

Ag nanoparticle catalyst based on Ga₂O₃/GaAs semiconductor nanowire growth by VLS method

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Abstract In this paper, we report the synthesis results of Ga₂O₃ semiconductor nanowires (NWs) on GaAs (100) semi-insulator substrate by vapor liquid solid (VLS) method. Our study based on Ag nanoparticle (AgNP) catalyst, in which prepared by conventional sol–gel method. As the GaAs wafer, after being deposited an AgNP layer in HF/AgNO₃ aqueous solution, which dried and loaded to vacuum-chamber. GaAs slices heated in vacuum-furnace by VLS method with two temperature modes. The results showed that the Ga₂O₃ NW morphologies and properties depend strongly on technological conditions, such as AgNP catalyst concentration, growth temperature, and vapor pressure. It is also indicated that the NW random grown over large area with the diameter in the region conform from 18 to 30 nm scale and lengths ranging from several tens of nm to a few hundred micrometers.

1 Introduction

During past decades, the semiconductor nanowire (NWs) has been interest due to their potential in low dimension such as nano science, nano material and nanotechnology [1–4]. Due to their low dimension properties, that they are controllable, tunable conductivity, variable and diameter dependent band gap, flexible surface chemistry, large

surface area, enhanced exciton binding energy, and increased surface scattering for electrons and phonons, etc. [1]. Especially, the Ga₂O₃/GaAs NW growth have attracted substantial attention for various applications on nanoelectronics, optoelectronics, and nanosensors, etc. [2–5], as well as the Ga₂O₃/GaAs NWs growth will expect many exciting opportunities on nanoscale science and technology [6–9].

Up to now, we have had many number of methods for purpose of synthesis the semiconductor Ga₂O₃ NWs such as vapor liquid solid—VLS, chemical vapor deposition—CVD, laser ablation catalytic growth—LCG, pulsed laser deposition—PLD, solution liquid solid—SLS, oxide assisted growth—OAG, and molecular beam epitaxy—MBE [1, 6–8, 10], and among them, the VLS method has been a closely and usefully method. Because research the VLS method began as early as in 1964 by Wagner et al. [10] for silicon whisker growth, and then this method has being applied for NWs growth on GaAs substrate. In this case, the VLS method strongly depends on many technological factors: the growing temperature, catalyst metal, vapor pressure and gas volume, the bulk and surface diffusion of the catalyst metal [7, 9, 11]. Secondly, the sizes of catalyst metal particles also strongly effect the seed nuclear formation on the solid surface, the features of the phase diagram of the catalyst metal–material system to NWs growth process [1, 7, 9, 12].

Although, there have had studies on the successful synthesis of Ga₂O₃/GaAs NW by using different catalyst metals and structures as: nano thin-films, and nanoparticle of Au, Ag, Pt, Fe, Cr, Ni materials. But most of them have deposited on the surface of wafer by physical deposition methods, for example thermal evaporation, direct current—DC/or radio frequency—RF sputtering, thermal effusion, etc. [9]. On the other hand, several kinds of deposition

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methods have existed high cost and difficultly controlled. In order to solve these drawbacks, another choice of the deposition catalyst metal is of importance to deposit materials on the GaAs surface [1, 9].

The sol–gel method has widely used to synthesize nanoscale materials, which can produce solid nanoparticle materials from small molecules (precursors). This mechanism uses either a chemical solution (sol short for solution) or colloidal particles (sol for nano particle) to form an integrated network in a continuous liquid (gel) [13]. In this case, the monomers (precursors) for synthesizing the Ag colloid consisted AgNO_3 salt and HF acid solvent. And then, these nanoparticles were dispersed in a solid and deposited on the substrate by spaying, dipping or doctor blade method.

According to our knowledge on both experimental and theory model, there has not been a combination between sol–gel and VLS method to grow $\text{Ga}_2\text{O}_3/\text{GaAs}$ NW, yet. Therefore, in this paper, continuing several our before works [6, 7, 11], we report the producing Ag nanoparticle (AgNP) on GaAs wafer by using sol–gel method, which has investigated to effects of the AgNP concentration, growth temperature on formation $\text{Ga}_2\text{O}_3/\text{GaAs}$ NW by VLS method. The morphology results and structural property of Ga_2O_3 NW are also discussed.

