

Comparison of electronic structure of as grown and solar grade silicon samples

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A comparison of the electronic structure of two different types of silicon materials viz., (i) as grown silicon and (ii) solar silicon has been carried out utilizing maximum entropy method and pair distribution function using powder X-ray data sets. The precise electron density maps have been elucidated for the two samples. The covalent nature of the bonding between atoms in both the samples is found to be well pronounced and clearly seen from the electron density maps. The electron densities at the middle of the Si-Si bond are found to be 0.47 and 0.45 e/Å³ for as grown silicon and solar silicon respectively. In this work, the local structural information has also been obtained by analyzing the atomic pair distribution functions of these two samples.

1. Introduction

The element silicon is a well known semiconductor and it has applications, which revolutionized the electronics industry. It is also used in the preparation of silicone, production of metallic alloys with iron, aluminum, copper and manganese, as deoxidizing agent in steel production, etc., [1]. Pure elemental silicon, when doped with traces of elements such as boron and phosphorous is one of the best semiconductors. It has a heap of applications in modern technology, because it was on the basis of semiconductors that transistors and diodes were invented which are the core of any analog or digital electronic circuit. The Si semiconductors are also used in power rectifiers or in solar cells [2].

Now a days, power generation is becoming a major problem and people are moving to renewable energy sources like solar energy. Solar energy is one of the most promising and secure sources of alternative energy which can reduce our reliance on fossil fuels and reduce pollution. As technology improves, we will be able to gather more and more energy, which will be a huge relief for a country in desperate need of power. For this effective usage of solar energy, we should have devices which will enable us to do so. Although solar platforms are evolving, solar grade silicon is still the primary energy producing material. As a result of the researches, silicon doped with some of the elements and indium tin oxide [3], cadmium telluride (CdTe) [4], titanium dioxide (TiO₂) [5] etc., are used as solar cells which are nothing but photovoltaic cells converting the light energy into electrical energy which can be utilized for domestic purposes.

Silicon is the second abundant element on earth in its oxide form. Solar cells are made of electronic-grade polycrystalline silicon, which is also used for making silicon computer chips which is more expensive. Solar grade silicon is an intermediate grade i. e., not very pure and therefore less expensive [2].

Many theoretical and experimental studies are available in literature for silicon as far as the bonding is concerned. For example, Lu and Zunger [6] compared the measured electron density distribution with *ab-initio* theoretical calculations within the local density formalism. Sakata and Sato [7] evolved the precise electron density of silicon by maximum entropy method (MEM) [8]. Using the maximum entropy method, the charge density distribution can be mapped on the desired two dimensional planes. The one dimensional electron density profiles can also be plotted along the bonding directions in order to find out the mid bond density between the atoms. This helps to find out quantitatively the bond charges which will help to find out the nature of bonding. In a work done by Saravanan et. al., [9] the mid bond density of silicon is found to be 0.554 e/Å³.

Due to its tremendous importance, we have undertaken a study on silicon solar cell (which is completely ready for mounting in a solar panel) by comparing its electronic charge distribution with an "unprocessed" silicon sample which we call as „as grown“ sample.

The present work can be considered to be the first attempt to study on solar grade silicon using X - ray powder data and the versatile tools like maximum entropy method (MEM) [8] and pair distribution function (PDF) [10]. MEM is a fool proof method which deals on statistically analyzing the experimentally observed structure factors by enforcing the entropy in the charge density calculated from them. The pair distribution function describes the probability of finding two atoms separated by a certain distance in the material under investigation. The PDF method [10] extracts structure - related information from powder diffraction data.

