I.P. KOVAL, YU.A. LEN, M.G. NAKHODKIN, M.O. SVISHEVS'KYI,
M.YU. YAKOVENKO

Taras Shevchenko National University of Kyiv,
Faculty of Radiophysics, Electronics, and Computer Systems
(4g, Academician Glushkov Ave., Kyiv 03022, Ukraine; e-mail: len@mail.univ.kiev.ua)

PACS 68.47.Gh

INTERACTION OF MOLECULAR OXYGEN WITH Si(001) SURFACE COVERED WITH A CHROMIUM OR TITANIUM MONOLAYER

The results of experimental researches concerning the initial stages of the interaction between the Si(001) surface covered with a chromium or titanium monolayer and molecular oxygen at exposures to 10^7 L (Langmuir) are reported. On the basis of experimental data, the coefficient of molecular oxygen sticking is calculated. It is shown that not only silicon but also titanium oxides are formed on the Si(001) surface covered with a titanium monolayer. The researches are carried out, by using the Auger electron spectroscopy method.

K e y w o r d s: oxidation, chromium, titanium, silicon.

1. Introduction

The researches of the interaction between molecular oxygen and the silicon surface covered with a thin layer of adsorbed impurity atoms, in particular, atoms of elements of the IV- and V-th groups and transition metals, are important for further improvement of the molecular-beam epitaxy technology and for understanding the fundamentals of adsorption processes. Silicides of transition metals, such as chromium, manganese, titanium, iron, and cobalt silicides, find applications in the manufacture and the development of modern integrated circuits, because they are characterized by a low specific resistance, high thermal stability, reliable contact to silicon, and structural stability at variations of the temperature. Recently, the studying of chromium and titanium silicides attracts most attention, because those elements and their alloys and compounds are widely applied in modern super-large-scale integrated circuits. For instance, titanium enters the composition of compounds that are used for the metallization and for the creation of superthin barrier layers on silicon. These are such multicomponent compounds as Ti–Pt, Ti–Pd–Au, and Ti–Pt–Au [1].

The shape change of Auger lines for titanium is of interest from the viewpoint of its relation to the chemical environment of titanium atoms. Depend-

ing on the silicide formation temperature, compounds with different stoichiometries can be formed, which, in turn, affects the mechanisms of oxide formation in metal–silicon systems [2]. Therefore, the search for a correspondence between the shape of Auger lines and the stoichiometry of surface compounds is important for further researches.

Experiments on the oxidation of the silicon surface covered with Cr and Ge films [3–6] showed that the presence of a superthin chromium or germanium film on the surface can increase the rate of oxygen accumulation by several orders of magnitude in comparison with the Si(001) silicon surface already at room temperature [3]. At the same time, there is a lack of information on the surface oxidation in the presence of other practically important transition metals, in particular, Ti. Hence, this work is aimed at studying the interaction between molecular oxygen and the silicon surface covered with a submonolayer coverage of Cr or Ti at its various exposures to O_2 at room temperature. The research was carried out with the help of the Auger electron spectroscopy method. We also analyze changes in the shape of titanium Auger lines, in particular, the behavior of satellite Auger lines Ti (354 eV) and Ti (364 eV). This was done for the determination of the stoichiometry of the formed titanium oxides.

2. Experimental Technique

Experimental researches were carried out in a working chamber of an ultrahigh vacuum installation with

oil-free pumping on the basis of a serial Auger spectrometer 09IOS-2. The composition of the residual gas atmosphere and the purity of oxygen and argon introduced into the vacuum chamber in the course of experiments were monitored with the help of a quadrupole mass-spectrometer MS-7303. The pressure of residual gases in the system during experiments did not exceed 10^{-10}–10^{-9} mm Hg.

Chromium and titanium were deposited on the Si(001) surface using the thermal sputtering from a filamentary source. The design of sources for the controllable sputtering of transition metals was described in work [7] in more details.

