02

Influence of resolution, escape depth, and defects on the line shape of $2p$-spectra from the Si(100) surface

© M.V. Kuzmin, S.V. Sorokina

Ioffe Institute,
St. Petersburg, Russia

e-mail: m.kuzmin@mail.ioffe.ru

Received September 30, 2024
Revised October 11, 2024
Accepted October 18, 2024

The results of quantitative and qualitative analysis of the fine structure of high-resolution (60 meV) $2p$-spectra from the Si(100)c(4×2) surface have been presented. The $2p$-line is simulated for various photon energies, energy resolutions, and density of structural defects in the Si surface layer. The upper limits of the experimental parameters (photon energy and resolution), at which the characteristic features of the spectra can be used as an indicator of the surface quality, are established. The spectrum sensitivity to vacancies in the surface dimer layer is estimated. The obtained results can be used as reference data when conducting experiments and processing the results of photoelectron spectroscopy of the Si $2p$-core level.

Keywords: surface, photoelectron spectroscopy, core level, surface core-level shift, silicon.

DOI: 10.61011/EOS.2024.10.60054.7124-24

Introduction

High-resolution photoelectron spectroscopy (PES) is used widely at present for diagnostics of surfaces, interfaces, and thin-film structures [1–3]. For example, core-level PES is used to record energy shifts of the inner shells of atoms on the surface (surface core-level shifts) [4]. These data provide an insight into the nature of bonds, the environment, and the charge state of the indicated atoms and may be regarded as „fingerprints“ of the atomic geometry of surface reconstructions.

Quantitative analysis of the fine structure of photoelectron (PE) spectra (specifically, their decomposition into individual components) is normally required for identification of surface shifts. In turn, detailed knowledge of the dependence of the line shape on experimental conditions is needed to decompose spectra. However, only a few papers focused on the systematic study of this relation (even for model systems: the best-known surfaces of semiconductors and metals free of foreign atoms and molecules) have been published to date.

The fine structure of high-resolution $2p$ spectra for the (100) face of silicon has recently been examined in detail in [5]. It was demonstrated that these spectra are formed by six components (spin-orbit doublets $2p_{1/2}-2p_{3/2}$), and the atomic nature of each of them was established. However, the results presented in the indicated study and in [6,7] did not clarify the dependence of characteristic features of the $2p$ spectra of Si(100) on the energy resolution and photon energy (in other words, the electron escape depth) within a wide range of values. It also remained unclear how sensitive the shape of the $2p$ line is to structural defects of this surface.

In view of the above, the present study was aimed at finding out how the above-mentioned experimental conditions (including the density of defects on the sample surface) affect the fine structure of the $2p$ spectra of the Si(100)c(4×2) face. Experiments were carried out at the MAX-lab synchrotron (Sweden). In addition, the $2p$ photoemission line shape for this surface was simulated under various conditions. The obtained data make it possible to reveal the main patterns of variation of shape of the $2p$ spectrum of the (100) silicon surface.

Methods

Experiment

Measurements were performed at channel I4 of the MAX-III storage ring at a residual pressure in the vacuum chamber of $3 \cdot 10^{-11}$ Torr. Spectra were recorded with a SPECS Phoibos 100 analyzer at a temperature of 100 K. Emission angle θ_e (measured relative to the normal to the surface) was varied to adjust the electron escape depth. The solid angle of electron collection was $\pm 1^\circ$. Full energy resolution ρ was 60 meV (at photon energy $h\nu = 130$ eV).

Samples were cut from a single-crystal silicon wafer with the (100) surface orientation doped with phosphorus (n-type). Its resistivity was $\sim 5\,\Omega \cdot$ cm. A series of short-term thermal annealings at 1530 K with the pressure in the vacuum chamber kept below $1 \cdot 10^{-9}$ Torr were performed to prepare an atomically clean surface. Following heating, a well-ordered structure (2×1) remained on the surface at room temperature. It transformed into c(4×2) upon cooling to 100 K. Low-energy electron diffraction

