STUDY OF SI SURFACE MODIFICATION WITH IRRADIATION, PLASMA AND ULTRASOUND FOR GAS SENSING APPLICATION

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In order to search the new physical principles for high sensitive and selective gas sensors on the base of porous silicon creating we examined gas sensitivity of the silicon surface modified with charge particle irradiation, chemical plasma and ultrasound. Single crystal Si and SiO_2/Si structures were irradiated with ions (6.8 MeV H, 27.2 MeV He, 290 MeV Ar, 372 MeV Xe, 710 MeV Bi), treated with chemical plasma with 80-100eV F-content and with ultrasound (P=0.5 W, 8 MHz). The sample's absorption properties were obtained from the analysis of the optical parameters changes (refraction index and absorption coefficient, and a thickness of near-surface region, too). The latest were studied by the method of multiangular monochromatic ellipsometry in test camera in ethyl alcohol, ammonia and acetone environment. Scanning electron microscope (SEM) and atomic force microscope (AFM) were used to analyze the surface morphology.

Protons and alpha particles were found to lead to the Si near-surface layer destruction of and an enhancement of the surface roughness. The proton irradiated samples revealed a higher sensitivity to the absorption of ammonia and acetone molecules. Plasma treated Si displays surface modification (loosening of near-surface layer), though, gas absorption is not clearly revealed. Optical properties of Si/SiO_2 structures depend on the dimensions and the depths of nanopores, created by the etching of latent tracks in dioxide after irradiation. The greatest optical constant changes occurred in irradiated with ^{209}Bi structures, where tracks penetrated the whole dioxide. Accordingly bismuth-irradiated structures have the best gas sensitivity. Ultrasound influences on the optical parameters of porous Si/SiO_2 structure (loosening of the near-surface layer). However, these changes are unstable; and optical characteristics relax to the initial value in time. The best result was obtained for SnO_2 /SiO_2 /Si structure, where nanopores etched in the Xe latent tracks areas, were filled with SnO_2.

Introduction

Gas sensors are used for environment and process monitoring and for homeland security as well as for biomedical research, drug development and medical diagnosis. Highly sensitive, small-sized and low cost sensors are required in all these fields. It appeared porous Si (PS) to be a unique and versatile material for such sensors.

PS has attracted significant attention for its optical properties. This nano-structured material is characterized with high surface to volume ratio. PS is biocompatible, bioactive and biodegradable by nature and offers surface topography controllable with nm resolution in three dimensions and allows chemical surface modification [1]. All that as well as inexpensive technique of fabrication and suitability for integration with silicon electronics makes PS especially attractive for sensor application.

In order to create porous Si surface a number of techniques was proposed [2, 3], and ion-beam irradiation seems to be highly promising. In the last case, irradiation of SiO_2/Si structure with high energy ions leads to the formation of the latent tracks along ion trajectories in SiO_2 layer [4]. These tracks are the elongated cylinders with diameters of 5-20 nm with the modified density and chemical bond. These cylinders are surrounded with undamaged matrix. A chemical etching in the suitable solution leads to the formation of nanometer pores in the latent track areas. Thus, the pores of fixed dimensions and definite geometry with controllable distribution may be created in SiO_2 layer on silicon wafer by means of ion-beam bombardment followed by chemical etching [3].

In this paper we present the results of the study of the absorption possibilities of silicon surface modified by means of high energy ion irradiation as well as chemical plasma and ultrasound treatment.

Experiment

Chemically polished single crystal n-Si(100) wafers with natural dioxide layer (d = 15nm) and SiO_2/Si structures with thermal SiO_2 layers ($d_{SiO2} \approx$ 500 nm) and with additionally deposited SnO_2 films were used.

i) Single crystal Si samples were irradiated in cyclotron U-120 (KINR-Kyiv) with 6.8 MeV protons (H) and 27.2 MeV α-particles (He).