The specimen surface was cleaned from surface films by sputtering the latter with the help of a beam of 1-keV argon ions and the following high-temperature annealing, by using the flash method. In the framework of this method, the temperature was drastically risen to 1200 °C, then decreased to 700 °C by making a 100 °C-decrement after every 5-min interval, and, at last, gradually cooled down to room temperature.

The sticking coefficient of molecular oxygen is a quantitative measure of the oxygen accumulation rate on the Si(001) surface covered with monolayers of Ti and Cr transition metals. The method of its calculation is described below.

Let us introduce the notations $I(\mathrm{Si})$, $I(\mathrm{Ti})$, and $I(\mathrm{O})$ for the intensities of Auger lines for silicon, titanium, and oxygen, respectively. If $I_0(\mathrm{Si})$ is the initial intensity of the Auger electron signal for a clean Si surface, after the sputtering of a titanium film of thickness d, the intensity of Auger electrons, $I(\mathrm{Si})$, decreases by k times,

$$k = \frac{\mathrm{I(Si)}}{\mathrm{I_0(Si)}}. \tag{1}$$

After the silicon surface with a sputtered titanium film was oxidized, we assume that saturated silicon oxide $\mathrm{SiO_2}$ was formed on it, which, in turn, reduces the intensity of the Auger line of silicon from the substrate. In Fig. 1, the scheme of the silicon oxide $\mathrm{SiO_2}$ formation under the titanium layer is exhibited.

The coefficient k is determined with the help of the expression

$$k = e^{-\frac{d}{\lambda \cos \theta}}, \tag{2}$$

where d is the thickness of the Ti or Cr film, θ the entrance angle of electrons into the analyzer of the
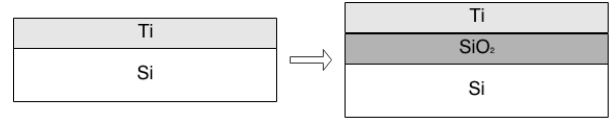

Fig. 1. Scheme of the arrangement of Ti and $\mathrm{SiO_2}$ layers on the Si(001) surface in the course of silicon oxide formation

cylindrical mirror type ($\theta = 42°$), and λ is the mean free path of Si Auger electrons in the $\mathrm{SiO_2}$ layer. The numerical value of the latter was determined with the help of software package QUASES-IMFP-TPP2M [8]. In order to consider the reduction of intensities as a result of the inelastic scattering in the metal layer and determine the parameter I_0 for oxygen and silicon, the measured intensities $I(\mathrm{Si})$ and $I(\mathrm{O})$ of corresponding Auger lines were divided by k.

The sticking coefficient η is the ratio between the number of particles N_1 remaining on the unit area of the specimen surface and the flux of oxygen molecules N_2,

$$\eta = \frac{N_1}{N_2}. \tag{3}$$

We consider that, on the surface, all oxygen molecules interact with silicon to form $\mathrm{SiO_2}$. Therefore, the number of molecules arriving at the surface can be evaluated using the relation

$$N_1 = 2n_{\mathrm{SiO_2}} d_{\mathrm{SiO_2}}, \tag{4}$$

where $n_{\mathrm{SiO_2}}$ is the concentration of oxygen atoms in the $\mathrm{SiO_2}$ layer of the thickness $d_{\mathrm{SiO_2}}$.

The total number of particles, which is calculated as the particle flux per unit area and per unit time, is determined by the formula

$$N_0 = 2I t, \tag{5}$$

where I is the particle flux, t the time, and the multiplier 2 corresponds to two oxygen atoms in the oxygen molecule. Taking into account that

$$I = \frac{P}{\sqrt{2\pi m_{\mathrm{O_2}} kT}}, \tag{6}$$

where P is the pressure, k the Boltzmann constant, T the temperature (293 K), and m the mass of an $\mathrm{O_2}$ molecule, and substituting expressions (4) and (5) into formula (3), we obtain the expression for the sticking coefficient,

