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Chemical creating the gold nanoclusters at GaP(001) surface and spectroscopy of their anisotropic plasmons

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Nanoclusters of gold are prepared at (001) surface of GaP crystals by a chemical method which does not require heating the sample. Characterization of obtained nanostructures Au/GaP was performed and their plasmons are investigated by reflection anisotropy spectroscopy technique. It is shown that the spectral feature at energy about 2 eV belongs to weakly anisotropic Au nanoclusters elongated presumably in crystallographic [110] direction at GaP(001) surface.

Keywords: gold clusters, gallium phosphide, polarization spectroscopy, anisotropic plasmons.

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Making and studying the novel nanostructures and materials based on semiconductors with noble-metal clusters are urgent for optoelectronics and nanophotonics [1]. One direction of this activity is creation at $A^{III}B^{V}$ semiconducting surfaces of gold nanoclusters possessing high-quality plasmons. As an example, three principally different types of anisotropic clusters of Au and its intermetallids were obtained in [2,3] in heating thin Au films at GaAs surfaces depending on their state. However, the mentioned technology of Au/GaAs structures fabrication has restrictions because high-temperature annealing of samples is necessary for clusters to be formed via chemical interaction of Au with GaAs.

In contrast to the cited works, here we develop a method of chemical preparation of Au nanoclusters on GaP(001) surfaces which requires no annealing the samples. With this method, novel structures Au/GaP are prepared, their characterization is performed and the spectra of anisotropic plasmons are investigated. It worthy noting that similar chemical methods for preparing Au films and particles from solution of gold-containing acid were used earlier for substrates GaAs and InP [4,5].

With the method proposed below for Au nanoclusters preparation, the surfaces of GaP(001) substrates are treated with a mixture of aqueous $2 \cdot 10^{-2}$ M solution of tetrachloroauric ($HAuCl_4$) and orthophosphoric (H_3PO_4) acids in volume fractions 5:1. Before treating, the surfaces are cleaned by boiling in trichloromethane, isopropanol, stands for 30 minutes in a solution of ammonia (NH_4) and are washed out by deionized water. Then, the substrates are immersed into gold-containing solution at temperature of 50°C, time of sample treating in solution being 10−20 minutes.

Under chemical contact of the anions $(AuCl_4)^-$ of solution with the atoms of GaP crystal surface, the oxidation-reduction reaction occurs resulting in transition of electrons from valence band of GaP to anions $(AuCl_4)^-$. Then according to the reaction

$$(AuCl_4)^- + 3e^- \rightarrow Au + 4Cl^-, \qquad (1)$$

trivalent gold reduces and stands out on the surface of crystal in the form of Au atoms. In turn, free adsorption positions appear on atomic bonds of Ga and P at surface GaP layer which are occupied according to (1) by anions Cl^- with formation of ion-covalent bonds. Finally, the reaction products $GaCl_3$ and PCl_5 (the latter hydrolyzes to $POCl_3$ in water-containing solution), which are soluble in phosphoric acid (H_3PO_4), are separated from crystal. This leads to microetching the surface of GaP(001) substrate. The described processes are presented by the formula:

$$3GaP + 8HAuCl_4 + 3H_2O \rightarrow 8Au + 3GaCl_3 + 3POCl_3 + 14HCl. \qquad (2)$$

The released atoms of gold possess high mobility at the crystal surface which is covered by acid H_3PO_4 from the solution. Random mutual collisions of migrating Au adatoms lead to formation in adsorption layer of gold associates, whose characteristic is abrupt reducing mobility with increasing the sizes. The sedentary associates become the centers for Au clusters to be formed. It is principal that Au/GaP structures with Au nanoclusters are formed as a result of low-temperature reaction (2) that is opposite to structures Au/GaAs which require strong heating for formation of Au clusters [3].

The obtained structures are characterized with help of scanning electron microscope (SEM) JSM7001F (JEOL, Japan), the results being presented in Fig. 1. The SEM image shows a layer of Au nanoclusters occurring at the surface GaP(001) treated in a solution of acids