Chemical plasma with F-content (ion energy is equal to 80-100eV) was also used.

ii) In order to reveal nano-sized pores in the region of latent ion tracks the Si/SiO_2 structures irradiated with Ar (290 MeV), Xe (372 MeV) and Bi (710 MeV) ions at the Joint Institute for Nuclear Research (Dubna, Russia) were etched in the buffer hydrofluoric (HF) acid.

Bi-irradiated *porous* SiO_2(d_{SiO2} =600 nm)/Si were treated by ultrasound (P= 0.5 W, 8 MHz, t= 2 h).

iii) For a part of samples the nanopores etched in SiO_2/Si structures were filled with tin dioxide (SnO_2). SnO_2 is known to be highly sensitive compound used in gas sensors [5]. SnO_2 layer formation included two steps. At first Sn layer was deposited by means of spray pyrolysis [6] and afterwards Sn layer was annealed in air at 600 °C for 2 hours in order to obtain SnO_2. The same procedure was carried out for the samples of single crystal Si and SiO_2/Si in order to fabricate SnO_2/Si and SnO_2/SiO_2/Si structures for comparison with SnO_2/*porous* SiO_2/Si.

Optical characteristics of samples were studied by the method of multiangular monochromatic ellipsometry. Refraction index n and absorption coefficient k, and also thickness d of near-surface region were calculated before and after irradiation from experimental dependencies of polarization angles ψ and Δ on the angle of incidence φ (in the vicinity of the Brewster angle) by solving the inverse ellipsometric equation. LEF-3M zero-ellipsometer (*λ*=632.8 nm) was used with the measurement accuracy 0.03° for ψ and 0.09° for Δ.

In addition, scanning electron microscope (Hitachi S-806) and atomic force microscope (Dimentional™ 300) were used to analyze the surface morphology and to choose the calculating model properly [4].

In order to study the gas absorption properties an experiment was carried out in test camera with the possibility of gas environment varying (ethyl alcohol, ammonia and acetone).

Results and discussion

i) The polarization angle's dependences *ψ(φ)* and *Δ(φ* were measured after some doses from 10^{14} to 10^{17} cm^{-2} and were compared with initial ones. The optical constants of Si near-surface region were calculated in the frames of "a thin oxide SiO_2 film on Si" model. Complex refraction index *N*=3.842-0.020i of initial sample agrees with tabular data. It has been found that the modification of optical parameters of the samples irradiated with high fluence is caused by the destruction of near-surface layer of the material and accompanied by an enhancement of the surface roughness. According to the AFM data a surface roughness increases (in 10 times greater for protons and in 20 times greater for α-particles in comparison with 0.5 nm value for initial sample). In spite of the same high-energy particles projected range (360 μkm) for both irradiation types Si surface is modified in different ways. Protons lead to the surface loosening (calculating *n* drops from 3.842 to 2.900); helium ions provoke surface compression (*n*=4,102). This last value is close to amorphous or polycrystalline Si [4]. A nature of effect is not clear. We suppose the surface loosening is due to preferable vacancy clusters, created by fast protons. For alpha-particle irradiation the destruction of the near-surface layer is more complicated. It occurs only at high dose ($10^{17}/cm^{-2}$), when a sufficiently large amount of radiation defects is present. It might be the defect self-ordering effect.

Despite the fact that we failed to discover pores in irradiated Si, the modified surface has revealed gas sensitivity. From experimental curves one can obtain the sensitivity S_ψ of the ellipsometric parameters to the absorption of different vapors by measuring the depth difference between minimal polarization angle ψ^{min} in *ψ(φ)* dependence for saturated vapors and without them by equation

$$S_\psi = \Delta\Psi / \rho_{sat} = (\psi^{min}{}_{sat} - \psi^{min}{}_0)/ \rho_{sat} , \qquad (1)$$

where ρ_{sat} is the saturated vapor density.