$$\eta = \frac{d_{\mathrm{SiO_2}}}{tP} \frac{\rho_{\mathrm{SiO_2}}}{M_{\mathrm{SiO_2}}} \sqrt{2\pi M_{\mathrm{O_2}} RT}, \tag{7}$$
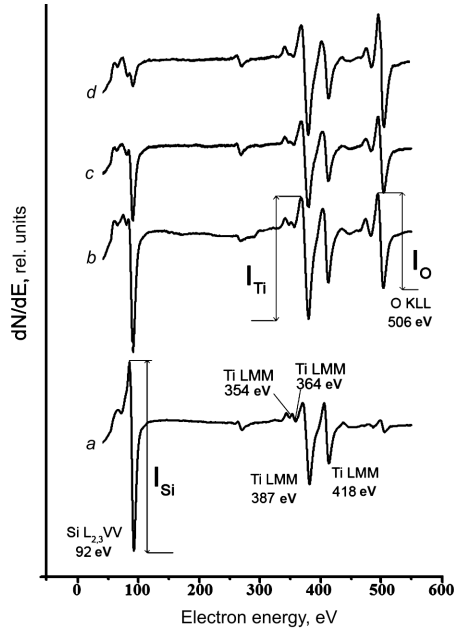
Fig. 2. Sections of dN/dE Auger spectra for the Si(001) surface covered with a titanium film for various exposures in the oxygen atmosphere: 0 (*a*), 5 (*b*), 500 (*c*), and 100000 L (*d*)
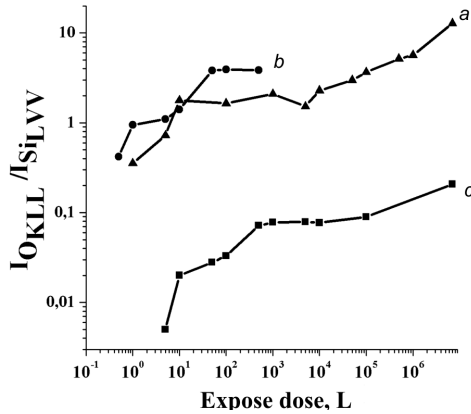

Fig. 3. Dependences of the ratio I_O/I_{Si} between the Auger line intensities on the exposure to molecular oxygen for various systems: (*a*) Si(001)–Ti–O$_2$, (*b*) Si(001)–Cr–O$_2$, and (*c*) pure Si surface

where ρ_{SiO_2} is the SiO$_2$ density, M_{SiO_2} the SiO$_2$ molar mass, M_{O_2} the O$_2$ molar mass, and R the universal gas constant. Substituting the known numerical values into Eq. (7), we obtain the following value of sticking coefficient:

$$\eta = \frac{d_{SiO_2}[\text{nm}]}{tP[\text{L}]} \times 7.325. \qquad (8)$$

The thicknesses of chromium, titanium, and silicon oxide films were calculated with the help of the method of quantitative Auger electron spectroscopy described in work [9]. In our researches, the thicknesses of chromium and titanium films were approximately equal to 0.2 nm. Substituting those values of d_{SiO_2} obtained at the given exposure dose into Eq. (8) made it possible to determine the value of sticking coefficient.

3. Results and Their Discussion

In Fig. 2, the silicon Auger spectra for the Si(001) surface covered with a titanium film sputtered at room temperature and obtained at various exposures to molecular oxygen (1 L = 10^{-6} mm Hg × s) are depicted. One can see that the spectra contain the Auger lines of silicon Si LVV (92 eV), titanium Ti LMM (387 and 418 eV), and oxygen O KLL (506 eV). As the exposure dose increases, the intensity of the oxygen Auger line O KLL grows, whereas the intensity of the silicon Auger line Si LVV decreases, which can testify to the formation of a new phase, silicon oxide.

