INTERACTION OF MOLECULAR OXYGEN WITH A SUBMONOLAYER Sb COVERAGE ON A Si(001) SURFACE

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The chemical content of oxides, which appear on a Si(001) surface previously covered with a submonolayer of adsorbed antimony atoms and exposed to molecular oxygen up to 10^8 L (1 L(Langmuir) = 10^{-6} Torr · s), has been studied experimentally by the methods of electron Auger and ionization spectroscopies. It has been shown experimentally for the first time that a submonolayer coverage of antimony on the Si(001) surface at exposures to molecular oxygen more than 10^6 L results in forming both the antimony and silicon oxides, the latter with a stoichiometric content close to that of SiO_2. This feature of Sb distinguishes it from Bi, in the presence of which only silicon oxides appear. This confirms our previous calculations of the adsorption energies of oxygen on the Sb/Si(001) and Bi/Si(001) surfaces. Among the reasons why the exposures that are required for silicon oxides to be formed in the Sb/Si(001) system are noticeably larger as compared with the Bi/Si(001) case, there may be substantially smaller strains and charge transfer between a surfactant and a substrate, which take place in silicon layers when antimony is being adsorbed. The quantum-chemical simulation of antimony oxide phases in submonolayer coverages on silicon showed that the values of the chemical shifts $N_{4,5}$ of the Sb levels are proportional to the variation of the effective charge of Sb atoms.

1. Introduction

The study of the interaction between molecular oxygen and a Si surface covered with a thin layer of adsorbed surfactant atoms, in particular atoms of the elements of the V group, is important both for the further improvement of the molecular-beam epitaxy technology and for the development of the fundamentals of adsorption processes. When being adsorbed, the surfactants are known to saturate the broken surface bonds of Si, thus passivating its surface. The Si surface passivated by a surfactant is resistant to the interaction with active gases, in particular molecular oxygen [1–5]. For example, the presence of an As monolayer on the Si(001) surface results in that the adsorption of oxygen and the formation of both As and Si oxides begin only at exposures larger than 10^{12} L [1]. Bismuth, when on the Si(001) surface and at large exposures to molecular oxygen (more than 10^5 L), stimulates the formation of silicon oxide with a stoichiometric content close to that of SiO_2, remaining, at the same time, in a not oxidized state on the surface of the silicon oxide layer [3]. This evidences for the formation of Si—O—Si bridge structures between the first and second Si layers and for the enhancement of atomic oxygen diffusion into the depth, as compared with a clean Si surface without any surfactant coverage. This fact agrees well with the results of previous calculations concerning the adsorption energies of atomic oxygen and the variations of bond lengths between the first and second Si layers at the M/Si(001) surface, where M = As, Sb, or Bi [5]. The content of oxides, which are created when oxidizing the Sb/Si(001) system, remains poorly studied until now. This system is characterized by the lowest charge transfer between the surfactant and the substrate, as well as by the smallest strains that arise in silicon layers at adsorbing the surfactant from the set As, Sb, and Bi [5]. Earlier, we showed that, in the Sb/Si(001)+O_2 system and at exposures not less than 10^6 L, there arise silicon oxides [4]. In this work, the results of researches obtained with the help of electron Auger and ionization spectroscopies are reported, which testify to that provided the exposures to O_2 are large ($10^4 - 10^8$ L) and owing to the interaction between molecular oxygen and the Si(001) surface with a Sb submonolayer coverage, Sb oxides do appear on the surface.

