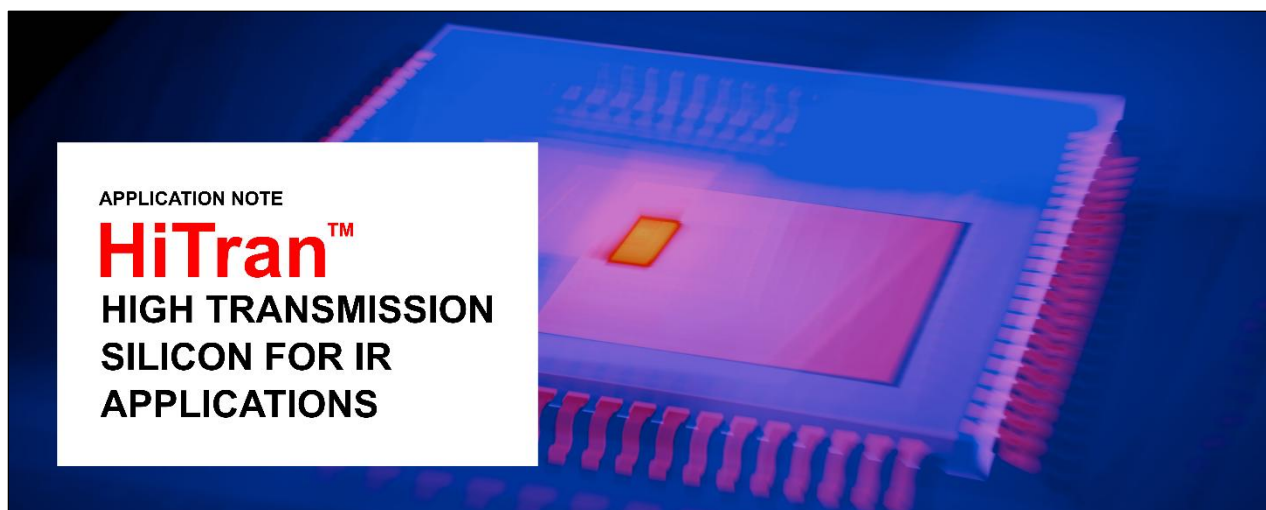


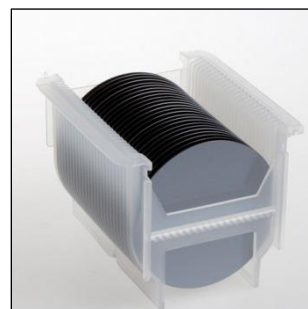


Infrared optical systems require materials that have very good transmission characteristics for infrared wavelengths as well as very good mechanical and thermal properties. Most of the applications for infrared materials involve harsh environmental impact on the material itself such as high/low temperatures and high pressures.

Many different choices in terms of material are possible for infrared systems. Most of them are specialised products that offer high transmission in certain windows of the infrared spectrum. The most important window is the 8-12 μm region (LWIR) that is used for thermal imaging systems around room temperature. Also, the LWIR region and the 3-5 μm region (MWIR) are the most commonly used windows for infrared detection because the atmosphere itself has high transmittance at these wavelengths.

Synthetic materials such as ZnS or ZnSe offer very high transmission in the LWIR region due to the very low index of refraction of these two materials. The increased transmission properties come at the expense of much higher cost and poor mechanical and poor environmental performance. Germanium is an alternative to ZnS and ZnSe in the LWIR window offering very high stability and low cost, but at the expense of transmission properties. The poor transmission properties originate from the high index of refraction limiting the transmission of uncoated samples to a maximum of 46%.

High Transmission (HiTran™) silicon has unique transmission performance across most of the infrared band including the far infrared region. The purity of HiTran™ silicon eliminates all extrinsic impurity related absorption over the entire infrared band. Intrinsic lattice vibrations in silicon reduce the transmission of infrared light of thick HiTran™ silicon in the extended LWIR wavelength band from 7-16 μm but in many cases HiTran™ silicon can replace the other infrared materials in this region.