2. X-ray analysis of the as grown and solar silicon samples

2.1. Structural refinements

The solar grade silicon used in this work was a sample which could be mounted on the solar panel. The unprocessed silicon sample used in this work is mentioned

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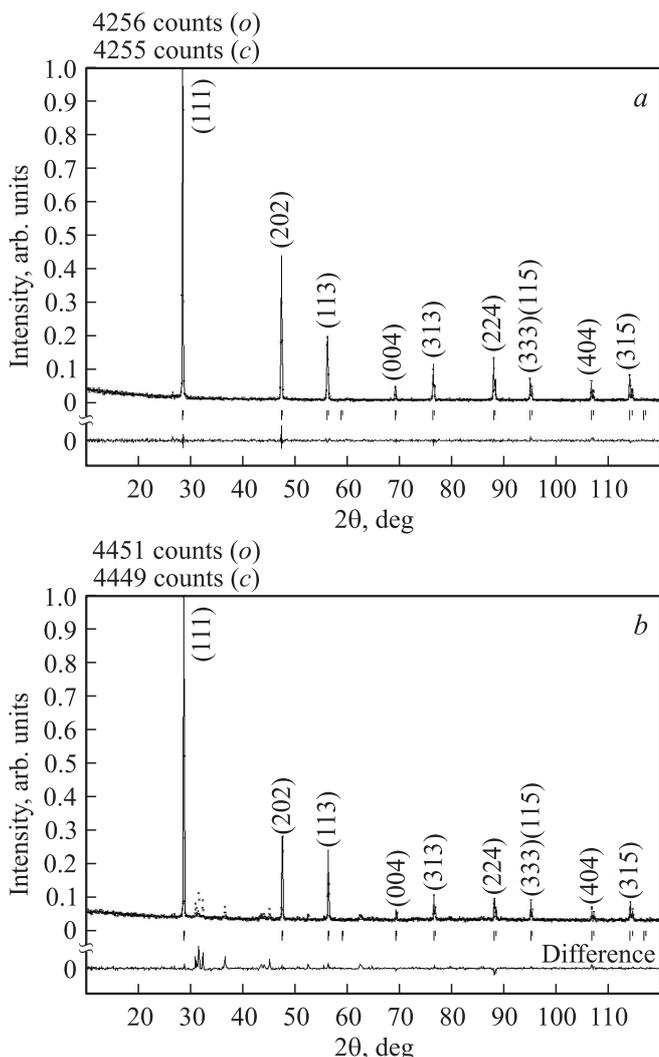


Figure 1. *a* — rietveld refined profile of as grown silicon; *b* — rietveld refined profile of solar silicon.

here as „as grown“ silicon sample. Both samples were ground separately into fine powders using agate mortar and pestle. Powder X-ray intensity data sets were collected both for solar silicon and as grown silicon using X-PERT PRO (Philips, Netherlands), X-ray diffractometer with a monochromatic incident beam, using $\text{Cu } K_{\alpha}$ (1.54056 Å) radiation. The 2θ range for both datasets was 10–120°.

Table 1. The Refined structural parameters

Parameters	As grown silicon	Solar silicon	Wyckoff value*
Cell parameter (Å)	5.4265(1)	5.4353(15)	5.4307
R_{obs} (%)	2.20	7.54	—
wR_{obs} (%)	2.43	6.79	—
R_p	9.58	12.22	—

Note: * Ref. [10].

The raw intensity data sets were processed using Rietveld method [11] through the software package JANA 2006 [12]. The Rietveld fitted observed and calculated profiles are given in Fig. 1, *a* and *b* for as grown silicon and solar silicon respectively. The refined results are given in Table 1. The refined cell parameters are 5.4265(1) and 5.4353(15) Å for as grown silicon and solar silicon respectively. The cell parameters in this work are in close agreement with the reported values 5.4307 Å [13].

2.2. Charge density analysis

The present analysis is focused on the electron density distribution using maximum entropy method (MEM) [8] and local structure using pair distribution function (PDF). Several reports on the electron density studies of various materials have been reported such as semiconductors like GaAs [14] ZnTe [15], fluorides like CaF_2 [16], LiF, NaF [17], and intermetallic compound like MnHg [18] using MEM. PDF analysis of samples of elemental Si and Ge has been reported by Saravanan et al [9]. Other studies based on the PDF analysis were also reported [10,19,20].