In the case of proton treatment (10^{16} cm^{-2}), a higher sensitivity to the absorption of ammonia and acetone molecules was observed in comparison with the sample without irradiation (Table).

Optical parameters of Si single crystal treated by F-rich plasma were calculated in the frames of the same model as for irradiation. It was found the decrease of refraction index and the increase of destructed layer thickness. Filling the measured camera with different gas vapors doesn't change layer thickness. Though, the subsequent growth of surface absorption coefficient observed in ammonia and acetone environment testifies a surface modification, too.

ii) Optical properties of irradiated SiO_2/Si structures depend on the ion energy and mass and, consequently, on dimensions and the depths of nanopores created by ion latent tracks etching in dioxide. It has been shown in our previous auxiliary SEM study [3] that swift Ar ions irradiation does not result in etched tracks in SiO_2. The chemical treatment of Xe- and Bi-irradiated SiO_2/Si structures results in the formation of non-uniform porous layers (the higher porosity in the upper near-surface layer). Thus two types of a model were chosen for optical parameters' calculation: (SiO_2/Si) - for Ar and (*porous* SiO_2/SiO_2/Si) - for Bi. The greatest optical constant changes occurred in structures irradiated with Bi. In our experiment Bi ions were characterized with the largest mass and highest energy. As the most developed surface is formed in this case, Bi-formed porous structures have also the best gas sensitivity. In order to calculate gas sensitivity by means of equation (1) the polarization angles ψ^{min} obtained from experimental *ψ(φ)* curves were used (see Table).

Sensitivity with the respect to the polarization angle ψ **S_ψ**, 10^4deg/gxcm^{-3}				
objects	Si		SiO_2/Si	
Vapors	Initial	Proton irradiated	Initial	Bismuth irradiated
Ethyl	20.0	9.21	2.62	60.7
ammonia	2.3	4.5	0.44	27.2
acetone	1.7	3.0	0.63	33.6

In order to study the ultrasound influence on the absorption properties of the modified surface SiO_2/Si structures with Bi-formed pores were treated by ultrasound (during 2 hours) and their optical properties were measured by ellipsometer. For a comparison standard structures were also treated by ultrasound. After sounding additional surface modification occurs in porous structures as the calculated thickness of destructed near-surface layer increases from 250 to 280 nm. Ultrasound induced changes are unstable. It was shown that experimental angular dependencies relax to the initial value in time.

iii) Pore formation in oxidized Si irradiated with swift ions is of a great interest. It is possible to create homogeneous or multi-layer nanowire and cluster structures on Si wafers by means of chemical and electrochemical pore filling with different materials [5]. We studied the optical and absorption characteristics of Xe-formed porous SiO_2/Si structures filled with SnO_2.

SnO_2 was formed on Si surface and on initial SiO_2 (d_{SiO2} =600 nm). Figure 1 shows the AFM-image of the surface of SnO_2/porous SiO_2/Si structure. One can see from the image that pores are nearly the same by dimensions.

For all types of structures optical parameters were calculated from experimental angular dependences according proper models.

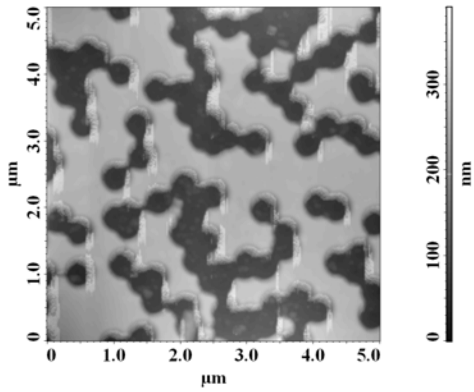

Figure 1. 2D AFM image of the SnO_2/ porous SiO_2 / Si structure

A model of "SnO_2 with thin SiO_2 film on Si" was chosen in the case of SnO_2 deposited on Si. "Two layers model" (SnO_2/*porous* SiO_2/Si) was taken for *porous* SiO_2/Si filled with SnO_2.