2. Method of Researches

Experiments were carried out on an ultrahigh vacuum installation described earlier in work [4] under the base pressure of 5×10^{-10} Torr. The $5 \times 30 \times 0.3$-mm^3 samples of B-doped Si(001) with specific resistances of $4.5 - 10$ Ω · cm were cut out of a Si plate and placed after a chemical treatment into a vacuum chamber. The preparation of the surface for measurements was similar to that described in work [6]. The absence of surface contaminations was monitored by the method of electron Auger spectroscopy. Antimony was thermally

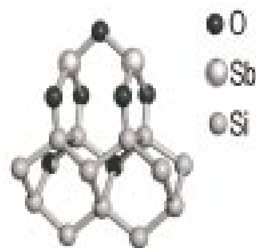

Fig. 1. Model of the cluster $O_5Sb_2Si_{15}H_{16}$ which was used in calculations. Hydrogen atoms are not shown

evaporated onto the Si(001) surface from a source of direct heating. The degree of coverage with Sb was monitored through an intensity relation between the Si and Sb Auger lines [4]. The Sb films on the Si(001) surface were annealed at a temperature of 650°C to form an ordered Sb coverage with the 2×1 reconstruction [7] and the degree of coverage $\theta_{\rm Sb} = 0.65$ monolayer. In order to diminish the possible dissociation of O_2 during the exposure, the experiments were carried out provided that the incandescent filaments of an ionization manometer, an electronic gun, and so on are switched off. To minimize the influence of electron-induced effects, some measurements were fulfilled in the 1×1-mm^2 raster mode. In so doing, no essential modifications of electron spectra caused by the action of the electron beam have been revealed.

The *ab initio* quantum-chemical calculations were made in the approximation of the restricted Hartree-Fock method, and a 3-21G* basic set was used for Si and Sb atoms. Calculations were carried out with the help of the GAMESS computer program [8]. In simulations, clusters that contained up to 66 atoms were used.

3. Results and Their Discussion

When calculating the chemical shifts of core levels, the geometrical structures for atomic oxygen that built itself into the bridge bonds were obtained first. For this purpose, the coordinates of Sb and O atoms, as well as the coordinates of the Si atoms of the first surface layer, were optimized. Calculations were made for $O_xSb_2Si_{15}H_{16}$ clusters, where $x = 0$, 1, 2, 4, and 5. An example of the $O_5Sb_2Si_{15}H_{16}$ cluster is presented in Fig. 1. The obtained values for the bond lengths and bond angles turned out close to those obtained by us earlier in a semiempirical approximation [9]. Afterwards, to calculate the shifts of core levels, larger clusters ($O_xSb_6Si_{29}H_{32}$) with the geometrical characteristics

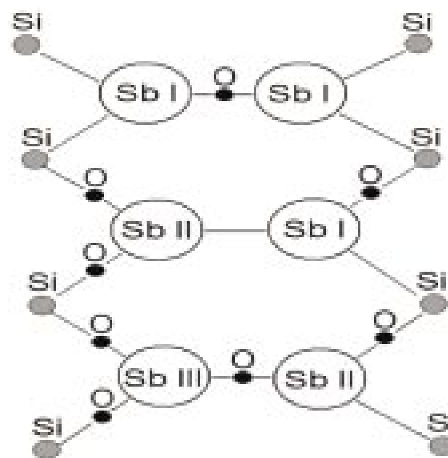

Fig. 2. Possible configurations of Sb atoms surrounded by O ones. The notations (I), (II), and (III) correspond to the configurations, where the Sb atoms possess one, two, or three neighbor O atoms, respectively

similar to those that had been obtained for smaller $O_xSb_2Si_{15}H_{16}$ clusters were used. For large clusters, the geometry optimization was carried out in a single iteration for saving computational resources.

The evaluated chemical shifts of the Sb core levels are quoted in the table. The notations (I), (II), and (III) indicate that a Sb atom has one, two, or three neighboring oxygen atoms (see Fig. 2). It is the availability of the latter in the Sb—O—Sb, Sb—O—Si, O—Sb—O, and 2O—Sb—O bridge bonds that causes the chemical shifts of Sb. Knowing shift amplitudes makes it possible to determine the stoichiometry of surface Sb oxides by methods of electron spectroscopy.

