Pair Distribution Function analysis of the structure of SiC nanowires

Stanislaw Gierlotka, Anna Danelska, Svetlana Stelmakh, Kazimierz Skrobas, Bogdan F. Palosz

Institute of High Pressure Physics "UNIPRESS" , Polish Academy of Sciences
Sokolowska 29/37 01-142 Warszaw, POLAND e-mail: xray@unipress.waw.pl

Experiments and data elaboration:

SiC nanowires were produced by combustion synthesis from PTFE and microcrystalline silicon in a CO atmosphere [1]. They were purified by firing at 700°C followed by etching in HF. Chemically pure material was subjected to fractionation in alcohol in order to remove residual bulky crystallites.
TEM images of the resulting material are shown in Fig.1. The reference sample was high purity commercial SiC with 400nm average size.
X-ray data were collected in a capillary geometry using Bruker D8 diffractometer with Ag anode, Goebel mirror and a strip detector.
The data were collected up to Q=21Å^{-1}.
Low temperature measurements were performed using Oxford Cryostream cooling sytem.
Experimental data reduction was done by PDFGetX2 software [2]. Theoretical calculations and fitting were performed with NanoPDF64 software [3].

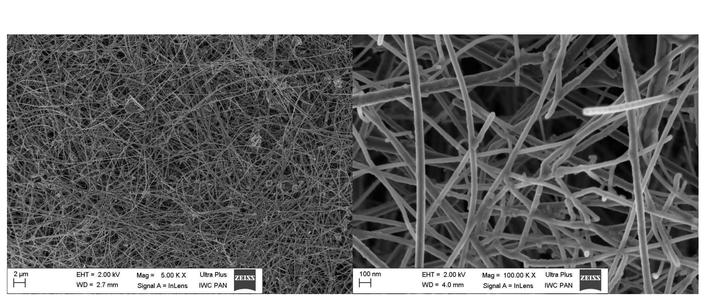

Fig. 1. TEM images of investigated SiC nanowires

How to tell bulk and rod-like nanocrystals apart based on Pair Distribution Function (PDF)?

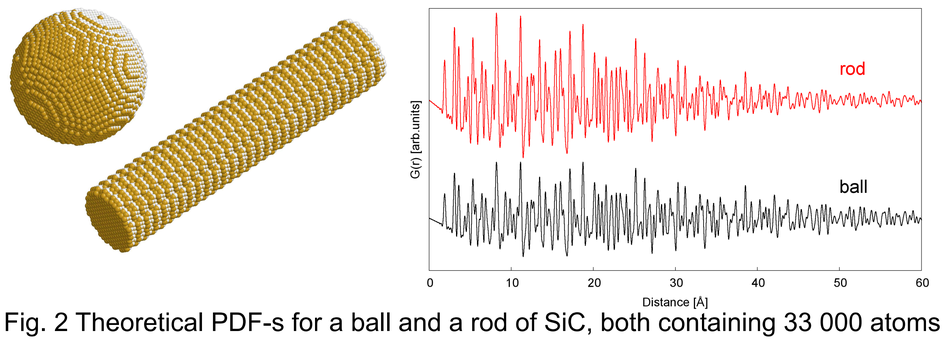

Fig. 2 Theoretical PDF-s for a ball and a rod of SiC, both containing 33 000 atoms

