

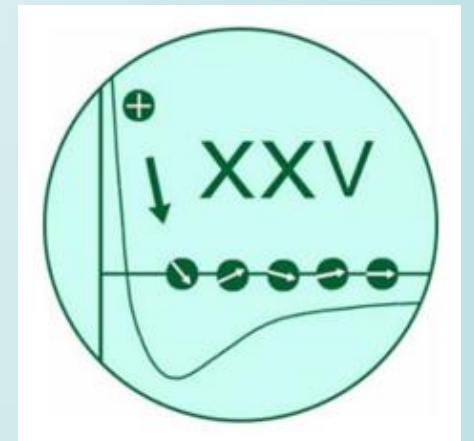
Ar⁺ IONS BOMBARDMENT EFFECT ON CORE-LEVEL BINDING ENERGIES OF THE *n*-GaAs SURFACE

E.A. Makarevskaya¹, S.Yu. Nikonov¹, D.A. Novikov¹, A.P. Solonitsyna¹, D.E. Marchenko², V.M. Mikoushkin¹



¹ *Ioffe Institute, Russian Academy of Sciences, 194021, St.-Petersburg, Russia*

² *Helmholtz-Zentrum BESSY II, German-Russian Laboratory, D-12489 Berlin, Germany*



Introduction

The x-ray photoelectron spectroscopy (XPS) is one of the most efficient techniques for diagnosing the material chemical compositions [1]. The circumstance hindering the XPS application is the necessity of removing the natural oxide layer and preparing an atomically clean surface of the studied material in ultrahigh vacuum. The most common technique for preparing such a surface is, perhaps, etching it with low-energy Ar⁺ ions.

However, we have revealed in analyzing the valence-band photoelectron spectra of the *n*-GaAs semiconductor [2] that the purely mechanical effect of Ar⁺ ions changes the Fermi level position with respect to the valence band edge and even the conductivity type of at least 1-nm layer, this thickness being equal to the mean free path (λ) of the photoelectrons under study. Binding energies E_B measured from the Fermi level may be also expected to vary within the ion-modified layer. To confirm this assumption, core-level photoelectron spectra were studied in this work. It was shown that variations in the binding energies caused by the conductivity type conversion under the action of Ar⁺ ions may be comparable with or higher than the chemical shift in the irradiated layer.

Results and Discussion

Fig. 2 presents a TRIM profile of Ar⁺ ions implanted into GaAs with energy $E_i = 1500$ eV. Using this profile, we assessed the thickness of the ion-modified layer. The thickness was assumed to be the Ar⁺ distribution FWHM, hence, $d \sim 2R_p = 5.4$ nm, where R_p is the easily determinable projected range.

Fig. 3 demonstrates an idealized band diagram of the *p-n* structure formed on the *n*-GaAs surface by the Ar⁺ ions implantation. Along with the valence and conductivity bands, the diagram presents the position of the Ga3d core level. One can see that in the region of the *p*- to *n*-layer transition the core level undergoes the same shift as the valence band edge. Therefore, it is possible to expect in the core-level photoelectron spectrum the presence of not only the main line of the surface *p*-layer but also of the *n*-layer contribution (satellite) shifted towards higher binding energies by about the bandgap width.

Fig. 4 presents the As3d photoelectron spectrum of *n*-GaAs irradiated with Ar⁺ ions. Besides the main line corresponding to the top *p*-layer, the spectrum contains a satellite line (tinted) corresponding to the unirradiated bulk *n*-layer. This line is shifted towards higher energies E_B by 1.1 eV. The *p*-layer thickness (5 nm) estimated through the satellite relative intensity appeared to be close to the TRIM estimate (5.4 nm).

Table I lists the Ga3d and As3d core-level binding energies measured from the Fermi level for atomically clean GaAs surfaces prepared by different methods. The main line energies E_B are in good agreement with previously acquired data published for crystalline, amorphous, and ion-etched GaAs surfaces [3-6]. The fact that the commonly known energies E_B are close to those obtained in this study for the main line means that they all correspond to GaAs with the *p*-type conductivity. The *n*-GaAs binding energies formerly absent in the data bases have been determined for the first time.

