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FREQUENCIES OF NORMAL VIBRATIONS OF OXYGEN COMPLEXES ON SILICON (111) FACE

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*The structure of molecular adsorption complex of O₂ molecule on Si(111) face as well as those of the products of its further transformations up to formation of SiO₄ - tetrahedron has been examined by means of density functional theory method (B3LYP, 6-31G**) within a cluster approach. Theoretically found IR-spectra of the adsorption structures have been compared with available literature data.*

Keywords: silicon surface, oxygen adsorption, infrared spectra, density functional theory method, cluster approach

INTRODUCTION

Despite appearance of new types of semiconductor materials [1], a role of crystalline silicon rises steadily in production of microelectronic devices [2]. When prepared by both the Chokhralsky method [3] and crucibleless zone melting [4], silicon monocrystals are saturated with oxygen and other admixtures. Oxygen as the main admixture in silicon controls the behavior of thermodonors, thermostability and lifetime of charge carriers, formation mechanism of micro-defects, as well as heteroformation efficiency. It also promotes occurrence of some phenomema stipulating performance of silicon-based micro-electronic devices [5]. That is why it should be expected that absolutely pure silicon has properties incapable of securing a normal operation of related microdevices. So, it is extremely important to develop methods of crystalline silicon production capable to guarantee the oxygen content proper for the working characteristics. Another way of oxygen ingress into silicon is adsorption of O₂ molecules onto a surface of silicon crystals followed by dissociation into atoms and their further insertion into Si-Si bonds [6-10].

Spontaneous oxidation of a crystalline silicon surface layer can be substantiated by thermodynamic considerations. Thus, the dissociation energy of oxygen molecule is of ~118 kcal/mol [11]. When inserting two so formed oxygen atoms into Si-Si bonds, an angular ≡Si-O-Si≡ bridge is formed. According to the experimental data [11], the ≡Si-Si≡ bond energy is

78 kcal/mol, that of Si-O one being 186 kcal/mol. If recounted for two oxygen atoms with taking into account the energy consumption to rupture the bond in an O₂ molecule (118 kcal/mol [11]), the total energy profit is of 470 kcal/mol. Besides, one should take into consideration that typical ≡Si-Si≡ bond length in silicon crystal is of 2.5 Å whereas average Si-O bond length in crystalline and amorphous silica forms is of 1.65 Å [12]. As the ≡Si-O-Si≡ angles of valence for various SiO₂ modifications are within 120 to 180°, the insertion of oxygen atoms into ≡Si-Si≡ bonds should not be believed to result in a considerable distortion of crystalline silicon lattice.

Hence, the importance of studies becomes obvious on spatial and electronic structure of the adsorption complexes of molecular oxygen on the surfaces of clusters of various configurations with presence of atomic oxygen within silicon bulk by means of both experimental and quantum chemical methods. In this article, in order to identify the structure of oxygen complexes on Si(111) face, the atomic vibration frequencies and forms have been calculated theoretically for these patterns and compared with known experimental data.

METHODS

The equilibrium spatial structures of adsorption complexes of O₂ molecules on the (111) and (100) faces of crystalline silicon were examined in works [13, 14] by means of density functional theory method (exchange-correlation functional B3LYP, basis set 6-31G**, program package GAMESS [15]) and a consequence was analyzed of the

formation stages of SiO_4 tetrahedron what is a structural element of all the silica modifications. The $\text{Si}_{26}\text{H}_{24}$ cluster was simulated for the Si(111) face. The results obtained coincided qualitatively and quantitatively with experimental data what gave grounds to believe that the clusters proposed and variant utilized of density functional theory method were suitable for calculation of IR-spectra of the adsorption complex and of the structures formed due to insertion of oxygen atoms into silicon surface layer.

The vibrations squared of normal vibrations were calculated as the eigenvalues of mass-weighted Hessians of the clusters simulating equilibrium configurations of adsorption complexes. The absence of the negative Hessian eigenvalues testified that the equilibrium configurations of adsorption complexes really related to local minima on the multidimensional potential energy surface rather than to transition states. The precision of potential energy calculations was of 10^{-6} a.u. and that of

determination of Cartesian coordinates – 10^{-4} a.u. Only frequencies and forms of normal vibrations involving oxygen atoms and molecules were analyzed and described.