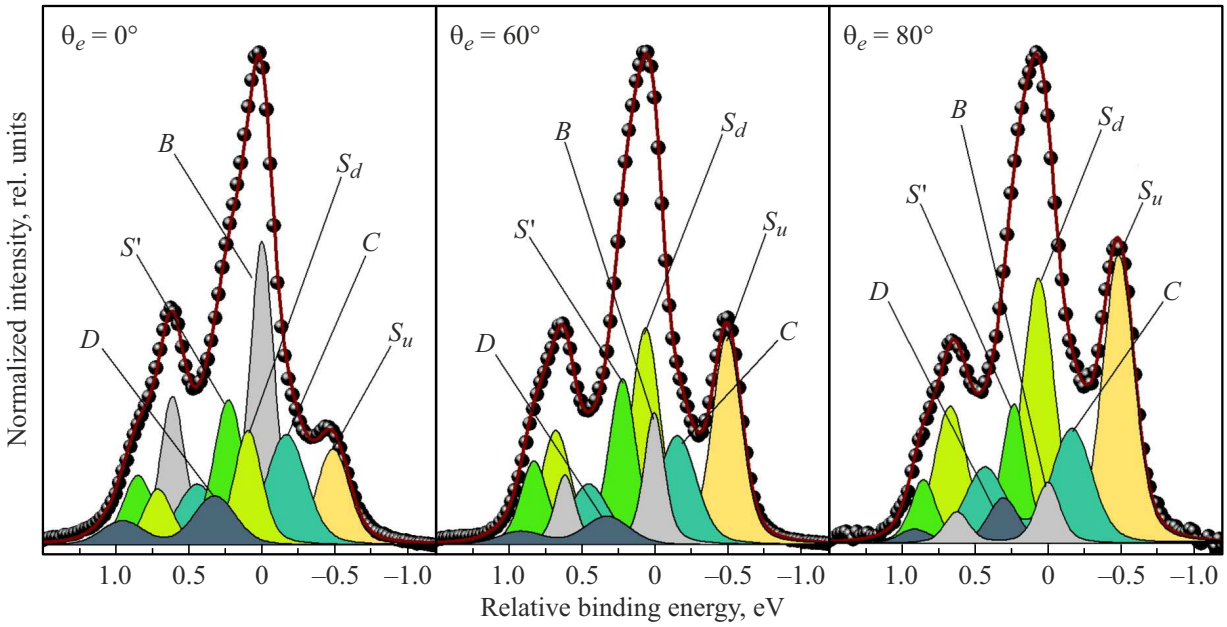

Figure 1. $2p$- spectra of the Si(100)with(4×2) surface at $h\nu = 130$ eV. Measurements were carried out at different emission angles θ_e.

and valence-band PES were used to monitor the surface structure and condition.

Simulation

Experimental $2p$ spectra were decomposed into spin-orbit doublets using the least squares method. The Shirley background subtraction method was applied [8]. The Voigt profile, which is a convolution of Lorentzian and Gaussian line shapes, was used as a model function. Lorentz broadening, which is associated with a finite lifetime of the photoexcited state of an atom with a hole at the $2p$ level; spin-orbit splitting; and the ratio of intensities of sublevels $2p_{1/2}$ and $2p_{3/2}$ (branching ratio) were fitting parameters fixed at the same level for all components. The number of components and the intensity and position on the energy scale of each component were variable parameters. Gaussian broadening ω_G was also varied for each component, since its value is determined both by the resolution and by the degree of local disorder of the sample crystal structure and, consequently, may vary with the lattice atom type.

Linear combinations of known spin-orbit doublets with given values of intensity and Gaussian width were used to calculate the spectra. The intensities of doublets were calculated based on the known values of mean free path in silicon [5,9]. The effects of photoelectron diffraction were neglected.

Results and discussion

Figure 1 shows the experimental $2p$ spectra of the Si(100)c(4×2) surface obtained at $h\nu = 130$ eV and three different values of $\theta_e = 0$, 60, and 80°. The results of measurements and decomposition of spectra are represented by circles and solid curves, respectively. It can be seen from Fig. 1 that a number of components contribute to the $2p$ line: the B doublet, which is induced by emission from the bulk silicon lattice, and five doublets S_u, S_d, S', C, and D, which correspond to emission from the surface layers and are shifted relative to the bulk component along the abscissa axis toward higher or lower binding energy values. For convenience, the position of the $2p_{3/2}$ sublevel of doublet B is set as zero on the energy scale.