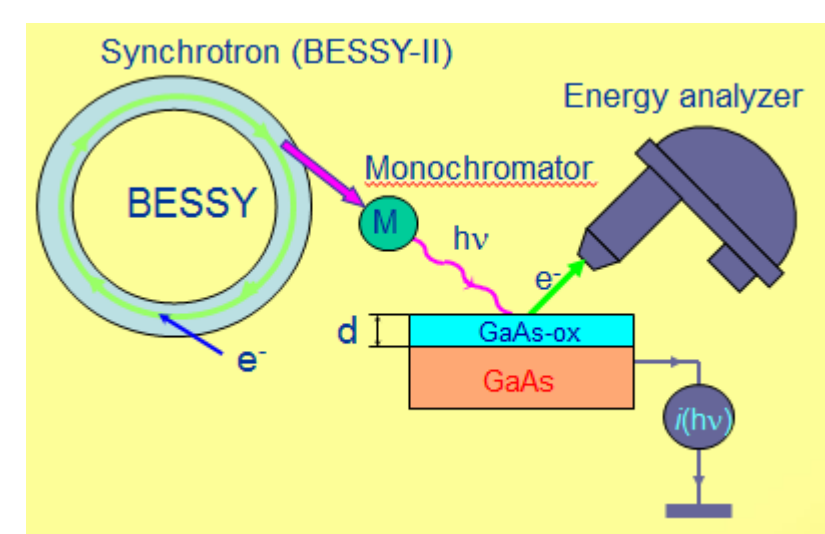


Fig. 1. Scheme of the experiment.

