Aluminum nanoparticles embedded into GaAs: deposition and epitaxial overgrowth by MOCVD

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Introduction

A novel trend in semiconductor nanophotonics is formation of artificial nonlinear fast optical medium. First example of such material is the low temperature grown GaAs with As precipitations. Other materials are produced in the multi−step technological processes based on the combination of lithography or self−assembling with sequential epitaxial overgrowth [1]. A new approach to introduction of metallic aluminum nanoparticles into gallium arsenide using only metalorganic chemical vapor deposition (MOCVD) stage is discussed in this report. Development of technology for producing metal nanoparticles on a semiconductor surface and further overgrowing them “in situ” into a semiconductor matrix would allow to create, by multiple repetitions of the process, a multilayer three−dimensional medium of metal−semiconductor microcontacts.

The objective is to study how metal (Al) nanoparticles can be formed on the GaAs surface under MOCVD conditions and how to recover epitaxial growth of GaAs after that. At this stage it is important to find optimal MOCVD conditions for fast smoothing of the growth surface.

Experiment

Epitaxial GaAs layers were grown by the MOCVD method on GaAs (100) substrates in a horizontal reactor under reduced to 100 mbar pressure. The sources of Ga, As, Al were $Ga(CH_3)_3$, AsH_3 and $AlH_3(CH_3)_2(C_2H_5)$ – dimethylethylamine alane (DMAA). Hydrogen was used as a carrier gas. The Al nanoparticles were formed “in situ”. The GaAs buffer layer with a thickness not less than 100 nm was always grown prior to deposition of Al. GaAs was grown at 600°C, Al was deposited at temperatures 160−500°C. Supply of arsine was stopped at least 0.5min before switching on the supply of DMAA into the reactor and during all the time of Al deposition. The main growth conditions were the same as in the case of growth of thin aluminum films from DMAA in MOCVD reactor described earlier [2].

We have investigated the properties of Al nanocparticles both on the surface and in the balk of GaAs by atomic force microscopy (AFM) on surfaces and cleaveges, electron diffraction, secondary ion mass spectroscopy (SIMS), photoconductivity and photoluminescence.

Results

When the quantity of Al deposition is small (structure A), a metal layer decorates the surface of a semiconductor film. Fig.1a shows AFM image of such a structure. The surface exhibits terraces which always appear in “step flow” epitaxial growth mode. The presence of aluminum on surface of the structure is revealed by the SIMS analysis. Fig.2 shows the dependence of the content of basic elements on the sputtering depth. It is clearly seen that the Al content is highest at the surface and decreases by 3 orders of magnitude in the bulk. An increase in the amount of deposited Al on GaAs (structure B) gives rise to formation of Al nanoparticles. Fig. 1b is an AFM image for a structure with aluminum nanoparticles. A transition from a smooth surface to that with nano−size objects (Fig.1b) is typical for the Stranski–Krastanov growth mechanism; however, there are no direct evidence to prove this is exactly the case for our process.

