Applied Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Ellipsometry of surface layers on a 1-kg sphere from natural silicon

Petr Klenovský[a], Jaroslav Zůda[b], Petr Klapetek[b,c], Josef Humlíček[a,*]

[a] CEITEC Masaryk University, Department of Condensed Matter Physics, Kotlářská 2, 611 37 Brno, Czech Republic
[b] Czech Metrology Institute, Okružní 31, 63800 Brno, Czech Republic
[c] CEITEC Brno University of Technology, Okružní 31, 63800 Brno, Czech Republic

ARTICLE INFO

Article history:
Received 15 July 2016
Received in revised form 23 August 2016
Accepted 25 August 2016
Available online xxx

Keywords:
Silicon
Surface layers
Ellipsometry
1-kg mass standard

ABSTRACT

We have investigated surface layers on a monocrystalline float-zone, n-type (2400–2990 Ωcm) sphere with the diameter of 93.6004 mm. Ellipsometric spectra in the visible–ultraviolet range reveals the presence of thin layers of amorphous Si as well as oxide overlayer. We have also prepared a series of flat Si samples, polished using slurries with 1–6 μm grits; the overlayers were examined by mid–infrared ellipsometry, including the range of polar vibrations of the Si—O bonds. AFM measurements on the sphere were used to test the models of its surface.

1. Introduction

Recent results in determining the Avogadro constant by counting the atoms in isotopically enriched Si spheres revealed that about one quarter of the total uncertainties is related to the surface [1,2]. The surface is of primary importance also in efforts to disseminate the new SI kilogram using spheres of natural silicon [3].

We have investigated spectroscopically, in NIR-VIS-UV, the surface layers on a monocrystalline float-zone sphere of the "secondary mass standard" [3] quality. After identifying a considerable presence of amorphous Si within the surface overlayers on the sphere, we have measured a series of flat Si samples; the device—grade Si surface (resulting from chemical—mechanical polishing, which removes the polishing damage), was mechanically polished using different slurries. Thus, we have simulated the near—surface conditions after different levels of polishing. In addition, the overlayers have been examined by mid-infrared ellipsometry; in particular, the range of the highest transverse and longitudinal vibrations proves to be sensitive to the Si-O bonding in the oxide overlayer. We have also performed AFM measurements on the sphere to obtain independent information on the models of its surface. Finally, comparisons of its mass with several steel etalons were performed in air and vacuum. Implications of the surface studies for the sphere's mass have been briefly summarized.

2. Samples and measurements

Silicon sphere purchased from Sartorius Weighing Technology GmbH is made of high-resistivity (2400–2990 Ωcm) float-zone single crystalline material with natural isotopic composition. Its average diameter is 93.6004 mm. It has been maintained mostly in air, with the exception of several weighing runs in vacuum. We have also polished several flat pieces of a high—purity Czochralski silicon wafer, having standard device-grade (100) surface obtained by chemo—mechanical polishing. Diamond pastes (with nominal grain sizes of 1, 3 and 6 μm) dispersed in water on polishing (glass—supported) fabric pads were used to mimic the damage introduced by mechanical polishing. These (flat) samples were cleaned in organic solvents and sprayed with clean air, the sphere was merely sprayed before the spectroscopic measurements.

For reflectivity measurements in NIR—VIS—UV range, Avantes 2048 pixel spectrometer (the spectral range from 1.2 to 5.1 eV) was equipped with a fiber reflectance probe as described in Ref. [4] and shown schematically in Fig. 1. We have used a thick homoepitaxial Si layer as the reference sample, having the reflectivity of bare Si covered by 3 nm oxide overlayer. The spot contributing to the registered reflectance signals is nearly circular, with the diameter of about 0.8 mm, and angles of incidence from the 0.2° to 1.7° at the 15 mm sample-probe distance. The VIS—UV ellipsometric data were acquired with a dispersive, rotating-compensator ellipsometer (Woolam VASE, shown in Fig. 1), at the angles of incidence from 67.5, 70, ... 80°, at an equidistant (0.02 eV) photon energy mesh.

* Corresponding author.
E-mail address: humlicek@physics.muni.cz (J. Humlíček).

http://dx.doi.org/10.1016/j.apsusc.2016.08.135
0169-4332/

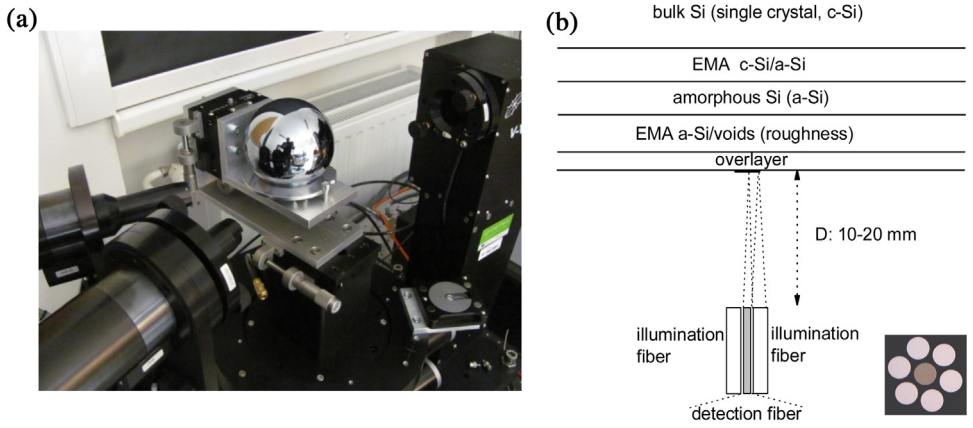

Fig. 1. (a)Si sphere mounted on the xyz holder of the Woolam VASE ellipsometer. (b) Layered system and the reflectivity setup (not to scale). Dotted lines show two limiting reflected rays; thick segment is the measured spot at the sample surface. Optical image at right bottom shows the termination of the reflectance probe with 6 illumination fibers surrounding the central detection fiber, each of 400 μm diameter.

