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CLUSTER SECONDARY ION EMISSION FROM THE NANOSIZED
SILICON SAMPLES

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КЛАСТЕРНАЯ ВТОРИЧНАЯ ЭМИССИЯ ИОНОВ ИЗ НАНОРАЗМЕРНЫХ
ОБРАЗЦОВ КРЕМНИЯ

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КРЕМНИДІҢ НАНОӨЛШЕМДІ ҮЛГІЛЕРІНЕН ИОНДАРДЫҢ КЛАСТЕРЛІК
ҚАЙТАЛАМА ЭМИССИЯСЫ

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Annotation

Time-of-flight secondary ion mass spectrometry was used to study cluster emission of three kind of Si samples with different dimensional features – massive single-crystal wafer, pressed pellet made of 60 nm in diameter particles and holographical grating consisted of the columns of 200 nm in height and 160 nm in diameter. It was shown that under 25 keV Bi_3^+ ion-beam bombardment both nanosized samples exhibited more intense negative cluster secondary ion emission as compared with massive Si sample. The «nanoscale effect of sputtering» was found to be more pronounced for large Si_n^- clusters with $n > 7$ and for pressed nanopowder pellet, in which individual particles are more isolated than in the columns formed holographic grating.

Key words: cluster; nanoparticles; negative ion emission; silicon; sputtering; time-of-flight secondary ion mass spectrometry.

Аннотация

Времяпролетная вторичная ионная масс-спектрометрия использовалась для исследования кластерной эмиссии трех видов образцов Si с различными размерными особенностями – массивной монокристаллической пластины, прессованной таблетки из частиц диаметром 60 нм и голографической решетки, состоящей из колонок длиной 200 нм и высотой 160 нм в диаметре. Было показано, что при ионно-лучевой бомбардировке Bi^3+ с энергией 25 кэВ оба наноразмерных образца демонстрируют более интенсивную отрицательную кластерную вторичную ионную эмиссию по сравнению с массивным образцом Si. Было обнаружено, что «наноразмерный эффект распыления» более выражен для крупных кластеров Si_n^- с $n > 7$ и для прессованной таблетки нанопорошка, в которой отдельные частицы более изолированы, чем в столбцах, образованных голографической решеткой.

Ключевые слова: кластер; наночастицы; эмиссия (выброс) отрицательных ионов; кремний; напыление; времяпролетная вторичная ионная масс-спектрометрия.

Андатпа

Өткен уақыт өлшемін қайталайтын ионды масс-спектрометрия 60 нм диаметрлі бөлшектерден престелген таблеткалардың массивті монокристаллической пластиналары мен ұзындығы 200 нм және биіктігі 160 нм диаметрлі колонкадан тұратын голографиялық торлардың түрлі өлшемдік ерекшеліктерімен Si үш түрлі үлгілерінің кластерлік эмиссиясын зерттеу үшін пайдаланылған. Көрсетілгендей, 25 кэВ энергиясымен Bi^3+ ионды-сәулелік бомбылау кезінде екі наноөлшемді үлгісі Si массивті үлгісімен салыстырғанда қарқынды теріс кластерлік екінші ионды эмиссиясын көрсетеді. Байқағанымыздай, бұл «наноөлшемді шашырату әсері» $n > 7$ -ден Si_n^- ірі кластерлер және

наноұнтақтарының престелген таблеткалары үшін өте байқалады, онда жекелеген бөлшектері, түзілген голографиялық торлар бағаналарына қарағанда анағұрлым оқшауланған.

Түйінді сөздер: кластер; нанобөліктері; теріс иондардың эмиссиясы (шығарындысы); кремний; тозаңдату; өткен уақыт өлшемін қайталайтын ионды масс-спектрометрия.