The reference experimental value of the ionization loss $N_{4,5}$ of Sb was obtained using a Sb film of several nanometers in thickness on the Si(001) surface. The thickness of the Sb film for these measurements was chosen such that the Si line was not registered in the Auger spectrum. The Sb ionization line (IL) $N_{4,5}$ with a loss energy of 33.5 eV and the Sb Auger line $M_5N_{4,5}N_{4,5}$ with an electron energy of 456 eV are depicted in Figs. 3 and 4, respectively, by curves *1*. After the exposure of 10^8 L of this specimen to molecular oxygen, a shift of the Sb ionization line $N_{4,5}$ ($\delta E = 2.5$ eV) of its spectrum towards higher loss energies was observed (Fig. 3, curve *5*). In the Auger spectra of the same surface, the intense $KL_{2,3}L_{2,3}$ line of oxygen is observed . A variation of the profile of the Sb Auger line $M_5N_{4,5}N_{4,5}$ (Fig. 4, curve *2*) also attracts attention.

No noticeable changes in the form and position of ILs $L_{2,3}$ of Si and $N_{4,5}$ of Sb were revealed on the Sb/Si(001)

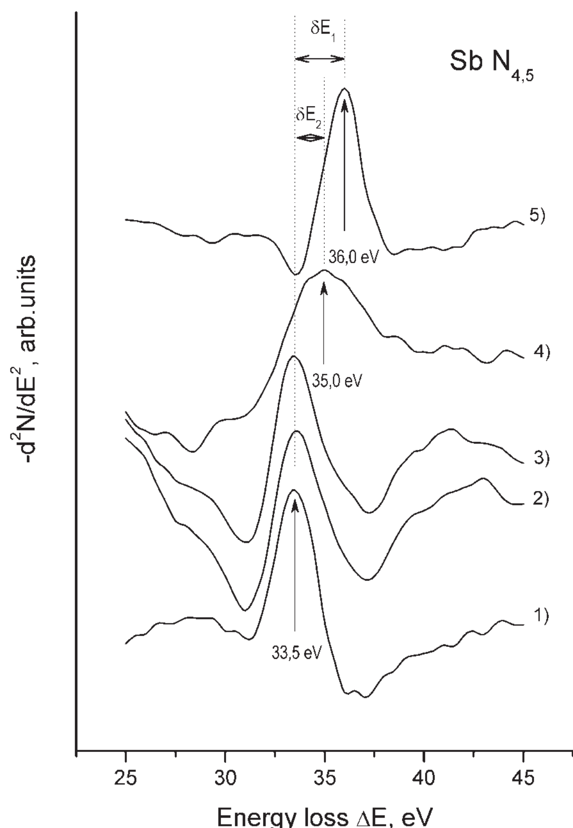

Fig. 3. Ionization line $N_{4,5}$ of a thick Sb film before (*1*) and after (*5*) oxidation by molecular oxygen (an exposure of 10^8 L), and of a submonolayer Sb coverage before (*2*) and after oxidation by molecular oxygen with exposures of 10^4 (*3*) and 10^4 L (*4*)

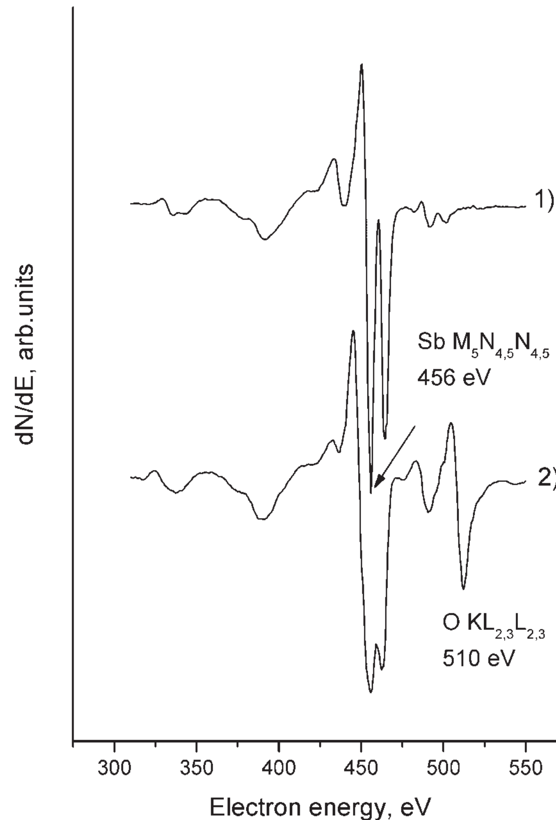

Fig. 4. Auger spectrum of a thick Sb film on the Si(001) surface before (*1*) and after an exposure of 10^8 L to O_2 (*2*)