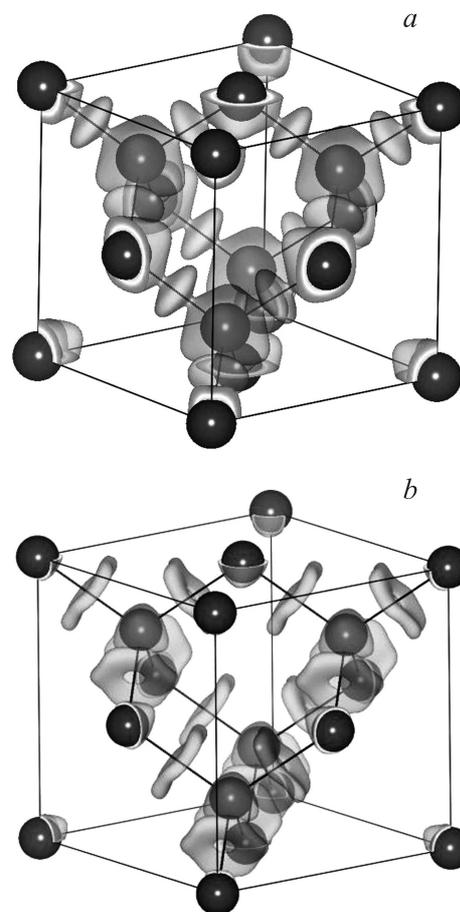


Figure 2. *a* — three dimensional isosurface of the electron density of as grown silicon; *b* — three dimensional isosurface of the electron density of solar silicon.

In the present work, the electronic structure analysis using MEM was carried out by the software package PRIMA [21]. For the 3D, 2D and 1D representation of the electron densities, the visualization software VESTA [22] was used. The three dimensional electron densities with similar iso-surfaces in the unit cell are shown in Fig. 2, *a* and *b* for as grown silicon and solar silicon respectively.

The two dimensional electron density contour maps on (100) plane (Fig. 3, *a* and *b*) and (110) plane (Fig. 4, *a* and *b*) have also been computed for as grown silicon and solar silicon respectively. The one dimensional electron density profiles along the [100], [110] and [111] directions are shown in Fig. 5, *a* and *b* for as grown silicon and solar silicon respectively.

Fig. 6 shows the one dimensional electron density only along [111] direction, for as grown silicon and solar silicon,

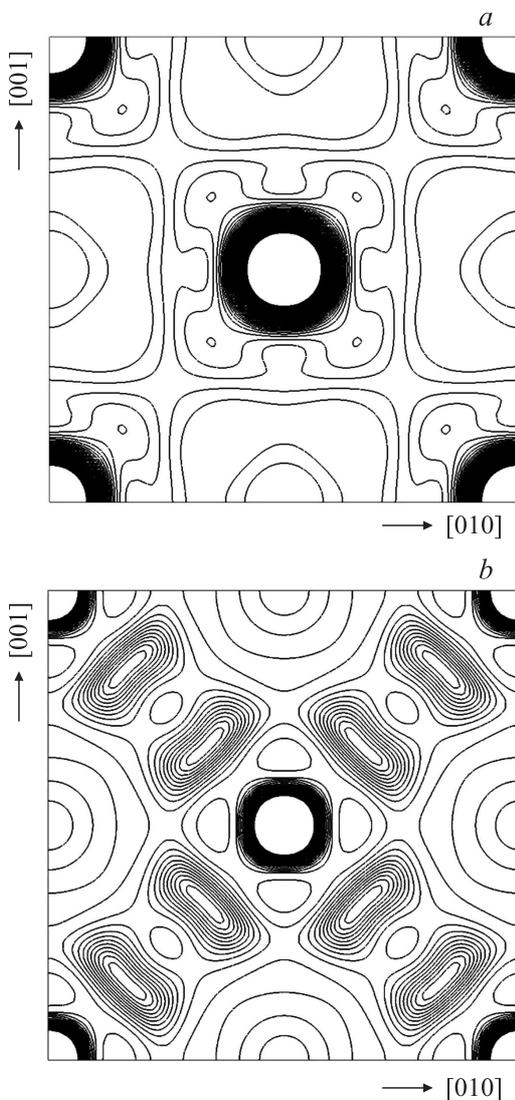


Figure 3. *a* — two dimensional charge density maps for the plane (100) of as grown silicon (Contour range is from 0.09 to 5.00 $e/\text{\AA}^3$. Contour interval is 0.03 $e/\text{\AA}^3$); *b* — two dimensional charge density maps for the plane (100) of solar silicon (Contour range is from 0.09 to 5.00 $e/\text{\AA}^3$. Contour interval is 0.03 $e/\text{\AA}^3$).

