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# Auger analysis of thallium oxide formed using a low-energy beam of oxygen ions

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> The effect of irradiation with low-energy oxygen ions on the composition and some properties of the layer formed on the thallium surface has been studied. It is shown that bombardment with oxygen ions leads to the formation of a two-dimensional oxide layer, which effectively passivates the surface.

Keywords: layer, spectroscopy, surface, energy, composition, bombardment.

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### Introduction

Thallium and its compounds are widely used in practice: vacuum electronics instruments, lenses, prisms, cuvettes for IR-range optical instruments, scintillation counters, etc. As per [1], it is known that as catalysts thallium oxides promote various reactions. The phenomenon of the hightemperature superconductivity was discovered in lamellar thallium-containing oxides [2]. Quite recently, the thallium oxide starts to be used in the semiconductor microcircuits as an insulating dielectric layer. It is produced by applying the non-thermic activation of physical-chemical processes by affecting the surface with various radiations and fields [3]. In this case, the oxides are usually produced by using highenergy oxygen ions (> 10 keV). In this case, as noted by the authors in [4], the surface modification is observed due to implantation of the oxygen ions, which results in generation of bulk oxide layers and hydroxide surface layers.

The references almost never contain studies devoted to investigating a metal surface after interaction with lowenergy oxygen ions. That is why the purpose of this study is to investigate a process of formation of the oxide film on the thallium surface and properties thereof, which is produced by using the oxygen ions with the energies < 1000 eV.

# 1. Experimental part

We have tried to reach our goal by using the Augerspectroscopy, which is quite sensitive to changing a chemical environment of surface atoms. This method exhibits bonded surface oxygen on spectra as changes of an Auger peak profile with their energy shifts by several electronvolts towards the lesser energies.

The studies were performed on a super-vacuum unit with non-oil pumping, and the electron Auger-spectrometer was used an analytical instrument [5]. During the measurements, the residual pressure in the operating chambers was at most  $1.5 \cdot 10^{-7}$  Pa. The specimen was bombarded with the oxygen ions by using a source with gas ionization by electron strike (O<sup>+</sup>, E = 600 eV,  $5\mu\text{A/cm}^2$ ). The same source was also used for producing an atomically pure surface, but in this case the heavy ions of argon (Ar<sup>+</sup>, 600 eV,  $5\mu\text{A/cm}^2$ ) were used. The specimen for investigation was a plate of Tl (99.99 at.%) with sizes  $10 \times 10 \times 1 \text{ mm}$ .

### 2. Results and discussion thereof

All the experiments started with producing the atomically pure surface of the specimen. Our data have been compared with the results of [6] to conclude that the pure surface is characterized by a double Auger peak ( $N_{6.7}O_{4.5}O_{4.5}$ ) with the energies 81.0 and 84.0 eV, wherein the energy position of  $N_{6.7}O_{4.5}O_{4.5}$  did not change in time (Fig. 1, the curve *I*). Together with no Auger peak of the impurity atoms, this fact confirmed the atomically pure surface.

Then, the surface had been studied after contact of the specimen in media with reduced partial oxygen pressure and with oxygen at the atmospheric pressure. As expected, our data well agree with reference data [6,7]. When the oxygen appeared on the specimen surface, it resulted in shifting the Auger peaks towards the lesser energies as caused by deformation electron shells due to changing the chemical environment.

Figure 1 shows the energy position of the Auger peaks of Tl  $N_{6.7}O_{4.5}O_{4.5}$  depending on the time of holding the specimen with the atomically pure surface in the vacuum of  $10^{-7}$  Pa (the curve 1) and the time of holding in the oxygen media with the partial pressure of  $10^{-2}$  Pa (the curve 2) and at the atmosphere pressure (the curve 3).

As per the data of [7], the energy position of the Auger peak of  $N_{6.7}O_{4.5}O_{4.5}$  after exposure in the oxygen medium at  $1 \cdot 10^{-2}$  Pa corresponds to a thin non-stoichiometric oxide layer (Fig. 1, the curve 2). The interaction of Tl with oxygen

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at the atmosphere pressure, when there is evident formation of the Tl<sub>2</sub>O bulk layer in the mixture with Tl<sub>2</sub>O<sub>3</sub> [1] provides the spectrum with the Auger peak of  $N_{6.7}O_{4.5}O_{4.5}$  with the energy of 80.0 eV (Fig. 1, the curve 3), starting from the 10 min exposure in oxygen.