The interpretation of surface components was discussed in detail in [5]. Let us list briefly the key findings. S_u and S_d

Parameters of components of the $2p$ line in Fig. 1. The notation is as follows: ΔE — surface shift, ω_G — Gaussian broadening, η — broadening induced by local disordering of the crystal structure, ω_L — Lorentzian broadening, ΔE_{SO} — spin-orbit splitting, and $I_{1/2}/I_{3/2}$ — ratio of intensities of sublevels $2p_{1/2}$ and $2p_{3/2}$ (branching ratio)

Component	ΔE, meV	ω_G, meV	η, meV	ω_L, meV	ΔE_{SO}, meV	$I_{1/2}/I_{3/2}$
B	–	143	130	70	610	1:2
S_u	−483	208	199			
S_d	78	204	195			
S'	225	159	147			
C	−163	256	249			
D	320	233	225			

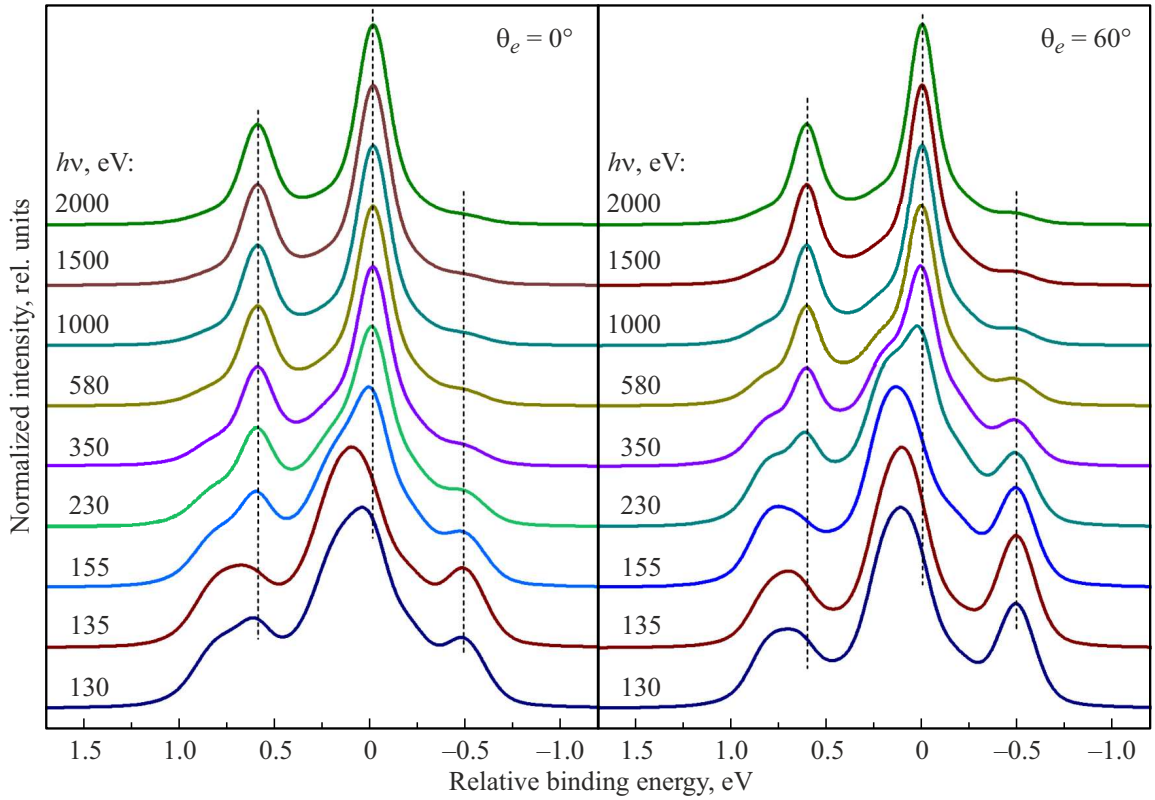

Figure 2. Dependence of the $2p$ line shape on photon energy $h\nu$. The simulation was performed for electron escape angle $\theta_e = 0°$ (left) and $60°$ (right).