Typical infrared applications that benefit from using HiTran™ silicon are

- Thermal Imaging Systems including Multicolour Infrared Systems
- Silicon Prisms, Gratings, Grisms, Lenses and Blanks
- Silicon Fresnel Lenses
- Passive Infrared Detector Filters
- Transmission windows for debris protection
- Micromachined infrared devices
- Silicon micro bolometers

This application note presents the properties of HiTran™ silicon. Emphasis is put on the transmission characteristics of HiTran™ silicon across the infrared band but also the mechanical and thermal characteristics of HiTran™ silicon will be covered.

Silicon technology is perhaps the most mature of all the solid state material technologies with the matureness being demonstrated for monocrystalline silicon over half a century. Since then, further refinement and development of the monocrystalline silicon by the floating zone technique has enabled unprecedented purity of the material approaching a 10N (99.99....%) status. Remaining impurity levels for nitrogen, oxygen and carbon are so low that they have no influence on the electronic and optical properties that determine the transparency/opaqueness of the material.

No pure conductor provides transmission in the infrared band because of electronic absorption (from overlapping valence and conduction bands) and free carrier absorption. In semiconductor materials where there is a bandgap between the full valence band(s) and the empty conduction band, the value of the bandgap determines the usefulness of the material as a transmission material in the infrared band. For photonic energies larger than the bandgap intrinsic electronic absorption is dominating the absorption coefficient. This is the case for pure semiconductor materials. For less pure semiconductor materials that have electronic states in the bandgap, extrinsic electronic absorption will be dominating the absorption coefficient. Free carrier absorption is dependent on the resistivity of the semiconductor material. Germanium has a maximum resistivity just above 50 Ωcm , whereas silicon has a maximum resistivity of around 100.000 Ωcm . Free carrier absorption is thus more dominant in germanium than in silicon and onset is at a much lower wavelength for germanium ($\sim 5\text{-}10\text{ }\mu\text{m}$). Manufacturingwise this puts an extra expense on the making of germanium because relatively small variations in the resistivity can cause big differences in the transmission characteristics in the infrared bands of interest.

Electronic absorption and free carrier absorption is highly dependent on the total number of coupling states between the incoming infrared light and the momentum vectors generated by the periodicity of the crystal and the number of free carriers. Therefore, in the regions of the infrared band where the light does couple to the crystal and in the absence of free carriers, the transmission of infrared light is independent of the material thickness.

Another source of absorption comes from the crystalline nature of the semiconducting materials. The individual atoms are arranged in a lattice form determining the energy bandgap of the semiconductor. Therefore, being confined in a periodic arrangement, the interaction of infrared light with the vibrational energy states (phonons) in the lattice result in various phonon absorption peaks from single phonon and multi phonon absorption events.

The fundamentals of infrared single phonon absorption are associated with coupling of incident infrared light with an oscillating electric field from charge motion in polyatomic/ionic crystals. In germanium and silicon single phonon absorption is absent because they are not polyatomic crystals. The individual atoms are covalently bonded to the neighbouring identical atoms leaving no space or opportunity for the neighbouring lattice points to have differently charged density states.

Multi phonon absorption exists in all anisotropic crystals because of lack of symmetry. Two modes of vibrations of atoms in the crystal can be defined; one where the atoms vibrate along the propagation direction of the incoming wave (longitudinal mode) and one where the atoms vibrate perpendicular to the propagation direction of the incoming wave (transverse mode). Furthermore, silicon has two atoms per unit cell in the crystalline structure. This enables a further splitting of the longitudinal and transverse mode into different branches dependent on whether the two atoms vibrate in phase or out of phase. In silicon the multi phonon absorption gives rise to 9 distinguishable peaks in the infrared spectrum ranging from 7-16 μm . The four most pronounced of these peaks are from 11-16 μm , where the absorption coefficient is in excess of 2 cm^{-1} . For the important wavelength around 9 μm the absorption coefficient is $\sim 1\text{ cm}^{-1}$. In Table I is summarised the calculated positions of the multi phonon absorption peaks.