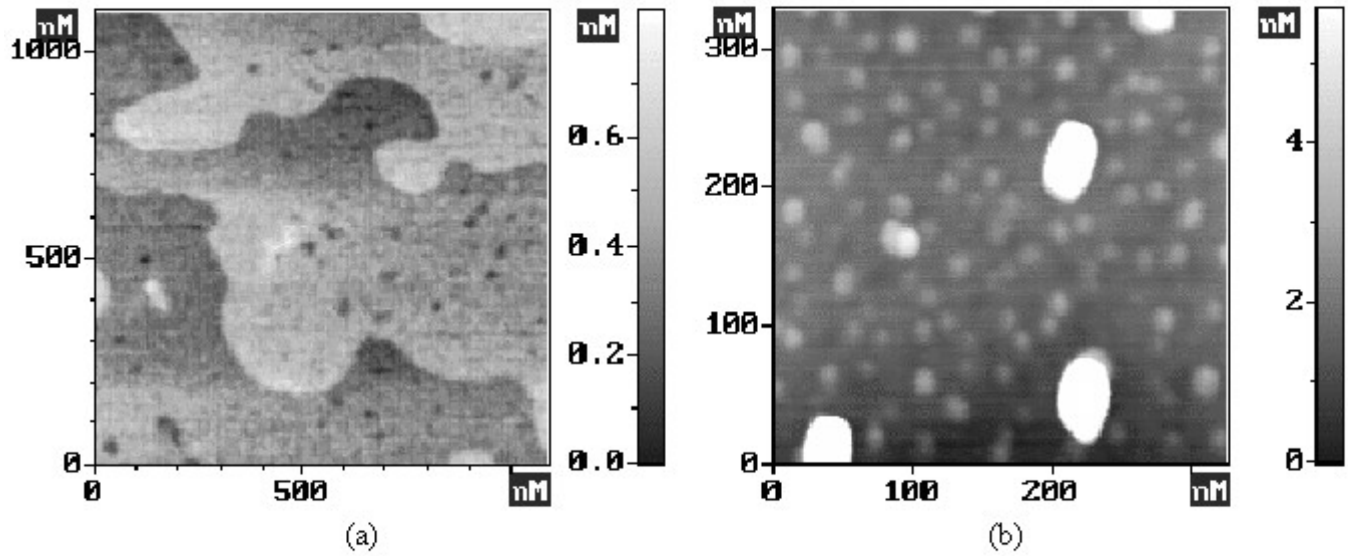


Fig. 1. AFM images of Al/GaAs structures with a low (a) and high (b) quantity of deposited Al, structures A and B, respectively.

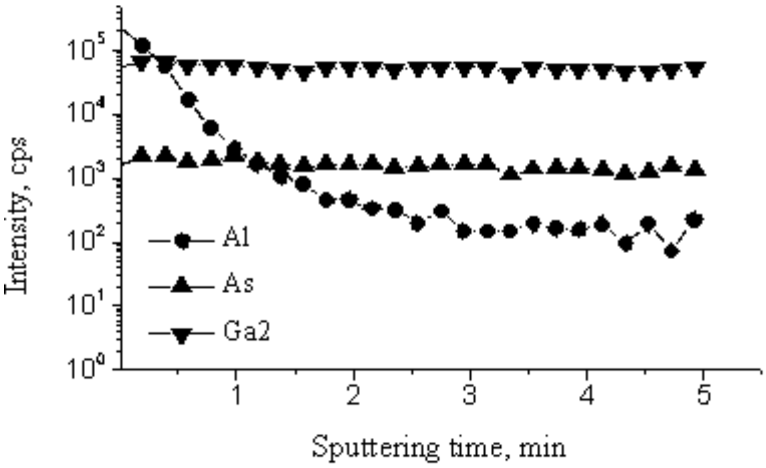


Fig. 2. Profilling of structure A by SIMS.

To model the conditions in effect when an Al layer is being overgrown with GaAs, structures A and B were subjected to annealing in AsH_3 at T=600°C during 1min. According to the AFM data, for structure A the annealing procedure caused no changes in the surface relief. Annealing of structure B leads to somewhat reduced in size Al nanoparticles, their density is also decreased. Such an effect may be due to Al diffusion from small clusters towards the GaAs region, which is accompanied by formation of AlAs resulting from arsenic saturation, or due to conversionof aluminum to volatile components, which are then removed from the reactor.

In the next set of experiments structures A and B were overgrown with GaAs varying in the effective thickness. The type of the obtained surface relief was the same for both original structures. AFM surface images of such structures are shown in Fig.3 – the effective thickness of overgrown layer is 2nm (structures A1 and B1), and in Fig.4 – the effective thickness of overgrown layer is 10nm (structures A2 and B2). As seen from the images, GaAs growth starts with formation of nuclei, further they coalesce. Such growth dynamics is characteristic of the Volmer−Weber mechanism. Growth of nanoparticles by this mechanism is connected exclusively with depositing of aluminum but not with possible rise of gallium droplets due to arsenic desorption. To verify this, we have grown a structure identical to B2, however there was switch off of the arsine supply, whilst Al deposition was not done. The surface relief of the resulting structure is typical for epitaxial layer−by−layer growth of GaAs on a misoriented GaAs substrate. A smooth surface with atomic steps is clearly seen. Fig.5. shows the electron diffraction patterns for structures A2 and B2. Structure A2 (Fig.5a) exhibits well−defined Kikuchi lines (from the substrate) and point reflections. This suggeststhat the top layer (GaAs) is essentially a single crystal. Structure B2 (Fig.5b) with a high Al content does not show any rings that are typical of a polycrystal, either. Additional point reflections may be attributed to the epitaxial aluminum or axially textured aluminum. No Kikuchi lines from the substrate are seen

