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# Effect of chemical passivation of GaAs(001) surface on anisotropy and orientation of gold nanoclusters formed on it and their plasmons

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The principal role of chemical passivation of GaAs surface in the formation on it of oriented anisotropic nanoclusters of gold is discussed. The nanoclusters are fabricated by thermal annealing of a gold film deposited onto GaAs(001) surface passivated as a preliminary by a monolayer of nitrogen or sulfur atoms. These atoms, bonded chemically to gallium atoms of the crystal surface, form a crystal lattice and prevent the chemical interaction of Au with GaAs. As a result of annealing, the arrays of anisotropic (elongated) nanoclusters of chemically pure Au oriented preferably in crystal $[1\bar{1}0]$ direction are formed on passivated GaAs(001) surface. The presence of strong anisotropy and orientation of Au clusters on passivated GaAs surfaces is established by the methods of probe diagnostics and of optical reflectance anisotropy spectroscopy and polarized reflection spectroscopy. Using an optical model of plasmonic polarizability of elongated Au spheroids, it is shown that the spectral features observed in polarized reflection originate from anisotropic plasmons of Au nanoclusters polarized mainly in direction $[1\bar{1}0]$ of crystal.

**Keywords:** semiconductor surface, nitride passivation, gold nanoclusters, anisotropic plasmons, polarized reflectance.

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## 1. Introduction

Combinations of noble-metal nanoclusters with semiconductors are promising for various applications in nanophotonics and photovoltaics. Practical importance of the metal–semiconductor composites is explained by the high quality of plasmons localized on metal clusters and the diverse optical and electronic properties of semiconductors. As to gold clusters on GaAs surface, fabrication of them was rather problematic until recently. The obstacle for that was dissociation of GaAs crystal in the places of its contact with gold, where the intermetallic phase $Au_2Ga$ appears [1]. The reaction observed at temperatures above 250°C leads to appearance of $Au_2Ga$ islands under the initial surface of crystal instead of Au nanoclusters on top. Therefore, the standard methods based on annealing the thin films of deposited gold are useless for fabrication of chemically pure Au clusters directly on GaAs surface.

Recently, it was shown [2–4] that the reaction of gold with GaAs in heating can be excluded by creating in between GaAs crystal and Au film an intermediate monolayer of nitrogen or sulfur atoms chemically bonded to gallium atoms of crystal surface GaAs(001). The monolayers of N or S atoms are created on GaAs(001) surface by means of its nitride or sulfide passivation before deposition of Au film. As a result, gold and crystal are separated by a chemically stable intermediate monolayer of gallium nitride or sulfide, which prevents from a contact between Au and GaAs in heating. Subsequent annealing of formed Au/N/GaAs or Au/S/GaAs structures makes possible to obtain chemically pure gold nanoclusters on passivated GaAs(001) surface of substrate.

This article demonstrates the exceptional importance of chemical passivation of GaAs(001) surface for fabrication of anisotropic gold nanoclusters on it. Studied here is the effect of passivating atomic layers on the shape and orientation of nanoclusters in a macroscopically anisotropic array formed on GaAs surface. The data of plasmon spectroscopy of anisotropic reflection and resonant polarization spectroscopy of plasmons localized on Au clusters are used to prove the anisotropy of gold clusters and their predominant orientation on the surface.

## 2. Structure and properties of passivated GaAs(001) surfaces

Passivation of surface of $A^{III}B^{V}$ semiconductor compounds is commonly used for reducing the density of surface states in the bandgap, the states being responsible for the Fermi level pinning and surface recombination. Similar states are characteristic of naturally oxidized surfaces of $A^{III}B^{V}$ semiconductors. As already noted, passivation implies the formation on semiconductor surface of an ultrathin layer of inert material preventing oxidation and creating no bandgap states. The methods of passivating GaAs(001) surface were elaborated earlier, which provide for on-surface formation of native oxides, oxide $SiO_2$ or nitride $Si_3N_4$ layers [5–7]. Such the passivating coatings are amorphous, their thicknesses are of a few nanometers, as minimum.

