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Plasmon spectroscopy of anisotropic gold nanoclusters on GaAs(001) surface passivated by sulphur atoms

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This work demonstrates how to create the structures Au/GaAs with perfect on-surface gold nanoclusters. In doing so, used is covering the GaAs substrate with chemically stable atomic monolayers of sulphur to prevent subsequently a chemical reaction of Au with GaAs. The structures Au/S/GaAs with monolayers of chemisorbed sulphur atoms are fabricated, characterized and studied by polarized reflection spectroscopy. The anisotropy of on-surface gold nanoclusters is established, and the anisotropic plasmons localized in Au clusters are investigated using the spectra of polarized reflection and interpreted theoretically.

Keywords: sulphide passivation, gold nanoclusters, plasmon anisotropy, polarized reflectance.

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1. Introduction

Noble-metal nanoclusters supporting high-quality plasmons in surface metal-semiconductor structures are of great importance for both fundamental science and applications in optoelectronics, photovolatics, nanophotonics, etc. Nanostructures Au/GaAs seem to be very prospective owing to plasmons of embedded Au clusters and optical properties of GaAs. In addition, remarkable chemical and physical stabilities of gold film and nanoclusters are of great utility. However, in standard conditions it is difficult to fabricate the nanoclusters because gold interacts chemically with GaAs at temperatures as low as 200°C. The related chemical reaction leads to dissociation of GaAs crystal and to formation of under-surface Au–Ga alloys instead of on-surface Au nanoclusters [1]. For this reason, no procedure is available to be efficient in annealing Au film and to ensure good adhesion of formed Au clusters to semiconductor surface. Thus, both fabrication technology and study of plasmonic Au/GaAs nanostructures are developed insufficiently. On this subject could be mentioned the only work dealt with Au nanoparticles prepared by ion beam bombardment of Au film sputtered over GaAs [2].

The present work is aimed at know-how fabricating and all-round studying the Au/GaAs structures with Au nanoclusters on GaAs(001) surface. The related technological problems were considered earlier for natural oxidized surfaces Au/GaAs [3] and nitridized surfaces Au/N/GaAs [3–5]. A principally new point of this work is to get pure-Au nanoclusters in structures Au/S/GaAs whose crystalline surface is stabilized preliminary by a chemisorbed atomic layer of sulphur. Formation of anisotropic on-surface Au nanoclusters in the structures Au/S/GaAs is verified by probe microscopy diagnostics. Such the Au nanoclusters are found to possess an unusual plasmonic anisotropy, established by reflectance anisotropy spectroscopy and explained theoretically. To note, the results presented below for Au/S/GaAs structures are similar in some respects to those obtained for Au/N/GaAs structures [5].

2. Stabilization of GaAs(001) surface by atomic monolayer of sulphur atoms

This work extends the idea that fabrication of chemically clean gold nanoclusters on GaAs surface is possible, if the deposited Au film and GaAs substrate are separated by a stable atomic layer impeding any contact of Au with GaAs. To form such a layer, we develop a chemical technology in which GaAs substrate undergoes the surface chemical sulphidation before deposition of Au film, just as it undergoes the nitridaton [4,5].

Sulphidation of GaAs(001) surface is performed by its chemical treatment in Na_2S water solution which removes the oxide layer and forms initially a layer of As-sulphides. Long-term treatment followed by annealing at 460°C leads to formation of on-surface layer consisting of sulphur atoms chemisorbed on Ga atoms of crystal in bridge-bond configuration [6].

The proposed atomic structure of GaAs(001) surface after chemical passivation by atoms denoted as X, in general, is shown in Fig. 1. In our case, the top layer X shown in Fig. 1, a is occupied by sulphur ($X = S$) atoms, and the same scheme being valid for nitridized GaAs(001) with $X = N$ [5]. The chemisorbed S atoms are strongly bonded to the next-layer Ga atoms of GaAs crystal, which, in turn, are bonded to As atoms underneath. The surface bonds S–Ga are significantly stronger than Ga–As bonds in

