Gold nanoclusters on GaAs(001) surface: atomic force microscopy and optical spectroscopy of plasmons

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Abstract. Gold nanoclusters of two different kinds are found to occur on annealing of thin Au films deposited on either oxidized or nitridized GaAs(001) surfaces. The morphology of Au/GaAs interfaces is characterized, and the gold nanoclusters are established to cause two resonant peaks in optical reflectance spectra at the energies of 1.6 eV and 2.15 eV. Using the data of reflection spectroscopy and theoretical analysis, we assign the latter peak to localized plasmons of Au nanoislands located on Au/GaAs surface. The former peak is attributed to plasmons of prolate Au nanoclusters buried in GaAs crystal just near its surface. As well, plasmonic anisotropy of Au nanoclusters formed on nitridized GaAs surfaces is detected using reflectance anisotropy spectroscopy.

1. Introduction

Metal-semiconductor structures with nanoclusters of metals supporting long-lived localized plasmons are of growing interest both for fundamental investigations and for applications in photovoltaics, nanophotonics, sensorics, etc. For preparation of such plasmonic structures especially promising are the gold nanoclusters, possessing high chemical and physical stabilities and high quality factor of plasmon resonances. Generally speaking, localized plasmons in Au clusters can be rather effective in the near-infrared and visible ranges up to the energy of 2.5 eV above which the plasmons are suppressed by interband electronic transitions in gold. As to Au nanoclusters formed on GaAs(001) substrates, no investigations of the related localized plasmons were reported earlier, probably, except for [1]. It seems to be mainly because of the technological obstacles for well-controlled preparation of Au nanoclusters with the proper adhesion to a substrate. To make a remark, earlier studies dealt with preparing Au-GaAs electrical contacts have been revealed that gold reacts chemically with GaAs even at rather low temperature of 350 °C leading to formation of Au-Ga alloys [2]. This chemical property hinders formation of Au nanoclusters in the conventional procedures based on annealing of deposited-Au thin films on oxidized GaAs surfaces. To weaken the reactivity of Au with GaAs substrate, we elaborate a chemical procedure of surface nitridation of GaAs substrates for using them to prepare Au nanoclusters at high temperatures.
The present paper reports on 1) the preparation of nitridized GaAs surfaces with Au nanoclusters, 2) the scanning probe diagnostics of Au/GaAs structures, and 3) the optical spectroscopy of plasmons belonging to dissimilar near-surface Au nanoclusters.

2. Preparation and diagnostics of samples

In our work, the gold nanoclusters are formed on various GaAs(001) substrates as a result of thermal annealing of deposited thin Au films, the thicknesses of the films being about of 10 nm as usual. To note, conventionally used are only Au films created on oxidized GaAs surfaces (except for Au catalyst droplets prepared on clean GaAs surfaces at MBE conditions [3]), which situations are defined as standard below. The oxidized GaAs surfaces are amorphous, and those consist of mixed oxide \( \text{Ga}_2\text{O}_3*\text{As}_2\text{O}_3 \) and an atomic As interlayer to occur in between the oxide and GaAs crystal. The \( \text{As}_2\text{O}_3 \) oxide and As atoms become volatile at temperatures above 300° C. When the two components are removed on annealing, the oxide layer becomes porous, and material contacts appear between the deposited Au and the surface of GaAs. At temperatures higher than 300° C, the dissociation of GaAs in the contact areas proceeds according the chemical reaction

\[
\text{Au} + \text{GaAs} = \text{Au(Ga)} + (\frac{1}{4})\text{As}_4. 
\]

This reaction leads to formation of Au-Ga alloy nanoclusters which are buried in GaAs substrate. As a consequence, considerable amount of gold penetrated into the substrate is found after the high-temperature annealing of Au/GaAs structures [2].

In our know-how method, nitridized GaAs substrates are applied whose peculiarity is presence on GaAs surface of a monolayer of GaN. Such a layer is prepared by nitridation of the substrate in hydrazine-sulfide solutions to protect Au from chemical contact with GaAs [4]. After deposition of gold onto nitridized GaAs substrates, we study surface morphology of obtained Au/GaAs nanostructures by scanning probe microscope NtegrA AURA (NT-MDT) at room temperature. The diagnostics show that before annealing the relief of as-deposited Au film is formed by grains whose lateral sizes are 15-20 nm, the in-surface distribution of grains being uniform on the average. Subsequent annealing of the film at 350°C during 30 min changes the relief leading to appearance of Au nanoclusters on the substrate surface, figure 1(a).

![Figure 1](image)

**Figure 1.** Surface topography image (a), and surface profile along the dashed line (b), measured for an Au/GaAs structure prepared on nitridized GaAs substrate after annealing at 350°C during 30 min. The initial thickness of Au film is estimated as 14 nm.

