National Institute of Standards & Technology

Certificate

Standard Reference Material® 640c

Silicon Powder
Line Position and Line Shape Standard for Powder Diffraction

This Standard Reference Material (SRM) is intended for use as a standard for calibration of diffraction line positions and line shapes, determined through powder diffractometry. A unit of SRM 640c consists of approximately 7.5 g of silicon powder bottled under argon.

Material Description: The SRM was prepared from ultra high purity, intrinsic silicon boules that were crushed and jet milled to a median particle size of 4.9 μm. The resulting powder was then annealed under gettered argon at 1000 °C for two hours [1] and bottled under argon. An analysis of X-ray powder diffraction data indicated that the SRM material is homogeneous with respect to diffraction properties.

Certified Value and Uncertainty: The certified lattice parameter for a temperature of 22.5 °C is

$$0.54311946 \text{ nm} \pm 0.00000092 \text{ nm}$$

The intervals defined by a value and its uncertainty in this certificate are 95 % confidence intervals for the true value of the mean in the absence of systematic error [2].

Expiration of Certification: The certification of this SRM is deemed to be indefinite within the stated uncertainties, provided the SRM is stored and handled in accordance with the instructions given in this certificate (see Storage section). This material degrades slowly with exposure to humidity. If excessive exposure is suspected, discontinue use.

Storage: SRM 640c was bottled under argon to protect against humidity. When not in use, store the unused portion of this powder tightly capped in the original bottle or in a manner with similar or greater protection against humidity.

This SRM was prepared and certified by J.P. Cline of the NIST Ceramics Division, R.D. Deslattes, J-L. Staudenmann, E.G. Kessler, L.T. Hudson, and A. Henins of the NIST Atomic Physics Division, and R.W. Cheary of the University of Technology, Sydney, Australia.

Statistical analysis was by provided J.J. Filliben of the NIST Statistical Engineering Division.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by R.J. Gettings and N.M. Trahey.

Stephen W. Freiman, Chief
Ceramics Division

Gaithersburg, MD 20899
Certificate Issue Date: 13 September 2000

Nancy M. Trahey, Chief
Standard Reference Materials Program

Source of Material: The silicon was obtained from Topsil Semiconductor Materials A/S, Frederikssund, Denmark[1]. The comminution was performed by Hosokawa Micron Powder Systems, Summit, NJ.

Certification: The SRM was certified with respect to lattice parameter, which, with a knowledge of the radiation wavelength and crystal symmetry, permits the computation of the diffraction line positions. The certified value was determined from X-ray diffraction data collected on a purpose built NIST diffractometer and analyzed using a *Fundamental Parameters Approach* convolution algorithm [3]. The homogeneity of the SRM material was verified with the *Fundamental Parameters Approach* profile fitting for Rietveld [4] analyses of conventional X-ray powder diffraction data.

The uniformity of the single-crystal silicon material was verified prior to comminution. These measurements were performed on the NIST lattice comparison apparatus [5] using 20 crystal samples taken from the supplied material. A total of 70 lattice comparison measurements covering the longitudinal and radial boule directions were made. The relative lattice variation of the input material implied from these measurements was $\pm 4 \times 10^{-8}$ (95 % confidence level).

The certification measurements of SRM 640c were performed on a diffractometer built for first principles lattice parameter measurements [6]. The source consisted of a 2.2 kW long fine focus, copper target X-ray tube operated at 2.0 kW. The beam preparation optic included a parabolic graded spacing multilayer tungsten/silicon mirror, followed by a flat uniform spacing nickel/carbon multilayer mirror. The dual multilayer optic of the diffractometer exhibited a bandpass of approximately 50 eV that transmitted the $K\alpha_1/K\alpha_2$ emission spectrum of the copper target without distortion. Data analysis procedures used the characterization of the copper $K\alpha_1/K\alpha_2$ doublet offered by G. Hölzer, et al. [7] as the linkage to the International System of Units (SI). The equatorial divergence of the incident beam was approximately 0.01 degrees; this insured the data were free from sample position, beam penetration, and centration errors. Axial divergence of the incident beam was limited by a 1.9 degree Soller slit. The goniometer was equipped with an auto-calibrating optical encoder resulting in an angular measurement uncertainty of approximately 9.7×10^{-7} rad (0.2″, that is 0.2 seconds of arc). The goniometer was capable of scanning both sides of the 2θ zero point. This permitted profile data to be collected symmetrically on either side of the direct beam, thus eliminating the 2θ zero error. Diffracted beam analysis was performed using an equatorial Soller collimator with a geometrical acceptance angle of 0.077 degrees. Axial divergence of the diffracted beam was limited by a 3.2 degree Soller slit. The goniometer radius was 300 mm. The diffractometer was equipped with a sample spinner that rotated the specimens at 1.26 rad/s (12 rpm) during data collection.

Ten units of SRM 640c were selected at random from the population of units during the bottling operation. Certification data were collected from five specimens prepared from material extracted from pairs of the SRM 640c units. Data were collected from selected regions of the diffraction pattern, each of which included one of the 11 allowed reflections accessible within the 2θ range of 25 degrees to 140 degrees. The two symmetric reflections associated with a given hkl reflection were scanned sequentially. The angular widths of the scan ranges were approximately 15 times the observed Full Width Half Maximum (FWHM) values of the profiles. The step width was chosen to include at least eight data points above the FWHM. The count time spent on each profile was inversely proportional to the observed diffraction intensity. The temperature of the specimen was recorded every 10th data point to an uncertainty of ± 0.01 °C.