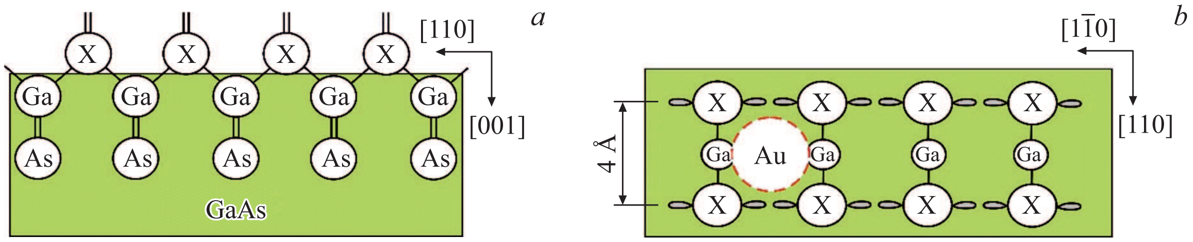

Figure 1. Side (a) and top (b) views of atomic structure of GaAs(001) surface, covered by chemisorbed atoms marked as X (standing for sulphur below), and the atomic layers Ga and As belonging to GaAs crystal. An atom of gold is shown in the scale of surface unit cell.

crystal bulk, and so the covering sulphide monolayer is able to protect the surface of GaAs crystal against its oxidation at atmospheric ambient and to stabilize its crystalline structure in the absence of natural oxide layer. The crystalline substrate facilitates the on-surface diffusion of Au adatoms in heating the structure.

Figure 1, *b* presenting the top view of sulphidized GaAs(001) surface displays that sulphur atoms (X = S) of upper layer form a square lattice with a period of 4 Å. A gold adatom with a diameter of 3.5 Å is also shown in Fig. 1, *b*, for comparison. In general, each chemisorbed atom X of upper layer possesses two dangling bonds whose orbital projections oriented along $[1\bar{1}0]$ direction are seen in Fig. 1, *b*. As to a surface sulphur atom, two of its dangling bonds are occupied by electron lone pairs. To compare with a surface nitrogen atom when X = N in Fig. 1, *b*, one of its dangling bonds is occupied by an electron lone pair and other forms chemical bond with hydrogen atom [5]. Presence of the dangling bonds causes the anisotropy of X/GaAs(001) surfaces themselves. At high temperatures it results in the anisotropic surface adatoms diffusion, whose rate is determined by direction-dependent activation energy. From Fig. 1, *b* one can conclude that the activation energy for diffusion of Au adatoms along the dangling bonds in $[1\bar{1}0]$ direction should be smaller than in perpendicular [110] direction, i.e. Au nanoclusters should grow anisotropically. This is why the shape anisotropy is anticipated for clusters formed on annealing Au films deposited on sulphidized GaAs(001) surfaces.

3. Preparation and diagnostics of samples

The nanostructures with on-surface Au nanoclusters are prepared on n-type GaAs substrates. After commercial cleaning, GaAs(001) substrate is subjected to the above chemical procedure of surface sulphidation. The latter is performed through the wet treatment of GaAs(001) crystal surface in saturated water solution of $Na_2S \cdot 9H_2O$, the treatment duration being about 10 minutes. After rinsing the prepared substrates in hot KOH-water solution and in deionized water, a 10 nm thick gold film is deposited thermally onto the sulphidized GaAs(001) surface in vacuum of 10^{-7} Torr. The sulphidized substrate is annealed at 460°C during 15 minutes prior gold deposition. To form on-surface Au clusters, the prepared Au/S/GaAs structures (Fig. 1) undergo annealing in the same chamber at temperature as high as 350°C. Such temperature activates the accelerated enlargement of Au grains in deposited Au film [7].

The surface morphology of ready nanostructures is characterized by scanning probe microscope (SPM) NtegrA AURA (NT-MDT) at room temperature. The diagnostics shows that before annealing the as-deposited Au film consists of grains with lateral sizes of 8–15 nm, which are distributed over the surface uniformly on the average [8]. Thermal annealing, as a whole, produces modification of surface Au film in the surface-stabilized structures. Figure 2 demonstrates $(1 \times 1)\,\mu$m image of an on-surface Au nanocluster array formed in Au/S/GaAs structure after annealing it at 350°C during 30 minutes.