originate from the upper (first) atomic layer of the c(4 × 2) structure, and their surface shifts are −483 and 78 meV, respectively (see the table). It is common knowledge that atoms of the upper layer form dimers with an asymmetric configuration: their axis is inclined to the surface plane, and the electron density shifts in part from lower atoms (corresponding to S_d) to the upper ones (S_u). The latter factor is the reason behind such a noticeable difference in energy of the indicated components (~ 0.5 eV).

Components S' and C (surface shifts of 225 and −163 meV, respectively) are associated with several atomic layers located below the upper c(4 × 2) reconstruction layer. S' is associated with atoms located in the second layer. They all have the same environment. Component C may be attributed to atoms in the third and fourth layers. They occupy at least five non-equivalent positions in the c(4 × 2) crystal structure, and the corresponding surface shifts are quite close to each other. It is impossible to determine the magnitude of these shifts accurately even at the high resolution level used here.

As for the D component, its atomic nature is not related to the regular structure of the silicon surface. It is induced by emission from local defects [5]. Therefore, this component is neglected in further analysis.

A comparison of the ω_G parameters for different components listed in the table provides additional data on the structural properties of the Si(100)c(4 × 2) surface. Doublet B has the smallest Gaussian broadening (143 meV). This is readily attributable to the fact that the crystal structure in the bulk has a higher degree of ordering than on the surface. The Gaussian width of PE peaks may be written as

$$\omega_G = \sqrt{\rho^2 + \eta^2},$$

where η is the broadening caused by local disordering of the crystal structure. This expression allows one to estimate the value of η for component B. The obtained estimate is 130 meV.

The surface doublet with the smallest Gaussian broadening is S' (159 meV). Its η value is 0.147 eV. The values of ω_G and η for the remaining components are given in the table. It is evident that doublet C undergoes the strongest broadening. This is attributable to the fact that several non-equivalent Si atoms contribute to this component.

Several important conclusions concerning the line shape in Fig. 1 may also be inferred from an analysis of the intensity of its components at different escape angles θ_e. It follows from the figure that the intensity of doublets S_u and S_d increases noticeably in the $\theta_e = 0 \rightarrow 60 \rightarrow 80°$ series, while the B doublet intensity decreases significantly. This is evidently caused by a change in the electron escape depth. As the θ_e value grows, the sensitivity of spectra to the surface (the bulk) increases (decreases). In the