2 Experimental procedures

The (100) GaAs semiconductor undoped single crystalline wafer with resistivity of $1.3\text{--}2.7 \times 10^8 \Omega\text{cm}$ was used as the substrate, which provided from AXT, Inc. The chemical HF 40 % solution, and 2.5 % (w/v) AgNO_3 powder reagents provided from Sigma Aldrich, Alfa Aesar, respectively. Before experiments, the GaAs wafers were cut of $0.5 \times 0.5 \text{ cm}^2$ pieces. The Ag deposition on the GaAs surface was done by immersing the wafers in the aqueous solution of 0.4 mM AgNO_3 and 0.14 M HF at 25 °C for 5, 20, and 35 s, respectively. According to previously reported of authors [14–17], we decided to use above concentration reagents and deposition time for AgNP high uniformity. Neither too sparse nor too dense, this condition chose to obtain the AgNP size diameter of range from 50 to 70 nm and $\sim 1 \times 10^{10} \text{ cm}^{-2}$ of particle density, respectively. After silver coated, the samples were rinsed with deionized water and dried at room temperature by pure nitrogen gas. For steps of the NW growth process, with which are experimentally carried out and repeated many times on the different investigation temperatures range from 650 to 830 °C at the low vapor-pressure inside of $\sim 10^{-1}$ Torr (listed Table 1). The growth temperature profiles in the closed quartz tube were automatically measured and controlled by a Keithley 2000 multimeter

(see Fig. 2b). And then, the morphology of NWs were investigated by field emission scanning electron microscope (FE-SEM) (Hitachi, Japan) equipment, energy-dispersive X-ray (EDX) techniques on JED-2300 AnalysStation equipment.

3 Experimental results and discussions

The Fig. 1a–c shown the AgNP densities and sizes on (100) surface GaAs substrate after AgNP deposited by the HF/ AgNO_3 solution. As same concentration of HF/ AgNO_3 solution and the different deposition times, we can see the density and size of AgNPs as a function of deposition time. The Fig. 1c shown the $\sim 2 \times 10^{10}$ of AgNP density, which is uniformly distributed in whole GaAs wafer surface. The diameter of the congregated particles are clearly observed ~ 70 nm of the short deposition time (Fig. 1a) and ~ 50 nm of long deposition time (Fig. 1c). Also, SEM cross-sectional image analysis of AG153 sample (Fig. 1d) shown that the average height and width of particles are ~ 70 , ~ 50 nm in range, respectively. These results can use to estimate the diameters of Ga_2O_3 NWs, which will be grown by below VLS mechanism. From the SEM results of AgNPs-coated, we shall select AgNP concentration as in Fig. 1c to next experiments. According to technology conditions [6, 7, 11], especially growth temperature was exactly controlled by a Keithley 2000 multimeter with two-steps as Fig. 2b. For step one at 400 °C of T_2 for 10 min, the AgNP will divide into smaller nanosize and adhere to the GaAs surface. These affected factors have still not understood yet to control in the first stage of VLS method, such as the contact angle, alloy temperature, and metal–crystalline. They can also use to determine the surface energy of a NW growth process [9, 18, 19].

For step two at (from 650 to 830 °C range) T_3 of different growth temperatures of this process (Fig. 2b), the gallium and oxygen atoms partly will be entered into the AgNP by surface absorb mechanism. Therefore, the NWs are immediately grown. So far, we also regard to investigate our experimental series due to the effect of NW morphologies at growth (T_3) temperature, and AgNP sizes. At the T_3 temperature, the NWs are continuously synthesized, in which will survey most of growth conditions depend on NW morphologies. The Fig. 3 shows the NW morphologies as a function of AgNP density that the NW successfully grown at 830 °C of substrate temperature and $\sim 10^{-1}$ Torr of vacuum–pressure inside quartz tube. In this case, we will investigate the effect of NW growth process depend on silver NPs density. At the high AgNP density (Fig. 3a, b), the NW has been random grown with very long of few hundred micrometers of length, and plentifully of area surface, as well as they also have smaller in

Table 1 Technological conditions for the experiments of Ga₂O₃/GaAs NW growth by VLS method

Samples	Vapor pressure inside the quartz tube (Torr)	AgNP deposition time (s)	As period heating up to T ₂ temperature			As period heating up to T ₃ temperature around eutectic temperature		
			t ₁ (min)	T ₂ (°C)	t ₂ (min)	t ₃ (min)	T ₃ (°C)	t ₄ (min)
AG151		5						
AG152		20						
AG153		35						
AG154	~10 ⁻¹	35	90	400	10	25	650	30
AG155	~10 ⁻¹	35	90	400	10	30	700	30
AG156	~10 ⁻¹	35	90	400	10	38	780	30
AG157	~10 ⁻¹	35	90	400	10	43	830	30
AG158	~10 ⁻¹	35	90	400	10	43	830	30
AG159	~10 ⁻¹	35	90	400	10	43	830	30
AG1510	~10 ⁻¹	35	90	400	10	43	830	30

