

Experimental and theoretical study of the effect of bombardment with Ar⁺ ions on the spectrum of valence electrons of a Si (111) single crystal

Yokub Ergashov^{1,*}, Boltaxodja Umirzakov¹, Nebodir Nurmatov², and Golib Otamurodov³

¹Tashkent State Technical University, 100095 Tashkent, Uzbekistan

²National university of Uzbekistan, 100174 Tashkent, Uzbekistan

³Head Scientific and Methodological Center, 100095 Tashkent, Uzbekistan

Abstract. The paper studies the effect of disordering of the surface layers on the electronic and optical properties of single-crystal silicon. An analysis of the photoelectron spectra shows that with complete amorphization of the surface density, the condition of Si valence electrons changes significantly. In particular, the positions of the main maximum of the electrons of the valence band of Si (111) shift by ~ 0.4 eV towards higher binding energies and the band gap E_g increases by 0.1-0.15 eV. The energy of a valence electron in amorphized silicon, which at low impurity concentrations, i.e. at low bombardment doses ($D < 10^{15} \text{ cm}^{-2}$), the potential M_{kk} and, therefore, the shift of the maximum of the density of states vary linearly with respect to concentration. At high impurity concentrations (at doses $D > 10^{15} \text{ cm}^{-2}$), corresponding to the transition to amorphous silicon, the concentration dependence of M_{kk} is very weak. Therefore, upon amorphization, the peak A of the density of states of the silicon valence band under consideration is shifted to the region of lower electron binding energies. The theoretical substantiation of the obtained experimental results is given.

1 Introduction

Experimental and theoretical studies presented in [1-5] have shown that atom deposition, ion implantation, laser irradiation and other effects in different crystals lead to a sharp change in the electronic and crystal structure of their surface region, and these changes are mainly due to the formation of nanoscale structures, changes in the stoichiometric composition and phase structure of the near-surface layer. In this case, it is of particular interest to study the processes of formation of nanocrystals and the dependence of their physical properties on the size and the presence of structural defects in them [1-5,7].

Any change in the physicochemical state of the surface (the appearance of vacancies and interstitial atoms, the introduction or substitution of an implanted impurity, the appearance of active centers, disordering, the formation of compounds, etc.) first of all leads to a change in the density of state of valence electrons, which is well reflected in the experimental spectrum of photoelectrons: change in the intensity, shape and energy position of existing peaks or their disappearance and the appearance of new peaks [6,8-22].

The study of these changes is very important in the development of multilayer nanofilm metal-dielectric-semiconductor (MDS) and semiconductor dielectric semiconductor (SDS) structures, electronic and optical devices, including solar cells.

The main purpose of this work was to experimentally study the effect of the disordering of the crystal lattice of the surface of single-crystal Si(111) on its electronic structure and optical properties, as well as to provide a theoretical explanation of the experimental results obtained.

2 The method of the experiment

Basic experiments were performed using the universal setup with several chambers under high vacuum ($P \sim 10^{-6}$ Pa). The given setup was based on a universal ultrahigh-vacuum facility (Chernogolovka, Moscow oblast) [19-21]

The object of the study was p type single crystal Si(111) in the form of disks with a diameter of 10 mm and a thickness of 1 mm. The disordering of the Si(111) surface was carried out by bombardment with Ar⁺ ions with an energy of $E_0 = 1 \text{ keV}$ with a variation in the ion dose within the range of 10^{13} to 10^{16} cm^{-2} . Before ion implantation, the Si surface was cleaned by heating to $T = 1200 - 1300 \text{ K}$ for 10 - 12 hours and pulsed heating to $T = 1500 \text{ K}$. The surface composition was controlled by Auger electron spectroscopy (AES) and high-energy electron diffraction (RHEED) methods.

To study the changes in the parameters of the energy zones and the density of state of valence electrons Si(111) during ion bombardment, we used the methods