As is seen from Fig. 2, many Au clusters are chain-like ones, some of which are outlined by white ellipses oriented preferentially along surface $[1\bar{1}0]$ direction. Similar gold

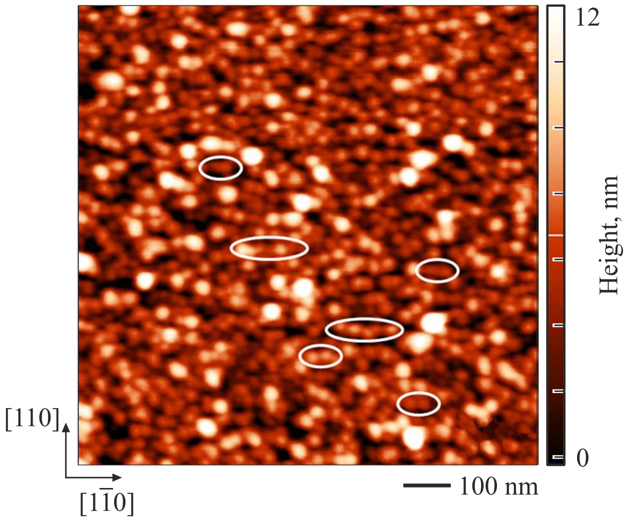

Figure 2. SPM topography image $(1 \times 1)\,\mu$m of Au/S/GaAs structure prepared on sulphidized GaAs(001) substrate after annealing at 350°C during 30 min. The thickness of deposited Au film is 10 nm. Elliptic lines are drawn around some chain-like Au nanoclusters.

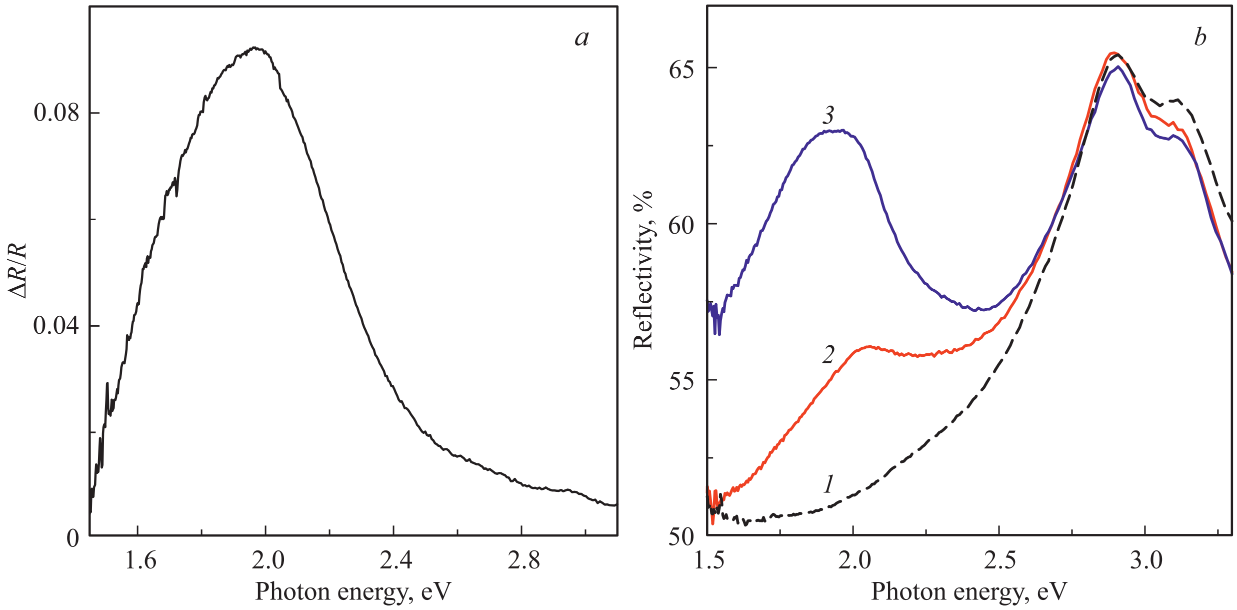

Figure 3. (*a*) Reflectance anisotropy spectrum measured for Au/S/GaAs structure after its annealing at 350°C. (*b*) Polarized reflectivity spectra of Au/S/GaAs structure measured before (*1*) and after annealing at 350°C with light polarized along [110] (*2*) and $[1\bar{1}0]$ (*3*) directions. Annealing duration is 30 minutes.

clusters have been observed also for Au/N/GaAs structure after annealing at the same temperature [5]. The chain-like clusters consist of 2–5 constituents whose in-plane dimensions are in the range 20–30 nm. For such a cluster the ratio of longitudinal-to-transverse size (along $[1\bar{1}0]$ vs [110]) is determined roughly by the number of its constituents. Thus, a pronounced shape anisotropy of Au nanoclusters is established for Au cluster arrays formed on crystalline GaAs(001) surface stabilized by chemisorbed S atoms. This fact does actually substantiate for Au/S/GaAs(001) structures the above postulate that the nanocluster anisotropy occurs due to different rates for Au adatom diffusion in $[1\bar{1}0]$ and [110] directions.

