Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 525-526

Compaction of nanosilicon pellets and sol-deposited films *via* high-vacuum annealing

Alexander A. Vinokurov, Sergei S. Bubenov, Nikolay N. Kononov, Tatiana A. Kuznetsova and Sergey G. Dorofeev

Sample preparation

Thermally oxidized weakly P-doped silicon (KEF-75, 320 nm oxide layer) was used as substrate material. Round gold marks (200-300 nm thickness) was vacuum-deposited on the substrates followed by SiO layer deposited through the same mask to prevent interaction between gold and Si nanocrystals (NCs) during annealing. After that the NC (undoped or P-doped) films were deposited through either spin-coating or high-speed centrifugation.

For annealing the samples were transferred to custom-shape (Figure S1) quartz ampoule with magnesium getter, as dispersed magnesium film absorbs water vapour and residual oxygen exceptionally well. The ampoule was then evacuated to 10^{-2} Torr and sealed. Magnesium was evaporated from an iron crucible with a punctured lid, pointing away from the samples' direction and towards the broadened part for higher area of getter film. Ampoule and crucible were degassed by heating at 10^{-5} Torr prior to the experiment. To disperse the magnesium the crucible was heated inductively, that allowed to avoid significant heating of the ampoule and its interaction with Mg film. The dispersion was repeated after 1 hour and 12 hours, and after a day the getter part of ampoule was removed by melting. The samples were then annealed for two hours at different temperatures, ranging from 300 to 1000°C.

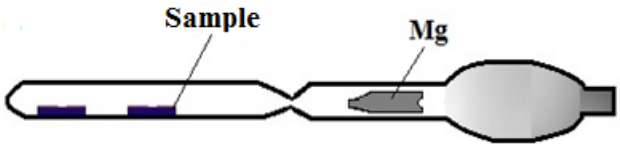

Figure S1 Scheme of quartz ampoule for vacuum-annealing of samples.

Density determination

Areal density was determined through attenuation of X-ray fluorescence (XRF) of the substrate. Gold was chosen as a material because the most intensive M-series lines M_5N_7 and M_4N_6 possess the energies of 2.1216 and 2.2033 keV, respectively, and are thus well absorbed by silicon (K-edge energy of 1.8339 keV, Figure S2). Theoretical values of mass attenuation coefficient were used: 2210, 37.0 and 22.8 cm2/g for M-series and L_3M_5, L_2M_4 lines, respectively.[S1] XRF spectra were recorded on a M1 Mistral (Bruker) spectrometer at 50 kV tube voltage, 800 μA current for 5 minutes. The ~200 nm thick gold marks used are essentially infinitesimal in thickness for L-series lines of Au (i.e. the intensity of the line is directly proportional to the thickness), while their thickness for M-series is intermediate (the dependence of signal on thickness is not linear). Due to this, each mark had to be studied individually before NCs deposition. Intensity of unresolved M-series line was divided over intensities of L_3M_5 and L_2M_4 after the background signal was subtracted. The resultant ratios were divided over the same ratios for the mark prior to film deposition to result in transmission in relation to these lines (T_{L3M5} иT_{L2M4}). Areal density D_s [g/cm^2] of NC films was calculated through the following: $D_s=\ln(T_{L3M5}/(37\text{-}2210))$ и $D_s=\ln(T_{L2M4}/(22.8\text{-}2210))$, and then averaged.

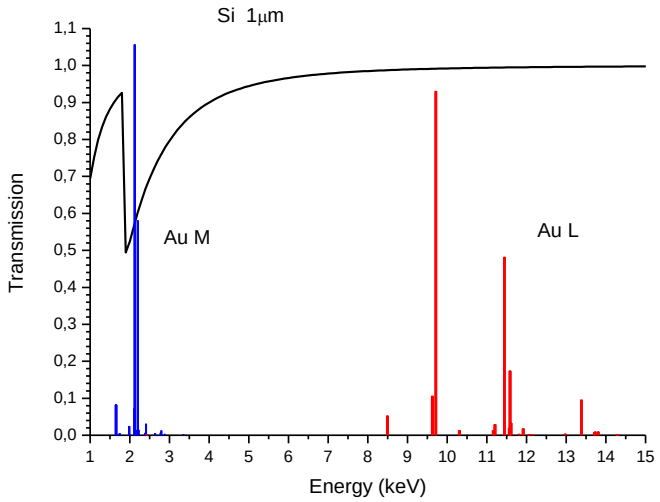

Figure S2 Theoretical X-ray transmission spectrum for 1 μm-thick with bulk silicon density (2.33 g/cm^3) modeled with PyMca software. Vertical lines are superimposed on the spectrum, that show the position and relative intensity of gold fluorescence lines.

UV-Visible absorption spectroscopy was employed as a secondary method to determine the areal density. The spectra were recorded on a Cary 50 (Varian) spectrophotometer. NC sols with concentrations of particles C_{sol} of 3 and 30 μg/cm^3 were used to calibrate the absorption. Absorbance at 400 nm wavelength was used for calculation, as in this region absorption by NC cores dominates the scattering of light on NC agglomerates, so the latter may be neglected. The areal density was calculated with the following formula: $D_s=C_{sol}\cdot L\cdot A_{film}/A_{sol}$.

SEM study of film morphology

Microphotographs of films, produced by centrifugation, are given in Figure S3. When comparing unannealed sample to the sample, annealed at 800°C, we can see that the former possesses a high number of small (~100 nm) voids. The annealed sample predominantly consists of densely packed particles. Voids are also present in annealed samples, but at a lower rate.

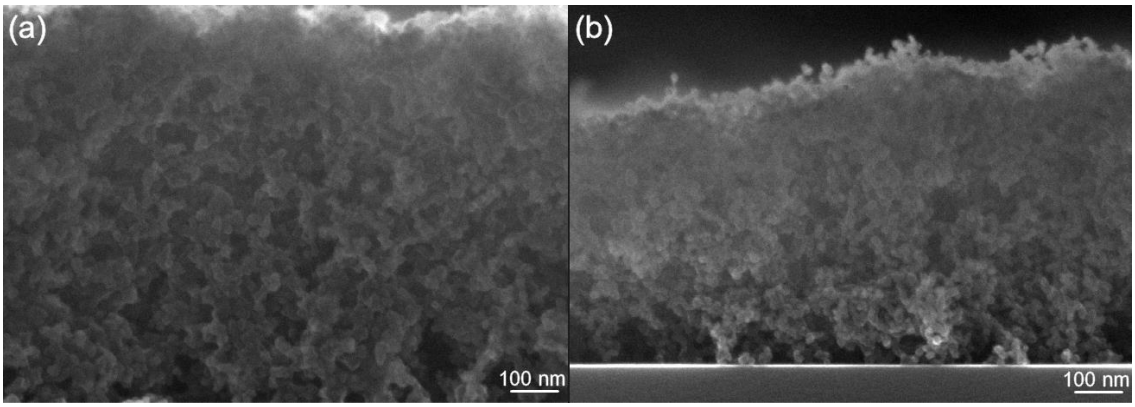

Figure S3 SEM end cleavage microphotographs of unannealed sample (a) and of sample, annealed at 800°C (b).

References

S1. M. A. Blokhin and I. G. Schweitzer, *Rentgenospektral'niy spavochnik* (*Rentgenospectral Handbook*), Nauka, Moscow, 1982 (in Russian).