The chemical nitride or sulfide passivation dealt with here means that a chemisorbed monolayer of nitrogen or sulfur atoms exists on GaAs(001) surface. The passivating N or S atoms are bonded to the layer of Ga atoms built in the lattice sites on GaAs surface, which were occupied by As atoms before passivation. Owing to high strength of formed chemical bonds N-Ga and S-Ga as compared with As-Ga bonds, the passivating monolayers of N or S atoms protect the surface of GaAs crystal from oxidation and from its contact with a deposited gold layer. It is important that the nitridized or sulfidized GaAs surfaces retain the crystal structure, which, in turn, can influence significantly the shape and orientation of metal clusters formed on it. This fact is the key in our work, since previous studies were for Au nanoclusters formed on surfaces having no crystalline structure (glass [8], polished quartz [9]).

A scheme of atomic structure for GaAs(001) surface passivated by nitrogen atoms was proposed in paper [3], and for the surface passivated by sulfur atoms is presented in [4]. In these cases, the scheme of valence bonding on passivated GaAs surface is similar, e.g. it is presented in Fig. 1 of article [4], and so it is not reproduced here. In [3], the data of diagnostics are reported for Au/N/GaAs structure, and Fig. 2 of article [4] shows similar results of diagnostics for Au/S/GaAs structure.

In cases under discussion, the electronic structure of passivating layer is anisotropic because passivating (N or S) atoms have dangling bonds whose projections onto (001) plane are oriented in $[1\bar{1}0]$ direction. The anisotropy of dangling bonds may result in the anisotropy of diffusion rate for Au atoms over passivated surface, which effect determines ultimately the anisotropy of formed gold nanoclusters. Further contents of this article give arguments for the anisotropy of gold nanoclusters with special emphasis on its study by optical methods.

The structures under study are formed on *n*-GaAs(001) substrates with an impurity concentration of $4 \cdot 10^{18}\,\mathrm{cm}^{-3}$. During nitride passivation of GaAs(001) substrates, their surfaces are subjected to chemical treatment in solution of hydrazine hydrate ($N_2H_4 : H_2O$) with a small addition of sodium sulfide ($Na_2S$) [2]. Sulfide passivation is performed by treating samples in aqueous solution of sodium sulfide, followed by vacuum annealing at temperature of 460°C [4]. Onto passivated surfaces of both types, an Au film of thickness $\sim 10$ nanometers is deposited by vacuum evaporation technique. Then, the prepared Au/N/GaAs or Au/S/GaAs structures are annealed in vacuum at temperature of 300°C. Atomic-force microscopy data [3,4] show that the arrays of Au nanoclusters are formed on the surfaces in Au/N/GaAs and Au/S/GaAs structures as a result of long-term (180−240 min) annealing. Dominating in the arrays are Au clusters having the form of chains oriented predominantly in $[1\bar{1}0]$ direction on GaAs(001) surface.

## 3. Spectroscopy of anisotropic Au clusters

The presence of anisotropy is established for Au clusters on GaAs surface using the optical reflection spectroscopy of polarized light and the differential reflectance anisotropy spectroscopy. The latter method measures directly the differential spectrum of reflectivity

$$\frac{\Delta R}{R} = 2\,\frac{R_{[1\bar{1}0]} - R_{[110]}}{R_{[1\bar{1}0]} + R_{[110]}} \qquad (1)$$

for light normally incident onto the surface GaAs(001) of crystal and linearly polarized in $[hk0]$ crystallographic direction. Signal (1) can appear only in the presence of optical reflection anisotropy, i.e. when $R_{[1\bar{1}0]} \neq R_{[110]}$. In our case, this makes the reflectance anisotropy spectroscopy to be, in essence, a reliable express method for detecting the optical anisotropy of Au clusters in the plane of GaAs(001) surface. To emphasize, the anisotropy signal $\Delta R/R$ from Au nanoclusters is one or two orders of magnitude larger than from a monolayer of valence bonds on reconstructed semiconductor surface.

