Optical reflectance of silicon implanted by silver ions

A. L. STEPANOV[a,b,*], Y. N. OSIN[b], V. V. VOROBEV[b], V. F. VALEEV[a], V. I. NUZHDIN[a]
[a]*Kazan Physical-Technical Institute, Russian Academy of Sciences, 420029, Kazan, Russia*
[b]*Kazan Federal University, 420008, Kazan, Russia*

The new results on the optical reflection of the Si surface layers implanted by silver ions at low energies of 30 keV over a wide dose range from 5.0×10^{14} to 1.5×10^{17} ion/cm^2 are presented. As the ion dose of irradiation was increased, a monotonic decrease in the reflection intensity in the ultraviolet region of the spectrum was observed, due to amorphization and macrostructuring of the Si surface. On the other hand, in the long-wavelength region, a selective reflection band appears with a maximum near 830 nm due to plasmon resonance of Ag nanoparticles synthesized during implantation.

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1. Introduction

A solution of the energy problem on the efficient conversion of solar radiation into electricity is one of the priority aim for fundamental and applied research. At present, in practice, to ensure the required level of absorption of solar radiation, solar cell elements from sufficiently thick plates of crystalline c-Si from 180 to 300 μm are used. At the same time, the main costs of manufacturing solar cells are determined by the price of growing and subsequent processing of thick-layer Si substrates. Therefore, it seems relevant and economically important to create 2D solar cells on thin Si (< 1 μm) layers with an amorphous or polycrystalline structures [1]. In addition, the area of functional applications for thin-layer solar cells could be widened, for example, when such elements ate integrating with modern compact optoelectronic microcircuits and Si-based devices.

The main limitation for the effective use of thin-film 2D solar cells is a low absorption in the visible region near the edge of the fundamental band, as in case of an indirect semiconductor Si. With the purpose of increasing the absorptivity of such solar cells, an approach was recently proposed that involves the include in the structure of thin Si layers of noble metal nanoparticles of small dimensions (< 30 nm) [2, 3], in which localized plasmon resonance excited under the light. Plasmon resonance manifests itself in intense absorption of light by metallic nanoparticles in the visible spectral range [4, 5], which provides an increased total absorption of a thin semiconductor layer containing metal nanoparticles [7]. Moreover, the local electromagnetic field arising near nanoparticles due to plasmon resonance can generate the appearance of electron-hole pairs in semiconductors [3]. In practice, nanoparticles from Ag metal are considered for solar cells based on Si, as the most promising in terms of the degree of efficiency of plasmon excitation and absorption [8].

Thus, it is important to find some technological ways to create and optimize thin-film 2D Si materials with metal nanoparticles. At present, various methods such as vacuum deposition, electron lithography, any chemical approaches, etc. are applied to form composite Si layers with Ag nanoparticles. Of particular interest is the technology of ion implantation, which is actively used in industrial Si microelectronics. Also, it was shown that an implantation of monocrystalline *c*-Si with ions B^+ and P^+ improves photovoltaic properties of Si that finds the development in solar cells [9]. On other side, studies on the synthesis of Ag nanoparticles in the Si matrix during ion implantation for applications in solar energy was not previously carried out. Recently, it was proposed a new technology for the formation of thin layers of porous Si with Ag nanoparticles (Ag:PSi) at low-energy high-dose (> 10^{16} ion/cm^2) implantation of *c*-Si by Ag^+ ions [10-12]. Later, ellipsometric measurements were also carried out in parallel with the observation of the back scattering electron diffraction for the Ag:Si surface obtained by implantation at low doses (< 10^{16} ion/cm^2) [13]. In order to further analysis of the Ag:Si layers, in particular, to obtain optical characteristics which are important for solar cells, for the first time a study of optical reflectance spectra for Ag:Si samples formed by ion implantation were realised in a wide range of ion doses from 5.0×10^{14} to 1.5×10^{17} ion/cm^2.

2. Experimental

c-Si plates with a polished surface and a crystallographic orientation (100) of 0.5 mm thickness were used as the substrate at present study. Implantation of *c*-Si was carried out by singly charged Ag^+ ions with an energy of 30 keV at a current density in the ion beam of 8 μA/cm^2 at different doses from 5.0×10^{14} to 1.5×10^{17} ion/cm^2 using an ILU-3 ion accelerator at residual vacuum

of 10^{-5} Torr and at room temperature of the irradiated samples.

