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Temperature-dependent low-Q scattering from silicon single crystals

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Abstract. It has been reported that the low-Q temperature-dependent scattering from silicon single crystals is due to the modification of the phonon curves arising from the presence of oxygen precipitates. Experimental evidence reported here shows that this assumption was incorrect. Furthermore, it is found that this scattering increases linearly with temperature in the temperature range from 300 K to 900 K.

1. Introduction

At low Q ($Q = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle and λ is the neutron wavelength) two types of scattering are observed from silicon single crystals. One is the usual small-angle scattering and arises from SiO_2 precipitates [1–4]. This scattering is not present in as-grown samples. It only appears in heat-treated samples and has been extensively used to study the precipitation of oxygen in silicon. This scattering may be anisotropic when the precipitates after long ageing times, become platelets. These platelets lie on {100} planes and have their long axis parallel to a ⟨110⟩ direction [5]. Thus this anisotropic scattering follows the cubic symmetry operations; this is due to the specific orientation of the precipitates with respect to the crystallographic axes of the crystal [6]. The other type of scattering, when azimuthally averaged, shows a characteristic peak which is at Q values around 1 nm^{-1}, when a neutron beam is incident along a ⟨111⟩ direction, and was first observed by Beddoe *et al* [7]. This characteristic peak should not be mistaken for the usual interference peak [8], often seen in SANS measurements, which arises from the inter-precipitate interference scattering and is observed when the volume fraction of the precipitates is larger than about 1% (the volume fraction of the oxide precipitates in silicon is a few ppm, thus such an interference peak is not observed). Furthermore, it was shown by Beddoe *et al* [7] that the intensity of this scattering decreased as the sample was cooled from room temperature to liquid-nitrogen temperature. At that time this scattering was thought to be thermal diffuse in origin. Since normal thermal-diffuse scattering would give zero scattering at these low Q values, it was proposed that

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the phonon curves are modified by the presence of the oxygen precipitates. This was supported by the scattering from a float-zone silicon single crystal which did not exhibit this characteristic peak. The temperature-dependent scattering was anisotropic and further work showed that this scattering follows the symmetry operations of the cubic system (threefold symmetry around ⟨111⟩, fourfold symmetry around ⟨100⟩ etc). In order to distinguish the temperature-dependent scattering from the precipitate scattering we refer to it in this paper as 'high-Q' scattering.

However, there were many questions which remained unanswered about this temperature-dependent scattering. Could the size of the precipitates modify this scattering? Was the scattering attributed to the precipitates temperature independent? What would the behaviour of the scattering be at high temperatures? Further work reported here was undertaken to answer these questions and to examine the validity of the assumptions made in explaining the origin of this scattering by Beddoe *et al* [7].

2. Experimental details

This work was carried out on the D11 instrument [9] at the Institut Laue–Langevin in Grenoble, France. Neutrons in the wavelength range 0.4 to 1.5 nm are transported via neutron guides from the liquid deuterium moderator down to the sample area 100 m away. The neutrons are monochromatized by a helical-slot velocity selector giving a wavelength resolution $\Delta\lambda/\lambda = 0.08$. The scattered neutrons are detected by a two-dimensional position-sensitive detector of 64 × 64 elements, each of 1 cm^2. The sample–detector distance can vary from 1.1 to 35 m and movable guide tubes positioned before the sample allow the employment of different incident angular resolutions so as to match the angular resolution defined by sample–detector distance.

All the experiments described here were made under vacuum using the evacuated sample vessel on D11. This avoids the parasitic scattering from air and window materials. For the low-temperature measurements a liquid nitrogen cryostat was used without any windows. The system vacuum used was adequate to avoid any water condensation on the sample. In order to study the temperature variation of the scattering from 300 K to 900 K a custom-built furnace made from gold-plated silica tubes was used. This furnace is ideally suited for a vacuum environment since it does not have any conventional insulation, relying instead on the very high infrared reflectivity of the gold film. The furnace was mounted coaxially with the beam direction and the sample temperature was controlled within ±2 K using an autotuning three-term temperature controller. For these experiments the sample–detector distance of 1.1 m was chosen, as this is the optimum distance to study the temperature-dependent scattering (see figure 1).