Figure 1 shows $\Delta R/R$ spectra measured for Au/N/GaAs structure after two successive annealings with total duration of 60 min (spectrum *1*) and 180 min (spectrum *2*) at temperature of 300°C. Before annealing, the $\Delta R/R$ signal is close to zero in the whole spectral region under study [3]. Appearance of $\Delta R/R$ spectra as a result of annealing is certainly evidence of appearance of optical anisotropy on GaAs(001) surface of Au/N/GaAs structure in accordance with formula (1). The only sources of anisotropy in Au/N/GaAs structures are Au nanoclusters, inasmuch as the cubic GaAs crystal and the possible residual Au film are optically isotropic. Spectra $\Delta R/R$ in Fig. 1 have the form of broad resonances whose maxima are located near the energy 2 eV characteristic of surface plasmons of gold particles. In view of this fact, we associate the observed resonant anisotropy signals $\Delta R/R$ (Fig. 1) with anisotropic plasmons localized on Au nanoclusters. Taking into account the data of probe diagnostics of Au/N/GaAs structures [3,4], we come to conclusion that the anisotropy signals $\Delta R/R$

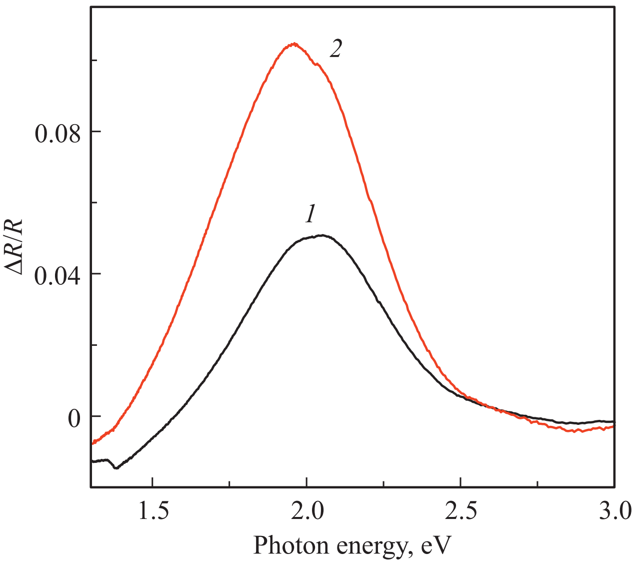

**Figure 1.** Reflectance anisotropy spectra $\Delta R/R$ measured for Au/N/GaAs structure after its annealing at temperature of 300°C for 60 (*1*) and 180 min (*2*).

plotted in Fig. 1 indicate a technologically conditioned shape anisotropy of Au clusters and the presence of their predominant orientation. When the heating duration increases, the signal $\Delta R/R$ increases, too (cf. spectra *1* and *2* in Fig. 1), that shows an increase of anisotropic spectral response with conserving the resonance characteristics.

More complete information on the spectra of anisotropic plasmons of Au nanoclusters formed on GaAs(001) surface is provided by reflection spectroscopy of linearly polarized light at normal incidence onto the surface. In this case, the reflection spectra $R_{[110]}$ and $R_{[1\bar{1}0]}$ with polarizations along [110] and $[1\bar{1}0]$ directions are measured separately, and those reliably identify the resonant contributions of plasmons having polarizations in [110] and $[1\bar{1}0]$ directions on surface plane. Figure 2 presents the spectra of normal reflection $R_{[110]}$ (*1*) and $R_{[1\bar{1}0]}$ (*2*) measured after annealing of Au/N/GaAs structure at 300°C for 180 min. The same „background“ contribution in spectra $R_{[110]}$ and $R_{[1\bar{1}0]}$ is conditioned by optically isotropic GaAs crystal and Au film. The presence of Au clusters anisotropy, established above with help of spectrum $\Delta R/R$, enables us to ascribe the observed difference $R_{[110]} \neq R_{[1\bar{1}0]}$ to optical anisotropy of plasmons localized on the nanoclusters.