Optical reflection spectra were measured with an AvaSpec-2048 (Avantes) spectrometer at a normal angle of incidence of the probing and reflected light beam to the surface of the samples through a coupled waveguide in the spectral range from 220 to 1100 nm at room temperature. The rear side of the Si sample was grounded and so scattered light from large microstructures did not produced a mirror reflection. Observation of the morphology and characterization of the crystallographic structure of the implanted Si surface was carried out with a scanning electron microscope (SEM) Merlin (Carl Zeiss). Crystallographic data were obtained by diffraction of electron backscattered diffraction (EBSD) using a NordLys HKL detector (Oxford Instruments). In addition, the analysis of the sample implanted surfaces was performed with an atomic force microscope (AFM) FastSkan (Bruker).

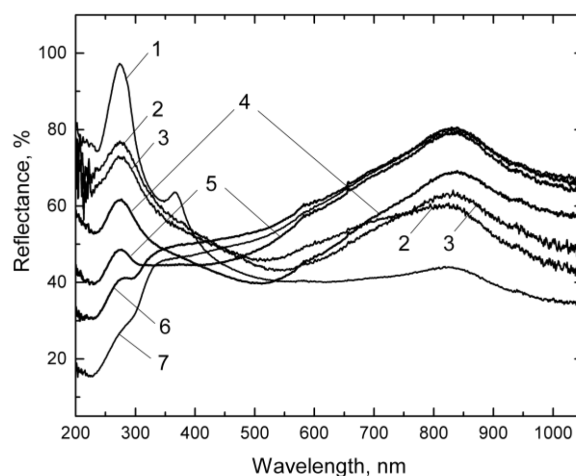

Fig. 1. Optical reflection spectra of unimplanted c-Si (1) and Ag:Si layers formed by implantation of Ag^+ ions by different doses: (2) 5.0×10^{14}; (3) 5.0×10^{15}; (4) 2.5×10^{16}; (5) 5.0×10^{16}; (6) 6.2×10^{16}; (7) 1.5×10^{17} ion cm^2

3. Experimental results and discussions

As was shown earlier, the thickness of the implanted layer in the Ag:Si sample formed upon irradiation of 30 keV with Ag^+ is 42 nm [10]. The penetration depth of light in the near ultraviolet spectral range in Si, as indicated in [14], is about 25 nm, which is within the thickness of the implanted layer.

The only known data on the optical reflection spectra of Si implanted with Ag^+ ions at an energy of 70 keV and only for quite low doses from 5.0×10^{12} to 5.0×10^{14} ion/cm^2 (< 10^{15} ion/cm^2) are limited to measurements in a narrow spectral range of 210 - 387 nm [14]. The reflection spectra of the Ag:Si layers formed in the present work at higher doses from 5.0×10^{14} to -1.5×10^{17} ion/cm^2 and for the unimplanted *c*-Si surface are shown in Fig. 1. The known reflection bands with maxima of 268 nm (4.56 eV) and 366 nm (3.39 eV), which are due to interband transitions near the *L* and *X* points of the Brullien zone, are found in the short-wave region of the *c*-Si reflection spectrum (Fig. 1, curve 1) [15] . In addition, for *c*-Si in the long-wavelength spectral region, a weekly intensity wide reflection band is observed with a maximum near 850 nm (1.45 eV). This band is present in the spectra of *c*-Si, given in various publications, for example [16], however, the nature of this band is not explained yet. Some private reports mention that a band with a maximum of 850 nm could be appeared in the case of various mechanical treatments of the Si surface, but, in any case, this circumstance requires a separate study.