RESULTS AND DISCUSSION

It was shown experimentally [16] that oxygen admixtures in bulk silicon give three absorption bands in the near-infrared region extrinsic to vibrations of Si atoms of crystalline lattice. An absorption band of great intensity with a maximum at 1106 cm^{-1} is observed at room temperature and another one near 515 cm^{-1} of much lower intensity. At the temperature below that of boiling nitrogen one more band appears with very sharp maximum at 1225 cm^{-1} .

There are somewhat different values of frequencies described in [17], namely 1205 , 1106 , and 515 cm^{-1} , that were referred to symmetric stretching, antisymmetric stretching, and flexural vibrations of the Si–O–Si angular triatomic fragment respectively (see Fig. 1).

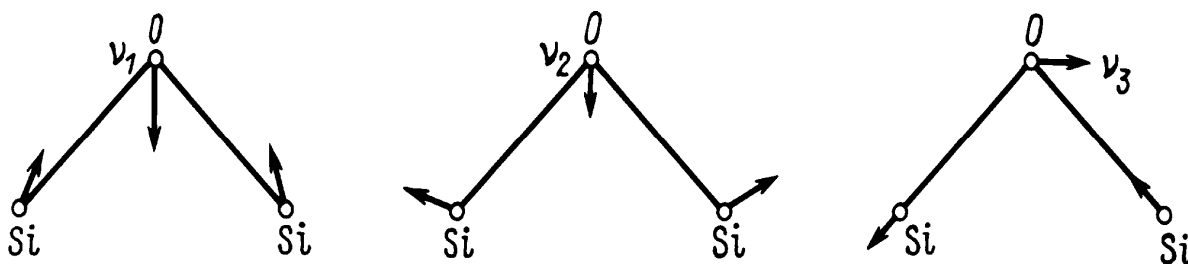


Fig. 1. A schematic sketch of normal vibrations of the Si_2O fragment

The absorption band at 1106 cm^{-1} is the most intensive and so it is usually utilized for determination of the content of interstitial oxygen atoms in crystalline silicon. At room temperature this band is wide enough, but it becomes narrow due to temperature decrease, its maximum being shifted toward higher frequencies. Additionally, at low temperature a splitting takes place of the band at 1106 cm^{-1} into two bands at 1135 and 1128 cm^{-1} .

One can believe that there is a unique correspondence of the band at 1106 cm^{-1} to antisymmetric vibrations of triatomic Si–O–Si fragment. As for identifying bands at 1205 and 515 cm^{-1} caused by presence of oxygen in silicon crystal lattice, there are no unique conclusions on their origin. Thus, starting from the structural analogy between triatomic $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ fragment and disiloxane molecule as well as similarity between IR spectrum of oxygen in silicon crystal

and that of disiloxane molecule, the authors of [18] jumped to a conclusion that the most probable origin of the band at 1205 cm^{-1} was a superposition of the band at 1106 cm^{-1} and that in far IR region at $\nu \approx 100\text{ cm}^{-1}$. Some bands were found [19] within a low-frequency region.

A lot of questions arise when the band at 515 cm^{-1} is interpreted. It was suggested in [20] to be probably caused by vibrations of separate oxygen atoms rather than interstitial ones.

Attention should be paid to the fact that a decrease or practical vanish of the absorption peak at 1106 cm^{-1} is accompanied in some cases by the appearance of new bands with maxima at 1220 , 1080 , 1036 , and 810 cm^{-1} that can testify the formation of an oxide film on the crystal surface. Summarizing a brief review of the experimental data on IR spectra of oxygen trapped in the bulk of crystalline silicon under preparation, one should

mention that they relate to a definite equilibrium between gas phase and solid and give no information on the frequencies of normal vibrations of atoms of the primary adsorption complex on solid surfaces. They can just give important information on the mechanism of initial stages of the interaction between molecular oxygen and crystalline silicon surface.

It was shown in [13] that when an adsorption complex is formed on a silicon face (111), the internuclear axis of oxygen molecule is oriented parallel to the face and the O–O distance increases from 1.24 (in isolated O₂ molecule) to 1.54 Å in the adsorption complex. At the same time, the charge of the diatomic –O–O– fragment reaches –0.8 a.u., so looking like an analogue of O₂[–] anion.

The frequency of O–O bond bending vibration of molecularly adsorbed oxygen is of 756 cm^{–1} whereas according to the experimental data for isolated O₂ molecule it equals to 1580 cm^{–1} and for isolated O₂[–] anion – 1089 cm^{–1} (see Table). It should be expected that for dianion O₂^{2–} this

frequency is even lesser. Rather low frequency of O–O vibration in the adsorption complex can arise from tridentate coordination of oxygen molecule with the face (111) silicon atoms and correlates with elongation of the bond mentioned in the surface complex.