Let us compare the reflection spectra $R_{[110]}$ and $R_{[1\bar{1}0]}$ (spectra *1* and *2* in Fig. 2), each containing a resonant feature (maximum) with a boundary conditionally drawn by points at the bottom. Spectrum $R_{[110]}$ polarized in [110] direction contains a resonance feature at energy of 2.2 eV. Spectrum $R_{[1\bar{1}0]}$ polarized along $[1\bar{1}0]$ direction has significantly more intense and broad feature in the range 1.7–2.1 eV. Presence of the resonance features at different energies in reflection spectra $R_{[110]}$ and $R_{[1\bar{1}0]}$ means the presence of plasmonic polarization anisotropy related to anisotropy of Au clusters. Following [3], we conclude that in an ensemble of Au clusters formed on the surface in Au/N/GaAs(001) structure during long-term annealing, dominating are clusters and cluster chains elongated in $[1\bar{1}0]$ direction, as were observed by atomic force microscopy in [3,4]. To add, significant rising in temperature of heating (up to 350°C), leads to dramatic changes of the cluster structure [2]. It is because gold penetrates into GaAs crystal through the holes occurring in nitride layer under heating and forms $Au_2Ga$ islands there. Also, it should be noted that for Au clusters formed on sulfidized GaAs(001) surface the features observed in polarized reflection spectra [4] are similar to those described here for nitridized Au/N/GaAs(001) structures.

To interpret the spectroscopy data for Au/N/GaAs(001) structures, we use a model of plasmon polarizability related to ellipsoids of revolution (spheroids) for anisotropic Au clusters. For spheroids with Au permittivity, such an optical model of clusters describes the spectrum of anisotropic plasmons, their polarization, and oscillator strength [3]. In the spheroid model, the components $\chi_{\alpha\alpha}(\omega)$ of diagonal polarizability tensor are associated with localized plasmons polarized in external wave field along the $\alpha$-semiaxes of spheroid with subwavelength sizes $a$ and $b$. The ratio $\eta = b/a$ determines the shape of spheroid, whereas the energies of plasmons having identical polarizations are equal to each other in spheroids with the same $\eta$. In accordance with the diagnostics data for Au nanoclusters [3], in Au/N/GaAs

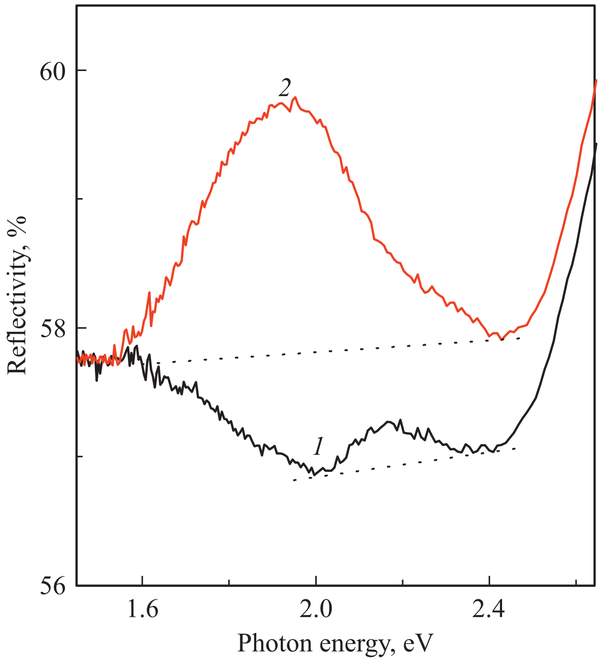

**Figure 2.** Normal incidence spectra $R_{[110]}$ (*1*) and $R_{[1\bar{1}0]}$ (*2*) of reflection of linearly polarized light, measured after annealing of Au/N/GaAs structure at 300°C for 180 min. The boundaries drawn by points are added from bottom to each observed spectrum to smooth it in the range of spectral feature and to highlight the feature symbolically.