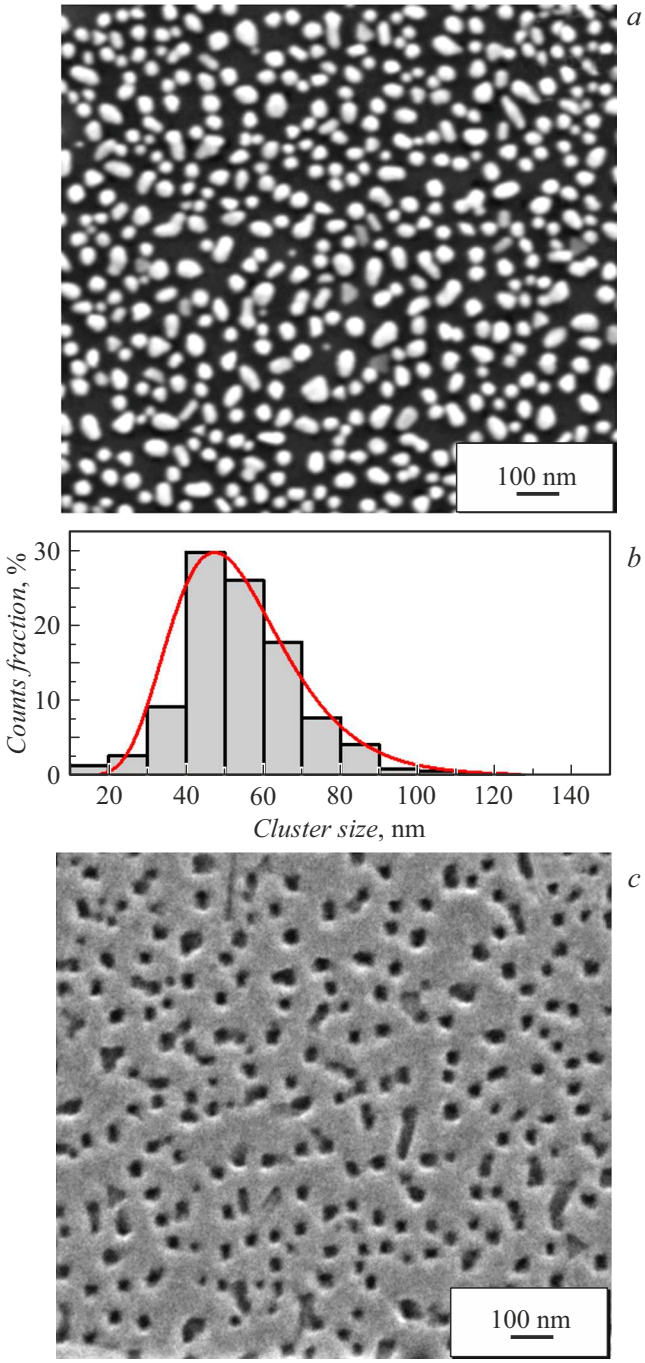

Figure 1. *a* — SEM image of $6\,\mu m^2$ area on Au/GaP(001) surface with gold nanoclusters; *b* — distribution of Au clusters over linear sizes, estimated from the squares of pits in the surface plane (smooth line is added for eye); *c* — SEM image of an area of the same surface GaP, as in fragment *a*, after removal of Au clusters and washing out.

$HAuCl_4-H_3PO_4$ for 20 minutes at temperature of 50 °C. Also, it is seen from Fig. 1, *a* that Au nanoclusters are distributed over the surface in random, but homogeneously on the average. The shape of clusters majority in the surface plane is close to circular, but seen is a tendency to their elongation and orientation. The histogram presented in Fig. 1, *b* gives the following estimations for the mean size of clusters and their standard deviation: $\langle a \rangle \approx 54$ nm and $\sqrt{\langle a^2 \rangle - \langle a \rangle^2} \approx 15$ nm. The SEM image seen in Fig. 1, *c* has been obtained after complete chemical removal of gold clusters from the surface of sample, like in [3]. In Fig. 1, *c*, numerous pits are seen on the sample surface GaP(001) which are the result of its etching during the oxidation-reduction reaction.

The results of Au/GaAs structures investigation [2,3] show that Au clusters formed at (001) surface of a semiconductor possess the anisotropy of shape and of plasmon polarization. In what follows, we show unambiguously the presence of plasmon anisotropy in structures Au/GaP and then investigate it by the method of plasmonic reflection anisotropy spectroscopy [6]. This method gives, under normal light incidence, the frequency dependence of the anisotropy signal

$$\frac{\Delta R}{R} = 2\frac{R_x - R_y}{R_x + R_y}. \qquad (3)$$

Here, R_α is the reflectivity of light linearly polarized along the α-axis (x or y) at GaP(001) surface. The signal $\Delta R/R \neq 0$ from Eq. (3) undoubtedly evidences for the existence of anisotropy ($R_x \neq R_y$), which means, in our case, the presence of shape anisotropy and orientation of clusters simultaneously. The setup for prompt revealing the anisotropy of clusters by direct registration of spectra (3) without measuring R_α is described in papers [2,3]. In the experiment, linear polarization of light incident onto surface of sample is modulated along crystallographic directions [110] and $[1\bar{1}0]$. Light reflected from the surface is detected with help of photomultiplier with the subsequent analyzing the signal using the lock-in amplifier which provides the sensitivity for signal $\Delta R/R$ on the level of 10^{-5}.

