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Anisotropic plasmons in Au/GaAs(001) structures with gold nanoclusters

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Abstract. The structures Au/GaAs(001) with gold nanoclusters are created by annealing of Au films deposited onto GaAs surface. The samples are diagnosed stepwise by scanning probe microscopy. Using reflectance anisotropy spectroscopy, Au clusters are established to possess plasmons with the in-surface anisotropy. The measured anisotropy spectrum consists of a resonant feature near the energy of 2 eV typical of local plasmons of Au clusters. The results are explained theoretically, and the new spectral feature is assigned to anisotropic plasmons of Au nanoclusters located on GaAs surface.

1. Introduction

Metal-semiconductor structures with metal nanoclusters supporting long-lived localized plasmons are of interest for fundamental studies and for various applications. In many fields, very promising are the structures with gold nanoclusters which possess chemical and physical stabilities and high-quality plasmon resonances. As to Au nanoclusters formed just on GaAs substrate, their controllable creation by conventional annealing of deposited Au film still remains technologically unattainable. This is because gold is able to react chemically with GaAs to form Au-Ga alloys [1] instead of Au clusters even at rather low temperature of 300 °C.

It was shown recently that chemical nitridation of GaAs surface in hydrazine-sulfide solutions before deposition Au film for annealing is a way for preparation of Au clusters just on GaAs surface [2]. In such a case, the monolayer of nitride GaN covering GaAs surface prevents the chemical interaction between Au and GaAs at elevated temperatures. It was demonstrated in [2], that annealing at 350 °C of Au/GaAs structures prepared on nitridized GaAs substrates results in formation of Au nanoclusters. Generally speaking, dissimilar Au clusters of two types can appear in different near-surface regions. The clusters of the new type II are the oblate-shaped Au nanoislands formed on nitridized GaAs surface, and the clusters of a standard type I are normally oriented Au nanowires buried into the crystal bulk. The two types of Au clusters specified below as on-surface and under-surface, are responsible for the resonant plasmon peaks observed in optical reflectance spectra at the energies of 2.15 and 1.6 eV, respectively. The cited results were obtained by non-polarized resonant optical spectroscopy [2], and the next fundamental question is about polarization and anisotropy properties of localized plasmons related with the gold clusters.

The present study is aimed at substantiating the concept of plasmonic anisotropy in nanocluster arrays formed at semiconductor surfaces, which effect was observed first for In nanoclusters on InAs(001) surface [3,4]. The new basic results are obtained for Au/GaAs structures with gold nanoclusters prepared on the nitridized GaAs(001) surface and characterized in details by probe microscopy technique. The plasmonic anisotropy is proved unambiguously by the optical modulation method of reflectance anisotropy spectroscopy, the results being verified theoretically.

2. Preparation and diagnostics of samples

The Au/GaAs structures are prepared on n-doped GaAs(001) substrates. The procedure of Au nanoclusters preparation is principally the same as developed in our work [2]. After conventional cleaning, the surface of GaAs substrate is nitridized in low alkaline (pH~10) hydrazine-sulfide solution during 10 min, washed in hot KOH-water solution and rinsed finally in deionized water. A gold film of 10 nm thickness is thermally deposited onto the nitridized GaAs(001) surface in vacuum of 10^{-7} Torr, and the prepared Au/GaAs structure undergoes annealing in the same chamber at 350 °C. Such a temperature activates the accelerated enlargement of Au grains in deposited Au film [5] and also provides formation of under-surface Au clusters [2]. In contrast with Ref. 2, in this work the duration of annealing stages is shortened down to 5 min, four annealing stages being done.

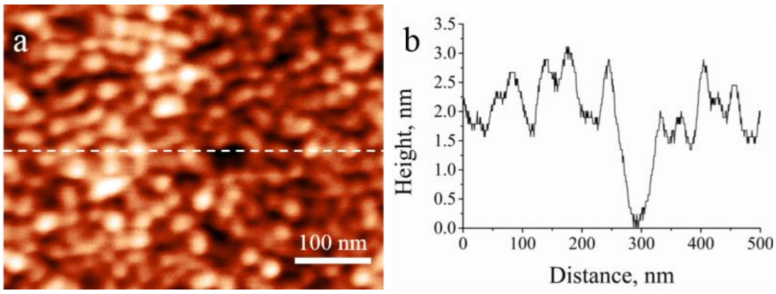

Figure 1. Surface topography image (a), and surface profile along the dashed line (b), measured for an Au/GaAs structure prepared on nitridized GaAs substrate after annealing at 350 °C during 5 min. The thickness of deposited Au film is 10 nm.