The scattering patterns were corrected for background and normalized to an absolute cross section using the scattering from a vanadium single crystal. In order to display the scattering patterns, different grey levels are used. Each little square corresponds to a detector element of 1 cm^2 (see, for example, figure 1); the darker the grey the larger the recorded neutron count. In order to study the temperature dependence of the scattering, the data were azimuthally averaged and are presented versus Q. The neutron wavelength for all the experiments (except one) was 0.9 nm, which is beyond the Bragg cut-off and thus any interference from Bragg scattering was eliminated.

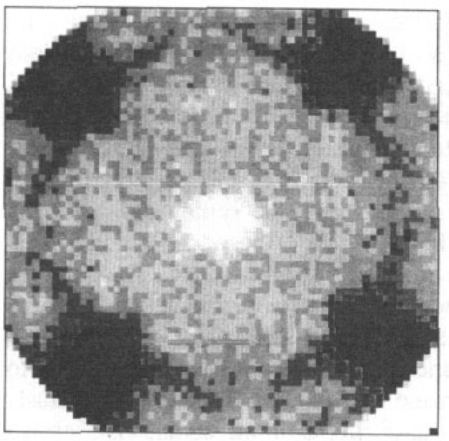

Figure 1. SANS from an as-grown Czochralski silicon single crystal. Neutron beam parallel to the [100] axis of the crystal (sample–detector distance = 1.1 m, λ = 0.90 nm).

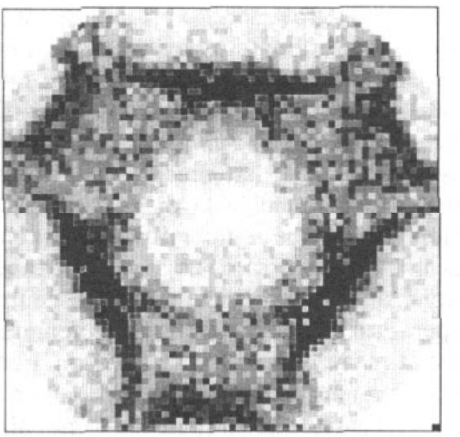

Figure 2. SANS from an as-grown Czochralski silicon single crystal. Neutron beam parallel to the [111] axis of the crystal (sample–detector distance = 1.1 m, λ = 0.98 nm).

3. Results and discussion

All the samples investigated were device-quality silicon single crystals and all but one, the float-zone crystal, were cut from Czochralski-grown dislocation free silicon. The various Czochralski-grown crystals studied had oxygen concentrations varying from 7 $\times$ 10^{17} to 2 $\times$ 10^{18} oxygen atoms per cm^3 according to current calibrations [10] and some were highly doped with carbon [11], antimony [7, 12], boron [13], or phosphorus [7]. The float-zone silicon single crystal contained $< 10^{15}$ oxygen atoms per cm^3.

In Czochralski-grown silicon single crystals two types of scattering are present: the centro-symmetric scattering around $Q = 0$ arising from the SiO_2 precipitates and the temperature-dependent scattering at higher Q values. The temperature-dependent scattering has the symmetrics of the cubic group, i.e. it has fourfold symmetry around the [100] axis and threefold symmetry around the [111] axis (figures 1 and 2). This scattering is not centrosymmetric like the low-Q scattering arising from precipitates and this can be seen in figure 2, where the pattern indicates a small misorientation of the [111] axis with respect to the incident beam. By increasing the angle of the [111] axis with respect to the incident beam, the non-centrosymmetric nature of the pattern becomes more apparent, for instance two of the three intense scattering areas can move outwards from the detector and the third one can move towards the detector centre. Further, by rotating the crystal, different cuts through reciprocal space can be seen by the detector.

The 'high-Q' scattering decreases linearly with temperature when the sample is cooled from room temperature to liquid nitrogen temperature, thus it was thought to be thermal diffuse (TDS) in origin [7]. Since TDS for a perfect crystal would be zero in this low-Q region, in order to explain the Q dependence of the scattering a modification of the normal phonon curves caused by the presence of the precipitates was proposed. If this is true, then the form of the scattering should depend on the size of the precipitates. A series of samples containing different size precipitates was