Wave number [cm^{-1}]	Wavelength [μm]	Absorption coefficient [cm^{-1}]
1448	6.91	~ 0.5
1378	7.26	~ 0.5
1121	8.92	~ 1.0
964	10.4	~ 1.5
896	11.2	~ 2.4
819	12.2	~ 2.1
740	13.5	~ 3.0
689	14.5	~ 1.0
610	16.4	> 9.0

Table 1. Location of the multi phonon absorption peaks and the approximate values of the absorption coefficient for monocrystalline silicon.

Electronic transitions, lattice vibrations and free carrier interactions dominate the absorption coefficient in different parts of the wavelength spectrum. Because of the high purity of HiTran™ silicon there is practically no extrinsic absorption from bandgap states or extrinsic impurities.

For HiTran silicon electronic transitions dominate up to 1.1 μm . From 1.2 μm up to 6.7 μm HiTran™ silicon is transparent with no or only little absorption coming from free carrier absorption. The small absorption contribution in this range can be eliminated by choosing a high resistivity HiTran silicon version. This can be seen from Fig. 1 where the calculated absorption coefficient of high resistivity HiTran™ silicon is compared with the calculated absorption coefficient of typical lower resistivity Czochralski silicon. From 6.7 μm to 20 μm lattice vibrations dominate the wavelength spectrum with the worst performance in terms of transmission being at 16.4 μm . From 20 μm and up free carrier absorption is dominating, but again, choosing a high resistivity HiTran silicon version will eliminate this absorption contribution completely ensuring more than 50% of transparency for uncoated samples.

This is shown in Fig. 2 where it is clearly seen that high resistivity HiTran™ silicon is transparent at far infrared wavelengths whereas typical lower resistivity Czochralski silicon becomes opaque. The effect of the thickness is very pronounced for the far infrared wavelengths. The higher the resistivity of the HiTran sample, the thicker the sample can be in order to preserve maximum transmissivity.

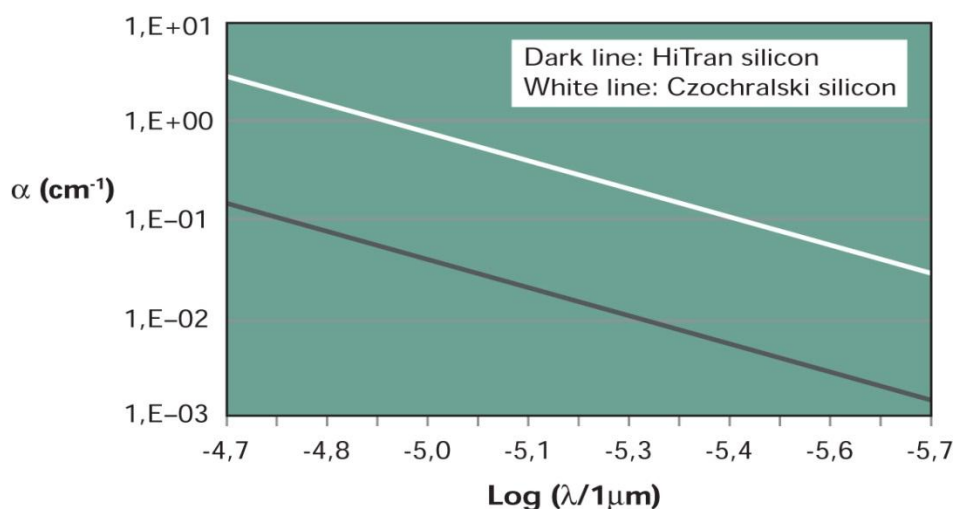


Fig. 1. Absorption coefficients for HiTran™ and Czochralski silicon as a function of the infrared wavelength (3-5 μm). Calculations are done by applying the Drude free carrier model. For the Czochralski silicon, a 50 Ωcm resistivity is assumed and for HiTran™ a 1000 Ωcm resistivity is assumed.

