SOME FEATURES OF THE AUGER ELECTRON SPECTRUM IN THE INTERACTION BETWEEN OXYGEN AND THE (111) SURFACE OF GaP

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The interaction between oxygen and the (111) surface of GaP is investigated at temperatures between 20 and 700°C by Auger-electron spectroscopy, low energy electron diffraction, and mass-spectrometry. A fine structure in the Auger-electron spectrum is detected and analyzed; it indicates that the interaction of oxygen with the GaP (111) surface may vary. At high temperatures the oxygen atoms interact with the gallium atoms to form various atomic surface structures. It is suggested that mixed Auger transitions in which both gallium and oxygen atoms participate are the most probable during formation of the structures.

OWING to the small depth from which they are emitted, Auger electrons emitted from the outer shells of the atoms of an investigated object by electron impact, serve as an effective tool for the study of the atomic structure and chemical composition of the near-surface region. Another no less important feature of Auger electrons is the possibility of investigating the bond between the surface atoms. Indeed, the energies of the outer electrons, and with them the spectrum of the Auger electrons, vary with the type of bond. The last-mentioned effects, however, are very small and require not only that the apparatus be sensitive but also that the experiment be performed under specially pure conditions.

We have used the methods of electron Auger spectroscopy, diffraction of low-energy electrons, and mass spectrometry to investigate the interaction of oxygen with the (111) surface of GaP. This investigation is of interest from the point of view of semiconductor technology.

The experiments were performed in an all-metal instrument. The Auger-electron spectrum was registered by the method of electronic differentiation of the current of inelastically scattered electrons with respect to energy[1]. To increase the sensitivity and resolution, we used a four-grid electron-optical system and oblique incidence of the primary beam of electrons on the investigated surface. The diffraction patterns of the low-energy electrons were obtained at normal incidence of the beam. The source of oxygen was BaO_2 powder, which decomposes when heated. The purity of the powder was verified with a mass spectrometer. An atomically-pure (111) surface of GaP was obtained by heating in a vacuum of 5×10^{-9}–5×10^{-7} Torr. The degree of purity was monitored by low-energy electron diffraction and by recording the spectrum of the Auger electrons from the investigated surface.

Figure 1 shows the Auger-electron spectra obtained after different stages of purification of the (111) surface of GaP. Spectrum (a), observed after the working vacuum has been obtained in the chamber, registers the usual composition of the adsorbed layer. Heating the crystal at 600°C leads to a partial purification of the surface, as shown by the Auger spectrum of Fig. 1b. The atomically pure (111) surfaces GaP was obtained by heating at ~ 680°C. Figure 2 shows the diffraction pattern of 27-eV electrons from the structure (111) GaP (1 × 1), which is the atomic structure of a pure (111) surface of GaP. Figure 3 shows the low-temperature part of the spectrum of Auger-electrons from an atomically pure (111) surface of GaP. The table lists the experimental and theoretical[2] values of the spectral-line energies corresponding to the Auger transitions indicated on the figure by arrows.

The atomically pure (111) surface of GaP was exposed to oxygen (pressure 10^{-8}–10^{-5} Torr) at 20°C for different time intervals. After each exposure, the oxygen was evacuated, low-energy electron diffraction patterns were observed, and the Auger-electron spectrum was plotted. The increase of the ratio of the background intensity to the diffraction-reflection intensity on the low-energy electron diffraction patterns was evidence of the disordered process of oxygen absorption on the (111) surface of GaP at room temperature. Three lines (510, 490, and 470 eV), corresponding to the $KL_{2,3}L_{2,3}$, $KL_1L_{2,3}$, and KL_1L_1 Auger transition of the oxygen atoms appeared in the Auger-electron spectrum and were distinctly registered (Fig. 4). With increasing exposure, the amplitude of the Auger-electron signal from the oxygen atoms increases, revealing a direct connection between the concentration of the impurity atoms on the surface and the magnitude of the signals from the Auger electrons.

Theoretical and experimental energies of Auger electrons

Auger transition of element	E, eV		Auger transition of element	E, eV	
	Theory**	Experiment		Theory**	Experiment
$M_3M_4M_4$(Ga)	56.8	59	M_2M_4V(Ga)	96—V	95
$M_2M_4M_4$(Ga)	60.7		M_3VV(Ga)	103—2V	105
M_3M_4V(Ga)	80—V	82	M_2VV(Ga)	107—2V	
M_2M_4V(Ga)	84—V		$L_{2,3}VV$(P)*	—	
M_3M_4V(Ga)	90.5—V	90	$L_{2,3}VV$(P)	118	120
$M_{2,3}VV$(Ga)*	—				

*Energy lost by the electrons of the corresponding Auger transition to plasmon excitation.

**V is the energy corresponding to the maximum electron density in the valence band relative to the energy of the Fermi level for GaP.