measured and their 'high-Q' cross section was found to be independent of precipitate size and heat treatment. Further, untreated samples with no measurable precipitate scattering were found to give the same 'high-Q' scattering. Figure 3 shows the radially averaged scattering around [100] from two silicon samples. One sample is as-grown, i.e. all the oxygen is in solution and low-Q scattering arising from precipitates is not observed. The other sample has been heat treated and, from the low-Q scattering, it can be deduced that precipitates have been grown (details of the precipitate scattering can be found in [3–6]). However, both samples give the same 'high-Q' cross section. In fact the temperature-dependent or 'high-Q' scattering was the same in all Czochralski-grown samples studied irrespective of impurity type (O, C, B, Sb or P) or concentration, provided that the neutron measurements were made at the same temperature. Thus the only measurement not showing the same 'high-Q' scattering was that made by Beddoe *et al* [7] on a float-zone silicon crystal. We thus decided to repeat this measurement. A much larger float-zone crystal than that used previously was investigated and showed the same 'high-Q' scattering as in all Czochralski grown silicon samples. The discrepancy between our new measurement on float-zone silicon and the measurement by Beddoe *et al* [7] can be attributed to two factors: (i) a small misorientation of the crystallographic axis could place the detector in areas of the reciprocal space where this scattering is either not present or not easily detectable, and/or (ii) the float-zone silicon used by Beddoe *et al* was five times thinner than the Czochralski samples, which makes the discrimination of the weak temperature-dependent scattering from the background very difficult. Thus we can conclude that all silicon crystals, with or without precipitates, containing oxygen atom concentrations from 2×10^{24} m^{-3} (Czochralski-grown) to less than 1×10^{21} m^{-3} (float-zone) give the same 'high-Q' cross section.

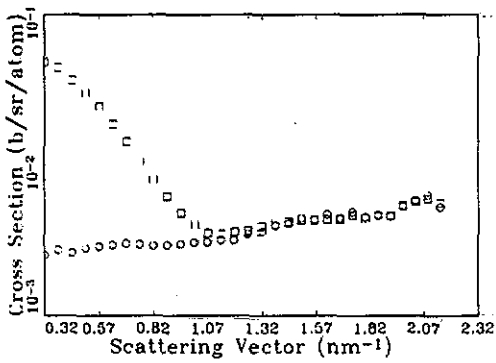

Figure 3. Radially averaged SANS from Czochralski-grown silicon. Neutron beam parallel to [100] axis of the crystal: ■, as-grown material, □, after precipitation of oxygen.

It is important to establish to what degree the scattering arising from the SiO_2 precipitates is temperature dependent. Thus a silicon sample with in-grown SiO_2 precipitates was cooled from room temperature to liquid nitrogen temperature and the precipitate small-angle scattering was measured *in situ*. A decrease in the low-Q scattering of a few percent was observed, whereas a fourfold decrease in the 'high-Q'

scattering was observed between room temperature and liquid nitrogen temperature. We may assume that the temperature-dependent scattering is extended to the low-Q region and thus the observed small decrease in the low-Q scattering with temperature can be attributed to the decrease of the temperature-dependent scattering lying underneath the precipitate scattering.

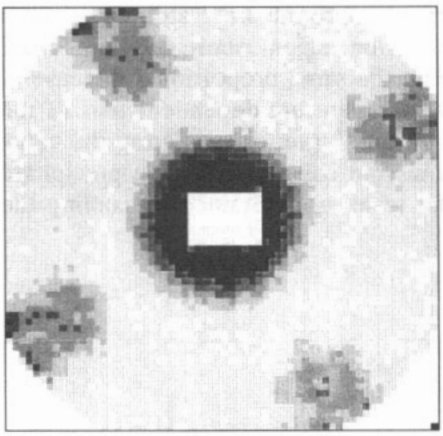

Figure 4. SANS from Czochralski-grown silicon after 72 h at 1025 K, measured at 300 K. Neutron beam parallel to the [100] axis of the crystal. Successive grey levels represent a fourfold increase in the intensity (sample–detector distance = 1.1 m, λ = 0.9 nm).

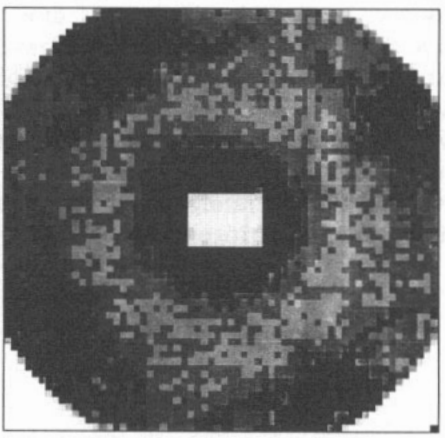

Figure 5. SANS from Czochralski-grown silicon after 72 h at 1025 K measured at 910 K. Neutron beam parallel to [100] axis of the crystal. Successive grey levels represent a fourfold increase in the intensity (sample–detector distance = 1.1 m, λ = 0.9 nm). Note the increase of intensity from figure 4.