4. Plasmon anisotropy spectroscopy of Au nanoclusters

The anisotropy of plasmons supported by gold clusters located on GaAs(001) surface is a consequence of the shape anisotropy of Au nanoclusters themselves. To study the plasmon anisotropy we apply the reflection spectroscopy of linearly polarized light below. The optical anisotropy is detected initially by the reflectance anisotropy spectroscopy. The latter modulation technique measures the anisotropy signal

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

as a function of photon energy. Here $R_{[1\bar{1}0]}$ and $R_{[110]}$ are the reflectivities of light waves linearly polarized in the directions $[1\bar{1}0]$ and [110] at normal incidence onto GaAs crystal surface (001), cf. Fig. 1. The measured reflectance anisotropy spectra $\Delta R/R$ are presented in Fig. 3, *a* for Au/S/GaAs structure annealed at 350°C during 30 min. By definition, the observed of spectrum $\Delta R/R$ is an unambiguous evidence for the presence of optical reflection anisotropy $R_{[1\bar{1}0]} \neq R_{[110]}$ due to anisotropic shape of Au clusters.

Next, the polarized reflectivity spectra $R_{[1\bar{1}0]}$ and $R_{[110]}$ of Au/S/GaAs structure are measured separately by spectrometer Cary 5000 for $[1\bar{1}0]$ and [110] polarized light at normal incidence onto (001) surface, the photon energies being 1.5–5.5 eV. Spectrum *1* presented in Fig. 3, *b* for Au-film/GaAs structure before annealing is insensitive to the polarization of incident light. It is because both thin amorphous Au film and cubic GaAs substrate are optically isotropic in the surface plane. After annealing at 350°C of Au/S/GaAs structure, its reflection spectra reveal strong polarization dependence in the spectral range below 2.5 eV. For light polarized along [110] direction, reflectivity spectrum *2* of Au/S/GaAs structure annealed during 30 minutes reveals a resonant feature at nearly 2 eV, Fig. 3, *b*. In contrast, reflectivity spectrum *3* for light polarized along direction reveals a broad resonant feature in the interval 1.7–2.1 eV. We ascribe the polarization-dependent features appeared in reflectivity spectra *2* and *3* in Fig. 3, *b* to plasmons of anisotropic Au nanoclusters, whose examples can be seen in Fig. 2. It should be emphasized that polarized reflection spectra *2* and *3* shown in Fig. 3, *b* for sulphidized GaAs(001) surfaces with Au clusters are similar to the related spectra measured for nitridized GaAs(001) surfaces [5]. This fact can be explained by using the substrates of the same type whose crystallography is generalized in Fig. 1.

5. Interpretation and discussion

For a disordered array of Au clusters, the plasmon polarization anisotropy would be undetectable. But it becomes observable, if the array of anisotropic clusters is ordered on the average, at least. Actually, Fig. 2 shows that the elongated Au nanoclusters are oriented predominantly along $[1\bar{1}0]$ direction, which fact allows us to treat the Au cluster arrays under study as rather ordered. As to inherent anisotropy of Au nanoclusters themselves, it is treated below in the elementary optical model of spheroids (ellipsoids of revolution) suitable for analyzing the shape anisotropy effect. The principal axes a and b (longest) of the spheroids are assumed to coincide with $[110]$ and $[1\bar{1}0]$ crystallographic directions of GaAs(001) substrate in accord with Fig. 2. Difference of lengths for semiaxes a and b (across and along the rotation axis of a spheroid) is responsible for different energies of dipole plasmons polarized along the axes a and b.

For a single spheroid, the energies of dipole plasmons are different for modes excited by incident light with polarizations along a and b axes and depend on the ratio $\eta = b/a$. For a set of single Au spheroids with different η located in air, Fig. 4 presents spectra of the dimensionless polarizabilities $|X^{(a)}(\omega)|$ and $|X^{(b)}(\omega)|$ calculated for plasmons polarized along a and b axes (i.e. for light polarizations $E \parallel [110]$ and $E \parallel [1\bar{1}0]$) [5]. The data of Fig. 4 predict the following. At $\eta = 1$ (an array of Au spheres) the plasmons are isotropic to result in $R_{[1\bar{1}0]} = R_{[110]}$ and $\Delta R/R = 0$ above. In increasing η for spheroids in accordance with the data of diagnostics (Fig. 2), the energy of plasmons polarized along semiaxes b ($[1\bar{1}0]$ polarization) shows considerable red shift and oscillator strength growth with η. In turn, plasmons polarized along semiaxes a ($[110]$ polarization) have very small blue shifts and oscillator-strength decreases. At that, the polarizability $|X^{(a)}(\omega)|$ is much smaller than $|X^{(b)}(\omega)|$, which is divided by 100 in Fig. 4.