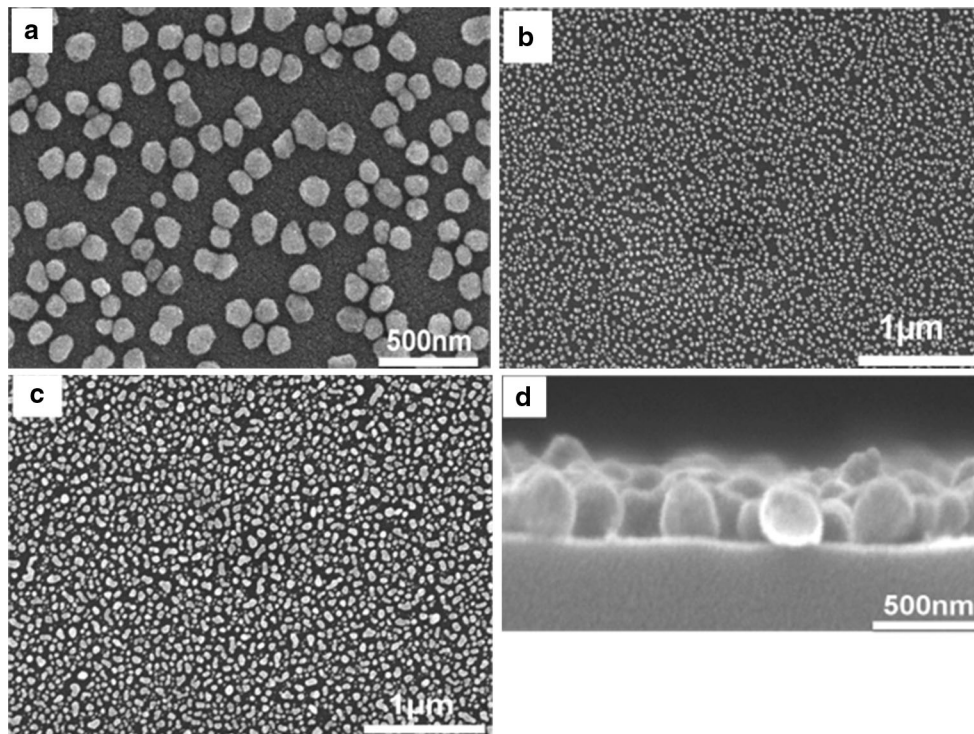


Fig. 1 Top view SEM images of AgNPs coated on the GaAs surface as a function of deposition time, **a** 5 s; **b** 20 s; **c** 35 s; and **d** SEM cross-sectional of AgNPs deposited on GaAs wafer for 35 s, as AG151, AG152, AG153 samples, respectively

diameter. In contrast, they have larger diameter and shorter length, in which we can see existent of Ag droplets on the top of the NW (Fig. 3c) that this phenomenon is in good agreement with the previously conventional explanation on VLS method [6, 7, 9, 10]. Also, they looked like tangly whisker structure and sidewall smooth shape. The different morphologies of NWs are often appeared during the NW

growth that due to effects of monocentric and polycentric nucleation and its combination with periodic stable and unstable growth. As a NW begins to grow, its height increases by an amount and the radius of the contact area decreases by an amount, then the NW growth continues, also the base of the NWs increases from the zero value follow Young’s model. The detail explains of this

Fig. 2 **a** The growth furnace scheme with 10^{-1} torr low vacuum quartz tube, and **b** the NWs growth by two steps temperature profile modes, where the growth temperatures T_3 are near the eutectic temperature T_e