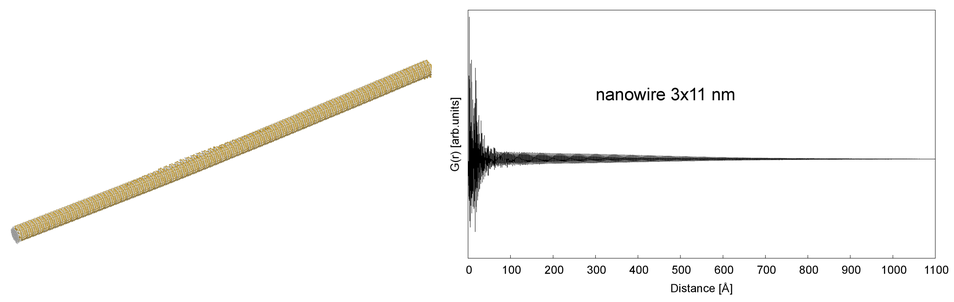

Fig. 3 Theoretical PDF for a 3x11nm wire of SiC containing 110 000 atoms

In a nanowire the relative abundance of low and high interatomic distances is different than in bulk crystals. The overall shape of the PDF function tells us about the shape of the crystallites. In a nanowire there is plenty of short interatomic distances and the long distances are smeared-out .

Can we see nanowires in PDF?

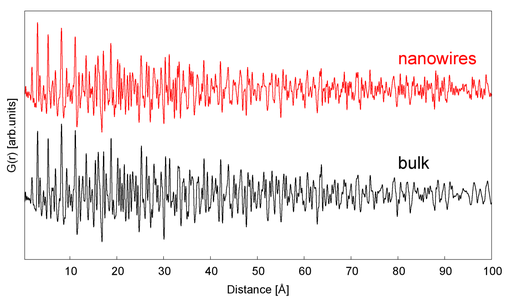

Fig. 4 PDF of nanowires and bulk SiC at room temperature

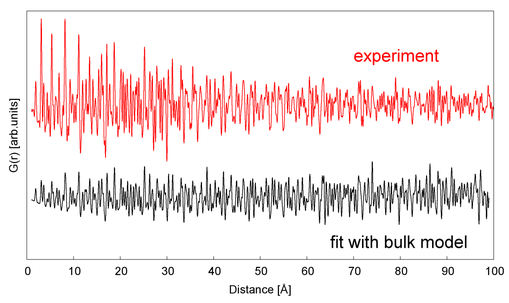

Fig. 5 PDF of nanowires at 100K and a fit of theoretical PDF for a bulk model. The crystal size returned by the software was 140 nm

The effect is not very strong but there is some excess of short distances. Most likely thicker wires, due to their bulk effect screen the thin onces.

Is crystal structure of nanowires similar to that of bulk crystals?

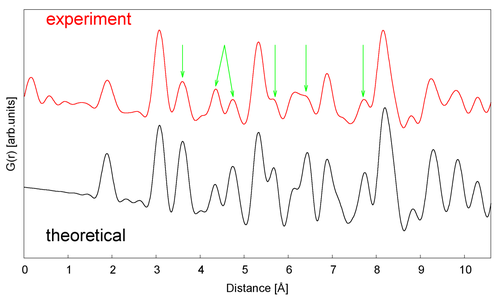

Fig. 6 Experimental PDF of nanowires compared to the theoretical PDF of perfect SiC structure

Abundance of some short distances in nanowires is diffrerent than in the perfect crystal structure of SiC - see green marks in Fig. 6.
It may be due to vacancies or due to the surface effects. Stacking faults, although present in nanowires cannot explain the effect.