surface with a submonolayer Sb film annealed at $T = 650°$C, after its exposure of 10^4 L to molecular oxygen. In Fig. 3, the Sb IL $N_{4,5}$ is shown before (curve *2*) and after (curve *3*) oxidation at room temperature. The Sb IL $N_{4,5}$ is evidently positioned at 33.5 eV both before and after oxidation. It is in agreement with the results of researches by the method of electron Auger spectroscopy where the submonolayer Sb coverage on the Si(001) surface at small exposures (up to 10^4 L) to oxygen was shown to hamper the interaction of molecular oxygen with the Si(100) surface owing to a reduction of the sticking factor [4].

At large exposures (above 10^6 L), a variation of the form of the Sb IL and a shift of its position by $\delta E = 1.5$ eV towards higher energy losses are observed. It becomes precisely appreciable at exposures to oxygen of more than 5×10^6 L. The Sb line $N_{4,5}$ is seen to broad and to shift towards higher energy losses (Fig. 3, curve *4*), which is most likely the consequence of a change of the chemical environment of antimony atoms and, hence, the electron binding energies at $N_{4,5}$ core levels.

Let us estimate the content of this oxide. Three groups of data concerning the dependences of chemical shifts of the Sb IL $N_{4,5}$ on the effective charge of the Sb atom, calculated following Pauling, are depicted in Fig. 5, namely: our experimental values of the chemical shifts of the Sb IL $N_{4,5}$, our calculated chemical shifts of Sb core levels $N_{4,5}$ (see also the table), and literature

Chemical shifts of the core levels of Sb atoms

Structures on the Sb/Si(001) surface	The Sb charge according to Mulliken	The Sb charge according to Pauling	Shift of the 4d core levels of the Sb atoms
Sb(I)	+0.57		0.68(0.55)
Sb(I)	+0.47	+0.47	1.15(0.16)
Sb(II)	+0.91	+0.94	2.07(1.01)
Sb(III)	+1.44	+1.41	2.84(2.29)

*N o t e. The values of shifts are quoted in eV with respect either to the vacuum level or (in parentheses) to the Fermi level. Notations (I), (II), and (III) mean that the Sb atom, for which the chemical shift is determined, has 1, 2, or 3 neighbor oxygen atoms, respectively (see the structure chart).

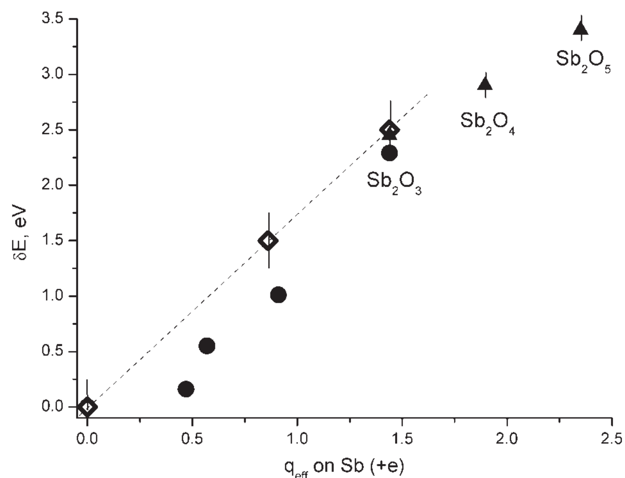

Fig. 5. Calculated chemical shifts $N_{4,5}$ of the Sb levels for Sb oxides with oxygen in a bridge position (circles), experimentally measured chemical shifts in Sb_2O_3, Sb_2O_4, and Sb_2O_5 [10, 11] (triangles), and experimentally measured shifts of the Sb IL $N_{4,5}$ (diamonds) as the functions of the effective charge of the Sb atom

experimental data on the chemical shifts of Sb core levels $N_{4,5}$ in known Sb oxides [10, 11]. From this figure, one can see that the oxide that is formed on the thick Sb film ($\delta E = 2.5$ eV) is most likely Sb_2O_3.