Surface morphology of obtained Au/GaAs nanostructures is characterized by scanning probe microscope NtegrA AURA (NT-MDT) at room temperature. The diagnostics shows that the as-deposited Au film before annealing consists of grains, whose lateral sizes are 15-20 nm, the grains being distributed over the surface uniformly on the average. Subsequent annealing of the Au film at 350 °C during 5 min changes the relief leading to appearance of Au nanoclusters on the substrate surface, as figure 1(a) shows. It is seen from figure 1(a) that the formed Au nanoclusters are randomly distributed over the surface; some of them form chain-like aggregates. From surface profile presented in figure 1(b) we estimate for Au nanoclusters the lateral sizes in the range 40-60 nm and the heights 1.5-2 nm. Since the latter are essentially smaller than Au film thickness of 10 nm, we conclude that annealing for 5 minutes does not break the film continuity.

3. Plasmonic reflectance anisotropy spectroscopy of Au nanoclusters

Detecting the anisotropy of Au/GaAs structure is performed by reflectance anisotropy (RA) spectroscopy. This optical modulation method measures the anisotropy signal

$$\frac{\Delta R}{R} = 2\,\frac{R_\alpha - R_\beta}{R_\alpha + R_\beta} \tag{1}$$

as a function of photons energy $\hbar\omega$. In equation (1), R_α and R_β stand for the reflectivities of normally incident light waves linearly polarized along the orthogonal axes α and β, which coincide with $[1\bar{1}0]$ and $[110]$ directions in the usual case of a cubic crystal with (001) reflecting plane. The method of RA spectroscopy possesses very high sensitivity to allow detecting the anisotropy signal (1) on the level of 10^{-5}.

It is principal that the anisotropy signal (1) from a bulk cubic crystal is zero. Then, appearance of nonzero signal $\Delta R/R \neq 0$ becomes an *unambiguous* sign that anisotropy exists on the surface of such a crystal. As a first demonstration of the in-surface anisotropy related with local plasmons, one can mention the observation of resonant plasmonic RA spectra of indium nanoclusters formed at InAs(001) surface [3]. From this viewpoint, the present work generalizes the basic idea of using plasmonic RA spectroscopy for detecting optical anisotropy of local plasmons of nanoclusters formed at the surfaces of $A^{III}B^{V}$ semiconductors. In what follows, the experimental data of RA spectroscopy are presented for Au nanoclusters at Au/GaAs(001) structures, and their theoretical interpretation is given.

3.1. Experimental results

The RA spectra $(\Delta R/R)_n$ are measured for Au/GaAs structures after each annealing stage (n=1, 2…). Before the first annealing of Au/GaAs structure, the RA signal is very weak on the level of $|\Delta R/R|$~10^{-3} typical of a clean GaAs(001) surface [7].