Introduction

Study on secondary ion emission (SIE) of silicon has a long story, and a great deal of the experimental data were collected in this field (see, e.g.,¹⁻³ and references cited therein). From the practical point of view, silicon due to its wide and successful application in micro- and nanoelectronics continues to be one of the major objects of sputter depth profiling by means of secondary ion mass spectrometry. From the theoretical point of view, this material is suitable for fundamental study on the mechanisms of neutral and charged cluster emission under the bombardment by mono- and polyatomic (cluster) ion-beams in the range of a several keV. However, there is a lack of experimental data on an influence of the dimensional characteristics of silicon samples, especially nanometric-sized, on their SIE. Before now, the most part of studies has been conducted with gold nanoparticles,^{4,5} and an amplification of cluster ion emission under the bombardment by different polyatomic primary ions was revealed (so called “nanoscale effect of sputtering”). In this work, we aimed at understanding the difference in SIE of silicon samples depending on their dimensional features.

Experimental details

Three kind of silicon samples were studied. Massive Si sample is a part of single-crystal wafer with (100) orientation and resistivity of 12 Ohm·cm (p-type doping by boron) obtained from IPM RAS (Nizhniy Novgorod, Russian Federation). Nanopowder Si sample was prepared by mechanical pressing of spherically-form nanoparticles into a 100–300 μm thickness pellet. Mean diameter of the particles produced at Shanghai Yao Tian New Material Co. Ltd (Shanghai, China) by plasma arc technique is estimated to be 60 nm with a density of 1.36 g·cm⁻³ and the bulk oxygen content lower than 2 at.%. Holographical grating sample consisted of the columns of 200 nm in height and 160 nm in diameter was fabricated at AMO GmbH (Aachen, Germany) by chemical etching of (100) single-crystal silicon wafer of 2 mm in thickness.

The SIE study of the above-mentioned Si samples was carried out at IPM RAS using a time-of-flight secondary ion mass spectrometer TOF.SIMS-5 by ION-TOF (Münster, Germany). The instrument operates in dual-beam mode employing continuous 1 keV/80 nA Cs⁺ ion-beam for the sputtering and pulsed 25 keV Bi₃⁺ cluster ion-beam for the probing with 45° incidence angles for both beams. In each experiment, the sputter ion-beam was scanned over an area of 250×250 μm² during 1 min to eliminate surface contaminations. Then, the probing ion-beam was used for mass spectra acquisition within an area of 40×40 μm², that is ca. 2.5 % in square around the center of sputtered zone. Both positive and negative secondary ion mass spectra in the range up to 1000 *m/z* were collected. In this work, only negative mass spectra are discussed. In our opinion, they are more informative since, in contrast to the positive ones, were not “polluted” by heavy Cs-contained secondary cluster ions originated from the preliminary ion-beam cleaning of the samples surface by Cs⁺ bombardment.

Results and discussion

Representative negative mass spectra of the Si samples measured under the steady state conditions, where the variation of signal intensities versus the time of measurements was negligible, are presented in Figure 1. Besides characteristic Si_{*n*}⁻ cluster ions, where *n* is a number of silicon atoms in cluster, the spectra contain the peaks of electronegative contaminations (C, O, OH, F, Cl and hydrocarbons), different oxide and hydroxide Si clusters. In our experiments, the maximal *n*-number for massive Si (Figure 1a) was found to be 11, while for nanopowder Si (Figure 1b) and holographic Si grating (Figure 1c) these

numbers were 17 and 16, respectively. It is interesting that Ninomiya et al.³ in their study on positive secondary ion emission of massive Si samples under large Ar^+ cluster ion bombardment also observed Si_n^+ clusters up to $n=11$.

