apparently associated with a compensation of internal mechanical stresses in the sample. The incorporation of clusters of Si–O bonds in silicon produces compressive stresses in the crystal, and the simultaneous incorporation of Si–C bonds should decrease these stresses and the internal energy of the system. Processes of this kind have been observed, for example, to accompany the implantation of oxygen ions in silicon plates.² Clusters of Si–N bonds can also serve, in principle, for compensating the mechanical stresses due to Si–O bonds, especially since the absorption maximum on the stretching vibrations of Si–N bonds in silicon nitride also lies near 12 $\mu$m. Although the nitrogen content in ordinary commercial silicon is much lower than the oxygen and carbon content (see, for example, Ref. 6), the lack of information about the initial material does not allow us to rule out this possibility completely.