* Corresponding author: vergashev@mail.ru

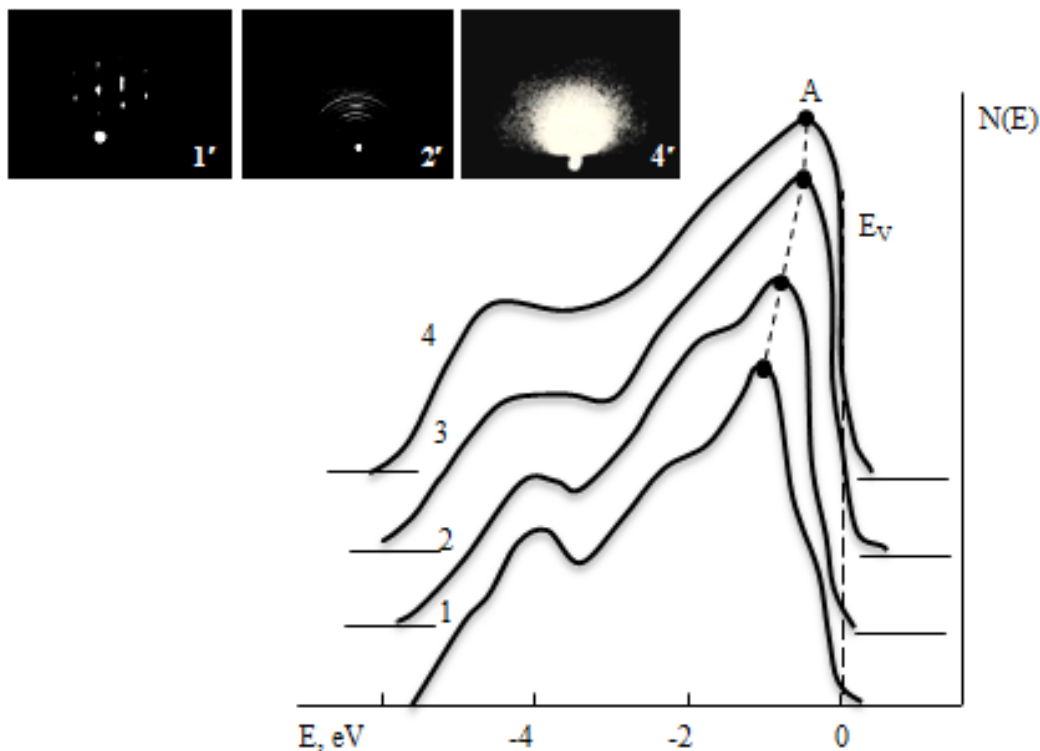


Fig. 1. Spectrum of photoelectrons and DFE-images (insert) of the Si(111) surface bombarded with Ar⁺ ions with E₀= 1 keV at various ion doses D, cm⁻²: 1 and 1'-0, 2 and 2'- 2·10¹⁴, 3·10¹⁵, 4 and 4'-10¹⁶.

of ultraviolet photoelectron spectroscopy (UVES) and measuring the intensity I of light passing through the sample (light transmittance K).

The study of the atomic depth distribution profiles was carried out using the (AES) method in combination with surface etching with Ar⁺ c E₀=1 keV ions at an angle of ~80° relative to the normal.

Annealing, ion bombardment, atom deposition, and all measurements were carried out in the same experimental setup at a vacuum no worse than 10⁻⁶ Pa. The degree of disordering of the surface was estimated from the fast electron diffraction patterns.

3 Results and discussion

Before ion bombardment, the surface of Si (111) was cleaned by prolonged heating at T=1200 K and short-term heating to T=1500 K in combination with soft etching of the surface with Ar⁺ ions.

At the same time, the total concentration of impurity C and O atoms on the surface did not exceed 0.5-1 at.% and practically did not affect the structure of the photoelectron spectrum.

Figure 1 shows the dynamics of changes in the spectrum (energy distribution curve - EDK) of photoelectrons and the RHEED of the image (in the insert) of the Si (111) surface when bombarded with Ar⁺ ions with E₀=1 keV at different doses.

The Ar⁺ bombardment was conducted perpendicular to the surface. In the based one, we will consider the change in the position and shape of the main peak A of

Si. It can be seen from Fig. 1 that, with an increase in the radiation dose, the peak A broadens, its amplitude decreases, and its position mixes towards higher energies (the upper edge of the valence band E_v).

In this case, the Si surface gradually transitions from a single crystal structure to a highly disordered amorphous state (insert Fig.1).

Under ion bombardment, the composition of the Si surface is practically unchanged, therefore, the observed changes are mainly explained by the disordering of the surface and near-surface layers.

At D=6·10¹⁵ cm⁻² complete amorphization occurs. However, all the features characteristic of amorphous Si was established at D=6·10¹⁶ cm⁻² and a further increase in D practically does not lead to a change in the spectrum of photoelectrons.

The table shows the values of the band gap E_g and the light transmission coefficient K for the Si(111) single crystal, measured before and after the amorphization of the surface.

The table shows that when the surface is disordered the band gap E_g increases slightly.

Despite this, the value of K at hv<E_g significantly decreases (hence, the absorption coefficient increases), which is mainly due to the appearance and increase in the concentration of different energy levels in the band gap due to disordering of the surface.

Change in the density of the state of the valence band Si (111), in the process of disordering the surface from a theoretical point of view. On the basis of Fig. 1, the dependence of the energy shift ΔE of the main Si peak A on the dose of Ar⁺ ions is constructed (Fig. 2). It is seen

Table 1. E_g and K values for Si(111) measured before and after surface disordering.

Sample	The structure of the surface	E_g, eV	$K, \text{v } \%$	
			$h\nu=0.8 \text{ eV}$	$h\nu=1.5 \text{ eV}$
Si(111)	Single crystal	1.1	85 ± 5	5 ± 1
$\text{Ar}^+ \rightarrow \text{Si}(111)$	Amorphous	1.25	40 ± 5	5 ± 1

that the largest shift of the peak A due to the amorphization of the near-surface layer is 0.4-0.45 eV.