Ellipsometric data $\psi(\varphi)$ i $\Delta(\varphi)$ show that there is an effective layer which consists of hard SiO_2 porous matrix, filled with SnO_2. Analysis of the absorption properties has shown that *porous* SiO_2/Si structures with the SnO_2 filled pores (whose length is less than the SiO_2 thickness) display the increase of the layer thickness from 200 to 220 nm in comparison with previous results of Bi ion-formed structures (when pores pierce the whole SiO_2 layer). where absorption in acetone vapors is observed,.

Conclusion

It was found that surface modification occurred for all kinds of treatments (high energy particles irradiation, plasma and ultrasound). This modification results in changes of optical parameters and the thickness of near-surface destruction region. However, it was found that irradiation only is suitable to the formation of surfaces sensitive to gases (ethyl alcohol, ammonia and acetone vapors). In turn, structures with thick oxide layers irradiated with heavy high energy ions reveal higher gas sensitivity with the respect to the polarization angle ψ (S_ψ increases in 20-30 times in ammonia and acetone vapors for SiO_2/Si and nearly twice for Si).

The best gas absorption is observed for SiO_2/Si structures irradiated with Bi. In this case highly developed nanoporous surface is formed after etching of the latent ion tracks. The *porous* SiO_2/Si samples filled with SnO_2 reveal pores nearly the same by dimensions and contribute to the further sensitivity grows.

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ИССЛЕДОВАНИЕ МОДИФИКАЦИИ ПОВЕРХНОСТИ КРЕМНИЯ С ПОМОЩЬЮ ОБЛУЧЕНИЯ, УЛЬТРАЗВУКОВОЙ И ПЛАЗМЕННОЙ ОБРАБОТОК ДЛЯ ИСПОЛЬЗОВАНИЯ В ГАЗОВЫХ СЕНСОРАХ

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С целью поиска новых физических принципов создания газовых сенсоров с высокой чувствительностью и селективностью на основе пористого кремния исследована чувствительность к газам поверхности кремния, модифицированного облучением, ультразвуком и химической плазмой. Монокристаллы кремния и структуры SiO_2/Si облучены ионами (6.8 МеВ H, 27.2 МеВ He, 290 МеВ Ar, 372 МеВ Xe, 710 МеВ Bi), обработаны химической плазмой с добавкой 80-100еВ F, а также ультразвуком (P=O.5 Вт, 8 МГц). Адсорбционные свойства образцов анализировались по изменению оптических параметров (комплексного показателя преломления) после обработки. Оптические характеристики поверхности и оксидной пленки измерялись по методике многоугловой монохроматической эллипсометрии в специально созданной камере в парах спирта, аммиака и ацетона. Показано, что 6.8 МэВ протоны и 27.2 МэВ α-частицы приводят к деструкции поверхностного слоя монокристалла, что сопровождается увеличением шероховатости поверхности. В облученном протонами Si возрастает чувствительность к парам ацетона и аммиака.

Оптические свойства структур *нанопор*SiO_2/Si зависят от размера и глубины пор, образованных при протравливании скрытых треков в облученном материале. Наибольшие изменения оптических свойств и, соответственно, наилучшая чувствительность к газам, наблюдаются в структурах, облученных Bi, где поры пронизывают всю толщину слоя SiO_2. Ультразвук также приводит к изменению свойств SiO_2/Si (заметное разрыхление приповерхностного пористого слоя, созданного травлением облученного материала), однако эти изменения нестабильны во времени. Обработка химической плазмой приводит к некоторой поверхностной модификации, но адсорбционные свойства материала не изменяются. Наилучший результат получен для структур SnO_2/*нанопор*SiO_2/Si, где поры, вытравленные на местах треков в облученных Xe структурах SiO_2/Si, заполнены диоксидом олова. В таких структурах поры одинаковы по размерам.