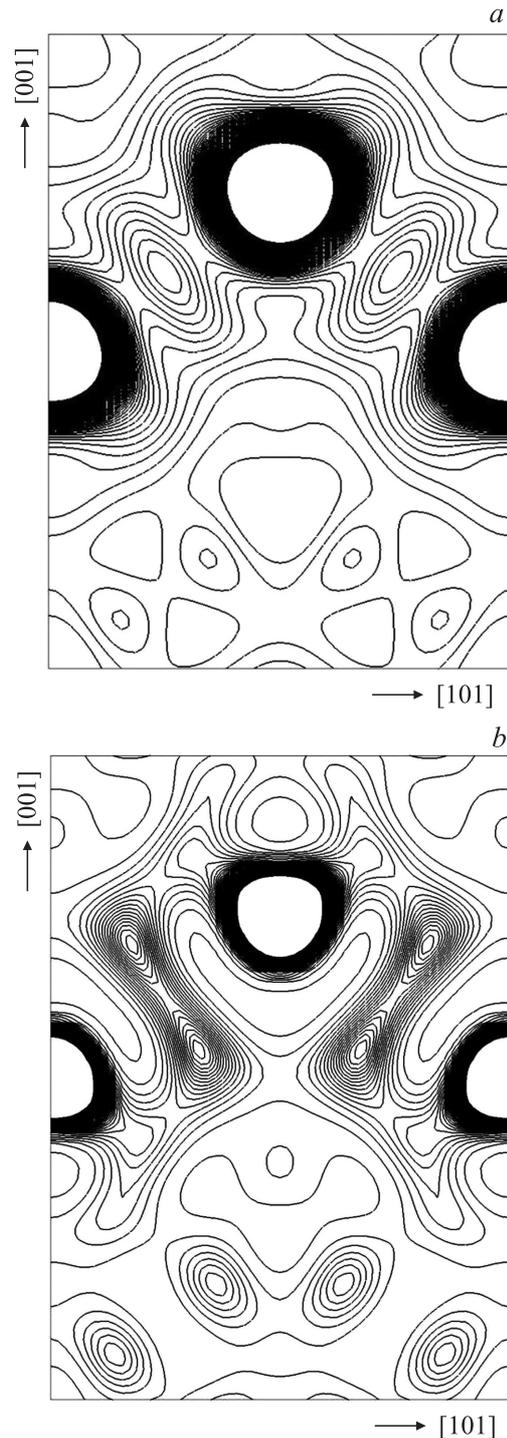


Figure 4. *a* — two dimensional charge density map for the plane (110) of as grown silicon (Contour range is from 0.09 to 5.00 $e/\text{\AA}^3$. Contour interval is 0.03 $e/\text{\AA}^3$); *b* — two dimensional charge density map for the plane (110) of solar silicon (Contour range is from 0.09 to 5.00 $e/\text{\AA}^3$. Contour interval is 0.03 $e/\text{\AA}^3$).

which visualizes the mid bond electron densities. The results of MEM analysis have been represented in Table 2. The electron densities along various directions have been presented in Table 3.

