Nanocrystalline silicon with twin faults and reduced Debye temperature

W. VOGEL
Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin, Germany

S. BOTTI, S. MARTELLI
ENEA, Dip. Innovatione, Settore Fisica Applicata, Centro Ricerche Frascati, P.O. Box 65, 1-00044 Frascati, Rome, Italy

Since the discovery of the visible photoluminescence (PL) of anodized porous silicon [1] a large effort has been focused on developing nanostructured silicon [2]. It still remains unclear whether quantum size effects or surface chemistry is causing the luminescence [3–9]. In order to overcome this problem much work has been recently devoted to produce regularly shaped silicon nanoparticles [3, 7, 10].

The object of the present letter is an accurate X-ray diffraction (XRD) study of spherical silicon nanoparticles, in order to investigate possible structural changes originating from the reduced dimension and the thermal stability of the nanostructured powders used as starting material for PL studies. The particles were synthesized by laser pyrolysis of silane gas (SiH₄) in a continuous flow reactor. The experimental set-up for laser synthesis has been described in detail elsewhere [11].

Two batches of nano-Si have been prepared by this technique: Si-608, mean size 8.7 nm, and Si-603 with a larger mean size (38.8 nm, averaged by mass) adopted as a reference powder standard. X-ray experiments were carried out with a Guinier counter diffractometer, equipped with an in situ reaction chamber which has been described elsewhere [12]. The nano-Si powder Si-608 was heated in vacuo up to a maximum temperature of about 1073 K without any measurable increase in the XRD line width. This outstanding resistance against coalescence and crystallite growth indicates a highly stable chemical state of the nano-Si surface, probably due to unavoidable surface oxidation which hinders Si atom diffusion between adjacent particles [2].

Accurate X-ray line profile measurements can also give information of internal particle defects, since internal lattice strains originating from dislocations and grain boundaries cause a noticeable increase of the integral line width of X-ray reflections with increasing reflection order [13]. Fig. 1 shows the plot of the integral line widths measured on the sample Si-608. The nearly constant values attest to the negligible amount of dislocation defects, the small variations can be ascribed to an additional broadening by (1 1 1) stacking faults [13, 14]. According to Warren [15], this broadening is proportional to $1.5\alpha + \beta$, were $\alpha$, $\beta$ are the probabilities of deformation faults and twin faults, respectively. The open symbols in Fig. 1 represent the theoretical line width, calculated with a major contribution due to size broadening, and a minor one due to planar defects. Assuming a spherical shape, the line broadening analysis gives a mass averaged sphere diameter of $D = 11.6$ nm, in close agreement with the transmission electron micrograph of Fig. 2, showing near-spherical particles with diameters between 8 and 15 nm.

The probability for planar defects deduced from Fig. 1 is $1.5\alpha + \beta = 0.22\%$. Most probably, twins are formed during particle growth and the stacking
fault contribution can be disregarded, i.e. \( \alpha \approx 0 \) [16, 17]. The number \( \beta = 0.002 \) means that, on average, every 1/\( \beta \), i.e. \( \sim 500^{th} \), (1 1 1)-plane is a twin plane. On average, each crystallite contains only 16 (1 1 1) planes, and the fraction of particles that are twinned can be estimated as \( \sim 3\% \). As far as the lattice parameter is concerned, a size dependent contraction \( \Delta R/R \) of the interatomic spacing is to be expected for spherical particles of diameter \( D \) on account of the surface stress \( f_r \) [18]:

\[
\Delta R/R = -(4/3)\kappa f_r (1/D)
\]

(1)

where \( \kappa = 0.306 \times 10^{-10} \text{ m}^2 \text{ N}^{-1} \) is the compressibility, and \( R = 0.2353 \text{ nm} \) is the bulk interatomic distance. Inserting the surface tension for liquid silicon \([19] \ \sigma = 0.725 \text{ N m}^{-1} \) we would expect \( \Delta R/R = -2.6 \times 10^{-3} \) from Equation 1, in contrast to an unchanged lattice constant for Si-608 in relation to the Si-603 reference sample (accuracy \( 3 \times 10^{-4} \)). The apparent contradiction can be related to the surface oxidation which reduces the surface free energy, hence the compressive stress experienced by the particles [20, 21].

Another interesting point is the variation in damping of the Bragg peak integral intensities observed with increasing temperature; this is related to lattic vibrations described by the Debye temperature. A reduced Debye temperature due to a softening of the thermal vibrations for the surface atoms has recently been observed for nanocrystalline \( \beta \)-Sn [22], for example. This damping is described by the Debye parameter \( B \) which is proportional, in the Einstein approximation, to \( \langle u^2 \rangle \), the mean square atomic vibrational amplitude:

\[
B = 8\pi^2\langle u^2 \rangle = (6\hbar^2/mk_B\Theta)(\exp(\Theta/T) - 1)^{-1}
\]

(2)

\( + 1/2 \)

where \( \Theta \) is the characteristic Debye temperature, \( T \) the absolute temperature, \( m \) the atomic mass, and \( \hbar \) and \( k_B \) the Planck and Boltzmann constant, respectively. By measuring the decrease of the 422-Si integral Bragg peak intensity versus temperature (Fig. 3), and by comparing it with the Debye model (solid line), the X-ray Debye temperature of the \( \sim 40 \text{ nm} \) size reference sample Si-603 was \( \Theta = 546 \pm 10 \text{ K} \), in close agreement with the literature data for bulk Si \( \Theta_{\text{bulk}} = 544 \pm 4 \text{ K} \) [23]. By contrast, the 8.7 nm samples (Fig. 3, circles) presented a Debye temperature reduced to 515 (±10) K. This implies that the influence of the surface on the vibrational properties becomes relevant only for silicon particles less than \( 10 \text{ nm} \) in size. Assuming that only the surface atoms have an anomalous large amplitude, the Debye parameter may then be written in terms of a surface and a bulk Debye contribution, respectively:

\[
B = dB_{\text{surface}} + (1 - d)B_{\text{bulk}}
\]

(3)

where \( d \) is the fraction of atoms exposed to the top layer. Approximating a silicon nanoparticle as a near-spherical shaped 18 shell cuboctahedron consisting of 42 254 Si atoms, sphere equivalent diameter 11.7 nm, with 3242 atoms exposed to the surface, the fraction \( d \) is equal to 0.08. Inserting the experimental Debye-parameter \( B = 0.00493 \text{ nm}^2 \), and \( B_{\text{bulk}} = 0.00443 \text{ nm}^2 \) [23], respectively, gives \( B_{\text{surface}} = 0.0107 \text{ nm}^2 \) with a related surface Debye temperature \( \Theta_{\text{surface}} = 350 \text{ K} \). To our knowledge, no other similar measurement has been performed, the only possible comparison is with single crystal investigations. Surface Debye temperatures in the range 230–240 K are reported depending on the adopted methods and techniques [24–27].

In conclusion, silicon nanoparticles produced by laser synthesis are perfect near-spherical ‘single crystals’, and only a small minority are twinned. Whereas the lattice parameters remain unaffected, the size reduction down to 10 nm induces a lowering of about 30 K in the Debye temperature, noticeable because of the increase in the surface to bulk ratio. The nanoparticles show an outstanding thermal stability up to 1073 K, probably related to the formation of a native a-SiO\(_2\) layer after air exposure. According to the ‘three-region-model’ of Kanemitsu [28] the interface region between the core and the surface oxide plays an essential role in the efficient visible PL.

References