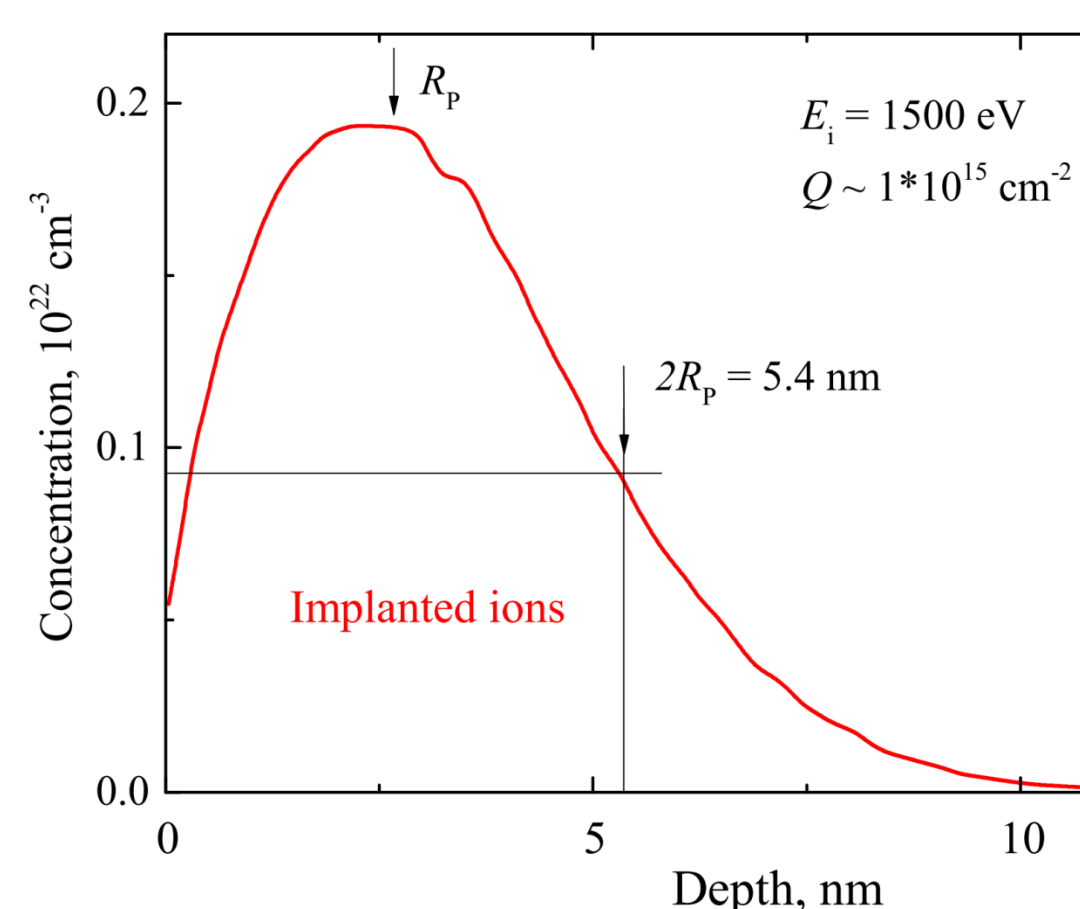


Fig. 2. TRIM profile of Ar⁺ implanted into GaAs with energy $E_i = 1500$ eV.

Table I. Ga3d and As3d core-level binding energies measured from the Fermi level for atomically clean GaAs surfaces prepared by different methods.

	Ga3d E_B , eV	Refs.	As3d E_B , eV	Refs.
GaAs-cleaved	19.2 19.4	[3] [4]	41.3	[3]
GaAs-chem. etch.	19.3	[4]		
GaAs-cat. evap.	19.0	[4]	40.9-41.0	[5]
GaAs-Ar ⁺ etched	19.0 18.5 19.4	[4] [5] [6]	41.0 40.7 41.5	[4] [5] [6]
<i>p</i> -GaAs - Ar ⁺ etched	19.35	this work	41.3	this work
<i>n</i> -GaAs - pristine	20.4	this work	42.4	this work

Experimental details

The experiment was carried out in ultrahigh vacuum by photoelectron spectrometer CLAM-4 (VG) at the Russian-German beamline of the BESSY-II storage ring (Berlin). The spectrometer energy resolution was $\Delta E_e \sim 300$ meV. The *n*-GaAs (100) ($n \sim 10^{18}$ cm⁻³) wafer was studied after irradiation with Ar⁺ ions 1500 eV in energy. Fluence $Q \sim 1 \times 10^{15}$ cm⁻² was sufficient to remove the natural oxide layer and a few layers of the material. The fact that the oxide layer has been removed was confirmed by the absence of the oxygen O1s peak in the survey spectrum measured at photon energy $h\nu = 650$ eV.