Table 2. Parameters from MEM refinement

Parameter	As grown silicon	Solar silicon
Number of cycles	49	210
Prior density, $\tau(r_i)$ ($e/\text{\AA}^3$)	0.7009	0.6975
Lagrange parameter (λ)	0.0148	0.0618
R_{MEM} (%)	1.1052	2.1694
wR_{MEM} (%)	2.0814	2.0246
Resolution ($\text{\AA}/\text{pixel}$)	0.0848	0.0849

Table 3. Electron density along various directions

Direction	As grown silicon		Solar silicon	
	Position (\AA)	Density ($e/\text{\AA}^3$)	Position (\AA)	Density ($e/\text{\AA}^3$)
[100]	1.2019	0.2049	1.3656	0.0919
[110]	1.1846	0.2707	1.3133	0.4832
[111]	1.1985	0.4730	1.1827	0.4492

Pair distribution function (PDF) is a method for the analysis of structure of the materials for which the short range order structure is not reflected in the long range order of the crystal. This method is modeled in real space. It has been used for the study of amorphous materials [23,24]. The structural information on nano scales can be obtained quantitatively by fitting a model directly to the pair distribution function [25,26]. If there are no short range deviations from the average structure, then it can be concluded that the PDF and the distance between the atoms computed from a crystallographic model is in good agreement [27,28].

In this work, the observed PDF's have been obtained from the software package PDFGetX [29]. Then a comparison of the observed and calculated PDF's has been made and analyzed for as grown silicon and solar silicon respectively using PDF [30]. The observed and calculated PDF's are shown in Fig. 7, *a* and *b* for as grown silicon and solar silicon respectively. The results of the PDF studies have been presented in Table 4.

3. Discussion

The rietveld refined profiles for as grown silicon and solar silicon were given in Fig. 1, *a* and *b* respectively. In the rietveld refined profile of solar silicon (Fig. 1, *b*), it is obvious that there are some additional peaks. These additional peaks in the profile of solar silicon correspond to the elements doped with silicon in order to use it as a solar cell. The elements present in the solar grade silicon sample were wollastonite (CaSiO_3), iron (Fe), tin (Sn), antimony (Sb), aluminium (Al), magnesium (Mg) and silica (SiO_2). The wollastonite itself may contain iron and magnesium in the substitutional position of calcium. Due to

the presence of all these elements in the solar silicon sample, the additional peaks representing the additional phases were there in the profile. Hence the reliability indices of the solar

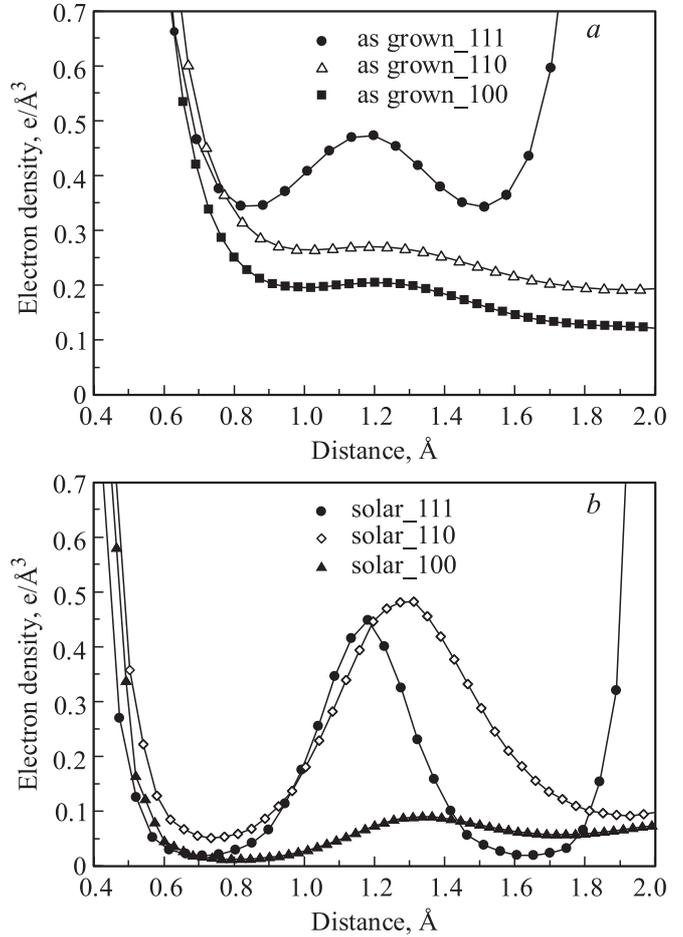


Figure 5. *a* — one dimensional charge density profile along the directions [100], [110] and [111] for as grown silicon; *b* — one dimensional charge density profile along the directions [100], [110] and [111] for solar silicon.