Considering, as an approximation, the dependence $\delta E = f(q_{\rm eff})$ for the Sb IL $N_{4,5}$ as linear [12], we may conclude that $q_{\rm eff}$ and, therefore, the stoichiometry of the submonolayer oxide correspond most likely to the structure of the type 2(Si—O)=Sb—Sb or =Sb—O—Sb—O—Si. Another reason for such a shift and a variation of the form (a substantial broadening of the IL (see Fig. 2, curve *4*)) can be a combination of the lines of not oxidized Sb ($\delta E = 0$ eV) and the line that corresponds to the structure 2(Si—O)=Sb—O— or Sb_2O_3 ($\delta E = 2.5$ eV). Both those cases considered above correspond to the formation of antimony oxides on the surface.

Fig. 6 shows the sections of the Si ionization spectra that include the Si line $L_{2,3}$ for the Si(001)+O_2 and Sb/Si(001)+O_2 systems which underwent the action of molecular oxygen with an exposure of 5×10^6 L. The sections of the ionization spectrum obtained for a clean Si(001) surface with an energy loss of 101 eV are presented in Fig. 6 by curve *1*. The position and the form of the Si IL $L_{2,3}$ are the same as those reported in work [13]. After exposing the Sb/Si(001) system to molecular oxygen, an additional line with an energy loss of 107 eV, which corresponds to oxidized silicon, appeared in its ionization spectra (Fig. 6, curve *3*). This

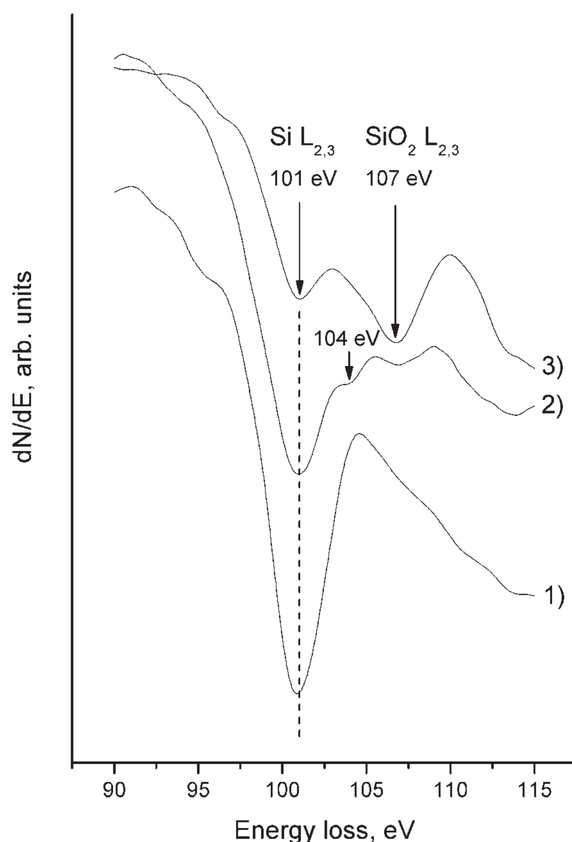

Fig. 6. Sections of ionization spectra, which include the Si IL $L_{2,3}$, of the clean Si(001) surface (*1*), Si in the system Si(001) + 5×10^6 L of O_2 (*2*), and oxidized Si in the system Sb/Si(001) + 5×10^6 L of O_2 (*3*)

line evidences for the formation of silicon oxides. This result coincides with our data obtained with the help of electron Auger spectroscopy [4]. In the ionization spectrum of the Si(001)+O_2 system (Fig. 6, curve *2*), only a weak shoulder from the side of larger energy losses (104 eV) is observed. This form of the IL is typical of the formation of non-saturated oxides SiO_x with $x < 2$ [13].