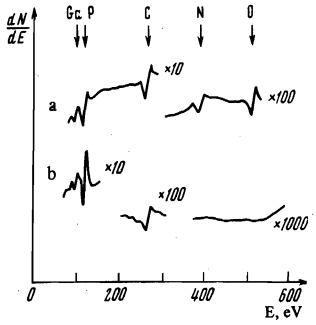

FIG. 1. Spectra of Auger electrons from the (111) surface of GaP: a–after the operating vacuum is reached in the chamber; b–after heating the crystal at 600°C; the energy of the incident electron beam was E_c = 2000 eV, the amplitude of the modulating signal was V_m = 3 V.

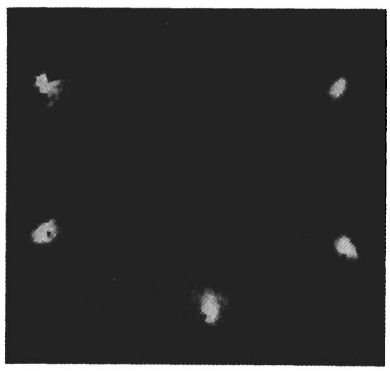

FIG. 2. Diffraction pattern of 27-eV electrons from an atomically pure (111) surface of GaP.

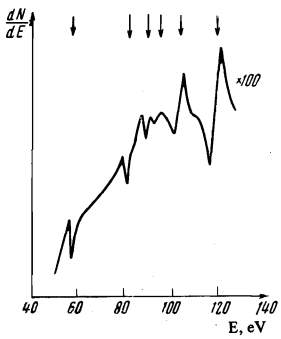

FIG. 3

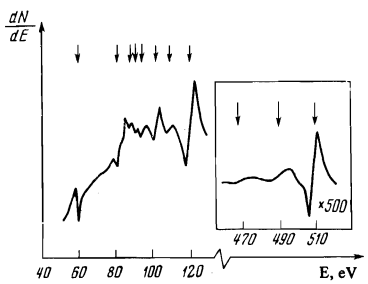

FIG. 4

FIG. 3. Low-energy part of the spectrum of Auger electrons from an atomically pure (111) surface of GaP. E_b = 600 eV, V_m = 2 V. The arrows show the positions of the Auger-electron lines.

FIG. 4. Low-energy part of the spectrum of Auger electrons from (111) of GaP after interaction with oxygen at room temperature; E_b = 600 eV, V_m = 2 V. In the right-hand side is shown the spectrum of the Auger electrons from the oxygen atoms; E_b = 2000 eV, V_m = 4 V.

Long exposures produce on the surface, besides oxygen, also carbon impurity atoms, apparently as a result of adsorption of CO or CO_2 from the residual atmosphere of the working chamber. The absence of discernible changes in the spectrum of the Auger electrons from the carbon and oxygen atoms, however, indicated that the rates of adsorption of CO and CO_2 on the investigated surface were low at high oxygen pressures. Prolonged exposures to oxygen produce changes in the low-energy part of the spectrum of the Auger electrons from GaP (Fig. 4). Thus, the lines 90 and 105 eV split into doublets, and the maximum of the high-energy lines of the doublet shifted toward higher energies when the surface concentration of the oxygen increased. According to the table, the 105-eV line is a superposition of the electron line $M_{2,3}VV$(Ga) of the Auger transition, the line corresponding to a loss of ~ 16 eV to plasmon excitation by the Auger electrons of the $L_{2,3}VV$(P) transition, and the 90-eV line corresponding to energy lost to plasmon excitation by the Auger electrons of the $M_{2,3}VV$(Ga) transition. Since the excitation energies of the bulk and surface plasmons are ~ 16 and 13 eV for a pure surface, the lines are difficult to resolve in the

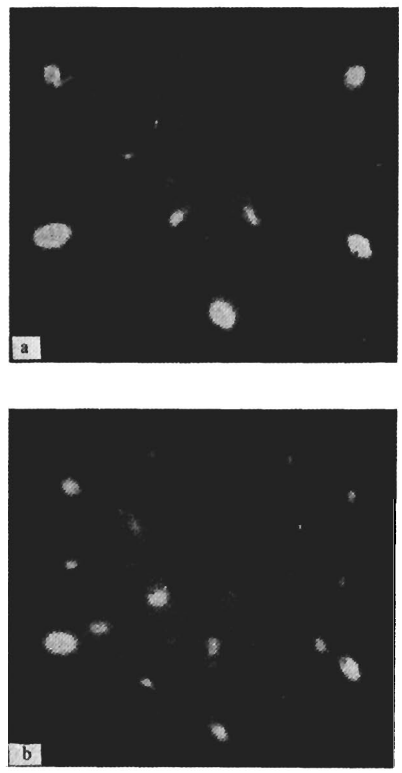

FIG. 5. Diffraction patterns of 27-eV electrons from atomic surfaces of the following structures: a–(111) GaP $(\sqrt{3} \times \sqrt{3}) \times 30°$–O, b–(111) GaP(2 × 2)–O.