The lateral sizes of Au nanoclusters estimated from figure 1(b) are in the range 60-80 nm, and the heights are 15-20 nm. On nitridized GaAs surfaces, formation of Au nanoclusters is apparently caused by recrystallization of the deposited Au film on annealing.
To sum up, for annealed Au/GaAs structures, the diagnostics data including STM and SEM results [5] reveal appearance of Au nanoclusters of two different types depending on the conditions of their preparation. These conditions, referred to as I and II, imply making use of oxidized or nitridized GaAs surface, respectively. To anticipate, it is shown below that the related type-I Au clusters are formed in GaAs bulk underneath of the initial Au film, while type-II Au clusters are formed mainly on the outer surface of As/GaAs structure. Consequently, the two types of GaAs surfaces provide a kind of chemical control over Au nanoclusters, while the Au deposition-annealing procedure itself is responsible for the physical properties of the clusters, particularly, for plasmons studied spectroscopically.

3. Spectroscopy of Au nanocluster plasmons

3.1. Reflectance spectroscopy

To substantiate firmly the idea concerning the two dissimilar types of Au nanoclusters, we investigate the localized plasmons of prepared nanocluster arrays. Optical reflection at normal incidence is studied with spectrophotometer Cary 5000 in the range 1.4-5.5 eV at room temperature. The effect of annealing on the reflectance spectra of Au/GaAs structure formed on nitridized GaAs surface is demonstrated in figure 2. In the absence of Au coverage, observed is the reflectance of GaAs(001) substrate, including peaks corresponding to the optical transitions $E_1$ and $E_1 + \Delta_1$ (2.9-3.2 eV) and to $E_0'$ (4.9 eV) in GaAs bulk. After deposition of 10 nm thick Au film onto GaAs(001) surface, a pronounced increase of reflectivity occurs at the energies below 2.5 eV due to electron plasma of Au. But the change of reflectivity is insignificant above the energy 2.5 eV, thus playing a role of the edge for plasmonic reflectance.

![Figure 2](image-url)

**Figure 2.** Spectra of normal optical reflectance from an Au/GaAs(001) structure before (1) and after (2) annealing it at 350°C for 15 minutes.

Next, we compare in figure 2 the initial (unannealed Au film) spectrum 1 with spectrum 2 measured for annealed Au/GaAs(001) structure. It is seen that in the range below 2.5 eV the reflectivity increases because two broad resonant features arise near 1.6 and 2.15 eV. Bearing in mind the surface morphology shown in figure 1 and more detailed data [5], we assign the two peaks to localized plasmons of Au nanoclusters formed after annealing. The plasmon-conditioned peaks occurring in the reflectivity spectra belong to arrays of dissimilar nanoclusters of types I (1.6 eV) and
II (2.15 eV) represented in figure 3(a). It is substantial that the higher-energy peak associated with type-II clusters is observed only for Au/GaAs structures prepared on nitridized GaAs(001) surfaces.

3.2. Theoretical background

To explain theoretically the data of optical reflection spectroscopy, we analyze them in the model shown in figure 3(a). It includes the three-layer “air/Au film/GaAs” and the arrays of Au clusters of type-I in GaAs and of type-II in air just on Au film. Following [6,7], we calculate the self-consistent normal-incidence reflectivity

\[ R(\omega) = \left| r^{(0)} + \sum_m \theta_m \Delta r^{(m)} \right|^2 = \left| r^{(0)} + \sum_m \theta_m \frac{\chi^{(m)}_{||}}{\lambda A_m} F^{(m)} \right|^2. \]  

(1)

Here, \( r^{(0)} \) is the amplitude reflection coefficient of the three-layer, and the contribution \( \Delta r^{(m)} \) is due to a layer of \( m \)-type Au nanoclusters (\( m = I, II \)), taken into account, if \( \theta_m = 1 \), and neglected, if \( \theta_m = 0 \). We consider Au nanoclusters to be presented by identical spheroids (ellipsoids of rotation) whose rotation axes are perpendicular to the crystal surface and the ratio of normal-to-lateral semi-axes lengths are \( \eta \), cf. [6,7]. The plasmonic contribution \( \Delta \chi^{(m)}_{||} \) is determined by the in-surface polarizability \( \chi^{(m)}_{||} \) of \( m \)-type spheroids making up a layer with a period \( A_m \), and \( F^{(m)} \) is the Fresnel-type phase factor at the wavelength \( \lambda \) of light.

![Figure 3.](image)

Figure 3. (a) - A scheme of Au/GaAs interface and reflection of light from it. (b) - Spectra of the plasmonic polarizabilities \( |\chi^{(m)}_{||}| \) calculated for prolate Au spheroids (\( m = I \)) with the ratios \( 1 < \eta < 5 \) (I-3) located in GaAs and for oblate Au spheroids (\( m = II \)) with \( 0.2 < \eta < 0.8 \) (I’-3’) located in air. (c) - Reflectivities \( R^{(I)} \) (I-4) of a three-layer with Au spheroids (\( m = I, 0.75 < \eta < 4 \)) situated in GaAs and reflectivity \( R^{(0)} \) (dashed) of the three-layer with 10 nm thick Au film in the absence of spheroids (\( \theta_m = 0 \) in Eq. 1).