As it follows from Fig. 1, for an Ag:Si sample implanted at the lowest dose of 5.0×10^{14} ion/cm^2, the intensity of the reflection band decreases with a maximum of 268 nm to 75% and a complete band loss at 366 nm relative to the *c*-Si spectrum (Fig. 1, curve 2) . The changes occurring in the optical spectrum of the implanted *c*-Si are explained by the amorphization of implanted surface layer (*a*-Si). Qualitatively similar patterns in changes of optical spectra were experimentally observed earlier for the implantation of *c*-Si with heavy ions (Ag^+, Sb^+, As^+, Xe^+) with an accelerating energy in the range from 40 to 100 keV for doses < 10^{15} ion/cm^2 [14, 16, 17]. It was concluded [14, 16] that these spectral changes are caused by amorphization of Si. Such reflectance change was not caused by possible morphological defects of the Si surface which could formed by implantation with small doses. Therefore Rayleigh scattering of light should not be considered to explain a decrease optical reflectance in the ultraviolet spectral region for low doses. Indeed, as follows from our observations of SEM, the surface morphology for the Ag:Si sample (5.0×10^{14} ion/cm^2) remains smooth and unchanged, as in the case of the initial *c*-Si plate (Fig. 2a). The formation of an amorphous layer for Ag:Si created by implantation is confirmed by the observations of EBSD. As a result of ion implantation, the crystallographic pattern from the Kikuchi lines for the original *c*-Si (Fig. 3a) is transformed into an image consisting of amorphous a-Si rings (Fig. 3b).

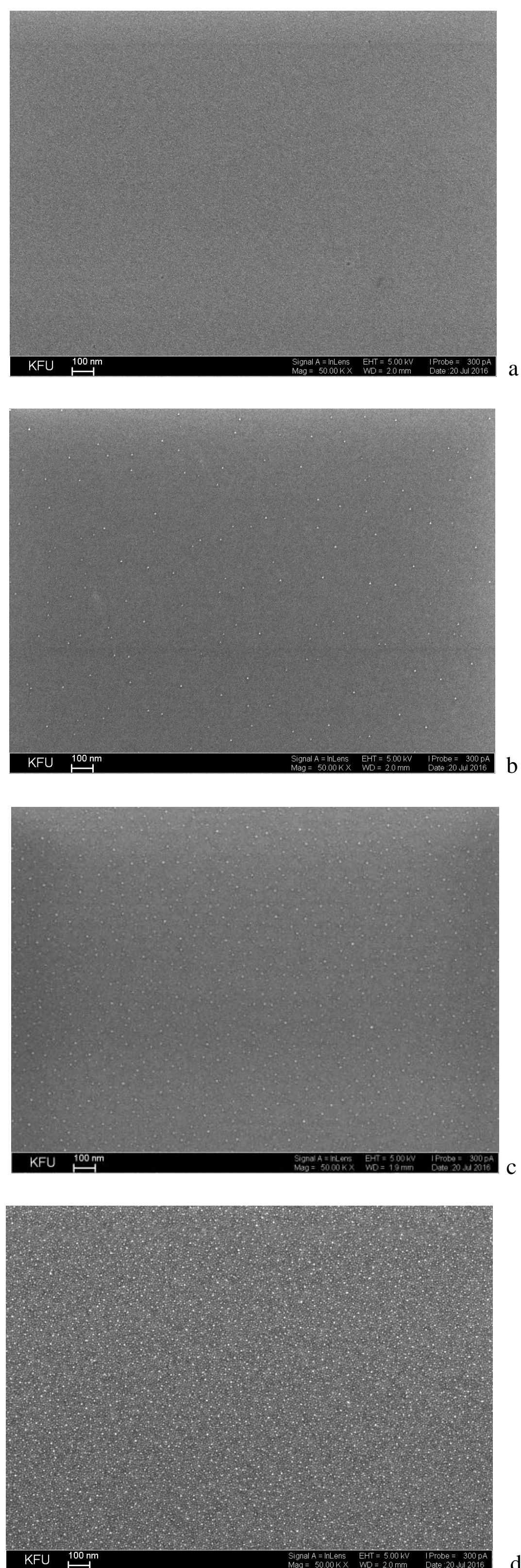

Fig. 2. SEM-images of unimplanted c-Si (a) and Ag:Si surfaces formed by implantation of Ag^+ ions by different low doses: (b)) 5.0×10^{15}; (C) 2.5×10^{16}; (D) 5.0×10^{16} ion/cm^2