In Fig. 3, the dependences of the intensity ratio between the oxygen and silicon Auger lines, $I_{O\ KLL}/I_{Si\ LVV}$, on the exposure dose in molecular oxygen are shown for the clean Si(100) surface (*a*), the Si(100) surface covered with a submonolayer chromium film, Cr/Si(001) (*b*), and the Si(100) surface covered with a submonolayer titanium film, Ti/Si(001) (*c*). One can see that oxygen is accumulated on the surface with a chromium or titanium submonolayer coverage much more intensively in comparison with that on the clean Si(001) surface already at exposure doses of 10–100 L. As the exposure dose increases, the intensity growth of oxygen Auger lines starts to gradually slow down. This behavior can be explained by the fact that a layer of saturated silicon oxide has already been formed on the surface, and the further growth of this layer is confined not only by the molecular oxygen dissociation, but also by the oxygen diffusion through the SiO$_2$ layer.

By analyzing the ratio between the number of oxygen atoms chemisorbed on the surface and the total number of atoms that arrive at the surface during the exposition, we obtained a number of values for the sticking coefficient of oxygen atoms on the Si(001) surface covered with a chromium or titanium submonolayer. For instance, Fig. 4 illustrates the depen-
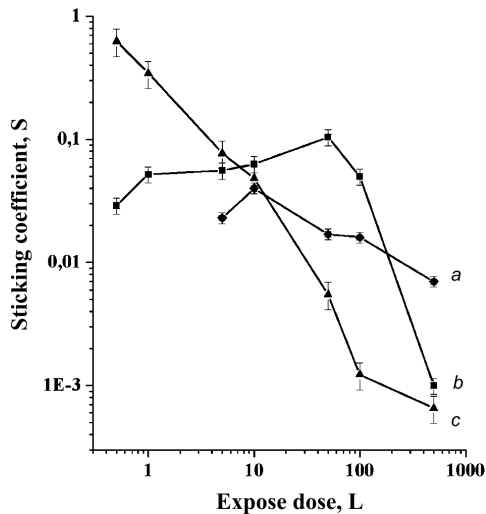
Fig. 4. Dependence of the molecular oxygen sticking coefficient on the exposure dose (on the logarithmic scale): (*a*) Cr/Si(001) annealed at 450 °C, (*b*) unannealed Cr/Si(001), and (*c*) unannealed Ti/Si(001)

Fig. 5. Modification of the titanium Auger peak with the growth of the exposure dose in the oxygen atmosphere and the correspondence to the formed oxides: Ti (*1*), $Ti_{0.75}O$ (*2*), TiO (*3*), Ti_2O_3 (*4*), and Ti_3O_5 (*5*)

dences of the sticking coefficient of molecular oxygen on the exposure dose to oxygen for the unannealed and annealed at 450 °C Cr/Si (001) surfaces, and also for the unannealed Ti/Si (001) surface. One can see that, at low exposures, the sticking coefficient is larger. As the exposure dose grows, the sticking coefficient decreases.

The largest value of sticking coefficients for the annealed Cr/Si(001) system is observed at an exposure of 10 L and amounts to approximately 0.04. At higher doses, it gradually decreases to a value of about 0.007 at an exposure of 500 L. The same dependence for the unannealed Cr/Si(001) system has a similar character. However, the attention should be paid to the fact that the largest value of sticking coefficient is reached already at an exposition of 50 L. The corresponding value amounts to about 0.1, which is by an order of magnitude larger that its counterpart for the annealed system. For the sake of comparison, we note that the sticking coefficient of molecular oxygen on the clean Si(001) surface amounts to approximately 0.0001 at room temperature. For the system Ti/Si(001), the largest value of sticking coefficient amounts to about 0.62 at an exposure of 0.5 L. As the exposure dose increases, this parameter quickly falls down, being equal to 0.0012 at an exposure of 5000 L.