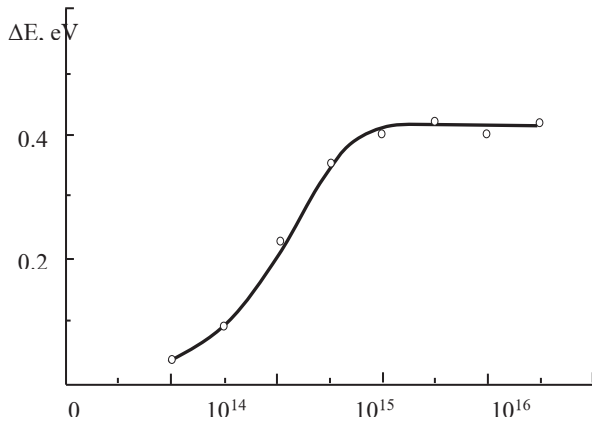


Fig. 2. Dose dependence of the energy shift of the main Si peak.

It is known [9, 10] that the state of an electron in a Si single crystal is described in the Bloch representation by the Green's function $G_0(\omega, k)$. Where ω is the frequency of the incident light, K is the quasiimpulse of an electron in the extended zone scheme.

The Green's function of an electron in an amorphous substance $G_{kk'}$ satisfies the Schredinger integral equation:

$$\hat{G}_{kk'} = G_0(k)\delta_{kk'} + G_0(k) \sum \hat{V}_{kk'} \hat{G}_{k'k} \quad (1)$$

where $\hat{V}_{kk'}$ is the matrix element of a random potential acting on an electron from the side of randomly located atoms of a substance, while the summation over K is performed over all states of electrons in the crystal.

K -describe the valence band of single-crystal Si, and K' -describes the band corresponding to ion-bombarded (amorphous) Si. δ -Dirac delta function expressing the law of conservation of energy when absorbing a photon.

Averaging equation (1) over the chaotic distribution of impurities, we obtain the equation for the Green's function $G' = \langle G \rangle$ of the valence band of Si

$$G'_{kk'} = C_0(k) + G_0(k)M_{kk}G'_{kk} \quad (2)$$

Where M_{kk} is the mass operator, which is the averaged effective complex potential acting on an electron from the side of chaotically located atoms.

The real part of this potential determines the shift of the maximum of the density of states, and the minimum part determines the broadening of the peaks. Peak broadening is not discussed in this article.

In the second order, perturbation theory, the shift of the maxima resulting from amorphization is proportional

to the mean square of the modulus of the random potential V :

$$M_{kk} = N \int \frac{dk'}{(2\pi)^3} \frac{\langle |\hat{V}_{kk'}|^2 \rangle}{\varepsilon_k - \varepsilon_{k'}} \quad (3)$$

where N is the concentration of defects, $\langle |\hat{V}_{kk'}|^2 \rangle$ is the mean-square fluctuation of the random interaction potential, the integral in (3) is understood in the sense of the main value.

The energy of the valence electron in amorphized Si ε'_k is equal to

$$\varepsilon'_k = \varepsilon_k + M_{kk} \quad (4)$$

where ε_k is the electron energy in the valence band of pure crystalline Si. The offset in the position of the peaks is determined by the value M_{kk} calculated by the formula (3).

The estimate shows that at low impurity concentrations, i.e. at low bombardment doses ($D < 10^{15} \text{ cm}^{-2}$), the potential M_{kk} and, consequently, the shift of the maximum density of states change linearly in concentration. At high impurity concentrations (at doses $D > 10^{15} \text{ cm}^{-2}$), corresponding to the transition to amorphous silicon, the concentration dependence of M_{kk} is very weak.

It is important to note that the value of M_{kk} is positive, since the main contribution to the integral (3) gives the state K' , whose energy is less than the energy ε_k . Therefore, during amorphization, the peak A of the density of states of the silicon valence band under consideration is shifted to the region of lower electron binding energies.

These theoretical results are consistent with the experimental data shown in Figs. 1 and 3. The energy shift is $\sim 0.4 \text{ eV}$.

4 Conclusion

Thus, we experimentally established a significant change in the density of the electronic states of the valence band of single-crystal Si(111) upon amorphization of its surface by ion bombardment.

In particular, ion bombardment leads to a displaced position of the main maximum A of the energy spectrum of Si(111) by $\sim 0.4-0.45 \text{ eV}$ towards higher energies, which is consistent with theoretical concepts.

It is shown that the complete disordering of the surface layers of Si leads to some increase in E_g , an increase by 15-20% of the light absorption coefficient at $h\nu \leq E_g$, and a significant decrease (1.5 times or more) in

the depth of diffusion of atoms of the contacting material into the depth of the target.

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