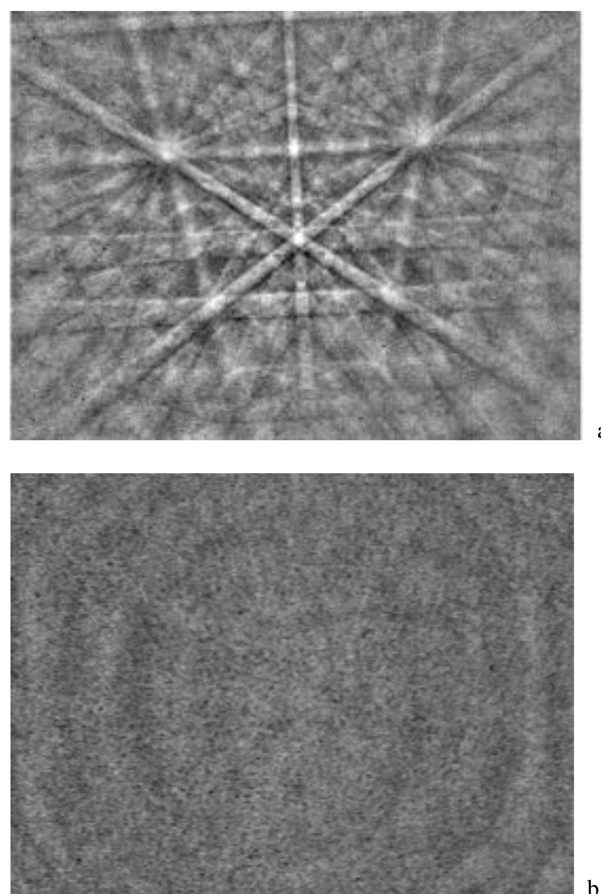

Fig. 3. EBSD-pictures of near-surface regions for unimplanted c-Si (a) and Ag:Si, formed by implantation of Ag^+ ions by a dose of 5.0×10^{15} ion/cm^2

In contrast to the earlier measurements of the optical reflectance spectra of implanted Si carried out in the ultraviolet region [14, 16, 17], at the present study, for all Ag:Si samples in the long-wavelength part of the spectrum from 500 to 1050 nm, for the first time a new broad band has been registered, the intensity of which increases from 60 to 80%, and the maximum shifts from 820 to 850 nm as the ion dose increases to 5.0×10^{16} ion/cm^2 (Fig. 1, curves 2-5). It should be mention that this new reflectance band placed in same spectral region as intrinsic week one of unimplanted *c*-Si (Fig. 1, curve 2). The development of this reflection band (Fig. 1, curves 2-5) is accompanied with dose increasing by the appearance in SEM-images of accompanying samples (Figs. 2b, c, d) bright spots against the background of a homogeneous gray Si surface, which, as suggested in [10-12], are ion-synthesized Ag nanoparticles. The average size of the nanoparticles is of the order of 5-10 nm (Fig. 2), as the ion dose increases, their number increases. Therefore, long-wavelength reflection bands with maxima of 820-850 nm in Ag:Si samples correlated with the reflection caused by plasmon resonance in Ag nanoparticles [4, 5]. Similar reflection was previously observed in the corresponding spectral visible area for plasmonic metal nanoparticles synthesized

by ion implantation in silicate glasses and polymers [18, 19].

To confirm the correspondence of experimentally observed long-wavelength reflection bands for Ag:Si samples with metallic nanoparticles, the extinction spectra of Ag nanoparticles placed in the Si matrix were simulated in the framework of the electromagnetic Mie theory by the approach given in [4]. Fig. 4 shows the extinction spectra of the Mi resonances of Ag nanoparticles of various sizes from 6 to 20 nm. As follows from the calculations, extinction bands appear in the spectral range from 700 to 950 nm, the maximum of which is shifted to the long-wave side with increasing nanoparticle sizes. These modelled resonance Mie bands appear in the same spectral visible range as the long-wavelength bands in the experimental spectra of Ag:Si samples (Fig. 1), which allows to conclude about their qualitative agreement. It should be mentioned that the experimental spectra are somewhat wider than the calculated spectra, so it could be assumed that the experimentally recorded reflection spectra consist of a superposition of the spectra of individual sets of Ag nanoparticles of various sizes. Estimates of the size distribution of Ag nanoparticles in Si were not carried out by us because of their smallness (Fig. 2).