For type-II oblate Au spheroids located in air, figure 3(a), the theory predicts a series of plasmonic polarizability \( |\chi^{(II)}_{||}| \) maxima ranged from 2.1 to 2.3 eV, if \( \eta \) is ranged from 0.2 to 0.8, figure 3(b). Similarly, for type-I Au prolate spheroids situated in GaAs a series of plasmonic \( |\chi^{(I)}_{||}| \) maxima is
predicted to range from 1.5 to 1.8 eV, if $\eta$ varies from 1 to 10. The related spectra $R^{(1)}(\omega)$ each calculated from Eq. (1) with the contribution $\Delta r^{(1)}$ of given- $\eta$ type-I Au clusters are presented in figure 3(c), spectra 1-4. The latter are compared with the reflectivity $R^{(0)}(\omega)$ (dashed) calculated for the above three-layer without Au clusters ($\theta_m = 0$ in Eq. 1).

This theory allows us to assign the reflectivity peak at 2.15 eV in figure 2 to plasmons of Au nanoislands formed on the outside surface of Au film in accord with the experiments revealing this peak only in the cases of nitridized GaAs substrates. Certainly, the low-energy peak (1.6 eV in figure 2) could appear experimentally too, but only if holes are burned through GaN monolayer on annealing. The low-energy peak is attributed to sub-surface type-I Au nanoclusters buried in GaAs bulk as nanowires elongated in direction of the surface normal. Given $\eta$ for spheroids of types I and II, the widths of related plasmonic features in calculated spectra, figures 3(b,c), are smaller than the widths of measured reflectivity peaks seen in figure 2. Taken into account a weak inter-spheroid interaction, the conclusion is not rejected [6]. If that is the case, the peaks of measured reflectivity should be considered as inhomogeneously broadened owing to a distribution of plasmon energies in the array of spheroids.

3.3. Plasmonic anisotropy

It is worthy to examine whether the localized plasmons of Au nanoclusters possess anisotropy, which property is established conventionally with the reflectance anisotropy (RA) spectroscopy, cf. [6,7]. This technique measures the anisotropy signal

$$\frac{\Delta R}{R} = 2 \frac{R_\alpha - R_\beta}{R_\alpha + R_\beta}$$

as a function of photons energy $h\omega$. In Eq. (2), $R_\alpha$ and $R_\beta$ stand for the normal-incidence reflectivities of light waves linearly polarized along the orthogonal in-surface axes $\alpha$ and $\beta$, usually being [1 10] and [110] for (001) surface of a cubic crystal. It is principal that the anisotropy signal (2) from the bulk of a cubic crystal is zero, then the result $\Delta R/R \neq 0$ is an unambiguous sign that a surface anisotropy exists in such a crystal.

![Figure 4](image)

**Figure 4.** Reflectance anisotropy spectra of Au/GaAs structure measured after annealing 10 nm film for 20 min at 310°C (1), for 20 min at 350°C (2), for 40 min at 350°C (3), and spectrum 4 presents the difference between spectra 3 and 2.
We measure RA spectra of Au/GaAs structures prepared on nitridized GaAs surfaces with deposited Au films. For an unannealed Au/GaAs structure, RA signal (2) in the range 1.4-2.8 eV turns to be almost zero that implies absence of in-surface anisotropy. After first annealing of the structure at 310°C, in RA spectrum a weak resonant feature 1 centered at about 2 eV appears, which can be ascribed to localized plasmons of type-II Au nanoclusters, figure 3(a). Further annealing at 350°C during 20 min transforms peak 1 into identical peak 2 with nearly seven-fold increased intensity. Finally, annealing for 40 min at 350°C changes strongly the intensity and shape of ΔR/R signal resulting in spectrum 3. The modification of RA spectrum induced by final annealing is presented by the difference 4 of spectra 3 and 2, which is centered at nearly 1.7 eV. We believe that appearance of the spectral feature 4 is caused by formation of near-surface type-I nanoclusters of Au-Ga alloy buried in GaAs. In general, the set of resonant RA spectra 1-4 (figure 4) give unambiguous optical evidence of existence of plasmonic anisotropy. In other words, the RA spectra argue that the plasmon-supporting Au clusters arrays formed on nitridized GaAs surface possess an in-surface anisotropy related with the shape of clusters or/and the structure of cluster arrays themselves, cf. [6,7].

4. Conclusions
This work has established that on annealing of a thin Au film deposited on GaAs(001) substrate Au nanoclusters are formed (I) in near-surface GaAs bulk and (II) on Au film, the result depending on the conditions of cluster preparation. The latter Au nanoclusters possessing localized plasmons observed at the energy about 2.15 eV are thought of as oblate-shaped islands. The former prolate-shaped Au clusters whose localized plasmons have the energy of 1.6 eV occur as a result of chemical reaction of Au with GaAs surface to thread into GaAs bulk perpendicularly to crystal surface. It is expected that this type of Au nanoclusters in Au/GaAs structures could provide the Ohmic contacts and influence the surface conductivity.

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