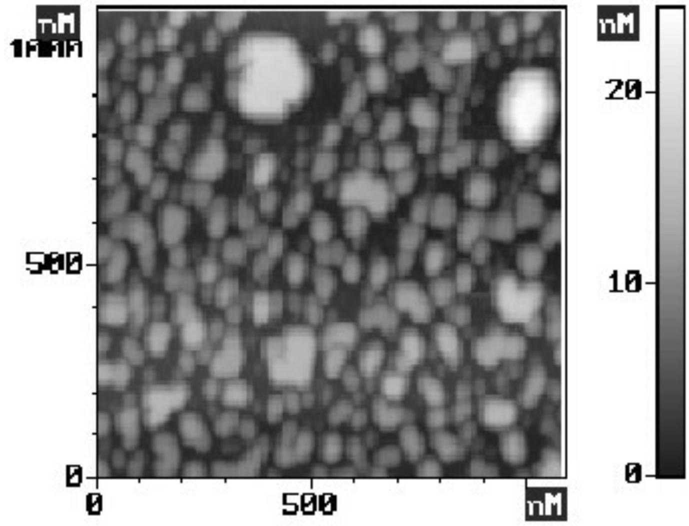


Fig. 3. AFM image of structure B1 (effective thickness of GaAs overgrowth is 2nm).

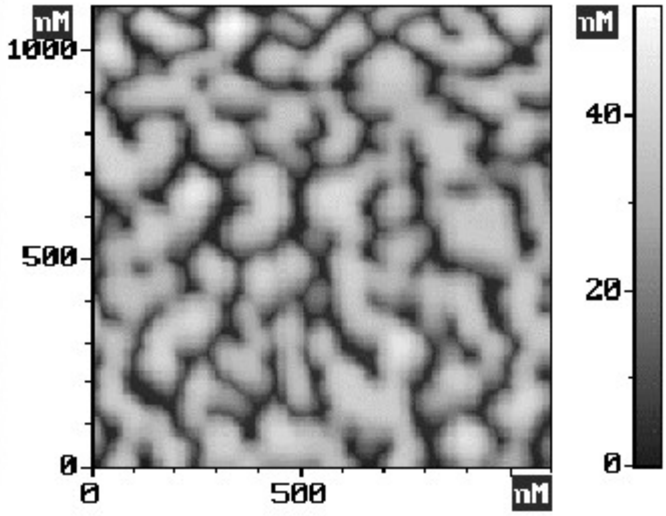
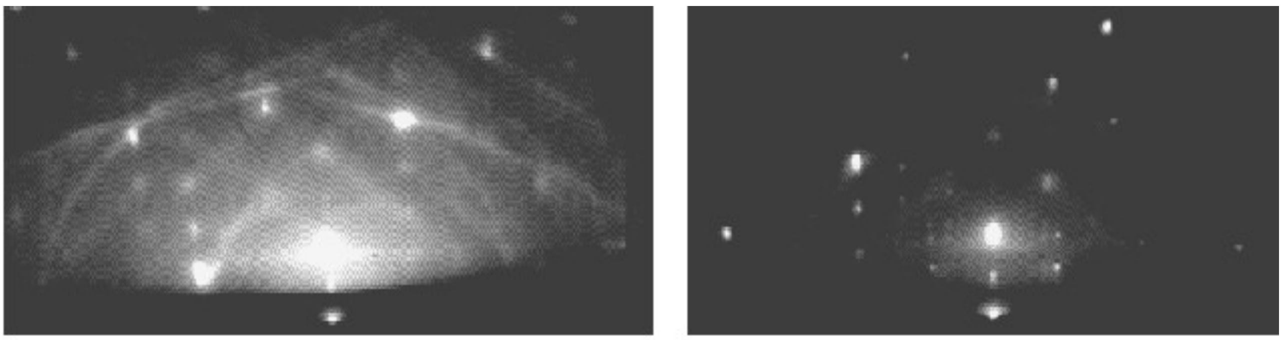


Fig. 4. AFM image of structure B2 (effective thickness of GaAs overgrowth is 10nm).



(a) (b)

Fig. 5. Electron diffraction patterns for structures A2 (a) and B2 (b) (effective thickness of GaAs overgrowth is 10nm).

