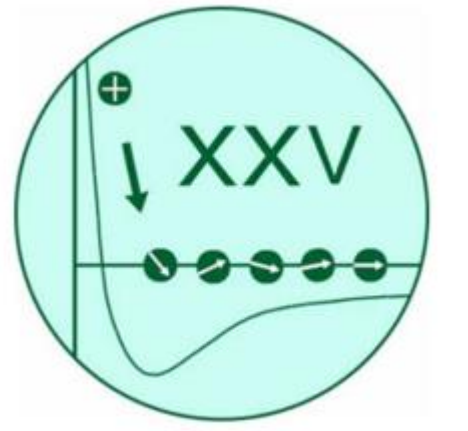




Introduction

In the last decade, Ga oxide (Ga₂O₃) remains one of the most intensely exploited wide-bandgap semiconductors [1]. The quite wide bandgap (4.85 eV) allows this oxide to play the role of dielectric at low (room) temperatures. The gallium oxide is quite valuable also because it is a part of the native oxide formed artificially or arising naturally on the surface of GaAs that is one of the most important semiconductors used in fast electronics. Hence, studying of such physical processes as atom diffusion in Ga₂O₃ and GaAs natural oxide still remains a topical problem.

Test object: GaAs natural oxide film 2-2.5 nm thick formed on the ion-etched GaAs surface and irradiated with Ar⁺ ions.

Ar⁺ ion irradiation of the oxide:

$E_i = 2500$ eV, $Q \sim 10^{14}$ cm⁻²

All the experiments were performed at room temperature

Calculation models and results

Radiation-vacancy mechanism

$$D = D_0 e^{-\frac{E_m}{kT}} (C_{eq} + C_{rad})$$

D_0 is calculated from the first principles [3].

C_{rad} is estimated by TRIM with essential corrections for possible recombination of defects and impossibility of As diffusion through certain vacancies [4].

C_{eq} is negligible as compared with C_{rad} .

E_m (migration barrier) for arsenic in Ga₂O₃ was assumed to be 0.9 eV based on the known experimental E_A of oxygen under the well-grounded assumption that the oxygen diffusion in Ga₂O₃ is interstitial and interatomic potential barriers are the same for oxygen and arsenic [5-9].

Figs. 3 presents the calculations of As diffusivity D_{As} (a) and diffusion lengths L for 10 and 60 min (b) vs. Q (dotted lines).

$D_{As} = 1.29 \cdot 10^{-19}$ cm²/s, $L_{10 \text{ min}} = 0.29$ nm, $L_{60 \text{ min}} = 0.72$ nm.

Conclusion: The radiation-vacancy diffusion mechanism does not provide the experimentally estimated rate of As room-temperature diffusion from the ion-irradiated GaAs oxide.

Interstitial diffusion mechanism

Contrary to GaAs, room-temperature interstitial diffusion of As is possible in Ga₂O₃ due to its larger cell sizes [3, 5].

In the case of high vacancy concentration, more probable is interstitial diffusion obeying the Frank-Turnbull formula [10] that takes into account the effect of vacancies:

$$D = D_0 e^{-\frac{E_m}{kT}} + D_0 e^{-\frac{E_m}{kT}} \cdot C_{rad}$$

D_{As} , $L_{10 \text{ min}}$ and $L_{60 \text{ min}}$ vs. Q are shown in Figs. 3(a) and 3(b) (solid lines).

At $Q \sim 10^{14}$ cm⁻² and $E_m = 0.9$ eV,

$D_{As} = 8.8 \cdot 10^{-18}$ cm²/s, $L_{10 \text{ min}} = 2.41$ nm, $L_{60 \text{ min}} = 5.9$ nm.

Conclusion: the model of room-temperature interstitial diffusion mechanism explains the arsenic removal from the irradiated oxide layer within the indicated duration of the measurement session. Almost the same parameters characterize the As diffusion in oxide As₂O₃ that is an essential part of the initial natural oxide.

Calculations of D_{As} and L for E_m of 1.0 [9] and 0.83 eV [10] (the maximal and minimal literature data on the oxygen E_A) showed that at $E_A = 1.0$ eV arsenic does not leave the oxide even in 60 min under any diffusion mechanism, while the radiation-vacancy mechanism at $E_A = 0.83$ eV ensures As removal by the very end of measurements (in 60 min) and the interstitial mechanism does the same in less than a minute.