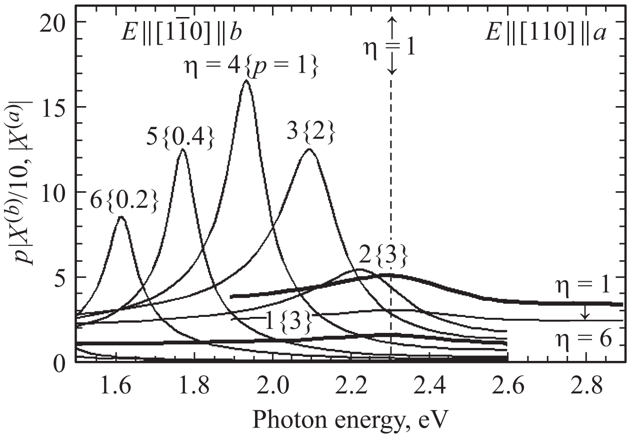

**Figure 3.** Spectra of dimensionless plasmonic polarizabilities $p|X^{(b)}|/10$ ($E \parallel [1\bar{1}0] \parallel b$) and $|X^{(a)}|$ ($E \parallel [110] \parallel a$) calculated for a model of prolate Au spheroids in vacuum with ratios of semiaxis lengths $\eta = b/a > 1$ indicated by integers in symbols $\eta\{p\}$. The vertical dotted line ($\eta = 1$) corresponds to plasmon energy of Au sphere. Factors $p$ included in symbols $\eta\{p\}$ hypothetically take account of relative contribution of spectral lines $p|X^{(b)}|$ into inhomogeneously broadened resonant feature of spectrum polarized in direction $[1\bar{1}0]$ (reflection spectrum $R_{[1\bar{1}0]}$ in Fig. 2).

structures Au clusters are oblong in $[1\bar{1}0]$ direction of GaAs(001) substrate. For prolate spheroids with $b/a > 1$, the orientation of axes $a \parallel [110]$ and $b \parallel [1\bar{1}0]$ relative to the crystallographic axes on GaAs(001) surface is assumed. At that, the diagonal components $\chi_{\alpha\alpha}(\omega)$ of plasmonic polarizability tensor of spheroids (nanoclusters) determine the resonant features (spectral bands) in reflection spectra $R_{[110]}$ and $R_{[1\bar{1}0]}$ (*1* and *2* in Fig. 2) for light polarized in [110] and $[1\bar{1}0]$ directions, respectively [3].

Dimensionless components $X^{(\alpha)}(\omega) = \chi_{\alpha\alpha}(\omega)/V$ of plasmonic dipole polarizability calculated for a prolate ($\eta = b/a > 1$) Au spheroid of volume $V$ are displayed in Fig. 3 in the forms $|X^{(a)}|$ and $p|X^{(b)}|/10$. For a spheroid with given $\eta$, the components $|X^{(a)}|$ and $p|X^{(b)}|/10$ have the form of elementary lines, whose maxima positions correspond to the energy of plasmons polarized along axes $a$ and $b$, respectively. The vertical dotted line $\eta = 1$ in Fig. 3 corresponds to plasmons of Au sphere, and it separates by energy the plasmons of Au spheroids polarized in parallel to the long axis $b$ (on the left) and to the short $a$ (on the right). The spectral lines $|X^{(a)}|$ and $p|X^{(b)}|/10$ of spheroids plasmons presented in Fig. 3 possess much smaller widths than the plasmon-determined resonant features (bands) in observed spectra *1* and, especially, *2* in Fig. 2. This means that the observed spectral features are inhomogeneously broadened, i.e. consist of narrow lines with different energies of maxima for Au clusters of different shapes (for ellipsoids with different $\eta$). The elemental lines $p|X^{(b)}|/10$ in Fig. 3 are classified by parameters $\eta\{p\}$, where $p$ expresses a hypothetical relative contribution of spheroids (plasmons) with a given $\eta$ into the resonance feature observed in spectrum $R_{[1\bar{1}0]}$.