The next stage of transformation of O₂ molecule adsorbed on silicon surface in a molecular way is its dissociation with formation of a top-top structure where both oxygen atoms saturate uncompensated valences of tricoordinated silicon atoms and Si–O bonds are oriented transversely to face (111). The frequency of bending Si–O vibrations is of 936 cm^{–1} in this case what is rather less than that for isolated SiO molecule (1241 cm^{–1}) (see Fig. 2). This fact testifies a considerable interaction between oxygen atom with lattice of crystalline silicon that is an initial condition of oxygen atom incorporation into Si–Si bond resulting in formation of an oxide layer on the surface.

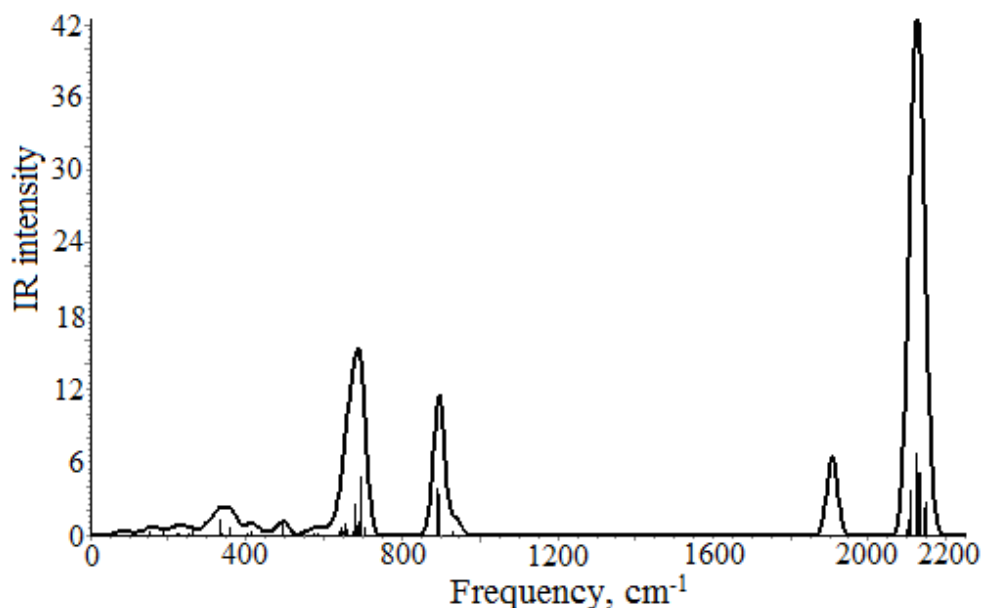
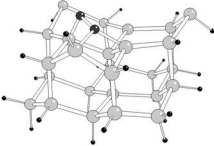
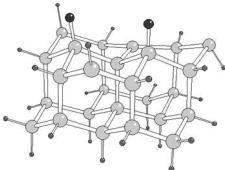
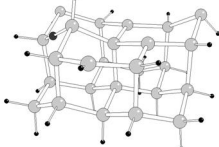
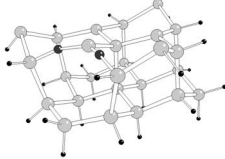
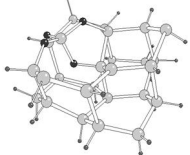


Fig. 2. Vibration spectrum of top-top adsorption complex

There is a representative value of the difference between symmetric (916 cm^{–1}) and antisymmetric (1044 cm^{–1}) stretching vibrations for ins-top structure where one O atom is incorporated into Si–Si bond and the second one occupies a top-position relatively to surface silicon atom (see Fig. 3). It reaches 128 cm^{–1} what is much more than a typical difference for isolated silicon-containing molecules. For the structure formed at the next stage when both

oxygen atoms incorporate into Si–Si bonds, both the frequencies of stretching O–Si–O vibrations and their intensities differ. Thus, for example, the intensity of symmetric stretching vibration is of 1.8 relative units whereas that of antisymmetric stretching vibration equals to almost 5 relative units. For SiO₄ tetrahedron formed on silicon surface, there is no essential difference between symmetric and antisymmetric stretching vibrations.