As known, for silicon oxides to be formed in the Sb/Si(001) system, considerably larger exposures than those in the Bi/Si(001) one are required (by more than one order of magnitude) [4,6]. The main reasons of this fact are substantially smaller strains and charge transfer between a surfactant and a substrate, which take place in Si layers, while antimony is being adsorbed [5].

Thus, we have found experimentally for the first time that if the Si(001) surface with a submonolayer of the Sb surfactant undergoes large exposures (more than 10^6 L) of molecular oxygen, the oxides both of silicon

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(possessing the Si—O—Si structure) and antimony (possessing either Sb–O–Sb or Si—O—Sb structure) are formed on the surface. This property of Sb distinguishes it from a Bi surfactant (Bi/Si(001)), in the presence of which only silicon oxides are formed. This fact agrees with our previous calculations of the adsorption energies of molecular oxygen on the Sb/Si(001) surface [9], where the possibility of the formation of bridge structures of three types for oxygen on the Sb/Si(001) surface, namely, Sb—O—Sb, Sb—O—Si, and Si—O—Si, was demonstrated. Such properties of Sb and Bi are to be taken into account, if one intends to use them in practice, as surfactants, for homo- and heteroepitaxy.

4. Conclusions

Using the method of ionization spectroscopy, a chemical shift of the position of the Sb IL $N_{4,5}$ by 2.5 eV towards larger energy losses, when oxidizing massive films of Sb, has been registered for the first time. The appearance of such a chemical shift of the Sb IL $N_{4,5}$ evidences for the sensitivity of the method to a chemical state of Sb atoms, with its value correlating with *ab initio* calculations of the shifts of Sb core levels $N_{4,5}$ in submonolayer oxides and with the known literature data concerning X-ray photoelectron spectroscopy for Sb oxide Sb_2O_3.

It has been shown experimentally for the first time that the oxides of both Sb and Si, the latter with a stoichiometric content close to that of SiO_2, are formed on the Si(001) surface with a submonolayer Sb coverage at the exposures to O_2 greater than 10^6 L. This property of Sb distinguishes it from a Bi surfactant, in the presence of which only silicon oxides are formed, which agrees with our previous calculations of the adsorption energies of oxygen on the Sb/Si(001) and Bi/Si(001) surfaces [9]. The reported data do not contradict our previous hypothesis concerning the role of strains in near-surface layers of Si and should be taken into account at homo- and heteroepitaxy.

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ВЗАЄМОДІЯ МОЛЕКУЛЯРНОГО КИСНЮ З ПОВЕРХНЕЮ Si(001), ВКРИТОЮ СУБМОНОШАРОМ СУРМИ

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Р е з ю м е

Методами електронних оже- та іонізаційної спектроскопії експериментально досліджено хімічний склад оксидів, що утворюються на поверхні Si(001), з попередньо адсорбованим субмоношаром сурми, після експозиції у молекулярному кисні до 10^8Л (1 Л (Ленгмюр) = 10^{-6} мм рт.ст.·с). Вперше експериментально показано, що при експозиціях у O_2, більших за 10^6Л, на таких поверхнях утворюються як оксиди сурми, так і оксиди кремнію, за стехіометричним складом близькі до SiO_2. Ця властивість сурми відрізняє її від вісмуту, у присутності якого утворюються лише оксиди кремнію, що узгоджується з нашими попередніми розрахунками енергій адсорбції кисню на поверхнях Sb/Si(001) та Bi/Si(001). Поміж причин необхідності помітно більших експозицій для утворення оксидів кремнію в системі Sb/Si(001), ніж у системі Bi/Si(001), можуть бути суттєво менші напруження та перенесення заряду між сурфактантом та підкладкою, що спостерігається в шарах Si при адсорбції Sb. Проведене квантово-хімічне моделювання оксидних фаз Sb у субмоношарових покриттях на кремнії показало, що величини хімічних зсувів $N_{4,5}$ рівнів сурми пропорційні змінам ефективного заряду на атомах Sb.