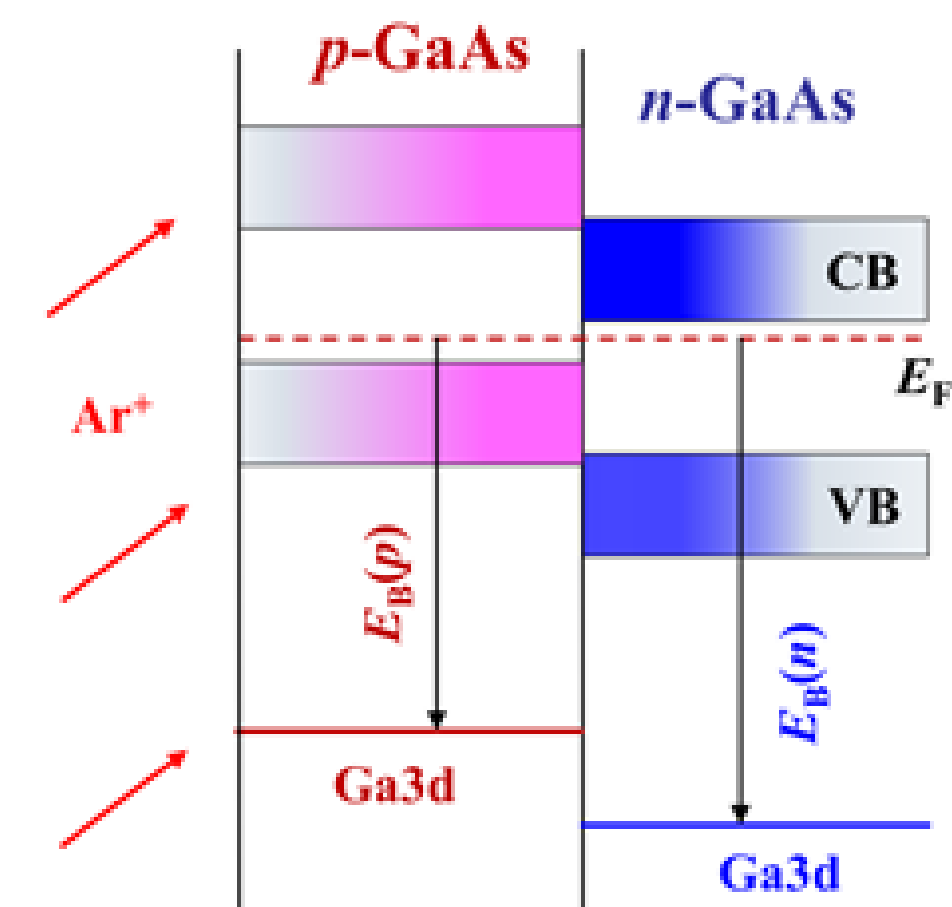


Fig. 3. A band diagram of the *p-n* structure formed on the *n*-GaAs surface by the Ar⁺ ions implantation.