Table. Frequencies of normal vibrations of adsorption complexes on crystalline silicon surface

Adsorption complex	Frequency of normal vibration (cm ⁻¹)		Intensity, relative units	Type of normal vibration
	calculated	observed [17, 19]		
molecular complex 	O–O bond			
	755	780	0.295	bending
top-top structure 	Si–O bond			
	934	990	0.334	bending asynchronous
	939	965	1.076	bending synchronous
ins-top structure 	O–Si–O angle			
	916	990	0.929	stretching symmetric
	1044	1046	1.880	stretching antisymmetric
	ins-ins structure 	O–Si–O angle		
1050		1075	1.888	bending symmetric
1044		1046	4.971	bending antisymmetric
SiO ₄ – tetrahedron 	O–Si–O angle			
	954	963	1.297	bending
	997	993	0.490	bending

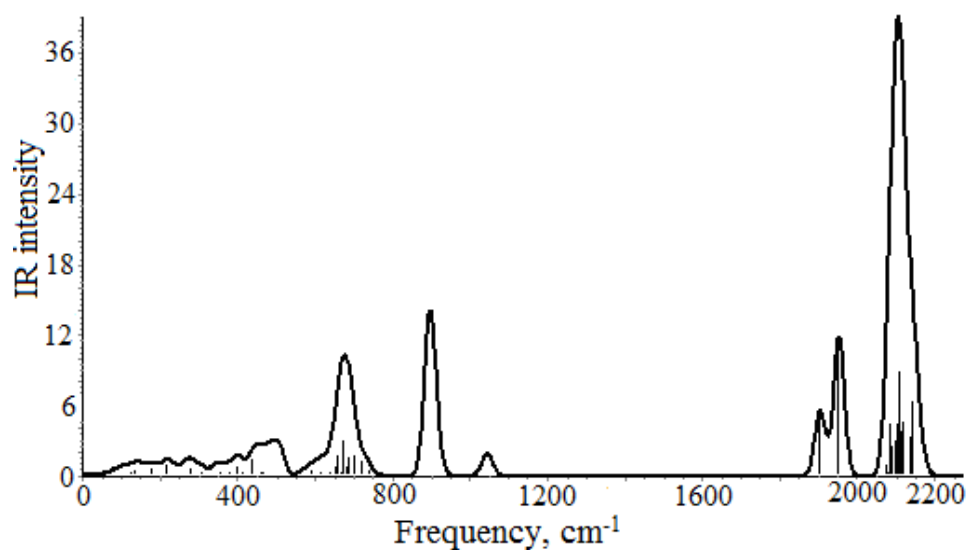


Fig. 3. Vibration spectrum of ins-top adsorption complex

CONCLUSION

Thus, calculated within harmonic approximation frequencies and forms of normal vibrations of atoms in the clusters presenting adsorption complexes of oxygen on the Si(111) face have demonstrated their dependence on the chemical environment of oxygen atoms what let it possible to indentify probable structure of surface complexes starting from the IR-spectra obtained. The frequencies and forms of normal vibrations of surface complexes with taking into account oxygen atoms have been also shown to differ from the corresponding characteristics of the structures

formed due to insertion of O atoms into bulk crystalline phase. This difference is evident, first of all, for top-top and top-ins structures where $\equiv\text{Si}-\text{O}$ bonds are stationed transversely to the face (111). The frequencies of both symmetric and antisymmetric stretching of O-Si-O angle for the ins-ins structure are close to those involving interstitial oxygen atoms.

The most intensive bands in IR-spectra are those related to stretching symmetric and antisymmetric vibrations of the atoms bound by siloxane bonds in both ins-ins structure and SiO_4 tetrahedra (4.9 and 1.9 relative units).

Частоти нормальних коливань кисню на поверхні силіцію (111)

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*Методом теорії функціоналу густини (B3LYP, 6-31G**) в кластерному наближенні розглянуто будову молекулярного адсорбційного комплексу молекули O_2 на грані Si(111) та продуктів його подальшого перетворення аж до утворення SiO_4 - тетраедра. Проведено порівняння теоретично розрахованих ІЧ-спектрів адсорбційних структур з літературними даними.*

Ключові слова: *поверхня кремнію, адсорбція кисню, інфрачервоні спектри, метод теорії функціонала густини, кластерний підхід*

Частоты нормальных колебаний кислорода на поверхности кремния (111)

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*Методом теорії функціонала густини (B3LYP, 6-31G**) в кластерному наближенні розглянуто будову молекулярного адсорбційного комплексу молекули O_2 на грані Si(111) та продуктів його подальшого перетворення аж до утворення SiO_4 - тетраедра. Проведено порівняння теоретично розрахованих ІЧ-спектрів адсорбційних структур з літературними даними.*

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