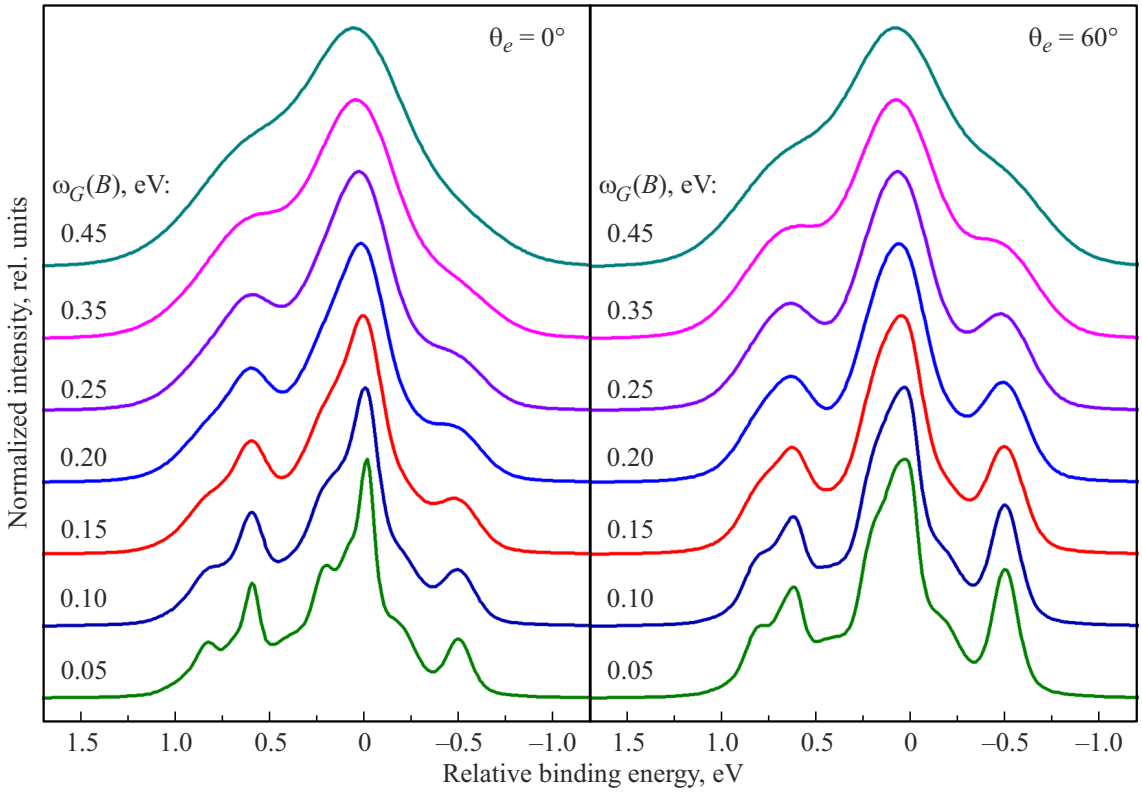

Figure 3. Dependence of the $2p$ line shape on full resolution (see text for details). The simulation was performed for electron escape angle $\theta_e = 0°$ (left) and $60°$ (right).

limit case (at $\theta_e = 80°$), the contribution of bulk silicon lattice atoms to PE emission is so insignificant that the recorded line shape matches almost completely the c(4×2) surface reconstruction. This spectrum is characterized by two features. One of them is a strongly pronounced peak at energies around -0.5 eV, which is associated with the $2p_{3/2}$ sublevel of doublet S_u. Its intensity decreases noticeably with decreasing θ_e values. This peak has almost no overlap with the other doublets in Fig. 1 and may be used as a surface state indicator even without quantitative decomposition of the spectra.

The second important feature is the fine structure of the main spectral maximum in the energy region around 0 eV. At $\theta_e = 80°$, the primary contributions to this maximum are produced by the $2p_{3/2}$ sublevels of surface doublets S_d, S', and C and the $2p_{1/2}$ sublevel of S_u (see Fig. 1). The pattern changes qualitatively in transition to $\theta_e = 0°$. The main contribution to the specified feature is provided by the $2p_{3/2}$ sublevel of the B component. This leads to narrowing of the maximum.

It follows clearly from the above that the features of fine structure of $2p$ spectra of Si(100) are related directly to both the surface state and the experimental parameters. To clarify this relation, we simulated the spectra for the c(4×2) reconstruction under different experimental conditions. Known components S_u, S_d, S', C, and B were used in calculations. Figure 2 shows two series of spectra obtained as a function of photon energy at $\theta_e = 0$ and $60°$.

In the case of normal emission, the most profound changes in line shape are observed in the $h\nu = 130-155$ eV region. The mean free path of electrons in silicon has a minimum (2.5–2.6 Å at $h\nu = 135$ eV) within this range [5]. This implies that the spectra in question are highly surface-sensitive. Indeed, their characteristic feature (well-resolved peak) at -0.5 eV has a high intensity, and the main maximum is broadened and shifted toward higher energies from the position of the bulk component (0 eV) due to the contribution of surface components. At $h\nu = 155$ eV, the mean free path increases, enhancing the contribution of the B doublet to photoemission. This leads to a reduction in intensity of the peak at -0.5 eV and a shift of the main maximum toward lower binding energies. As the photon energy increases further, the bulk contribution becomes dominant, the feature at -0.5 eV vanishes gradually, and the spectrum assumes a shape typical of the bulk silicon lattice (in this case, the contribution of surface components is virtually zero). It can be seen from Fig. 2 that the spectral feature at -0.5 eV vanishes at a quanta energy upward of 350 eV.