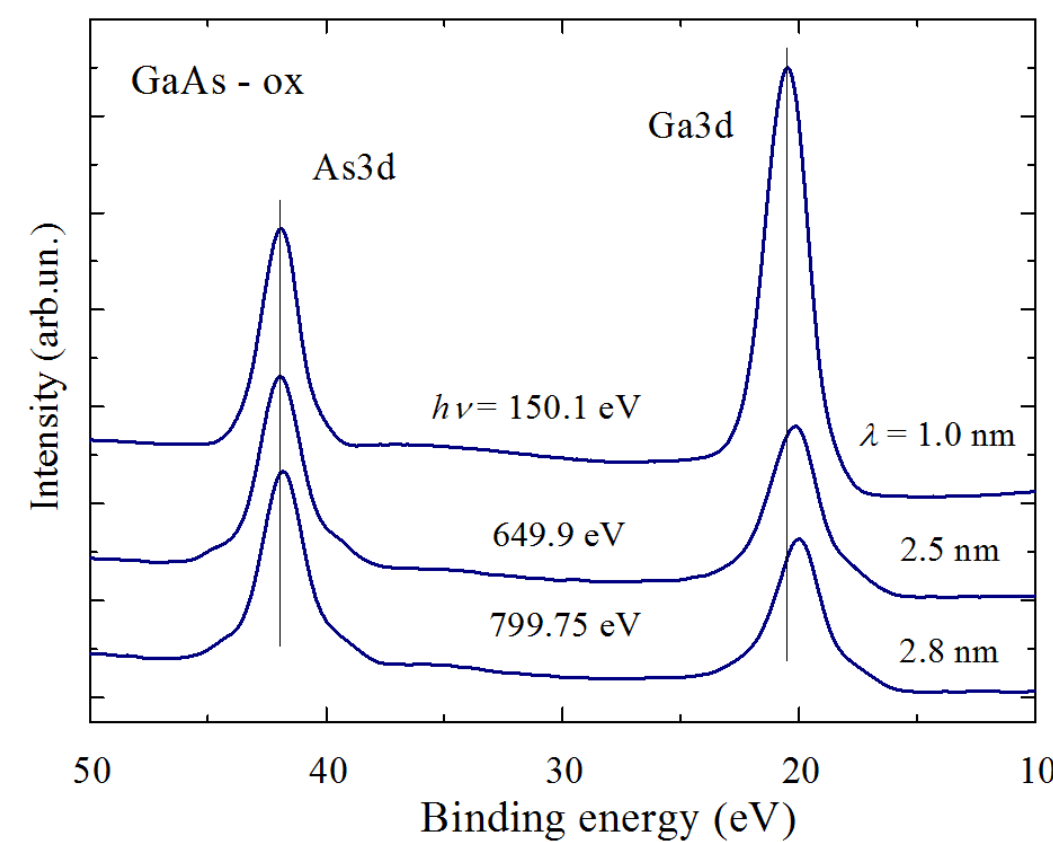


Fig.1. As3d and Ga3d spectra. The photon energies ($h\nu$) and mean free paths (λ) are indicated. Probing depth varies with $h\nu$.