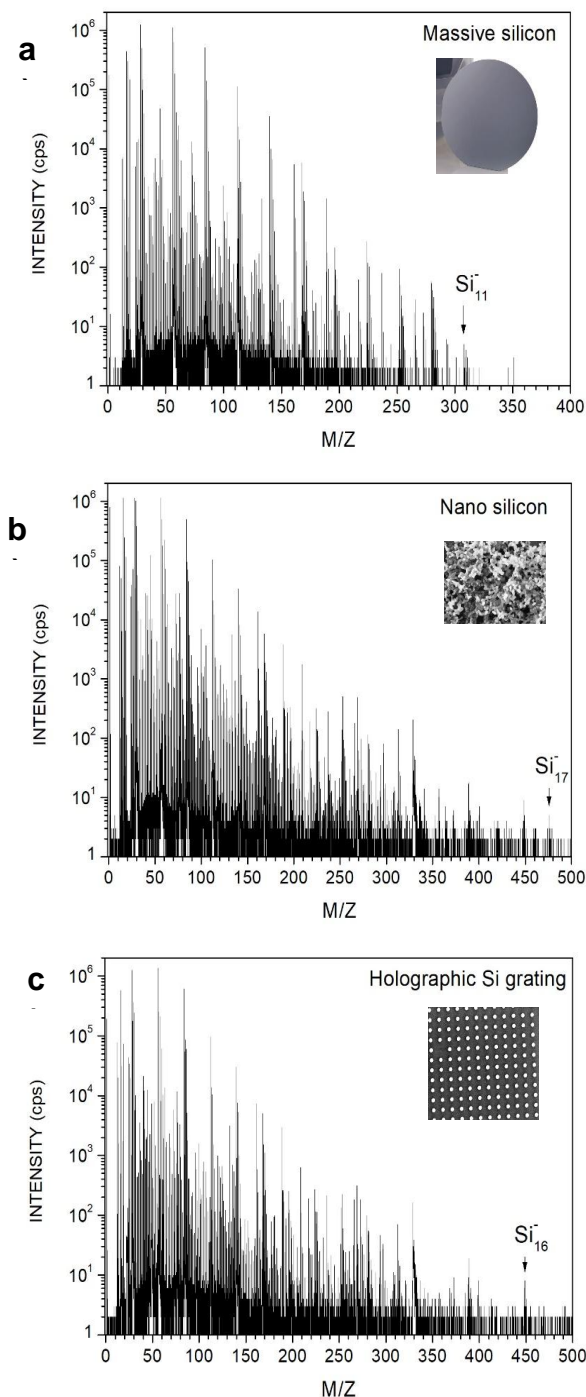


Figure 1 Massspectra of negatively charged secondary ions acquired for the different silicon samples under 25 keV Bi_3^+ ion-beam bombardment: a) massive single-crystal wafer, b) nanopowder pellet, c) holographic grating

In Figure 2, the intensities of $^{28}\text{Si}_n^-$ ($n = 2-11$) peaks of nanopowder pellet and holographic grating scaled to the intensity of the corresponding peaks of massive Si sample are shown. One can see that the intensity of large silicon clusters, starting from $n > 7$, become greater for both nanosized samples as compared with massive Si, and this difference is more pronounced for nanopowder pellet. It should be mentioned that all mass spectra presented in Figure 1 were acquired under the same experimental conditions including the potentials of an electronic multiplier and the coefficients of amplification/discrimination of the registration system of a TOF.SIMS-5 mass spectrometer. By that reason, the mass-spectral noise observed in Figures 1b,c for nanosized samples in the mass range higher than 300 m/z can be also attributed to the cluster secondary ion emission, but not to the apparatus artifacts of the measurements.