Figure 2 presents the measured spectra *1* and *2* of reflection anisotropy $\Delta R/R$, accordingly, in the absence and presence at GaP(001) surface an ensemble of Au nanoclusters shown in Fig. 1, *a*. The reflection anisotropy spectrum 2 related to an ensemble of Au nanoclusters has a characteristic resonant dip at energy about 2 eV which is absent in spectrum *1*. According to Eq. (3), the presence of the dip means that $R_y > R_x$ in choosing the axes $x \parallel [1\bar{1}0]$ and $y \parallel [110]$ at GaP surface. We ascribe the observed resonant dip in the spectrum $\Delta R/R$ of Au/GaP(001) to plasmons of anisotropic Au clusters, like in papers [2,3] for structures Au/GaAs(001). Presence of the only resonant feature $\Delta R/R < 0$ in spectrum *2* in Fig. 2 means that the frequencies of the maxima in spectra $R_y \neq R_x$ entering in Eq. (3) are close to each other. At that, spectrum *2* differs principally from spectra $\Delta R/R$ belonging to strongly elongated and definitely oriented clusters [3], of which characteristic are two wide and significantly remote features with different signs. As well, should be noted presence in spectrum *2* in Fig. 2 of a weak feature at energy of 2.25 eV which is related with indirect interband transition in GaP [7];

the latter is activated owing to plasmonic nanoclusters of Au. Arrow in Fig. 2 points the unrelated with plasmon feature which is due to transitions E_1 in GaP crystal bulk.

To interpret the observed spectra, use following [8] the model of spheroids with the semi-axes lengths $a < b$ taking account of the elongation of Au clusters seen in Fig. 1, *a*. A nanospheroid Au with subwavelength a and b possesses anisotropic surface plasmons, polarized along its principal axes. Quasi-homogeneous electric field $\mathbf{E}$ induces the dipole moment $\mathbf{p} = \hat{\chi}\mathbf{E}$ of plasmons having the polarizability tensor $\hat{\chi}(\omega) = \hat{\chi}' + i\hat{\chi}''$. When the plasmon polarizability is taken into account, the coefficients of normal reflection $R_\alpha = |r^{(0)} + \Delta r_\alpha|^2$ of light with linear polarizations $\alpha = x, y$ enter Eq. (3). These are expressed through the coefficient $r^{(0)}$ of light reflection from crystal and anisotropic contributions Δr_α due to plasmons. Below, in calculating the latter we neglect the interaction between dipole plasmons of different clusters (Fig. 1, *a*), and the effect of image forces from the substrate include formally in the frequency $\omega_{\alpha,n}$ of plasmon with polarization α in n-th cluster.

In the experimental spectrum $\Delta R/R$ in Fig. 2, the resonant dip with minimum at energy of $\hbar\omega_R \approx 2$ eV we attributed above to plasmons localized at Au clusters. For the energy of such a plasmon calculated for a sphere with Au parameters from [9] to be close to $\hbar\omega_R$, one needs to take $\varepsilon_* \gtrsim 6$ for dielectric constant of environmental medium. Such the value (intermediate between permittivities of air and GaP) signifies that Au clusters probably are situated in a transition layer between air and GaP. This conclusion is consistent with SEM image of GaP surface in Fig. 1, *c* which shows a nanostructured relief after removal of Au clusters. The width $\hbar g_R \approx 0.4$ eV of the dip in spectrum $\Delta R/R$ in Fig. 2 is significantly larger than the width $\hbar\varepsilon''(\omega)\omega^3/\omega_p^2 \approx 0.12$ eV of the elemental spectral line expressed by the polarizability component $|\chi_{\alpha\alpha}(\omega - \omega_{\alpha,n})|$ of plasmon with $\omega_{\alpha,n} \approx \omega_R$. This obliges to assume analogously [3] that spectra $\Delta R/R$ and R_α are broadened inhomogeneously owing to dependence of plasmon frequencies $\omega_{\alpha,n}$ on cluster shapes.