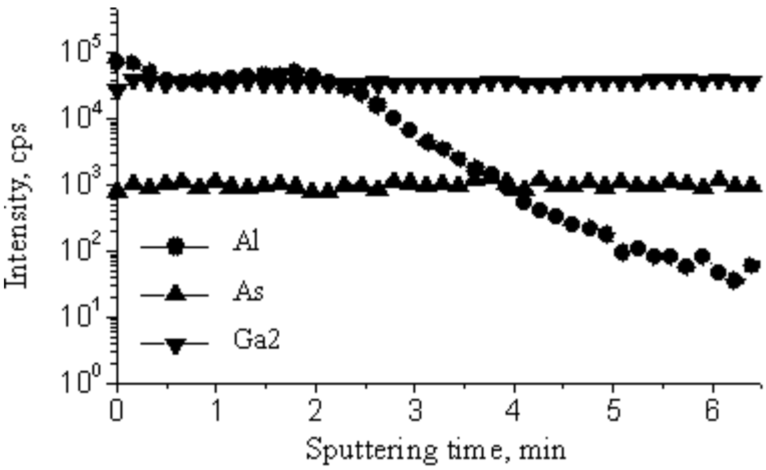


Fig. 6. SIMS profilling of structure A2 (effective overgrowth thickness is 10nm).

any longer because the Al layer is thicker here and there are Al islands formed. SIMS profiling for structure A2 also finds out aluminum on top of GaAs (Fig.6). As seen from the figure, the Al concentration remains practically the same until some sputtering depth is reached, after that it starts decreasing. High Al content even on the surface of the structure is apparently related to peculiarities of the GaAs overgrowing of Al nanoparticles. These peculiarities consist in island overgrowth of Al layer with GaAs, when at the early stages between GaAs islands remains uncovered Al which is detected by SIMS. Since GaAs grows over Al nanoparticles as monocrystal, further overgrowth leads to coalescence of GaAs islands ending up in a smooth surface.

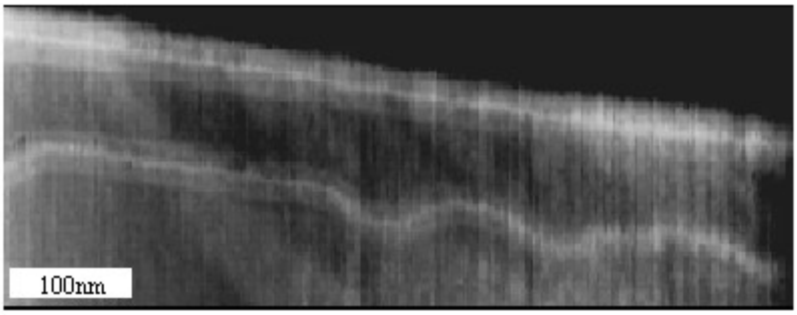


Fig. 7. AFM image of cleavage of GaAs/Al/GaAs structure. White strips belong to AlAs layers, introduced for marking position of growth front.

Photoconductivity and photoluminescence spectra showed, that thin GaAs and InGaAs layers groun over the layer of Al nanoparticles exhibit good optical quality. Crystallographic perfection is confirmed by the presence of growth steps seen in AFM. Fig.7 shows the AFM image of a cleaved structure, where two layers of AlAs, each 10nm thick, were formed during the process of Al nanoparticles overgrowth with GaAs. The first mark layer of AlAs was grown when the effective thickness of deposited GaAs was ~ 10nm, the second − after the GaAs thickness had reached the effective value of about 100nm. It is seen in the picture that the first AlAs layer (lower) bends replicating the shape of the growth front at early stages of the overgrowth process. The second AlAs layer is flat: the islands here have coalesced forming smooth surface of GaAs. Besides, SIMS profilling of structure A2 was accompanied by charging effect of the surface of sample. Such an effect may be associated with saturation of aluminum with arsenic and with formation of an intermediate layer of AlAs which features good dielectric properties. A similar analysis of structure A, though, revealed no surface charging (Fig.2), which is evidence of the presence of a conducting layer (Al) on this surface.

Conclusion

The regularities of Al layer growth on GaAs at high temperatures (up to 500°C) have been studied. It is shown that an excess in the critical thickness of Al layer gives rise to formation of Al nanoparticles. It was shown that Al nanoparticles grown at high temperatures (500°C) appeared on GaAs surface with a short delay after starting DMAA flow in the reactor. Conditions for forming Al nanoparticles with a height of 1−2nm, with a base in the range of 20−30nm, and surface density more than 10^{11} per cm^2 were established. Evolution of Al nanoparticles with increasing temperature up to 600°C for growth of monocrystalline layer of GaAs was observed.

It was found that growth of GaAs over the Al nanoparticles or Al treated surface begins with formation of nanodimensional nuclei which is typical for the Volmer−Weber growth mechanism. Monocrystalline GaAs layers, GaAs/AlAs and GaAs/InGaAs heterostructures with good optical quality were successfully grown over Al nanoparticles. Smoothing of the grown front was observed at the optimal conditions when the total thickness of capping layers is more than 100nm.

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