All of the above numbers and statements apply for room temperature conditions. There are, however, quite a few temperature dependent effects to take into account in order to have a more complete picture of the suitability of a certain infrared material. All of the intrinsic optical properties of an infrared material are highly dependent on the

ambient temperature. Adding to this, other temperature dependent effects such as Rayleigh scattering can come into play but extrinsic impurity scattering is still ruled out for HiTran™ silicon because of the high purity of the material.

For HiTran™ silicon the electronic absorption edge is shifted downward with decreasing temperature because the energy bandgap increases. This effect is not very pronounced for silicon in comparison with germanium. Free carrier absorption is also reduced for lower temperatures because of the freeze out of the freely moving carriers. The biggest impact of temperature is in the wavelength region where lattice vibrations are governing the absorption. Reducing the ambient temperature has impact on the exact value and width of the absorption peaks.

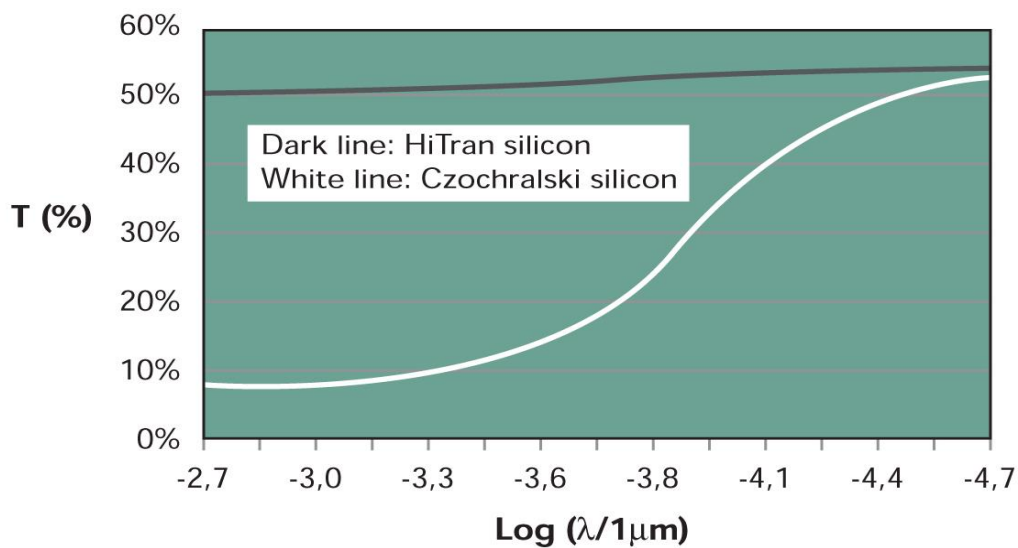


Fig. 2. Far infrared calculated absorption coefficients for HiTran™ silicon and typical Czochralski silicon (20-2000 μm). Calculations are done by applying the Drude free carrier model on 5 mm thick uncoated samples. For the Czochralski silicon, a 50 Ωcm resistivity is assumed and for HiTran™ a 1000 Ωcm resistivity is assumed.

Thermal expansion of the material is an effect that has to be taken into account in dimensioning the infrared components and systems. Thermal expansion is much lower for silicon than any other infrared materials and adding to that the high thermal conductivity of silicon makes silicon an especially good choice for heat stable, infrared systems working at elevated temperatures. Those applications are mostly concerned with industrial surveillance in hot working environments. The associated infrared window of interest is from 3-5 μm , where transmission properties of HiTran™ silicon are indeed very good.