As follows from Fig. 3, given a shape (given $\eta$) of a spheroid, the polarizability maximum is larger and the resonance energy is smaller for its plasmon polarized along axis $b \parallel [1\bar{1}0]$ than for plasmon polarized along axis $a \parallel [110]$ (cf. [3]). Then, in an ensemble of spheroids the spectral range for plasmons with polarizabilities $|X^{(b)}|$ is an order of magnitude larger than for plasmons with polarizabilities $|X^{(a)}|$. Also, it is seen that for given contributions $p$ of spheroids with different $\eta\{p\}$ (shapes), the spectral position and shape of envelope drawn through the maxima of spectral lines $p|X^{(b)}|/10$ agrees qualitatively to characteristics of the spectral feature observed in spectrum $R_{[1\bar{1}0]}$ (spectrum *2* in Fig. 2). The inhomogeneous broadening of spectrum polarized in [110] direction is determined by the same distribution of lines $|X^{(a)}|$ over $p$ as the distribution of $|X^{(b)}|$ lines. According to Fig. 3, such inhomogeneous broadening of $|X^{(a)}|$ spectrum should result in a weak and relatively narrow spectral feature with energy above 2 eV, which agrees well to the feature observed in spectrum $R_{[110]}$ (spectrum *1* in Fig. 2). It should be noted that in addition to the resonant plasmon contribution the spectra of polarizabilities $|X^{(a)}|$ and $|X^{(b)}|$ (Fig. 3) imply a „background“ component (non-resonant, but weakly dependent on frequency). The latter is related to difference between the permittivities of ellipsoid material (without electron gas) and environment. The presence of such a „background“ can explain, at least in part, the difference between spectra obtained from $R_{[110]}$ and $R_{[1\bar{1}0]}$ (Fig. 2) after separation of resonant features with their conditional pointed boundaries.

## 4. Conclusions

We have demonstrated that annealing a thin Au film deposited on GaAs(001) surface results in formation of an ordered array of anisotropic gold nanoclusters, if the surface is passivated by a monolayer of nitrogen or sulfur atoms, which prevent from the reaction of gold with GaAs. The nature of cluster anisotropy is determined by temperature and duration of film annealing, which can also affect the continuousness of passivating layer. After annealing at temperatures that do not allow breaking the structure of passivating layer, the Au clusters of prolate shape are formed on GaAs(001) surface with predominant orientation in $[1\bar{1}0]$ direction. When temperature increases significantly, holes appear in passivating layer through which Au penetrates into GaAs substrate and chemically interacts with it to form clusters of alloy Au with Ga. Then, the elongation of Au clusters in $[1\bar{1}0]$ direction of surface plane decreases appreciably, though does not disappear. The observed elongation of Au clusters in $[1\bar{1}0]$ direction is assumed to be due to the anisotropy of surface chains of dangling bonds, whose consequence may be the anisotropy of thermally stimulated diffusion of gold atoms over passivated surface of GaAs(001) crystal. If so, the above results mean that the diffusion rate of Au atoms should be larger in $[1\bar{1}0]$ direction than in [110] direction. As well, it should be anticipated that the diffusion anisotropy postulated for gold on passivated GaAs surfaces is a general property of the diffusion of metal atoms on the surface of semiconductor crystals.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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