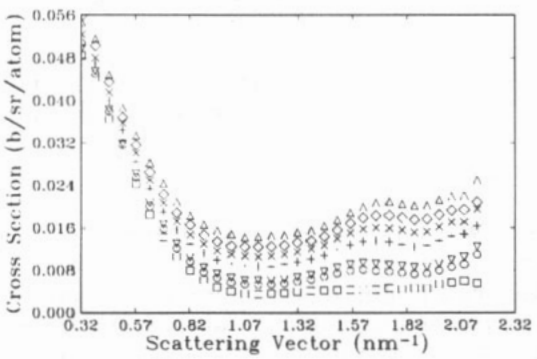

Figure 6. Temperature dependence of the radially averaged SANS. Neutron beam parallel to [100] axis of the crystal. □, 300 K; ○, 390 K; ▽, 455 K; +, 610 K; ×, 710 K; ◇, 805 K; △, 910 K (sample–detector distance = 1.1 m, λ = 0.9 nm).

In order to establish the temperature dependence of the 'high-Q' scattering at higher temperatures, a Czochralski-grown silicon crystal was heated from 300 K to 910 K *in situ* in the neutron beam. In order to limit precipitate formation during the measurement, the sample was pre-treated for 72 h at 1025 K. The scattering increased as the temperature was increased, but the pattern remained the same (figures 4 and

5). Figure 6 shows the radially averaged cross section versus scattering vector for different temperatures. We observe that the peak moves to higher Q values linearly with temperature (figure 7) and a fourfold increase of the peak cross section is observed between 300 K and 910 K (from 5 mb str^{-1} $atom^{-1}$ to 22 mb str^{-1} $atom^{-1}$). Figure 8 shows the temperature dependence of the scattering at two indicative scattering vectors: $Q = 1.13$ nm^{-1} (corresponding to the lowest scattering) and $Q = 1.68$ nm^{-1} (middle of the peak). From figure 8 we can conclude that the magnitude of the cross section varies linearly with temperature. An increase of 10 mb str^{-1} $atom^{-1}$ between 300 K and 910 K is observed in the low-Q cross-section region, where the small-angle scattering from precipitates is found. This is about the same proportional increase as that observed at the peak, if we assume that the temperature-dependent part of the low-Q scattering at 300 K is around 3 mb str^{-1} $atom^{-1}$ (i.e. extrapolating the value of the cross section at $Q = 1.07$ nm^{-1}). Thus, we can conclude that the precipitate scattering is temperature independent (the same result was obtained by cooling the sample to liquid nitrogen temperature).

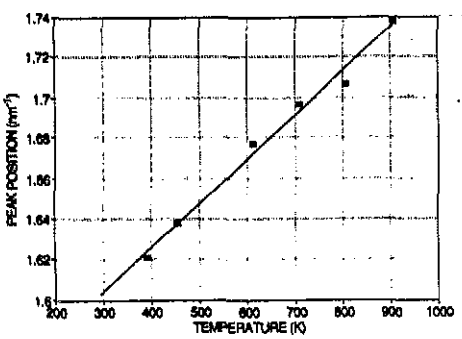

Figure 7. Variation of the position of the 'high-Q' peak with temperature (sample–detector distance = 1.1 m, λ = 0.9 nm).

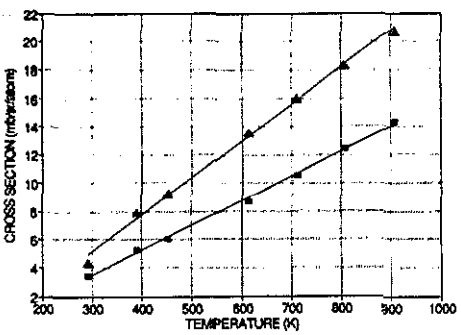

Figure 8. Variation of the scattering cross section versus temperature: ■, $Q = 1.13$ nm^{-1}; ▲, $Q = 1.68$ nm^{-1} (sample–detector distance = 1.1 m λ = 0.9 nm).