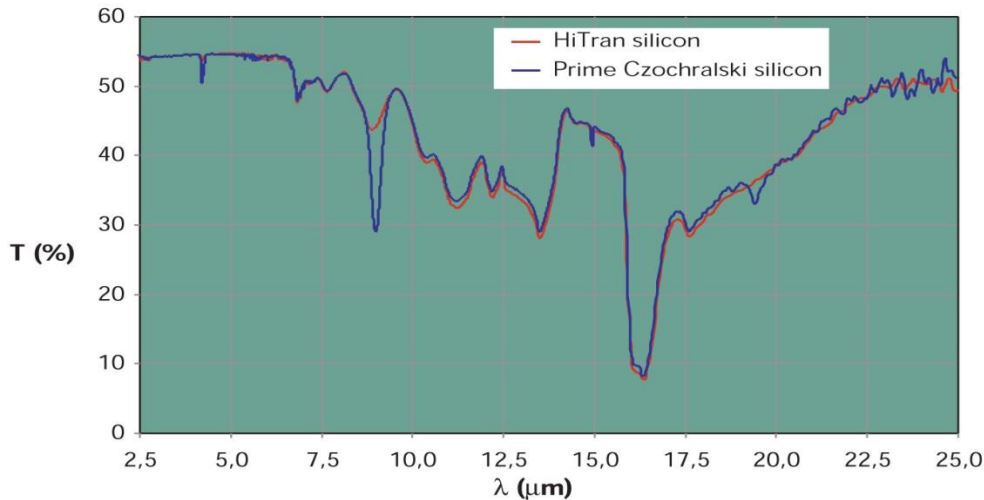


Fig. 3. Infrared transmission spectra for 2.2 mm thick uncoated, polished HiTran™ silicon and 2.0 mm thick uncoated, polished prime Czochralski silicon. Oxygen concentrations for prime Czochralski silicon and HiTran™ silicon is $6 \times 10^{17} \text{ cm}^{-3}$ and $5 \times 10^{15} \text{ cm}^{-3}$, respectively.

In Fig. 3 is shown the transmission properties of HiTran™ silicon and Czochralski silicon in the wavelength range from 2.5 μm to 25 μm . The transmission of infrared light through a sample of thickness d with parallel, smooth surfaces can be calculated by use of Eq. 1 below:

$$T(\lambda) = \frac{(1-R(\lambda))^2 \times e^{-\alpha(\lambda)d}}{(1-R(\lambda))^2 \times e^{-2\alpha(\lambda)d}} \quad (\text{eq. 1})$$

Where λ is the infrared wavelength, $R(\lambda)$ is the wavelength dependent reflectivity and $\alpha(\lambda)$ is the wavelength dependent absorptions coefficient. $\alpha(\lambda)$ comprises the wavelength dependent absorption coefficients that has been discussed above. That is the electronic transition absorption below 1.1 μm , the lattice vibration absorption from 7-20 μm and the free carrier absorption that is in principle valid throughout the full wavelength spectrum.

The reflectivity, $R(\lambda)$ is given by

$$R(\lambda) = \frac{(n(\lambda)-1)^2 + k(\lambda)^2}{(n(\lambda)+1)^2 + k(\lambda)^2} \quad (\text{eq. 2})$$

Where $n(\lambda)$ is the wavelength dependent refractive index and $k(\lambda)$ is the wavelength $T(\lambda)$ dependent extinction coefficient.

Fig. 3 clearly shows the benefit of using HiTran™ silicon in comparison with standard Czochralski silicon, which is being sold as optical grade silicon. Transmission is better for HiTran™ and the higher purity of HiTran™ eliminates extrinsic impurity peaks at different designated wavelengths.

In the wavelength region from 3-5 μm the minimum transmission is 53% for HiTran™ uncoated samples. At wavelengths just around 4 μm there is an impurity absorption coming from interstitial oxygen in Czochralski silicon.