A qualitatively similar pattern is observed at $\theta_e = 60°$. The electron escape depth decreases in grazing emission (in the present case, by a factor of 2). This is the reason why the threshold values of photon energy shift upward.

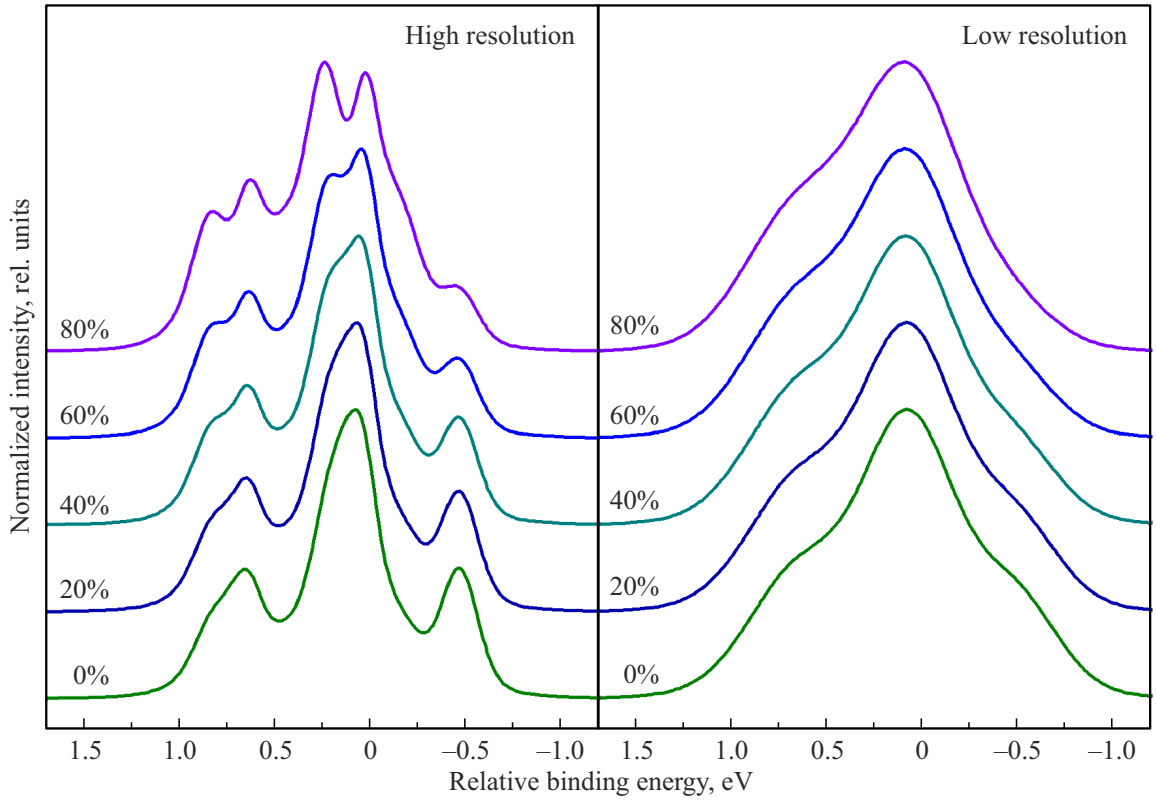

Figure 4. Dependence of the fine structure of $2p$ spectra on the number of surface defects of silicon. Calculations were performed for a photon energy of 130 eV. High-resolution and low-resolution spectra are shown in the left and right panels, respectively. See text for further details.

It follows from a comparison of the two series of spectra in Fig. 2 that the upper limit of photon energies at which the $2p$ line features may be used to assess the surface state is ~ 230 eV at $\theta_e = 0^\circ$ and ~ 580 eV at $\theta_e = 60^\circ$.