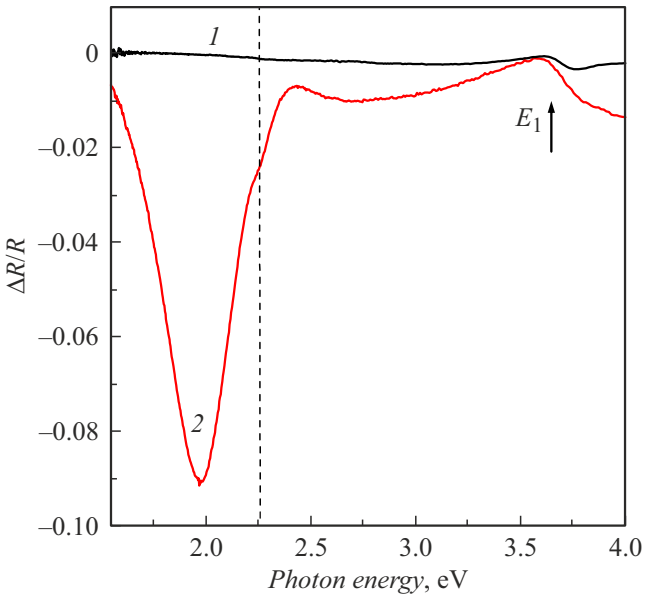

Figure 2. Reflection anisotropy spectra $\Delta R/R$ of light from GaP(001) surface measued in the absence (*1*) and the presence (*2*) of an ensemble of Au nanoclusters which is shown in Fig. 1, *a*. Dashed line corresponds to energy 2.25 eV of indirect interband transition in GaP.

Next, we discuss the character of inhomogeneous broadening for observed plasmonic spectra under the following suppositions. The polarizability $|\chi_{\alpha\alpha}(\omega - \omega_{\alpha,n})|^2$ of plasmon with polarization along the α-axis in n-th spheroid is expressed by the Lorentzian having maximum with frequency $\omega_{\alpha,n}$ and width γ_α with $\gamma_\alpha \ll \omega_{\alpha,n}$ [3]. The inhomogeneously broadened spectrum of plasmons consists of lines $|\chi_{\alpha\alpha}(\omega - \omega_{\alpha,n})|^2$ with close frequencies $\omega_{\alpha,n}$ for each axis α along which clusters are oriented on the average. The spectrum is obtained by averaging over the plasmon frequencies $\omega_{\alpha,n}$ (over the numbers n) with a distribution function having the mean frequency $\overline{\omega}_\alpha$ and width δ_α. As a result of averaging with the Cauchy distribution, one gets for inhomogeneously broadened spectra with polarizations $\alpha = x, y$ the following (cf. with [3]):

$$\frac{\Delta R}{R}(\omega) = A_x^{(-)} L_x(\omega - \overline{\omega}_x) - A_y^{(-)} L_y(\omega - \overline{\omega}_y), \qquad (4)$$

$$R_\alpha(\omega) = R^{(0)}(\omega) + A_\alpha^{(+)} L_\alpha(\omega - \overline{\omega}_\alpha), \qquad (5)$$

$$L_\alpha(\omega - \overline{\omega}_\alpha) = \frac{\omega\Delta_\alpha/2}{(\omega - \overline{\omega}_\alpha)^2 + (\Delta_\alpha/2)^2}. \qquad (6)$$

Here, the width $\Delta_\alpha = \gamma_\alpha + \delta_\alpha$ of inhomogeneously broadened peak includes the constants of homogeneous γ_α and inhomogeneous δ_α broadenings, and coefficients $A_\alpha^{(\mp)} > 0$ are calculated with taking into account the sizes of Au clusters shown in Fig. 1.

The inhomogeneously broadened spectra $\Delta R/R$ and R_α presented in Fig. 3 are calculated from Eqs. (4)–(6) with the following values of parameters (eV): $\hbar\overline{\omega}_y = 2$, $\hbar\overline{\omega}_x = 2.1$, $\hbar\gamma_y = 0.2$, $\hbar\gamma_x = 0.15$, $\hbar\delta_x = \hbar\delta_y = 0.15$. It is seen that inhomogeneously broadened spectrum $\Delta R/R$ depicted by curve *1* in Fig. 3 is in good agreement with experimental spectrum *2* shown in Fig. 2. Independently averaged coefficients R_y and R_x of light reflection calculated from Eq. (5) are shown in Fig. 3, for completeness.