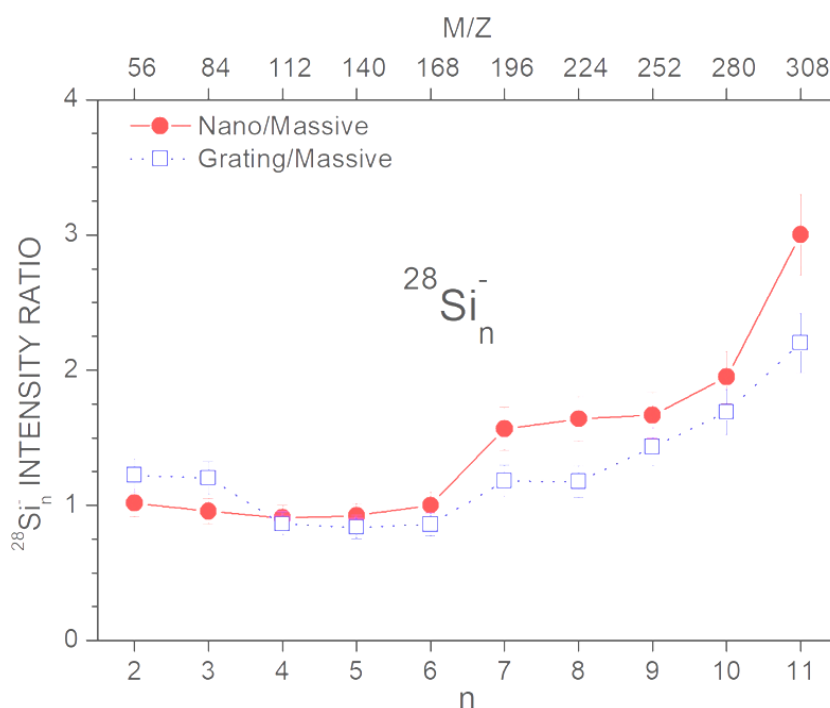


Figure 2 Intensity of $^{28}\text{Si}_n^-$ ($n = 2-11$) clusters of nanosized samples scaled to the intensity of the corresponding clusters of massive Si

In Figure 3a, the total ion intensities calculated for each sample in the mass interval $\Delta M = 56$ amu within the mass range from 0.8 to 400 m/z are presented in the histogram form. Each mass interval, starting from the second one, includes two peaks of the main isotope Si cluster ions (the first interval, from 0.8 to 57 m/z , includes atomic Si^- and Si_2^- peaks). Up to 169 m/z (in the initial three mass intervals), the difference in total ion intensity between massive and nanosized samples is rather small. However, for heavier masses the nanosized samples exhibit more intense SIE, especially in case of nanopowder pellet. In Figure 3b we presented these data scaled to the corresponding intensity of the mass intervals of massive silicon. One can see that for $m/z > 300$ the scaled total ion intensities of nanosized samples surpass the similar data of massive Si more than in an order of magnitude.