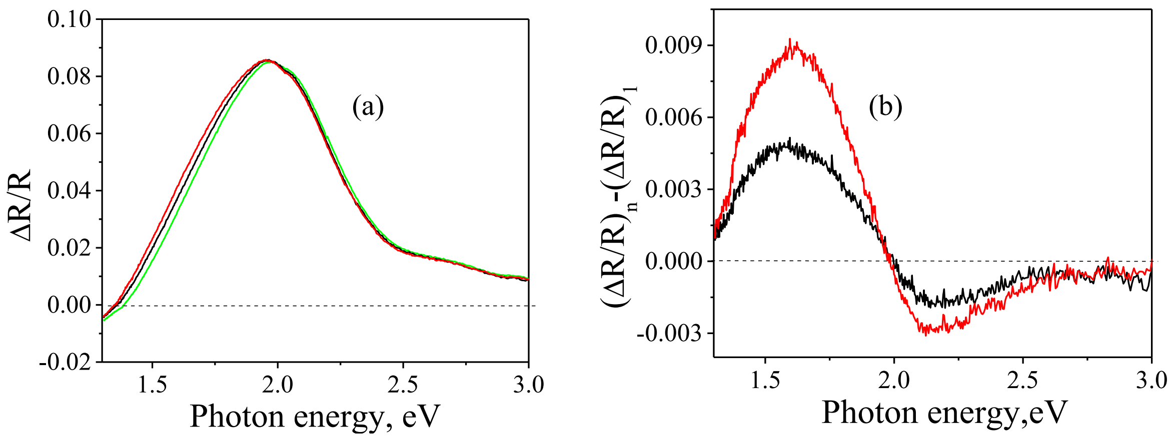

Figure 2. (a) - RA spectra $(\Delta R/R)_n$ of a Au/GaAs(001) structure measured after three ($n = 1$, 2 and 3 from right to left) successive 5-minute annealings at 350 °C. (b) – Differences $(\Delta R/R)_n$-$(\Delta R/R)_1$ for n=2 and 3 (black and red).

Figure 2(a) shows that just after first annealing (n=1) a rather broad resonant feature appears which is peaked at the energy about 2 eV consistent with the plasmonic energy of Au clusters [2]. Further successive annealings (n = 2, 3) produce very small low-energy shifts of the peaked RA feature shown in figure 2(a). In accordance with the above diagnostics data (figure 1), we assign the spectra $(\Delta R/R)_n$ to localized plasmons of Au clusters formed on annealing of Au film deposited on GaAs(001) surface. The plasmonic RA signals $(\Delta R/R)_n \approx 8\%$ seen in figure 2(a) for a nitridized Au/GaAs structure are by one-two orders of magnitude stronger than the signals from clean GaAs surface.

The further insight in annealing-induced modification of RA spectrum detects the spectral differences $(\Delta R/R)_n$-$(\Delta R/R)_1$ shown in figure 2(b) for n = 2 and 3 (black and red). These differences demonstrate that the annealing stages $n = 2$ and 3 give rise to increasing the successive contributions to anisotropy signal at about 1.6 eV, i.e. at the energies of localized plasmons of under-surface Au clusters [2]. In conformity with Ref. 2, the observed shift of RA peak in prolonged annealing of a Au/GaAs structure can be ascribed to formation of some under-surface (type-I) Au clusters due to chemical reaction between Au and GaAs. From figure 2(b) it follows that plasmons of the under-surface Au nanoclusters exhibit the same sign of anisotropy relative to crystallography directions $[1\bar{1}0]$ and [110] as the on-surface Au clusters appearing first on nitridized GaAs surface. Such the similarity could be associated with anisotropy of Au cluster formation processes.

3.2. Theoretical interpretation

Next we interpret the observed RA spectra within a theory of plasmonic RA spectroscopy developed after [2,4,6]. Consider a three-layer medium "air/Au film/GaAs" in the presence of Au nanoclustes array. In a self-consistent approximation [4,6], the reflectivity at normal incidence of light wave with linear α -polarization entering equation (1) is

$$R_\alpha = | r^{(0)} + \Delta r_\alpha |^2 \ . \tag{2}$$

Here, $r^{(0)}$ is the Fresnel-type reflection coefficient of the above in-plane isotropic three-layer without clusters. The resonant contribution Δr_α due to plasmons of Au clusters implies the presence of anisotropy $\Delta r_\alpha \neq \Delta r_\beta$ providing $\Delta R/R \neq 0$ in equation (1).

The optical anisotropy of Au clusters is introduced through their dipole-plasmon polarizabilities. Keeping in mind possible existence of Au clusters of types I or/and II [2], we introduce the related polarizability tensors with the components

$$\chi^{\mathrm{I,\,II}}_{\alpha\beta} = \delta_{\alpha\beta}\ \chi^{\mathrm{I,\,II}}_{\alpha\alpha}(\omega) \tag{3}$$

marked by indices I and II. Then, we consider a model of the three-layer with a monolayer of identical quasi-point dipoles with plasmonic polarizabilities (3) of type either I or II, each layer occupying its own rectangular lattice with the period $A^{\nu}_{\alpha,\beta} << 1/k_0 = c/\omega$, $\nu = \mathrm{I, II}$. Within a self-consistent approach [2,6], the anisotropy term in equation (2) in general consists of the Au cluster contributions with $\nu = \mathrm{I, II}$, cf. [2],

$$\Delta r_\alpha = \sum_{\nu=\mathrm{I,\,II}} \frac{k_0 \tilde{\chi}^{\nu}_{\alpha\alpha}}{A^{\nu}_{\alpha} A^{\nu}_{\beta}}\ F^{\nu} = \sum_{\nu}\ \Delta r^{\nu}_{\alpha} \ . \tag{4}$$