Therefore, for optical grade silicon which is mostly based on Czochralski, transmission above 50% for uncoated samples cannot be guaranteed. The optical grade sample that has been used for measuring the transmission as a function of the wavelength in Fig. 3 was fabricated with oxygen control methods resulting in relatively low levels of oxygen ($6 \times 10^{17} \text{ cm}^{-3}$). However, values are still two orders of magnitude larger than in HiTran™ silicon. Standard Czochralski silicon has up to 10x of this level of oxygen ($6 \times 10^{18} \text{ cm}^{-3}$) and, therefore, absorption is even more pronounced in standard Czochralski silicon. Around 9 μm this will give cause transmission to drop below 20%. In standard Czochralski silicon transmission is always lower than 20% (uncoated samples) at and around 9 μm and will make the impurity absorption peak around 4 μm even more pronounced.

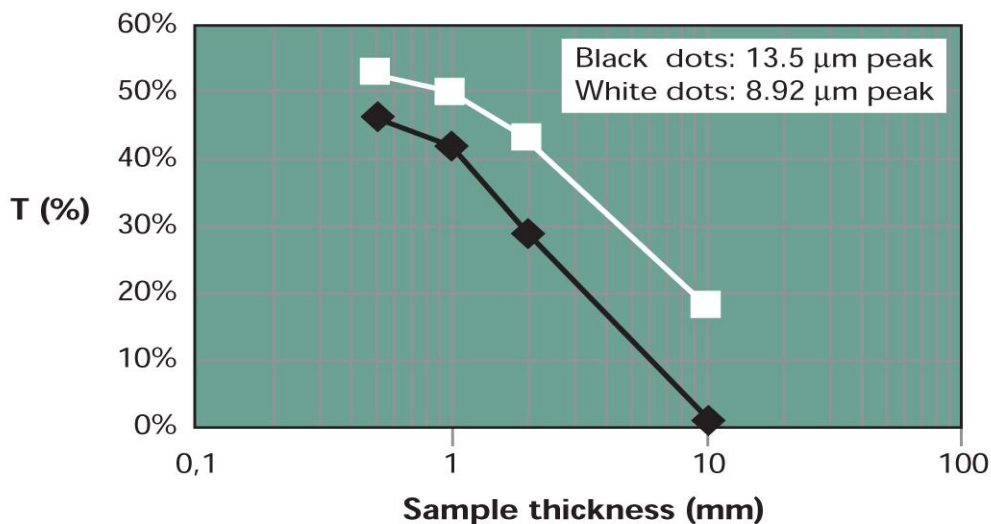


Fig. 4. Measured transmission at 8.92 μm and at 13.5 μm as a function of the uncoated sample thickness for HiTran™ silicon.

The usefulness of HiTran™ silicon over Czochralski silicon is clearly demonstrated in Fig. 3. In comparison with germanium, HiTran™ silicon suffers from multi phonon absorption peaks in the extended LWIR wavelength band, but because of the lower refractive index of silicon as opposed to germanium there are quite a few applications that can benefit from using HiTran™ silicon in the extended LWIR wavelength band. In Fig. 4 is shown the measured transmission of HiTran™ uncoated samples as a function of the thickness of the sample of the dominating peaks at 8.92 and 13.5 μm . The 8.92 μm peak is of course the most important of these two peaks and from Fig. 4 it can be seen that more than 40% transmission is achievable for uncoated samples around 2.5 mm in thickness and that more than 50% transmission is achievable for uncoated samples around 1 mm in thickness. The 13.5 μm absorption

peak is outside the 8-12 μm range but for multicolour systems working up to 15 μm it is important to have the thickness dependence outlined. As shown in Fig. 4 more than 40% of transmission is achievable for uncoated samples less than 1 mm in thickness. Further, the fact that with proper broad band anti reflection (BBAR) coating the transmission can easily approach 100% in selective regions, HiTran™ is indeed a good candidate for infrared optics in the extended LWIR wavelength band.

One important application of HiTran™ silicon is for high power lasers like the CO₂ gas laser. Normally, silicon is only considered technical superior to germanium for CO₂ laser applications because of the hardness and thermal conductivity and is thus only being considered as a potential mirror substrate. However, with the availability of HiTran™ silicon with good transmission properties in both the MWIR and the LWIR wavelength range, windows and lenses in silicon become attractive solutions in systems where ruggedness and weight are important factors. The improved ruggedness comes about because of the hardness and the fact that silicon is not as brittle as is germanium. Having only about half the weight density of germanium improves the total weight of the infrared system.