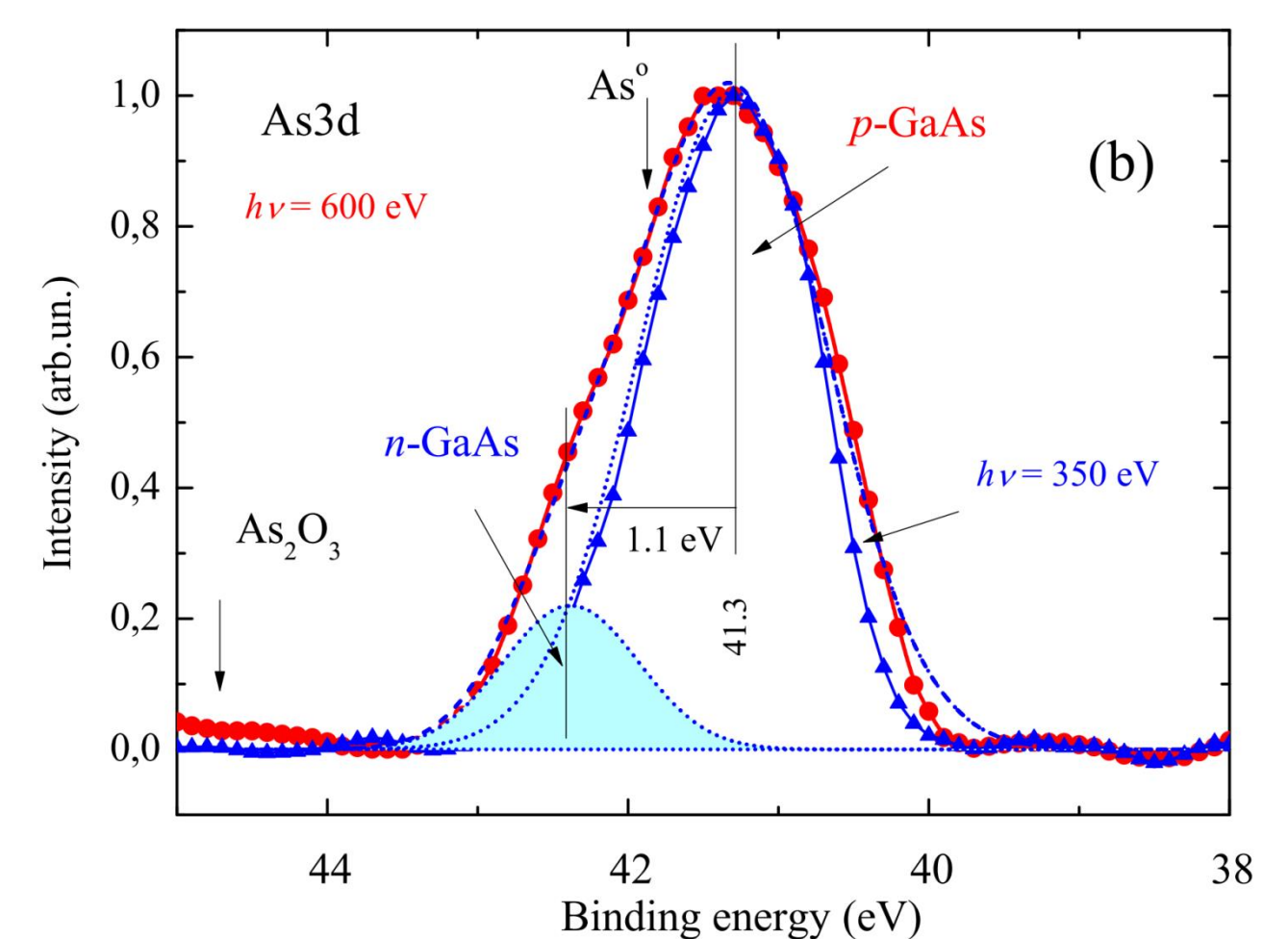


Fig. 4. The As3d photoelectron spectrum of *n*-GaAs irradiated with Ar⁺ ions.

Conclusions

This study has demonstrated that bombardment with Ar⁺ ions strongly affects core-level binding energies of the *n*-GaAs surface via the variation in the Fermi level position leading to the conversion of the irradiated layer conductivity type.

The shift caused by the ion-induced change of the conductivity type may be comparable with or higher than the chemical shift.

By determining the conductivity-conversion shift, we have revealed that all the commonly known As3d and Ga3d binding energies relate to *p*-GaAs. Binding energies for *n*-GaAs were determined in this study for the first time.

References

- [1] D. Briggs, M.P. Seah, Eds., Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy, John Wiley & Sons, New York, 1983.
- [2] V.M. Mikoushkin, V.V. Bryzgalov, S.Yu. Nikonov, A.P. Solonitsyna, D.E. Marchenko, EPL **122**, 27002 (2018).
- [3] C.R. Brundle, D. Seybold, J. Vac. Sci. Technol. **16**, 1186 (1979).
- [4] Y. Mizokawa, H. Iwasaki, R. Nishitani, S. Nakamura, J. Electr. Spectr. Rel. Phen. **14**, 129 (1978).
- [5] C.D. Wagner, W. M. Riggs, L.E. Davis, and J.F. Moulder, «Handbook of X-ray photoelectron spectroscopy», Perkin-Elmer Corporation, Physical Electronics Division, 1979.
- [6] V.M. Mikoushkin, V.V. Bryzgalov, S.Yu. Nikonov, A.P. Solonitsyna, M.M. Brzhezinskaya, J. Surf. Invest.: X-ray, Synchrotron Neutron Tech. **6**, 971 (2012).

Acknowledgements

This work was supported by the Russian Science Foundation (Project N 17-19-01200-P). The authors also thank Helmholtz Zentrum Berlin (HZB) for the allocation of synchrotron radiation beamtime and the Russian-German Laboratory at BESSY II Helmholtz Zentrum (Berlin) for the support in the synchrotron radiation experiments.