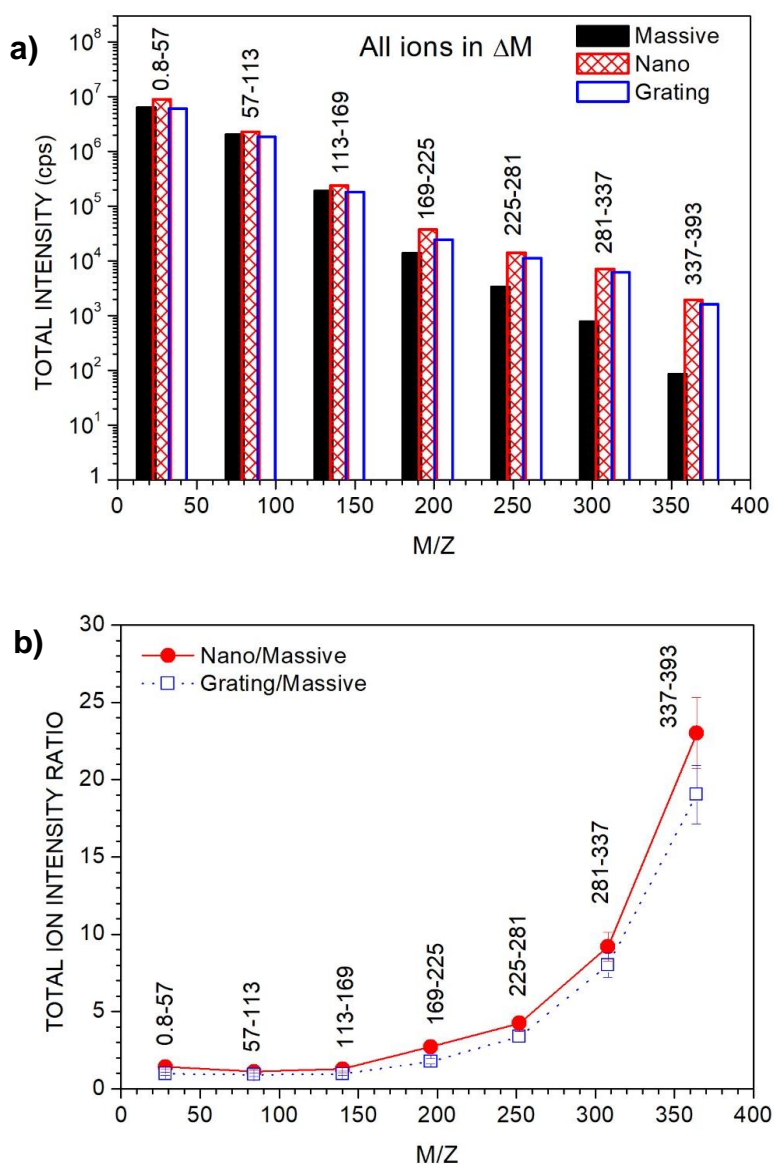


Figure 3 Total intensity of all secondary ions calculated into the mass intervals shown in the panel: a) as–received data, b) the data scaled to the corresponding intensity of the mass intervals of massive Si

In the first approximation, the peak intensity I_n of siliconcluster secondary ions composed of n individual atoms can be presented as

$$I_n \propto (Y * \beta_n^-)_n * N, \quad (1)$$

where Y_n is the cluster sputter yield, i.e. an average number of clusters ejected off the sample per incident primary ion, β_n^- is the negative ionization probability, i.e. the fraction of the sputtered cluster flux that is ionized, and N is the atomic density of silicon in the sample to be sputtered. Of course, this is very schematic approximation, which leaves out of account in full measure the complexity of the processes occurring during cluster secondary ion emission,

particularly under polyatomic (cluster) ion bombardment. However, basing of this factorization one able analyzing and discussing the data obtained in this work.

The atomic density of massive Si sample is higher than that of nanosized samples. It means that a greater number of atoms are involved in the sputter process in massive Si as against nanosized samples. However, an efficiency of sputtering, especially for the large (“populated”) clusters, with bigger n , should be higher for nanosized samples since for nanoparticles, even not fully isolated as in our experiments, more favorable conditions for the development of nonlinear collisions cascades inside these particles are realized. Besides, the channels of energy dissipation of the bombarding ions within the volume of each particle are limited, which results in higher density of energy released in this volume. In the upshot, an amplification of cluster SIE is observed, that is “nanoscale effect of sputtering” (see Figure 2, 3). Such effect is more pronounced for nanopowder pellet because of the particles in this sample are more isolated than in the columns formed holographic grating. In our opinion, the ionization probability β_n^- of the clusters emitted from nanosized samples is higher as against massive ones since the charge formation and/or exchange processes mainly occur in the surface and near-surface region of nanoparticles possessing greater surface energy and the ratio of surface/bulk atomic concentration. It should be noted that at present time the understanding of ionization phenomena responsible for the charge formation of emitted cluster (or its survival) is at rudimentary stage, and detailed discussion of such topic is beyond the scope of the present article.

Conclusion

We experimentally showed that nanosized Si samples in the form of pressed pellet made of ca. 60 nm in diameter individual particles and holographical grating consisted of the columns of 200 nm in height and 160 nm in diameter under 25 keV Bi_3^+ ion-beam bombardment exhibit more intense negative cluster secondary ion emission as compared with massive Si sample. The “nanoscale effect of sputtering” is more pronounced for large Si_n^- clusters with $n > 7$ and for pressed nanopowder pellet, in which individual particles are more isolated than in the columns formed holographic grating. Our further studies will aim clarifying the dependence of this effect on the size, type and degree of isolation of nanoparticles, which allows more efficiently using the nanoscale sputtering for the perfection of our sputtering-type high-current sources of homogeneous and heterogeneous cluster ions.^{6,7}

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