Here, F^{ν} is a phase factor of Fresnel theory, and $\tilde{\chi}^{\nu}_{\alpha\alpha}$ stands for the effective polarizability of α-polarized plasmon in ν-type Au cluster, $\tilde{\chi}^{\nu}_{\alpha\alpha}$ taking account of interaction of a given plasmon with the other intra-layer plasmons and their images [4,6]. The contribution Δr^{ν} in equation (4) is due to a lattice of identical ν-type clusters possessing the effective polarizability tensor $\hat{\tilde{\chi}}^{\nu}$ being a response on the local field. It is worthy to note that physically Au nanoclusters of the two alternative ν-types appear separately and so analyzed theoretically. The joint effect of the clusters can appear experimentally on longterm annealing when the burning of nitridized GaAs surface and subsequent penetration of Au through the holes of nitridized layer can lead to formation of type-I Au clusters in GaAs. Figure 3 explains theoretically how plasmons of Au clusters of types I and II appear in reflectivity spectra in accordance with experiment [2].

Thus, figure 3 discriminates the reflectivity spectra of type-I (under-surface) and type-II (on-surface) Au clusters, occurring in different regions of a structure Au/GaAs depending on the state of GaAs surface [2]. The classification was introduced earlier for in-plane isotropic arrays of Au clusters, and here we classify the in-plane anisotropic clusters in the same terms. Experimentally [2] it was found that Au clusters of type I occur in usual (non-nitridized) Au/GaAs systems where Au reacts chemically with GaAs substrate. As a result, type-I Au clusters are formed as under-surface nanowires elongated into GaAs bulk, the energies of their plasmons are 1.6-2 eV. As stated above, we get type-II Au nanoclusters with the know-how procedure of surface nitridization making impossible any interaction between Au and GaAs. The related on-surface oblate clusters (nanoislands) occur in vacuum on GaAs surface, their plasmon energies are above 2 eV depending on the oblateness of Au islands. The reflectivity $R^{\nu}_{\alpha}(\omega)$ calculated from equation (2) in the presence of the only ν-type Au clusters are presented in figures 3(a) for ν = I and 3(b) for ν = II. Dash line shows the related reflectivity $R^{(0)} = | r^{(0)} |^2$ for in-plane isotropic three-layer without Au clusters. The peaks of the series ν = I are seen to be in the range 1.5 eV (nearly spheres of Au) up to 1.8 eV (rather long Au wires). The peaks of another series ν = II are located from 2 eV (very oblate Au islands) up to 2.3 eV (nearly spheres of Au) .

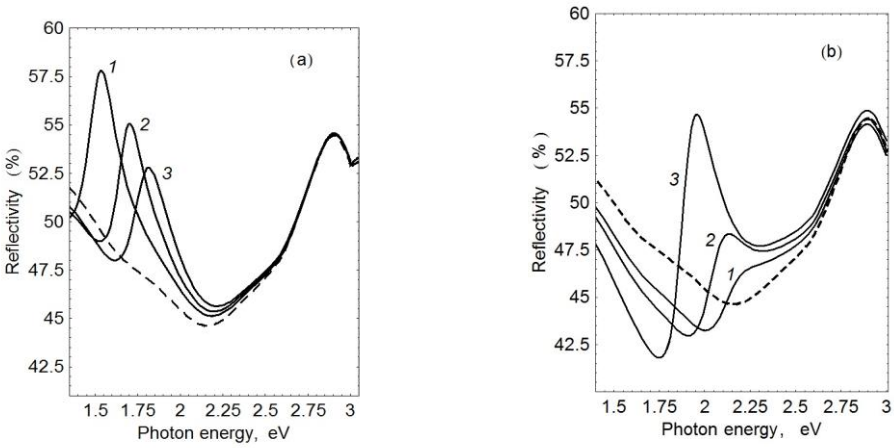

Figure 3. Reflectivity spectra calculated for the three-layer "air/Au film/GaAs" with the following Au clusters: (a) Au nanowires of type-I in GaAs bulk, (b) Au nanoislands of type II in air above nitridized GaAs surface. In both panels dashed line show the reflectivity $R^{(0)} = |r^{(0)}|^2$ of the three-layer without Au clusters.