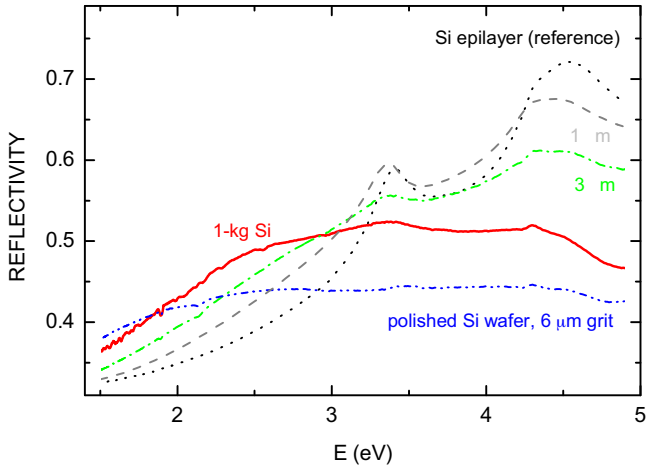

Fig. 2. Normal—incidence reflectance of Si sphere (solid line), homoepitaxial Si layer (dots), and two Si wafers polished with the slurries of 1, 3 and 6 μm grain size (dashed, dash—dotted and dash—dot—dotted lines, respectively).

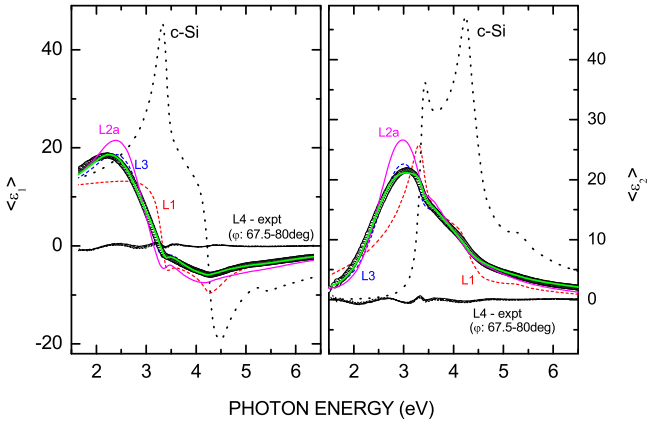

Fig. 3. Measured pseudodielectric function of Si sphere (symbols) and homoepitaxial Si layer (dots, black). Four of the model lineshapes of Table 1 are shown by thin dots (L1, red), thin solid line (L2a, magenta), thin dashed line (L3, blue), thick solid line (L4, green). The differences between the last model and experimental data are also shown (6 thin, mostly overlapping lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

No focusing optics has been used in collecting the ellipsometric spectra.

Mid—infared ellipsometric spectra were taken with the Woolam IR-VASE instrument, using the spectral resolution of 4 cm^{-1}. The angles of incidence were 65 and 70°. All reflectivity and ellipsometric measurements were performed at the temperature of 22–24 °C.

Surface images have been obtained with the AFM Explorer (Thermomicroscopes), using high—aspect tips in the contact mode. Custom built holders were used to mount the microscope head and the silicon sphere.

3. Results and discussion

3.1. NIR—VIS—UV reflectance

We have started our investigations with reflectance measurements. The spectra shown in Fig. 2 were taken against homoepitaxial Si layer. The signal registered by the central detection fiber is lowered by the spread of light upon reflection on the curved surface of the sphere; the effect increases with the distance of the reflectance probe from the sphere. We have therefore determined an appropriate multiplication factor by comparisons of the spectra taken with several distances from the flat and curved surfaces. While the uncertainty of the signals relative to the Si epilayer reference is typically well below 1%, the use of the normalization factor leads to the uncertainty of about 2–3% with our alignment of the reflectance probe.

These results indicate a substantial coverage with amorphous Si, leading to the loss of sharp spectral features due to the E_1 and E_2 electronic transitions at 3.4 and 4.3 eV, respectively. The UV part of the spectra, with rather small penetration depth of light, suggests our polishing with the 3 and 6 μm slurries brackets approximately the loss of crystallinity of the sphere.

3.2. VIS—UV ellipsometry

Measured and model ellipsometric spectra are shown in Fig. 3 in the form of the pseudodielectric function, i.e., the measured pairs (ψ,Δ) interpreted as resulting from a semiinfinite isotropic sample.

These spectra differ significantly from those of the bare single-crystal Si and also from the latter covered with a thin oxide overlayer, driven to unreasonably large thickness by the L1 model of Table 1. The blank entries in Table 1 mean the absence of the corresponding layer in the stack. The uppermost surface layer has always been included with the assumption of having the refractive index of glassy SiO_2; however, it comprises also volatile substances (mostly water). We have observed their removal by the weighing in vacuum, as described below. We have subse-

Please cite this article in press as: P. Klenovský, et al., Ellipsometry of surface layers on a 1-kg sphere from natural silicon, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2016.08.135