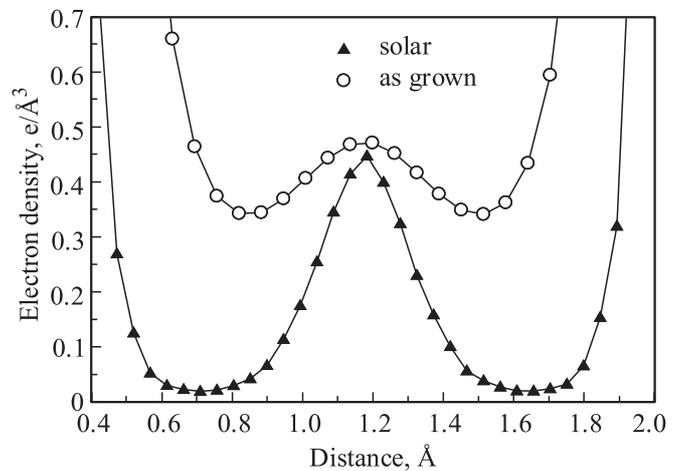


Figure 6. One dimensional charge density profile along the [111] direction for as grown silicon and solar silicon.

Table 4. Bond lengths from PDF analysis

Bond length	Distance observed r_2 from PDF (Å)	Distance calculated* r_1 (Å)	Distance calculated r_3 from PDF (Å)	% difference $\frac{r_2-r_1}{r_1} \cdot 100$
Si-Si (as grown)	3.92	3.84	3.82	2.08
	4.70	4.30	4.32	9.30
	5.76	5.77	5.68	0.17
	6.72	6.93	6.74	3.03
	7.76	7.69	7.98	0.91
Si-Si (solar silicon)	8.46	8.81	8.04	3.97
	3.84	3.84	3.90	0.00
	4.56	4.30	4.32	6.05
	5.74	5.77	5.72	0.52
	6.66	6.93	6.72	3.89
	7.74	7.69	7.98	0.65
	8.58	8.81	8.04	2.61

Note: * Ref. [31].

silicon sample are high (see Table 1). Table 1 shows that the cell constant of solar grade silicon (5.4353(1) Å) is slightly greater than that of as grown silicon (5.4265(15) Å). This may be due to the incorporation of the variety of dopant

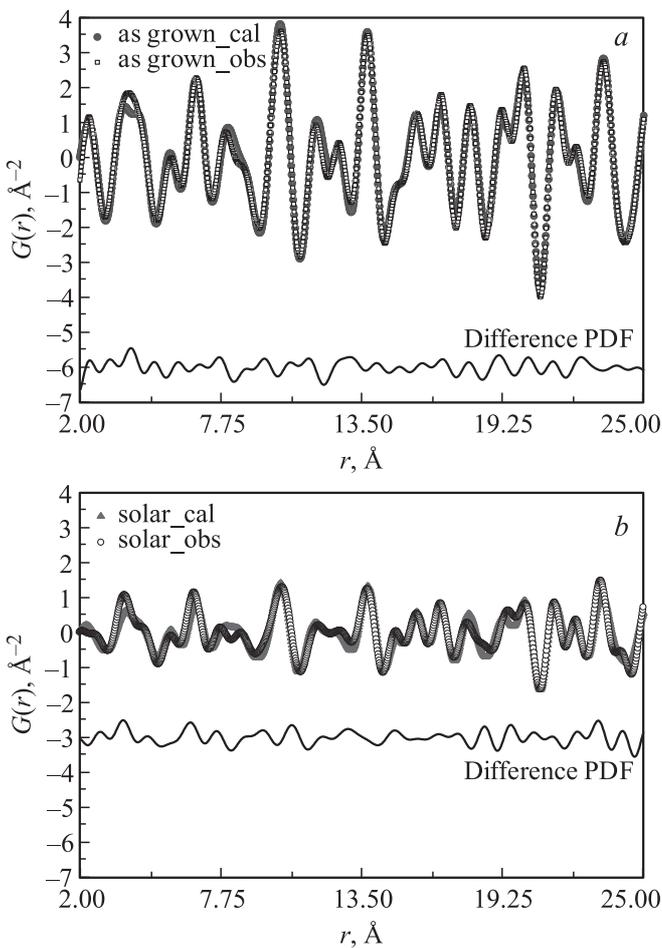


Figure 7. *a* — the observed and calculated PDF of as grown silicon; *b* — the observed and calculated PDF of solar silicon.