Figure 3 shows two series of $2p$ spectra obtained at a fixed value of $h\nu = 130$ eV and different full resolution levels. For convenience, the Gaussian width for the bulk component was used as a quantitative measure of resolution. It can be seen from Fig. 3 that the characteristic features of the $2p$ line become increasingly blurred and less noticeable as the Gaussian broadening parameter increases from $\omega_G(B) = 0.15$ eV (this value corresponds to $\rho = 75$ meV at $\eta = 130$ meV). At $\omega_G(B) = 0.45$ eV (corresponds to $\rho = 431$ meV), the $2p$ spectrum assumes a shape close to the one typically observed in X-ray PE spectroscopy with the Mg K_α and Al K_α lines used as excitation radiation (an almost symmetrical line shape without pronounced features). Note also that the vanishing of the characteristic „shoulder“ in the energy region of -0.5 with $\theta_e = 0^\circ$ actually occurs at $\omega_G(B) \geq 0.35$ eV ($\rho = 325$ meV).

The expected shape of spectra in the ultrahigh resolution region (at $\omega_G(B) = 0.05$ and 0.10 eV) is shown in the lower part of Fig. 3. It should be emphasized that the formation of a $2p$ line with such a small Gaussian width is a very difficult, if not impossible, task at present. To accomplish this, one needs not only to increase the energy resolution (in particular, reduce the temperature of experiments to a level significantly lower than 100 K), but also to develop a procedure for preparation of a silicon sample with a significantly higher degree of ordering of the crystal structure. For example, the values of $\rho = 22$ meV and $\eta = 45$ meV are required to achieve parameter $\omega_G(B) = 0.05$ eV. It is clear that this is currently beyond the realm of possibility.

As was already noted, the fine structure of $2p$ spectra may be used to monitor the Si(100) surface state at the atomic level. Vacancies in the rows of dimers formed in the first atomic layer (missing dimers [10]) are one of the most common types of defects for the c(4×2) surface reconstruction. It is evident that the emergence of such vacancies should be accompanied by a change in the shape of $2p$ spectra.

In the final part of this work, we consider the issue of their sensitivity to these defects. Figure 4 presents the $2p$ lines modeled for surfaces with different densities of missing dimers, which are expressed as a percentage per one monolayer. It was assumed for simplicity that the state of atoms in the underlying layers does not change when a vacancy forms. Two series of spectra corresponding to high and low resolution levels ($\omega_G(B) = 0.15$ and 0.45 eV, respectively) are shown in the figure. In both cases, the emission angle was 60°. It is evident that the fine structure

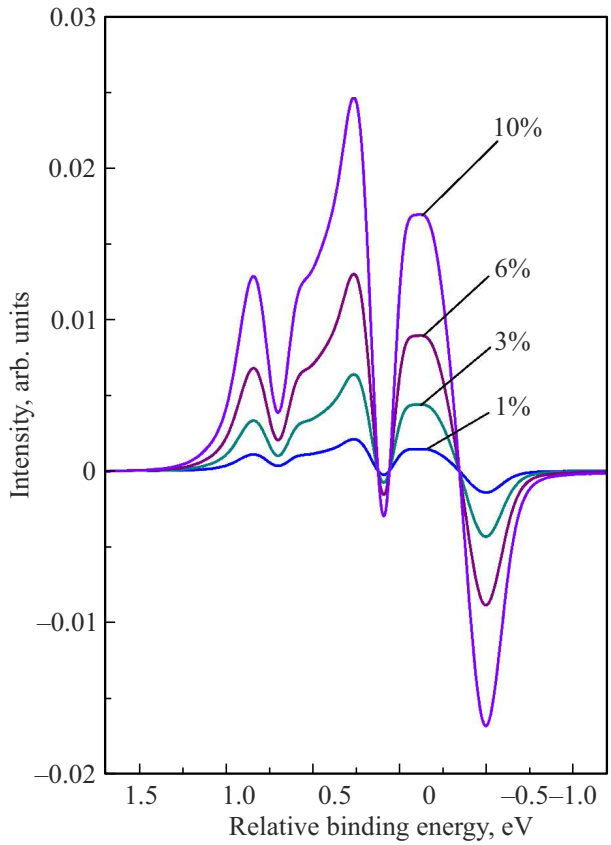

Figure 5. Difference spectra obtained at various densities of surface defects (numbers next to the curves).

of spectra gets blurred significantly at low resolution, and it becomes rather difficult to assess the degree of influence of defects on the line shape qualitatively. In the high-resolution case, qualitative changes in shape become clearer. An increase in the number of defects leads, most notably, to a reduction in the intensity of the low-energy peak induced by component S_u. Other parts of the spectrum do also change; for example, splitting of the other two maxima at $0-0.25$ eV and $0.65-0.90$ eV is observed.