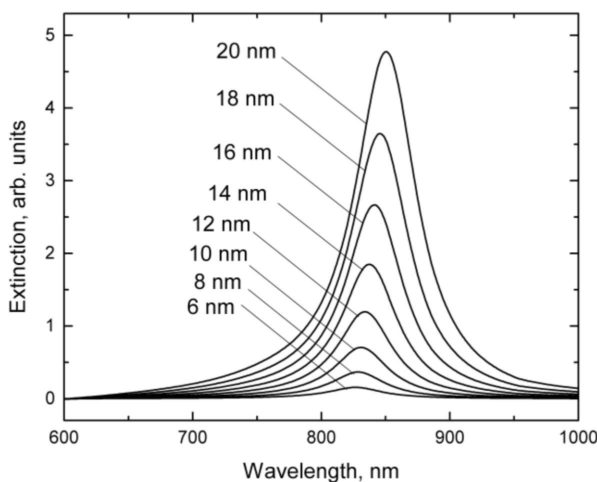

Fig. 4. Modelled optical extinction spectra of Ag nanoparticles in the Si matrix different nanoparticles sizes indicated for each spectrum

It should be noted that the calculations of the extinction spectra for Ag nanoparticles in the Si matrix (Fig. 3) are supported by independent simulations using the electrostatic approximation approach or the finite difference time domain (FDTD) technique for particle size of the order of 20 nm [20]. For such modelling, there is a qualitative agreement on the spectral position of the resonant absorption (reflection) bands of Ag nanoparticles with Mie calculations (Fig. 3) and experimental dependences (Fig. 1). An increase in the absorption of a thin Si layer after implantation by Ag-ions with energies of 58 - 78 keV and doses of 1.0×10^{16} - 1.75×10^{16} ion/cm^2 was reported in [21]. The authors of this work in the discussion also associated such effect with the formation of Ag nanoparticles with a size up to 20 nm in the irradiated Si layer, although plasmon absorption of nanoparticles was not discussed.

Another distinctive feature of the dose dependence for the optical reflection of Ag:Si samples in the long-wavelength spectral region (Fig. 1) is the invariance of the shape and intensity of the plasmon band of reflection of Ag nanoparticles in the high dose range 5.0×10^{16} - 1.5×10^{17} ion/cm^2. This circumstance, apparently, was explained by the previously considered effect [22], which consists in the fact that upon reaching a certain dose and with active sputtering of the surface, the distribution profile of the implanted ions in the sample depth does not change. Another words, the number of implanted Ag^+ ions is comparable to the fraction of the same ions sputtered from irradiated Si surface. Similarly, the number of ion-synthesized nanoparticles, starting with a certain dose (~ 5.0×10^{16} ion/cm^2) of implantation in the Ag:Si layer, also does not change. The experimentally observed sputtering of the Si surface during high-dose implantation with Ag^+ ions was demonstrated in [10, 11].

In contrast to the long-wavelength reflectance band of Ag nanoparticles on the short-wavelength part of the spectrum (220-420 nm) of the Ag:Si sample it is observed a monotonous integral decrease in the reflectance intensity of Si with increasing ion dose from 5.0×10^{14} to 1.5×10^{17} ion/cm^2 (Fig. 1). If, as it was discussed here, this regularity for a band with a maximum of 268 nm at low implantation doses is explained by amorphization of Si, then for the higher doses the effect of structuring the irradiated Si surface should be considered for an explanation of the integral decrease in the reflection intensity, as predicted in Refs [15, 16]. Indeed, as follows from electron-microscopy observations of implanted samples (Fig. 5a), starting at approximately an irradiation dose of 6.2×10^{16} ion/cm^2, in addition to the formation of Ag nanoparticles, SEM images clearly reveal the destruction of a smooth Si surface. Implantation of Si with higher doses leads to the formation of a porous structure on its surface (Fig. 5b), as a result of intense surface sputtering upon irradiation with silver ions [10]. Similarly, a developed surface for Ag: Si is also observed on the AFM (Fig. 6). As seen in this figure, the dimensional parameters of the surface structures are comparable with the wavelengths of ultraviolet light. Therefore, such structures have to initiate the Rayleigh scattering of light in all possible directions (not only from the mirror direction), which causes the observed integral decrease in intensity in the short-wave region of the reflection spectrum (Fig. 1). It is known that porous and fibrous materials based on Si with similar microstructures, similarly to the present study, exhibit intense diffuse Rayleigh scattering in this spectral region [23, 24].