Peak positions were determined via the *Fundamental Parameters Approach* as implemented in TOPAS [8]. The refined parameters that were allowed to vary with the individual profiles included peak position, intensity, parameters of a linear background function, and the FWHM of a Lorentzian profile used to describe the extent of particle size induced broadening and equatorial divergence of the incident beam. The parameters which were constrained over the entire 2θ range included the intensities and positions of the $K\alpha_2$ and satellite [9] components of the Cu Kα emission spectrum, and a parameter describing the convolution of two "top hats" (i.e., a triangle function) used to model the transmission function of the equatorial Soller analyzer. The data sets from each side of the direct beam were refined separately. Certified lattice parameters were determined from the 422, 333, 440, 531,

[1]Certain commercial equipment, instruments, or materials are identified in this in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

and 620 reflections which were located in the angular region, 80 degrees to 130 degrees 2θ, wherein the effects of axial divergence are minimal. Axial divergence parameters used in the "full" axial divergence model [10] of TOPAS were set to 3.8 degrees and 6.4 degrees for the primary and secondary axial Soller slit angles, respectively. The lattice parameter was computed from each hkl reflection using the Cu $K\alpha_1$ wavelength of 0.15405929 nm [7]. The data collection temperature associated with each hkl lattice parameter was the average of eight readings; four from each of the two profiles. The temperature readings used were those that straddled the $K\alpha_1$ and $K\alpha_2$ lines from each reflection recorded during the X-ray data collection. The lattice parameters were then corrected to the reference temperature of 22.5 °C using a thermal expansion coefficient of 2.581×10^{-6} °C^{-1} [11].

X-ray diffraction (XRD) data for homogeneity testing were collected on two specimens removed from each of the 10 aforementioned units of the SRM material. The XRD data for this testing were collected on a Siemens/Bruker D5000 diffractometer of θ-θ geometry equipped with a 2.2 kW copper tube operated at 1.8 kW, a sample changer/spinner, a graphite post monochromator, and a scintillation detector. The goniometer radius was set to 215 mm, the divergence slit was set to 0.8 degrees, and a 0.2 mm receiving slit was used. Data were collected from selected regions that included the 11 allowed reflections accessible within the 2θ range of 25 to 140 degrees. The peaks were individually scanned in ranges that straddled the Kα doublet by at least 20 times the observed FWHM. The step widths were chosen to insure at least 8 data points above the FWHM and count times were also chosen so that the profile maxima had approximately the same X-ray count values. TOPAS was used to carry out the *Fundamental Parameters Approach* to profile fitting for a Rietveld analysis of the silicon profile data. The scale factors and parameters of a linear background function were allowed to vary for each profile. All other parameters were constrained across the full pattern. These included the intensities and positions of the $K\alpha_2$ and satellite components of the Cu Kα emission spectrum, the FWHM of Lorentzian profiles to describe the extent of particle size and strain induced profile broadening, terms indicating the position and intensity of the "tube tails" [12], the axial divergence angle of the diffracted beam, the sample displacement and linear attenuation terms, and the lattice parameter. Homogeneity of the SRM feedstock was judged in the context of variation in the lattice parameter and, secondarily, in the profile shape parameters.

Information Values: The *Fundamental Parameters Approach* analyses performed for the homogeneity testing included the refinement of the FWHM of a Lorentzian profile to account for sample induced broadening. The angular dependence of the FWHM, degrees 2θ, was found to fit the relation, $\text{FWHM} = 0.0065(5)/\cos\theta + 0.0086(6)\tan\theta$. The first term is interpreted as the crystallite size contribution, indicating a mean crystal size of 1.4 μm, while the second can be interpreted as a microstrain term. Such a microstrain level increases the breadth of the 533 profile by approximately 0.02 degrees. The information values for computed peak position and particle size distribution as determined by laser scattering are given in Table 1 and Figure 1, respectively.

Table 1. Peak Positions Computed for SRM 640c Using Cu Kα Radiation, λ = 0.15405929 nm

h	k	l	2θ, degrees
1	1	1	28.4409
2	2	0	47.3003
3	1	1	56.1193
4	0	0	69.1261
3	3	1	76.3718
4	2	2	88.0247
5	1	1	94.9463
4	4	0	106.7009
5	3	1	114.0834
6	2	0	127.5330
5	3	3	136.8789

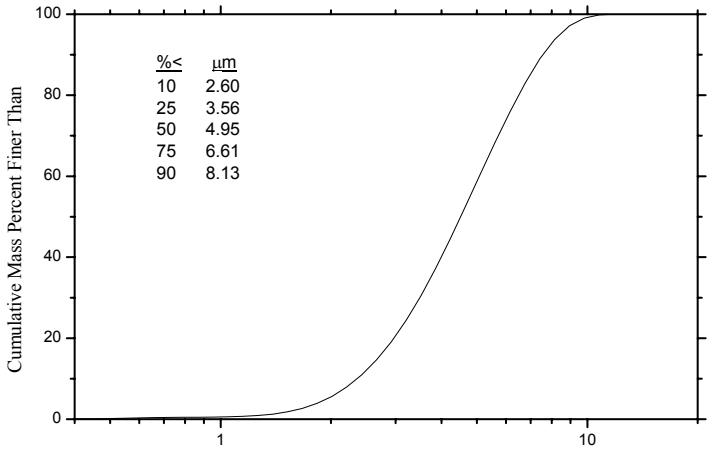

Figure 1. Typical Particle Size Distribution as Determined by Laser Scattering

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Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.