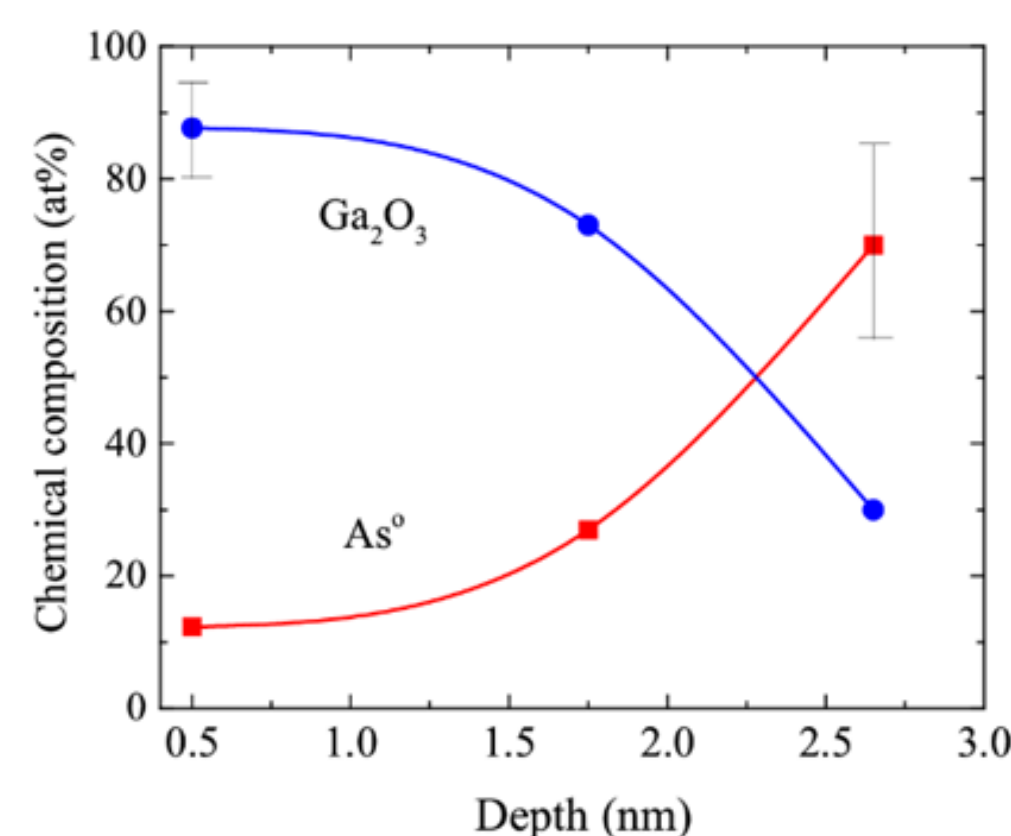


Fig.2. Depth profile of chemical composition of the ion-irradiated GaAs oxide.