In summary, HiTran™ silicon offers very attractive properties across most of the infrared band. Transmission starts at 1.2 μm and up to 7.0 μm there is no bulk properties that is limiting the transmission. From 7.0 μm to around 20 μm the lattice configuration limits the transparency of HiTran™ silicon with 9 designated absorption peaks. However, for the LWIR wavelength range the transparency are superior to germanium for sample thicknesses below 2.5 mm as are the other bulk properties (thermal conductivity, hardness and so on). This means that there are many cases where HiTran™ can be considered a good solution for application in the LWIR wavelength range. For far infrared wavelengths >20 μm HiTran™ including THz frequencies, silicon is superior to Czochralski silicon because of the unique bulk resistivity methods in the making of the HiTran™ silicon. In Table II is summarised all important parameters of HiTran™ silicon.

Physical Properties	
Symbol	Si
Atomic Number	14
Atomic Weight	28.086
Crystalline Structure	Diamond Cubic
Density (g/cm ³)	2.3291 (298 K)
Atomic Density (atoms/cm ³)	4.96×10^{22} @20°C
Lattice Constant (Å)	5.431
Dielectric Constant	11.8
Refractive Index 4 μm	3.4255
Dn/dT (°C ⁻¹)	1.6×10^{-4}
Surface Tension (dyne/cm)	736
Modulus of Rupture (MPa)	125
Breaking Strength, Compression (MPa)	120
Mohs Hardness	7
Hardness, knoops (kg/mm ²)	964<100>, 948 <111>
Bulk Modulus (GPa)	102
Youngs Modulus (GPa)	131<100>, 187 <111>
Poisson's ratio	0.279 (125-375K)
Elastic Constants (cm ² /dyne)	$S_{11}=7.68 \times 10^{-13}$, $S_{12}=2.14 \times 10^{-13}$, $S_{44}=12.56 \times 10^{-13}$
Elastic Coefficients (dynes/cm ²)	$C_{11}=16.57 \times 10^{11}$, $C_{12}=6.39 \times 10^{11}$, $C_{44}=7.96 \times 10^{11}$

Thermal Properties	
Melting point (°C)	1412
Boiling point (°C)	2878
Heat capacity (cal/(mol*K))	4.78 (solid phase)
Heat of fusion (cal/g)	264
Coefficient of Thermal Expansion (10 ⁻⁶ /K)	2.33 @25°C
Solid Thermal Conductivity (W/(m*K))	163 @25°C

Electronic Properties	
Intrinsic Resistivity (Ω*cm)	2.87x10 ⁵
Intrinsic Electron Drift Mobility (cm ² /(V*s))	1450
Intrinsic Hole Drift Mobility (cm ² /(V*s))	480
Bandgap (eV)	1.11 @25°C
Temperature Dependence of Bandgap (eV/oC)	-2.4x10 ⁻⁴
Number of Intrinsic Electrons (cm ⁻³)	1.5x10 ¹⁰
Bulk resistivity (Ωcm)	30-30.000
Debye Temperature (°K)	640

Chemical Properties	
Solubility Water (300 K)	Insoluble
Acids (300 K)	Insoluble
Organic Solvents (300 K)	Insoluble

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Topsil GlobalWafers A/S

Topsil is a world leading supplier of ultrapure silicon for the global semiconductor industry. Engaging in long term relations with customers, Topsil focuses on premium quality, an efficient production process and a safe delivery of products.

Float-Zone FZ silicon is the high-purity alternative to crystals grown by the Czochralski CZ method. Based on extensive knowledge, expertise and significant investments in new technology, facilities and equipment, Topsil FZ silicon products are ideal for the most demanding purposes in conversion and control of electrical power.

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