The thallium specimen is bombarded with the oxygen ions (600 eV,  $5\mu$ A/cm<sup>2</sup>) to provide for the spectra similar to those obtained in the medium with the partial pressure of oxygen  $1 \cdot 10^{-2}$  Pa. The energy position of the Auger peak of thallium was also at E = 82.5 eV, but the ratio of the amplitudes of the Auger peaks of oxygen and thallium  $I_{\rm O}/I_{\rm TI}$  was significantly different from that obtained at the oxygen pressure of  $1 \cdot 10^{-2}$  Pa.

Figure 2 shows the kinetics of the change of the amplitude ratio of the Auger peaks of oxygen (KLL) and thallium in exposure in the oxygen medium  $1 \cdot 10^{-2}$  Pa (the curve *I*)



**Figure 1.** Energy position of the Auger peak of N<sub>6.7</sub>O<sub>4.5</sub>O<sub>4.5</sub> Of thallium depending on holding in oxygen at the various partial pressures:  $I = 1.5 \cdot 10^{-7}$  Pa (the atomically pure surface);  $2 = 1 \cdot 10^{-2}$  Pa;  $3 = 10^5$  Pa.



**Figure 2.** Dependence of the intensity ratio of the Auger peaks of  $I_{\rm O}/I_{\rm II}$  on the time of exposure in the oxygen medium  $10^{-2}$  Pa (*I*) and on the time of irradiation by the oxygen ions (600 eV,  $5 \mu$ A/cm<sup>2</sup>) (2).



**Figure 3.** Appearance of the thallium specimens after holding in the atmosphere conditions (10<sup>5</sup> Pa, the humidity 70%, 298 K) during two days. *1* — pre-bombarded by the oxygen ions (600 eV,  $5 \mu A/cm^2$ ) during 60 min, 2 — the reference specimen.

and when irradiated by the oxygen ions (600 eV,  $5 \mu A/cm^2$ , the curve 2). It is clear that after the 10 min bombardment by the oxygen ions the Tl surface is characterized by higher intensity ratios  $I_O/I_{Tl}$ , whereas the surface concentrations have been calculated using  $I_O/I_{Tl}$  to provide the values close to the stoichiometric composition of Tl<sub>2</sub>O. The depth analysis by means of the ion probe (Ar<sup>+</sup>, 600 eV) has shown that a single-layer oxide film was obtained.

The obtained results can be explained as follows. As per [8], it is known that the interaction of the ions with the surface and their activity is defined a relationship of the energy and the ion current density. The bombardment by the low-energy ions at the high irradiation doses results in appearance of the large number of surface defects. Point defects, like vacancies, and agglomerations of the point defects created by the ion bombardment on the surface are adsorption centers, which amplify oxygen adsorption.

In our case, there is no implantation of the low-energy ions and no formation of the thick oxide layer at the energies of  $O^+$  600 eV, as it is a single-layer film as per profiling data for the specimen surface. It should be noted that the produced oxide film passivates the thallium surface. It is confirmed by the fact that holding the TI specimen irradiated by the oxygen ions during two days in the atmosphere conditions (10<sup>5</sup> Pa, humidity 70%, 298 K) did not result in the change of the surface color, whereas in several minutes the reference specimen was covered by a thick black layer consisting in the oxides Tl<sub>2</sub>O and Tl<sub>2</sub>O<sub>3</sub> [9] (Fig. 3).

#### Conclusions

Based on the experimental studies, it has been found:

1. The bombardment of the thallium surface with the lowenergy oxygen ions resulted in the energy shift of the Auger peak of Tl  $N_{6.7}O_{4.5}O_{4.5}$  towards the lesser energies.

2. Simultaneously with the chemical shift of the Auger peaks, there was evident increase in the amplitude ratio  $I_{\rm O}/I_{\rm Tl}$  to the values corresponding to the Tl<sub>2</sub>O stoichiometry.

3. The specimen depth profiling has shown that the produced  $Tl_2O$  oxide film was a single-layer one and its density ensured the passivation of the thallium surface.

# **Conflict of interest**

The authors declare that they have no conflict of interest.

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