As was shown in work [10], the chemical composition of titanium oxides, which depends on the expo-
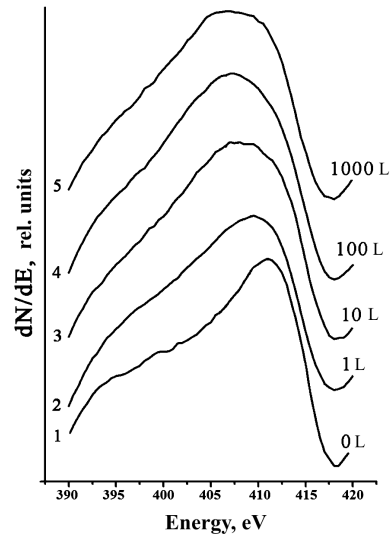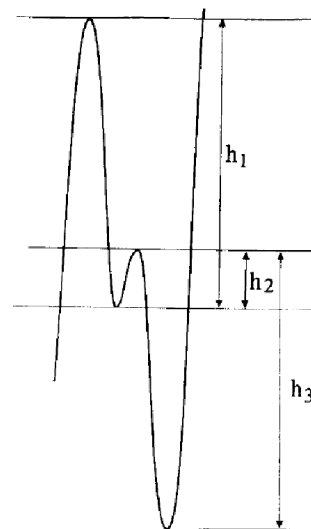

Fig. 6. Satellites of Auger lines Ti 354 eV and 364 eV in SrTiO. Notations are the same as in work [11]

sure dose, can be determined from the shape and the shift of the main Auger peak of titanium (418 eV), as is demonstrated in Fig. 5. However, in this work, we applied a different method proposed in work [11]. It consists in that variations in the form of titanium satellites at 354 and 364 eV are considered. At the oxidation, they acquire shapes shown in Fig. 6. In this method, for the determination of the amount of
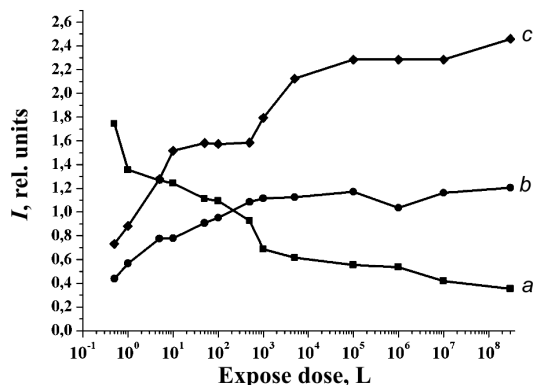
Fig. 7. Dependences of the parameter Ω (*a*) and the ratios O(510 eV)/Ti (387 eV) (*b*) and O(510 eV)/Ti(418 eV) (*c*) on the exposure dose in the oxygen atmosphere
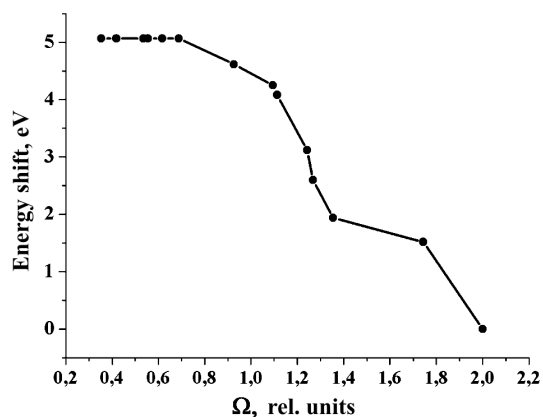

Fig. 8. Interrelation between the parameter Ω and the titanium oxidation degree (shift of the titanium Auger line)

titanium oxides, the following formula is introduced:

$$\Omega = \frac{h_2 + h_3}{h_1}. \tag{9}$$

Here, the quantities h_1, h_2, and h_3 are defined in accordance with Fig. 6.

In order to obtain the initial information concerning the regularities of oxidation processes in the system, it is necessary to establish how the intensity ratios for Auger lines change at the oxidation. In Fig. 7, the dependences of the intensity ratio between the oxygen (510 eV) and titanium (386 eV) Auger lines, the intensity ratio between the oxygen (510 eV) and titanium (418 eV) Auger lines, and the parameter Ω on the oxygen exposure dose are exhibited. One can see that the oxygen-to-titanium ratios grow with in-

crease of the dose, which testifies to the enrichment of the system with oxygen and an increase of the oxygen concentration. The ratio O(510)/Ti(418) illustrates all that more pronouncedly.