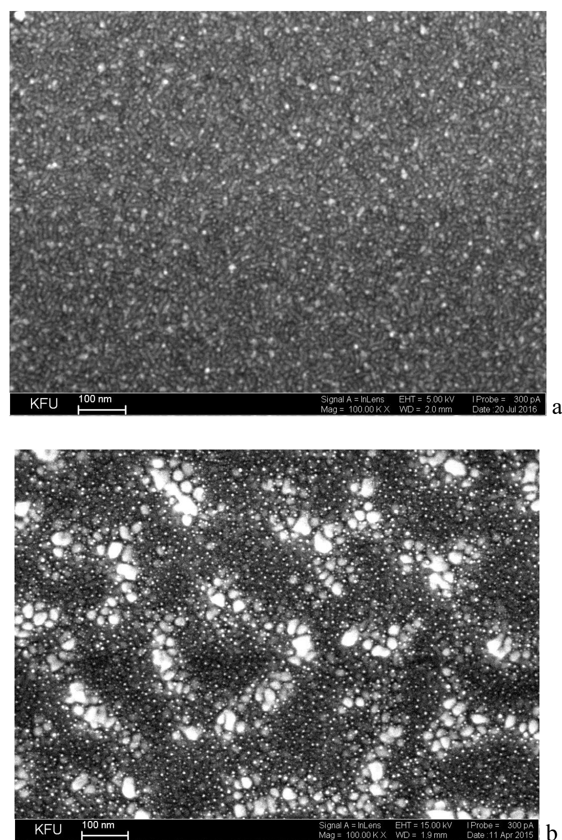

Fig. 5. SEM images of the Si surface implanted with Ag^+ ions at doses: (a) 6.2×10^{16} and (b) 1.5×10^{17} ion/cm^2. Images are shown on an enlarged scale, in comparison with Fig. 2

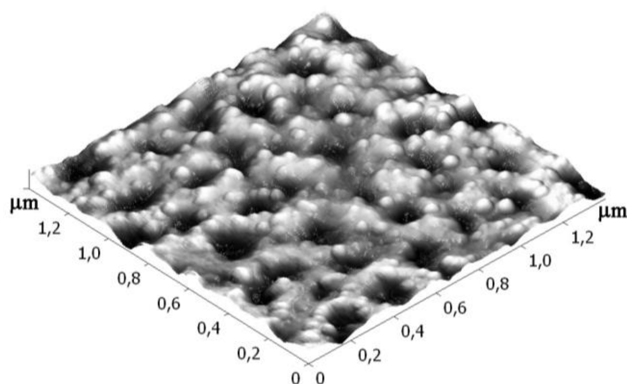

Fig. 6. AFM image of the Si surface implanted with Ag^+ ions at a dose of 1.5×10^{17} ion/cm^2

4. Conclusion

For the first time the optical reflection spectra of the Si surface implanted with Ag^+ ions at low energies over a wide range of doses from 5.0×10^{14} to 1.5×10^{17} ion/cm^2 were studied. The characteristic features of the reflection spectra of Ag:Si samples are a low level intensity in the spectral ultraviolet region (< 400 nm), caused by amorphization and macrostructuring of the Si surface, as well as the presence of a selective plasmon resonance band of Ag nanoparticles with a maximum of about 830 nm. The formation of Ag nanoparticles is observed by SEM and AFM when Si is implanted with Ag^+ ions at high doses. A successful experimental demonstration of the potential use of ion implantation for the synthesis of Ag nanoparticles in a thin Si layer suggests the prospects of using this technology for the development of thin-film solar cells.

Acknowledgements

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* Corresponding author: aanstep@gmail.com