Difference spectra, which represent the remainder of subtraction of the spectrum of an ideal surface with no vacancies from the spectrum of a surface with a given number of vacancies, were obtained in order to evaluate quantitatively the sensitivity of spectra to defects. Several difference spectra corresponding to different numbers of defects are shown in Fig. 5. It is evident that the curves deviate more and more from the zero level as the surface quality deteriorates. Naturally, the capacity to detect such deviations is tied directly to the signal-to-noise ratio for the experimental spectrum. This was used to estimate the sensitivity of the spectrum at $\theta_e = 60^\circ$ in Fig. 1. Its signal-to-noise ratio is $\sim 8.1 \cdot 10^2$. It follows from Fig. 5 that the $2p$ spectrum is sensitive in this case to $2-3\%$ of a defect monolayer on the Si(100)c(4×2) surface.

Conclusions

The structure and shape of the $2p$ line for the Si(100)c(4×2) reconstruction at $h\nu = 130$ eV and different values of θ_e (different electron escape depths) were investigated. Quantitative parameters of the $2p$ spectra components were obtained, and their main features, which depend on the experimental conditions and may serve as an indicator of the surface state, were determined. Modeling of $2p$ spectra with different $h\nu$, θ_e, and numbers of vacancies in the surface dimer layer was performed.

The obtained data suggest that $2p$ spectra may be used to monitor the Si(100) surface quality at $\rho \leq 300$ meV and $h\nu \leq 580$ eV (at $\theta_e = 60^\circ$). The sensitivity of $2p$ spectra to surface defects was determined. In the present case, this sensitivity is $\sim 2-3\%$ of a monolayer.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] C.S. Fadley. Surf. Interface Anal., **40**, 1579 (2008). DOI: 10.1002/sia.2902
[2] D. Wolverson, B. Smith, E. Como, C. Sayers, G. Wan, L. Pasquali, M. Cattelan. J. Phys. Chem. C, **126**, 9135 (2022). DOI: 10.1021/acs.jpcc.2c00981
[3] Y. Kayser, C. Milne, P. Juranic, L. Sala, J. Czapla-Masztafiak, R. Follath, M. Kavcic, G. Knopp, J. Rehanek, W. Blachucki, M.G. Delcey, M. Lundberg, K. Tyrala, D. Zhu, R. Alonso-Mori, R. Abela, J. Sa, J. Szlachetko. Nature Communications, **10**, 4761 (2019). DOI: 10.1038/s41467-019-12717-1
[4] J.W.F. Egelhoff. Surf. Sci. Rep., **6** (6–8), 253 (1987). DOI: 10.1016/0167-5729(87)90007-0
[5] M.V. Kuz'min, A.A. Monyak, S.V. Sorokina. Fiz. Tverd. Tela, **66** (7), 1213 (2024). DOI: 10.61011/FTT.2024.07.58397.132
[6] H. Koh, J.W. Kim, W.H. Choi, H.W. Yeom. Phys. Rev. B, **67**, 073306 (2003). DOI: 10.1103/PhysRevB.67.073306
[7] P.E.J. Eriksson, R.I.G. Uhrberg. Phys. Rev. B, **81**, 125443 (2010). DOI: 10.1103/PHYSREVB.81.125443
[8] D.A. Shirley. Phys. Rev. B, **5**, 4709 (1972). DOI: 10.1103/PhysRevB.5.4709
[9] C.J. Powell, A. Jablonski. *NIST Electron Inelastic-Mean-Free-Path Database,* Version 1.2, SRD 71 (National Institute of Standards and Technology, Gaithersburg, MD, 2010).
[10] R.M. Tromp, R.J. Hamers, J.E. Demuth. Phys. Rev. Lett., **55**, 1303 (1985). DOI: 10.1103/PhysRevLett.55.1303

Translated by D.Safin