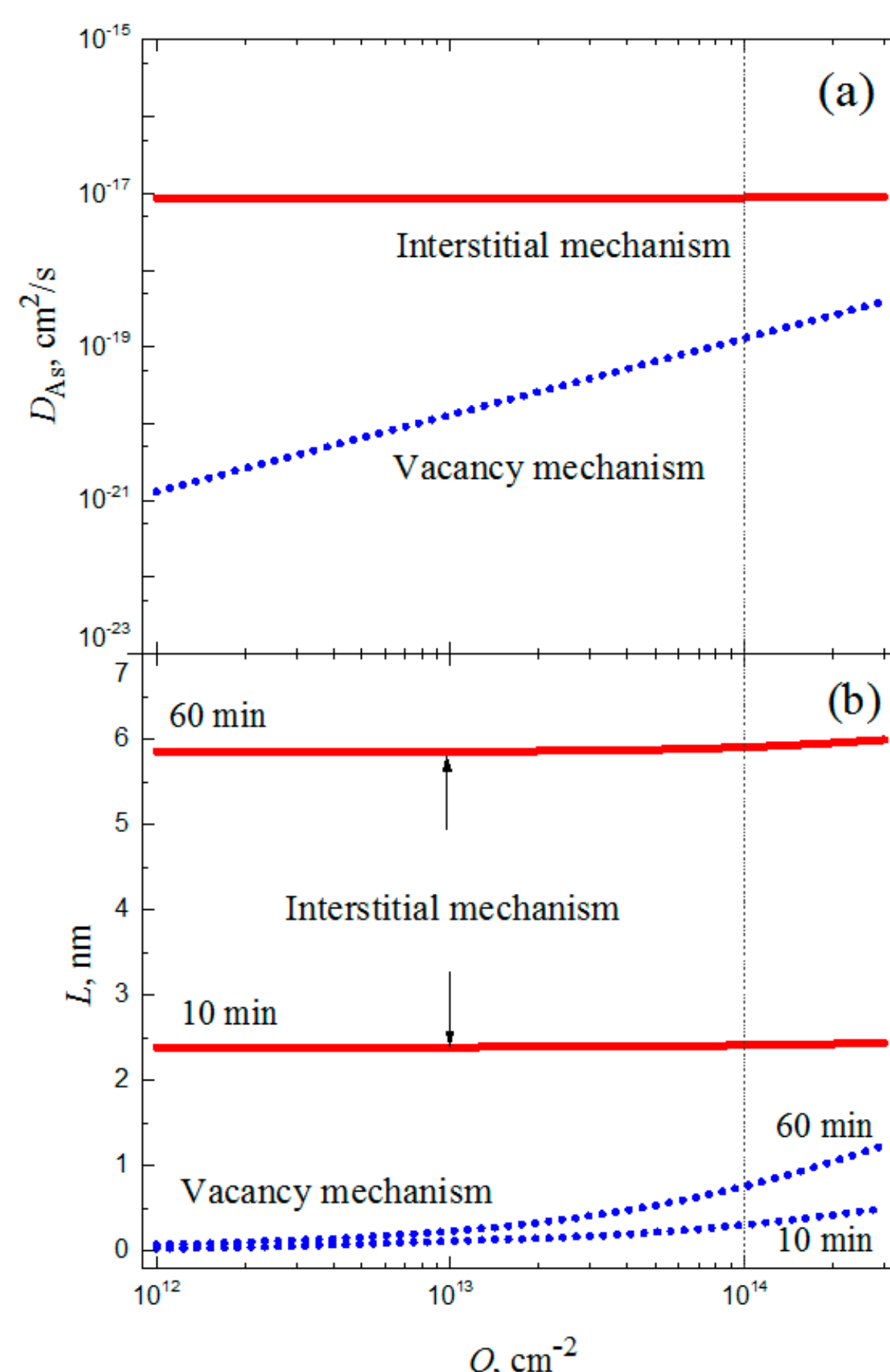


Fig. 3. As diffusion coefficient D_{As} (a) and diffusion length L for 10 and 60 min (b) vs. Q for different diffusion mechanisms.

Experimental details and results

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A GaAs natural oxide film 2-2.5 nm thick formed on the preetched GaAs surface was stored under normal conditions for ~6 months (sufficient for room-temperature self-restoration of the GaAs crystal structure [3]) and then irradiated with Ar⁺ ions. After that, XPS spectra of the sample were measured.

Depth profile of chemical composition of the irradiated oxide derived from XPS spectra (Figs. 1, 2) showed that

Ar⁺ ion irradiation of the GaAs natural oxide almost fully (by 90%) converts it into Ga₂O₃ down to the depth of 2-2.5 nm.

The qualitative model of the oxide modification suggested in [2] implied the As chemical bonds breakage with Ar⁺ ions and intense room-temperature diffusion of As atoms from the oxide layer through radiation vacancies.

The measurements lasted from 10 to 60 min after irradiation. Thus, As left the oxide not later than in 60 min.

In this work, a more detailed quantitative analysis of the paper [2] experimental results concerning the arsenic atoms diffusion in the oxide was performed.

Conclusions

Arsenic diffusion from the ion-irradiated natural oxide layer proceeds preferentially through the interstitial mechanism that is especially energetically favorable at room temperature and relatively low fluences ($Q < 10^{15}$ cm⁻²). Due to its high efficiency, the interstitial diffusion may affect also the dynamics of the GaAs surface oxidation which is known to be accompanied by emergence of elemental arsenic.

References

- [1] S.J. Pearton, J. Yang et al., Appl. Phys. Rev. 5 (2018) 011301.
- [2] V.M. Mikoushkin et al., Surf. Coat. Technol. 344 (2018) 149.
- [3] H. Mehrer, "Diffusion in solids", Springer Science & Business Media, 2007, 654 pp.
- [4] J.F. Ziegler, J.M. Manoyan, Nucl. Instr. Meth. B 35, 215 (1988).
- [5] D. Shaw, "Atomic diffusion in semiconductors, Plenum Press, London and New York, 1973.
- [6] A. Rim and R. Beserman, J. Appl. Phys. 74 (1993) 897.
- [7] A.V. Bobyl et al., Semiconductors 46, (2012) 814-824.
- [8] A. Heiden, et al., Phys. Chem. Chem. Phys. 21(8) (2019) 4268.
- [9] J.F. Wager, J. Appl. Phys., 69 (1991) 3022.
- [10] J.P. Stark, Solid State Diffusion, Malabar, FL: Krieger Publishing, 1983.

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