Another interesting phenomenon occurs when we change the incident wavelength from 0.9 nm to 0.6 nm (figures 1 and 9). One would expect the four lobes to move towards the centre of the detector, clearly this is not observed in figure 9. However, before concluding that the cross section does not scale with Q, one has to remember that the incident wavelengths of 0.9 nm and 0.6 nm do not scan the same area in reciprocal space. This is due to the Ewald sphere having a large curvature because of its small radius ($1/\lambda$). Taking this into account, and the fact that the four observed lobes at 0.9 nm are confined to a small area of Q space, their absence in the 0.6 nm measurement could be explained. A further point is that, if the lobes do move with Q, then as the four lobes move to the centre of the detector their size would be reduced and they would move closer to each other. This, combined with the worsening resolution at the centre of the detector, could merge the four lobes,

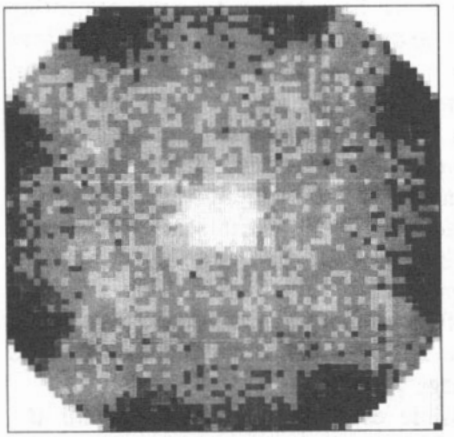

Figure 9. SANS from an as-grown Czochralski silicon single crystal. Neutron beam parallel to the [100] axis of the crystal (sample–detector distance = 1.1 m, λ = 0.6 nm; same sample and orientation as in figure 1).

thus giving rise to isotropic scattering. In either case the eight lobes observed at the corners of the detector in the 0.6 nm measurement are new features in reciprocal space which have moved into the detector area. However, this reasoning cannot exclude the possibility that the temperature-dependent scattering, partly or wholly, is arising from inelastic or quasi-elastic effects.

4. Conclusions

In this paper we have established that the temperature-dependent 'high-Q' scattering is the same in Czochralski-grown silicon crystals, independent of the presence and the size of SiO_2 precipitates. The same scattering in magnitude and shape is observed in a float-zone silicon single crystal which contains two orders of magnitude less oxygen than the Czochralski-grown crystals. Thus, we may conclude that this scattering is not connected in any way with the presence of oxygen in the silicon samples. Furthermore, we have established that the scattering does not change its shape as the sample is heated from 300 K to 910 K, but its intensity increases linearly with temperature. This, combined with previous results which showed the linear decrease of the scattering on cooling the sample, establishes a linear dependence of the scattering from 70 K to 910 K.

The neutron wavelength used for most of the measurements was 0.9 nm with a resolution of 8%. Hence, since the Bragg cut-off of silicon is 0.626 nm, Bragg or multiple Bragg scattering does not account for the 'high-Q' scattering. Elastic diffuse scattering arising from lattice relaxation around impurities was found not to match the observed 'high-Q' scattering for any reasonable lattice relaxation [7]. The incoherent scattering length for silicon is zero, so there is no elastic incoherent scattering. The velocity of sound in silicon is greater than the velocity of neutrons of wavelength 0.9 nm, thus phonon creation processes cannot occur. From the energy resolution and the angular range spanned by the detector on D11, we calculated the loci of the possible energy and momentum transfers for normal and Umklapp processes. These calculated loci did not intersect with the phonon curves for silicon determined by Dolling [14]. Beddoe *et al* [7] proposed that the temperature-dependent scattering arises from the modification of the phonon curves by the presence of the precipitates

and was probably thermal diffuse scattering. Here we have shown that this scattering is not connected with the oxygen precipitates and is not influenced by variations in the concentration of oxygen, carbon, boron, antimony or phosphorus. However, a modification of the phonon curves by some other impurity at sufficiently high concentrations (hydrogen?) cannot be excluded. A modification of the phonon curves near the centre of the Brillouin zone would give the observed magnitude, shape and temperature dependence of the scattering. A change of the incident wavelength from 0.9 nm to 0.6 nm does not show a scaling of the cross section with scattering vector. However, this experiment does not necessarily indicate that the scattering is inelastic. Beddoe *et al* [7] performed time-of-flight experiments which showed no evidence of any inelastic contribution with energy transfers greater than 0.3 meV. The linear dependence of the scattering with temperature might be explained with either TDS (quasielastic) or inelastic events with small energy transfers (<0.3 meV).

In this paper we have excluded some possible explanations to account for the origin of the temperature-dependent scattering. However, its origin and how it is connected with the presence of impurities in silicon and our understanding of the fundamental properties of silicon is still a matter to be resolved.

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