To conclude, the nanoclusters of gold has been created at GaP(001) surface as a result of its chemical reaction with the solution of gold-containing acid. With the methods of SEM characterization and of optical spectroscopy, the presence of shape anisotropy of the Au clusters has been found. It is shown that the elongated Au clusters are oriented presumably in [110] direction at GaP surface, just as in structures Au/GaAs studied earlier [3].

Conflict of interest

The authors declare that they have no conflict of interest.

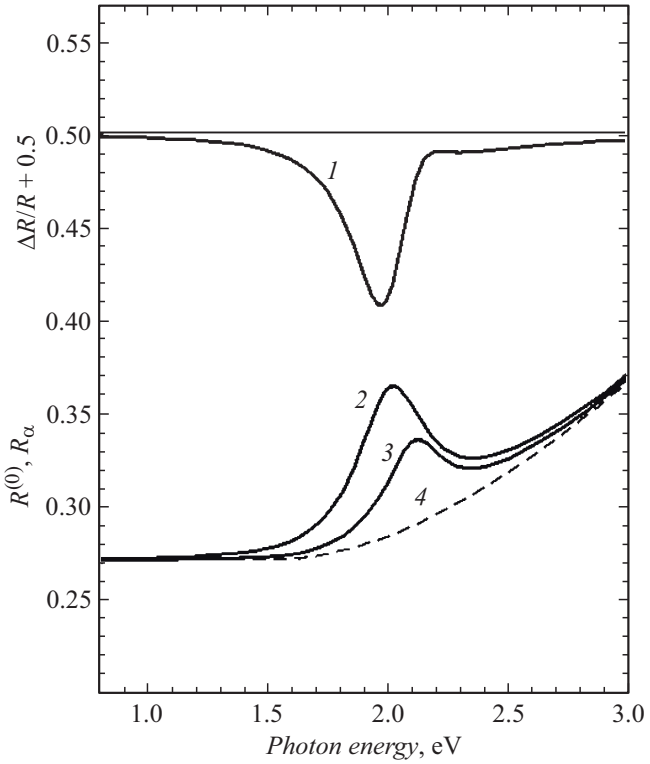

Figure 3. Theoretical inhomogeneously broadened optical spectra of reflection anisotropy $\Delta R/R + 0.5$ (*1*) and of polarized reflection R_y (*2*) and R_x (*3*) from GaP surface with Au clusters. Dashed line shows spectrum $R^{(0)}$ (*4*) of light reflection from crystal in the absence of clusters. Calculated with parameters of GaP from [7] and Au from [9]; spectrum $\Delta R/R$ is shifted above by 0.5, for convenience.

References

[1] A.A. Toropov, T.V. Shubina, *Plasmonic Effects in Metal-Semiconductor Nanostructures* (Oxford Univ. Press, 2015).
[2] V.L. Berkovits, V.A. Kosobukin, V.P. Ulin, P.A. Alekseev, F.Yu. Soldatenkov, V.S. Levitskii, Phys. Status Solidi B, **259**, 2100394 (2022). DOI: 10.1002/pssb.202100394
[3] V.L. Berkovits, V.A. Kosobukin, V.P. Ulin, P.A. Alekseev, B.R. Borodin, F.Yu. Soldatenkov, A.V. Nashchekin, S.A. Khakhulin, O.S. Komkov, Surf. Sci., **742**, 122437 (2024). DOI: 10.1016/j.susc.2023.122437
[4] Y.A. Goldberg, D.N. Nasledov, B.V. Tsarenkov, Instrum. Exp. Tech., **14** (3), 899 (1971).
[5] S.Y. Sayed, B. Daly, J.M. Buriak, J. Phys. Chem., **112**, 12291 (2008). DOI: 10.1021/jp803888g
[6] V.L. Berkovits, V.A. Kosobukin, V.P. Ulin, A.B. Gordeeva, V.N. Petrov, JETP Lett., **98** (10), 614 (2014). DOI: 10.1134/S0021364013230033
[7] D.E. Aspnes, A.A. Studna, Phys. Rev. B, **27** (2), 985 (1983). DOI: 10.1103/PhysRevB.27.985
[8] V.A. Kosobukin, A.V. Korotchenkov, Phys. Solid State, **58** (12), 2536 (2016). DOI: 10.21883/ftt.2016.12.43871.164
[9] P.B. Johnson, R.W. Chrystie, Phys. Rev. B, **6** (12), 4370 (1972). DOI: 10.1103/PhysRevB.6.4370