At the same time, the parameter Ω behaves differently. As the exposure and, accordingly, the oxidation degree increase, it decreases, similarly to what was obtained in work [11]. Probably, such a behavior is typical of not only the system of titanium oxides in the composition of $SrTiO_3$, which was studied in work [11], but also of the Ti–O_2 systems in general.

Figure 8 illustrates the interrelation between the parameter Ω and the oxidation degree of titanium (the energy shift of its Auger line). In correspondence with Fig. 5, the energy shift of the titanium line can be identified as a shift that, in the given energy interval, can be related to titanium oxide with a certain stoichiometry. This means that, on the basis of the calculation of the parameter Ω, the chemical composition of titanium oxides can be determined. This is an alternative method to establish the fact of the titanium oxide formation on the silicon surface. Moreover, it allows not only the presence of titanium oxides to be confirmed, but also specific titanium oxides to be identified.

4. Conclusions

It is established that titanium and chromium submonolayer films adsorbed on the Si(001) surface at room temperature accelerate the process of silicon oxidation. The sticking coefficient of molecular oxygen on the Si(001) surface covered with a titanium and chromium submonolayer coverage is three orders of magnitude larger than the corresponding value for the clean Si (001) surface. For the first time, it is shown that the information on the stoichiometry of titanium oxides in the Si(001)–Ti–O_2 system can be obtained with the help of relations between the parameters of Auger line satellites Ti(354 eV) and Ti(364 eV) for titanium deposited on the silicon surface.

1. X. Liu, K. Song, R.W. Davis, M.H. Hu, and C.-E. Zah, in *Proceedings of the 54th Conference on Electronic Components and Technology* (2004), Vol. 1, p. 798.
2. B.-Z. Li, S.-F. Zhou, F. Hong, G.-B. Jiang, P. Liu, A.-M. Zhang, and M. Chao, J. Vac. Sci. Technol. B **6**, 1974 (1988).
3. I.P. Koval', Yu.A. Len', and M.G. Nakhodkin, Visn. Kyiv. Univ. Ser. Fiz. Mat. Nauky **4**, 255 (2007).

4. J. Engstrom, D. Bonser, M.M. Nelson, and T. Engel, Surf. Sci. **256**, 317 (1991).

5. C.H. Choi, D.-J. Liu, J.W. Evans, and M.S. Gordon, J. Am. Chem. Soc. **124**, 8730 (2002).

6. J. Engstrom, D. Bonser, and T. Engel, Surf. Sci. **268**, 238 (1992).

7. I.P. Koval', Yu.A. Len', and M.G. Nakhodkin, Visn. Kyiv. Univ. Ser. Fiz. Mat. Nauky **1**, 275 (2006).

8. http://www.quases.com/products/quases-imfp-tpp2m/.

9. O.D. Protopopova and V.A. Gorelik, *Auger Spectra of Pure Materials* (Sci. Res. Institute, Ryazan', 1984) (in Russian).

10. C.N.R. Rao and D.D. Sarma, Phys. Rev. B **25**, 2927 (1982).

11. Z. Tass, G. Horvath, and V.K. Josepovits, Surf. Sci. **331–333**, Part A, 272 (1995).

І.П. Коваль, Ю.А. Лень,
М.Г. Находкін, М.О. Свішевський, М.Ю. Яковенко

ВЗАЄМОДІЯ МОЛЕКУЛЯРНОГО
КИСНЮ З ПОВЕРХНЕЮ Si(001), ВКРИТОЮ
МОНОШАРАМИ ХРОМУ ТА ТИТАНУ

Р е з ю м е

Подано результати експериментальних досліджень початкових етапів взаємодії молекулярного кисню при експозиціях до 10^7 Л (Ленгмюр) з поверхнею Si(001), вкритою моношарами хрому або титану. На основі експериментальних даних розраховано коефіцієнт прилипання молекулярного кисню та показано, що на поверхні Si(001), вкритій моношаром титану, утворюються не тільки оксиди кремнію, а й оксиди титану. Дослідження проводились за допомогою методу електронної оже-спектроскопії.