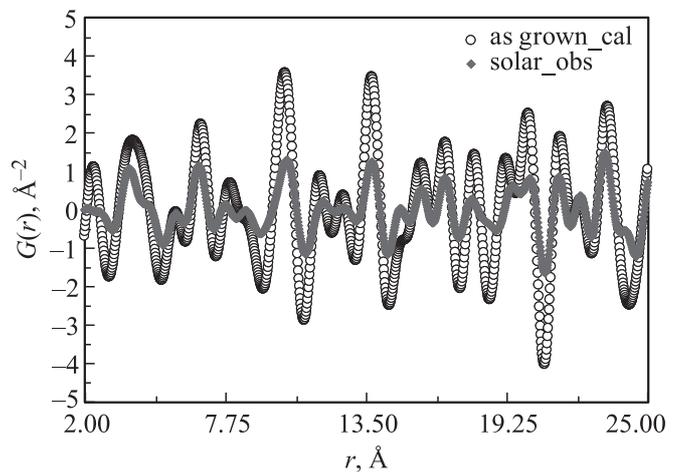


Figure 8. Comparison of the observed PDF of as grown and solar silicon.

atoms in solar silicon and hence the increase in average atomic size.

The additional charges present in the three dimensional structure of solar silicon and the deviation of the charges from the tetrahedral shape (Fig. 2, *b*) is due to these dopants. From the two dimensional charge density mapping, it is clear that the charge density distribution in the solar silicon sample is considerably higher than that of the as grown silicon sample (Fig. 3 and 4). The mid-bond densities of as grown silicon and solar silicon are 0.483 and 0.449 e/Å³ respectively (Table 3). This shows that the binding charges between two silicon atoms in as grown silicon are greater than that of the solar silicon. The may be due to the interaction of silicon atoms in solar silicon with other atoms doped silicon. The charges may be shared with the other atoms which are bound to silicon in the system.

The electron clouds in solar silicon are having more spatial distribution and the mid-bond electron density in

this case is slightly smaller than that of as grown silicon as revealed by the one dimensional electron density profiles (Fig. 6). The several processing methods through which the solar cell has undergone have improved the crystalline quality. Also, there is a reduction in bonding strength in solar silicon compared to as grown silicon which is essential for easy charge movement.

The observed and the calculated pair distribution functions are given in Fig. 7, *a* and *b* for as grown and solar silicon respectively. The observed PDF of the as grown silicon and solar silicon are compared in Fig.8. The PDF profile for as grown silicon is fitted well. The differences in the PDF profile of solar silicon are due to the additional phases of silicate compounds such as wollastonite. Table 4 gives some neighbor distances up to around 9 Å from the origin. Very close matching of the neighbor distances is visible between calculated and observed values, both for as grown and solar silicon which shows that there are no short range deviations from the average structure [28,31,32]. The average deviation between the observed and calculated neighbor distances is around 0.027 and 0.025 Å for as grown silicon and solar silicon respectively. These deviations are not uniform for the systems, i.e., and the local structural undulations in the neighbor distances vary depending on the local electronic charge distribution in both the systems. In solar silicon, the local changes in the electronic charge distribution are more enhanced due to the changes in the charge distribution due to other coating materials.

4. Conclusion

The electronic and local structure of solar and as grown silicon samples have been studied and compared in terms of atomic size difference, local structure and electron density. An increase in the atomic size is seen in solar silicon. Studies like the present one are highly essential to understand the physical and conducting properties of solar materials.

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