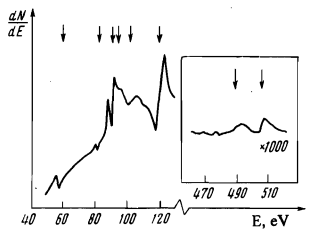

FIG. 6

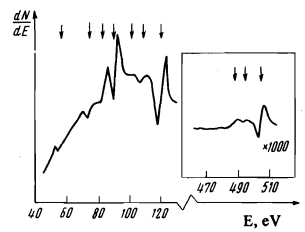

FIG. 7

FIG. 6. Spectrum of Auger electrons from the atomic surface structure (111) GaP$(\sqrt{3} \times \sqrt{3}) \times 30°$–O at E_b = 600 eV and V_m = 2 V. For the Auger electrons from the oxygen atoms (insert), E_b = 200 eV and V_m = 35 V.

FIG. 7. Spectrum of Auger electrons from the atomic surface structure (111) GaP(2 × 2)–O at E_b = 60 eV and V_m = 2 V. For the Auger electrons from the oxygen atoms (insert), E_b = 2000 eV and V_m = 3.5 V.

spectrum. However, oxygen absorption changes the excitation energy of the surface plasmons (energy ~ 10 eV), shifts the energy-loss lines toward higher energies, and increases the resolution of the doublets[3].

A second run of experiments on the interaction of oxygen with the (111) surface of GaP was performed at increased crystal temperatures. After keeping the GaP crystal at 300°C in an oxygen medium (2×10^{-5} Torr) for 10 minutes, we observed formation of the atomic surface structure (111) GaP($\sqrt{3} \times \sqrt{3}$) × 30° − O, the pattern of diffraction of 27-eV electrons form which shown in Fig. 5a. Figure 6 shows the spectrum of the Auger electrons from the atomic surface structure (111) GaP($\sqrt{3} \times \sqrt{3}$) × 30° − O. The Auger-electron spectrum differs considerably from the case of interaction at room temperature. The Auger-electron line from the oxygen atoms became distorted and was shifted about ~ 2 eV toward the low-energy side. The limited resolution of the apparatus at high voltages did not make it possible to estimate more accurately the value of the shift. The line intensities of the 59, 82, and 105 eV Auger electrons decreased, whereas the intensity of the 90-eV line increased.

The next stage of the interaction of oxygen with the (111) surface of GaP was observed after soaking the crystal in an oxygen medium at 5×10^{-5} Torr for 15 minutes at 350°C. Diffraction of the low-energy electrons (Fig. 5b) has shown that the atomic surface structure (111) GaP(2 × 2) − O was produced. Additional changes were observed in the spectra of the Auger electrons obtained from the structure (111) GaP(2 × 2) − O (Fig. 7). The Auger-electron line from the oxygen atoms increased in intensity and shifted towards the low-temperature part of the spectrum. On the low-energy side of the $KL_{2,3}L_{2,3}$ line of the Auger electrons there appeared a weak satellite line, due apparently to energy loss to plasmon excitation. The 105 eV line decreased further in intensity, while the 90 eV line increased. A new line, 74 eV, appeared. The 82 and 105 eV line split into doublets.

The differences between the Auger-electron spectra clearly illustrate the difference existing between the character of the interaction of the oxygen with the (111) surface of GaP at room temperature and at higher temperatures. Adsorption at room temperature affects the energy of the surface plasmons. The energies of the adsorption bonds are apparently low and lie outside the sensitivity limit of the apparatus. A number of new effects in the Auger-electron spectra are observed in the course of interaction at increased temperatures: first, a shift of the position of the Auger-electron line from the oxygen atoms; second, a shift of the position, a change in intensity, and the appearance of new lines in the spectrum of the Auger electrons from the gallium atoms. The line shift of the oxygen Auger electron line is probably connected with a change in the energy of the electron shells of the oxygen atoms as a result of the chemical bond. A similar shift was observed for SiO_2 produced on an atomically pure Si surface[4].

The changes observed in the spectrum of the Auger electrons from GaP interacting with oxygen are difficult to interpret, since the energy model of the surface state, the state density in the valence band, and the distribution of the electrons in the bands are all unclear. Certain assumptions can be made, however. The 105 eV Auger-electron line for the atomically pure (111) surface of GaP is due to two processes, namely electrons of the Auger transition $M_{2,3}VV$(Ga) and energy lost to plasmon excitation by the electrons of the $L_{2,3}VV$(P) Auger transition. The chemical compounds produced by the oxygen and gallium atoms at increased temperatures are the possible cause of the mixed Auger transitions. Vacancies in the $M_{2,3}$ shells of the gallium atoms can be filled by electrons from the L_2L_3 shells of the oxygen atoms, and the excess energy goes to detach electrons from the outer shells of both the gallium and the oxygen atoms. It is probable that the 90-eV line corresponds to the mixed Auger transition $M_{2,3}$(Ga)$L_{2,3}$(O)V(Ga, L). Naturally, with increasing binding and with increasing amount of oxide, the probability of the mixed Auger transitions increases, and with it the change in the relative intensities of the spectral lines of the Auger transitions. The appearance of doublets is apparently due to the change of plasmon energy following production of a complex surface layer.

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