Nanowires at low temperature

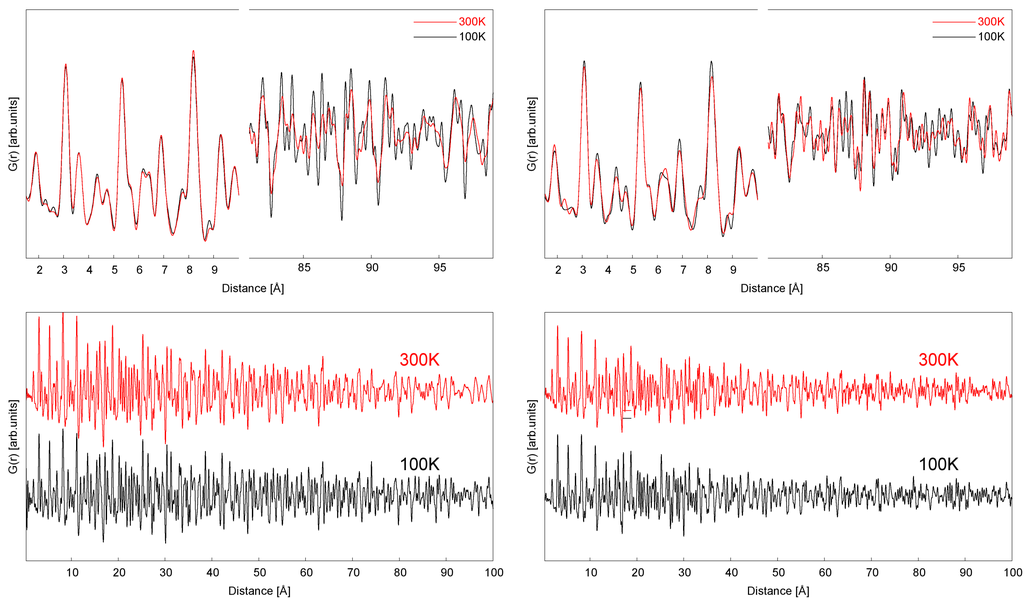

Fig. 7 PDF of bulk SiC at room temperature and at 100K

Fig. 8 PDF of nanowires at room temperature and at 100K

In bulk crystals peaks corresponding to larger interatomic distances become narrower as temperature decreases, while in nanocrystals they are narrow already at room temperature and don't change while temperature decreases. Broadening of the nearest-neighbour distances does not change with temperature neither for bulk SiC nor for nanowires. A possible explanation is the directional confinement of the phonons in the wires due to their elongated shape.

Molecular Dynamics

Simulations were performed using DL_POLY Classic software from Daresbury Laboratory. It was noticed that nanowires do not remain perfectly strainght during the simulation. If the initial structure is that of a perfect SiC wire adopts a wavy and slightly twisted shape - Fig.9 , while in the presence of stacking faults the wire tends to bend - Fig.10.

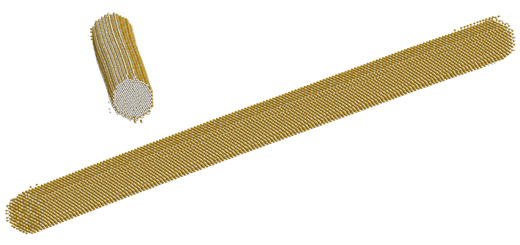

Fig. 9 MD simulation of SiC nanowire without stacking faults

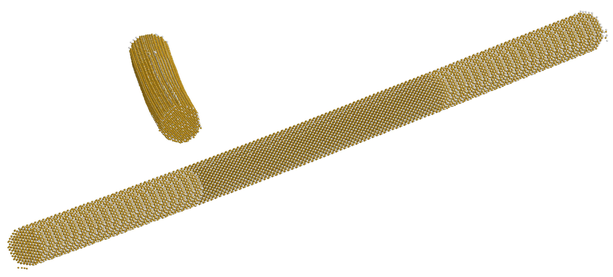

Fig. 10 MD simulation of SiC nanowire with 2 stacking faults

References

1. A. Huczko *et al* , Ultrafast self-catalytic growth of silicon carbide nanowires, Journal of Materials Research, 26, 24, 3065-3071, (2011)
2. X. Qiu, J. W. Thompson, and S. J. L. Billinge, PDFgetX2: A GUI driven program to obtain the pair distribution function from X-ray powder diffraction data, J. Appl. Cryst. 37, 678-678 (2004) http://www.pa.msu.edu/cmp/billinge-group/programs/PDFgetX2/
3. K. Skrobas, S. Gierlotka, B. Palosz and S. Stel'makh NanoPDF - the computer program to simulate and analyze the Pair Distribution Function of nanocrystals, EPDIC14, Aarhus, Denmark (2014) http://www.unipress.waw.pl/soft/crystallography/nanopdf/

The research was supported by the NCN (Polish National Science Center) grant UMO-2011/03/B/ST5/03256.