The reflectivities $R_\alpha^\nu(\omega)$ are basic for analysis of RA spectra (1) which are considered separately for Au clusters of types I and II. Turning to experimental data (figure 2), the nature of RA spectra is illustrated in figure 4 in conformity with type-II Au clusters appearing on nitridized GaAs surface, index ν = II being omitted. The related reflectivity spectra $R_\alpha(\omega)$ and $R_\beta(\omega)$ in figure 4 possess the same plasmonic feature whose polarization components are slightly shifted ($|\omega_\alpha - \omega_\beta| << \omega_\alpha, \omega_\beta$) from each other because of the difference $\omega_\alpha \neq \omega_\beta$ of plasmon frequencies for the orthogonal in-plane polarizations α and β. The normalized difference of spectra R_α and R_β calculated from equation (1) is exactly RA spectrum $\Delta R/R$. To emphasize, all the modulation spectra in figure 4 include the related resonant features associated with a given local plasmon mode, neither of them being a single line in the usual spectral interpretation and thus require a special treatment, like that developed in [4].

Theoretical RA spectra of type-II Au clusters are presented in figure 5. Given a localized plasmon frequency, the magnitude of $\Delta R/R$ is larger for clusters of larger size (compare spectra *1* and *2*). In turn, an increase of the plasmon frequency (a decrease of oblateness of clusters) results in high-energy shift of $\Delta R/R$ peak (the transition to spectrum *3* in figure 5). Since the plasmonic peaks in figures 3-5 are apparently narrower than their experimental counterparts (Ref. 2 and figure 2 above), the observed spectra can be thought of as inhomogeneously broadened because of a statistical distribution of in-surface shapes of Au clusters.

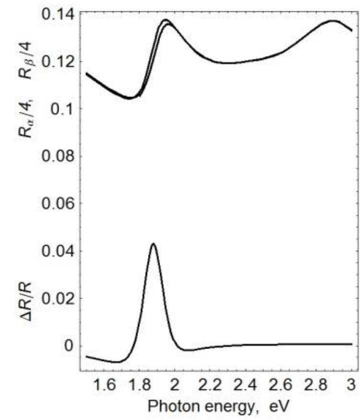

Figure 4. Polarized reflectivity spectra R_α and R_β (multiplied by 1/4) of a nitridized three-layer with anisotropic Au clusters of type II whose α - and β -polarized plasmons have different energies. The RA spectrum $\Delta R/R$ is calculated from equation (1) with spectra R_α and R_β inserted.

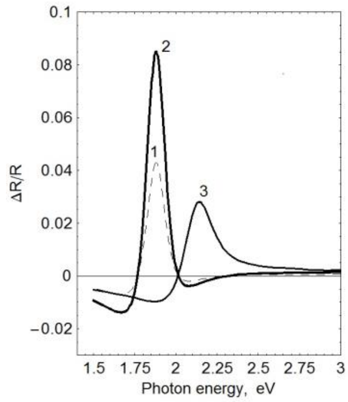

Figure 5. Reflectance anisotropy spectra $\Delta R/R$ calculated for the same model of type-II Au clusters located on nitridized surface as in figure 4.

4. Conclusions

We have established that structures Au/GaAs(001) with gold nanoclusters created by annealing of Au film deposited onto either oxided or nitridized GaAs surface possess in-surface optical anisotropy. The fact is discovered owing to observation of a broad resonant feature at plasmonic energy of 2 eV by reflectance anisotropy spectroscopy. It is shown experimentally and theoretically that RA spectra reveal unambiguously the existence in Au/GaAs(001) of anisotropy of local plasmons of Au nanoclusters. The results obtained for Au/GaAs(001) with gold nanoclusters together with our earlier results on indium nanoclusters on InAs surface [3,4] shows that the concept of plasmonic anisotropy in metal cluster arrays formed at semiconductor surfaces is general.

Acknowledgements

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