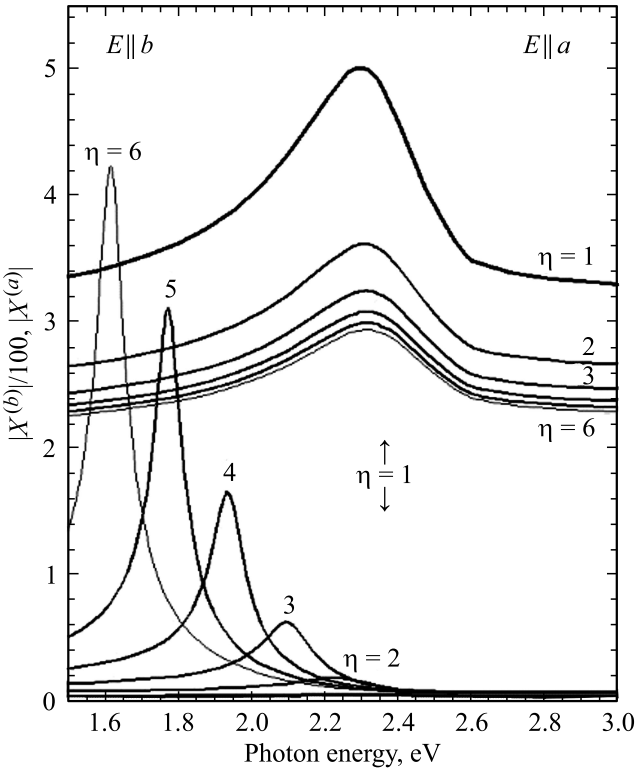

Figure 4. Spectra of dimensionless plasmonic polarizabilities $|X^{(a)}|$ and $|X^{(b)}|$ calculated for gold nanoclusters in a model of prolate spheroids ($\eta = b/a > 1$) located in air. The spectra are marked by integers $\eta = b/a$. Left set for $|X^{(b)}|$ ($E \parallel [1\bar{1}0] \parallel b$) and right set for $|X^{(a)}|$ ($E \parallel [110] \parallel a$) correspond to plasmon polarizations along and across the rotation axis b of a spheroid, respectively.

The calculated series of spectra ($E \parallel a$ in Fig. 4) explains the weak feature centered at about 2.1 eV in spectum *2* in Fig. 3, *b*, the related plasmons being polarized across the chains seen in Fig. 2. Another series ($E \parallel b$) explains the maximum of spectrum *3* in Fig. 3, *b* appearing at nearly 2 eV due to plasmons polarized along the chains. Rather large difference is found between the bandwidth of spectrum *3* in Fig. 3, *b* observed for $E \parallel [1\bar{1}0]$ polarization and the widths of calculated elementary lines of series $E \parallel b$ in Fig. 4. It means that polarized spectra in Fig. 3 are inhomogeneously broadened due to a distribution of ellipsoids (plasmons) over η, cf. [5]. Interpreting the broad resonant feature of observed spectrum *3* in Fig. 3, *b* as a set of narrow plasmonic lines of Au clusters (of spheroids in Fig. 4), we estimate that $1 < b/a < 5$ in our experiments.

6. Conclusions

It has been established that the sulphide monomolecular layer fabricated on GaAs(001) crystal surface before covering it with gold film prevents henceforth a chemical reaction of Au with GaAs substrate in heating. In this way, the formation of pure-Au nanoclusters on semiconductor surface is provided, if the surface is covered by a layer of sulphur atoms. The shape of Au clusters formed on such a layer is shown to possess a strong anisotropy related unambiguously with the crystallography of substrate with sulphur overlayer. The anisotropy of so formed Au clusters (and their plasmons) seems to be due to anisotropic diffusion of Au adatoms over the anisotropic relief of GaAs(001) crystal surface. The found and above-discussed plasmonic anisotropy is expected to be a common property of metal nanoclusters formed on crystal surfaces (001) of A_3B_5 semiconductors.

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Conflict of interests

The authors declare no conflict of interest.

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