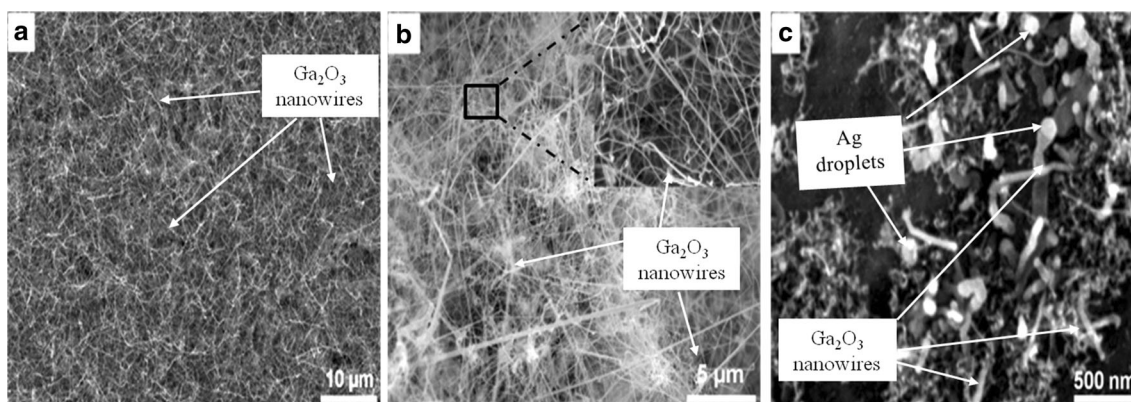
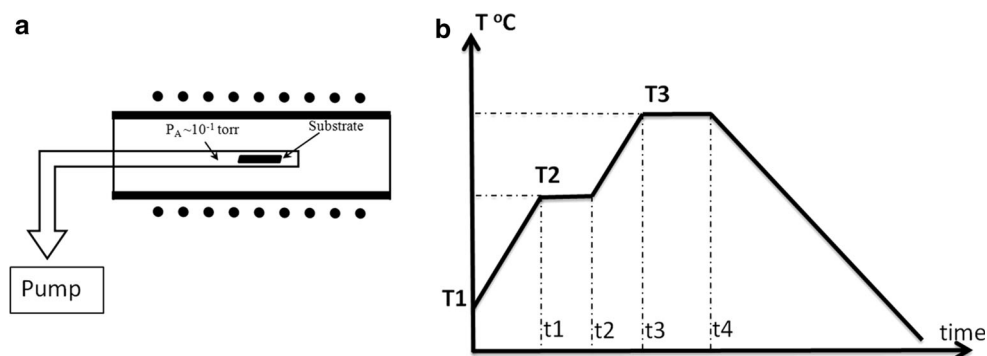


Fig. 3 SEM image results of Ga_2O_3 NW morphologies which depend of different AgNP densities on GaAs surface at same growth temperature and pressure **a** 20 s, **b** 35 s, **c** 5 s of AgNP deposition times, as AG158, AG159, and AG1510 samples, respectively

mechanism could be found elsewhere [1, 2, 7, 9–11]. As far, these NW morphologies (Fig. 3a, b) will better candidate to nano electric circuit, nanosensor, and applications in the future.

The Fig. 4 shows the investigation results of NW which depend on different substrate temperatures at the similar AgNP density. As you see the Fig. 4a–c, the NWs have successfully synthesized as a function of substrate temperature, that mean the NWs can easily grow at the higher substrate temperature ($\sim T_e$), as well as longer in length. This believed due to low impurity incorporation at high growth temperature [9]. To more detailed explain, we need to understand eutectic point (T_e) of Ag–GaAs alloy [20] and the important role of AgNP catalytic during growth process. At the nearly T_e (Fig. 4d), and phase edge region of catalytic liquid alloy, in which can rapidly absorb a vapor to become stability levels of thermodynamic equilibrium state, and then a new crystal growth can subsequently appear as nucleated seed at the liquid–solid interface. However, if growth temperature is too high (above T_e) causing a significant amount of gallium and oxygen desorption then reduce the NW quality. On the

other hand, the high substrate will reduce impurity of alloy and just only alloy phase desired to form NW nuclear seeds [9], as well as the high growth temperature ($>850^\circ\text{C}$) is unacceptable for the real usage. But the advantages of high growth temperature is offset ($\sim T_e$) by the degrading effect of vacancies from contamination.

The Fig. 5 shows EDX measurement result of Ga_2O_3 NW on AG159 sample which grown at 830°C of substrate temperature for 30 min. Among NW length, the structure composition of NW has similar chemical element. From the EDX results, the wt% composition magnitudes of NW configuration are Oxygen of 47.99 wt%, Gallium of 37.60 wt% and small Carbon amount impurity of 7.10 wt%. Also, we obtained the Arsenic of 7.31 wt%. Evidence of the residual As molecular small amount was absorbed on the NW surface by physical absorption during cooling down process of the substrate. Nevertheless, this As amount will not effect on NW structure and they also will disappear at As vapor temperature/or high temperature. To deeply understand these mechanisms, we can consider the surface physical absorption/or desorption mechanism.

Fig. 4 SEM image results of Ga₂O₃ NW morphologies which depend of different growth temperature with similar AgNPs density on the GaAs surface **a** 650 °C, **b** 700 °C, **c** 780 °C **d** 830 °C, as AG154, AG155, AG156, and AG157 samples, respectively

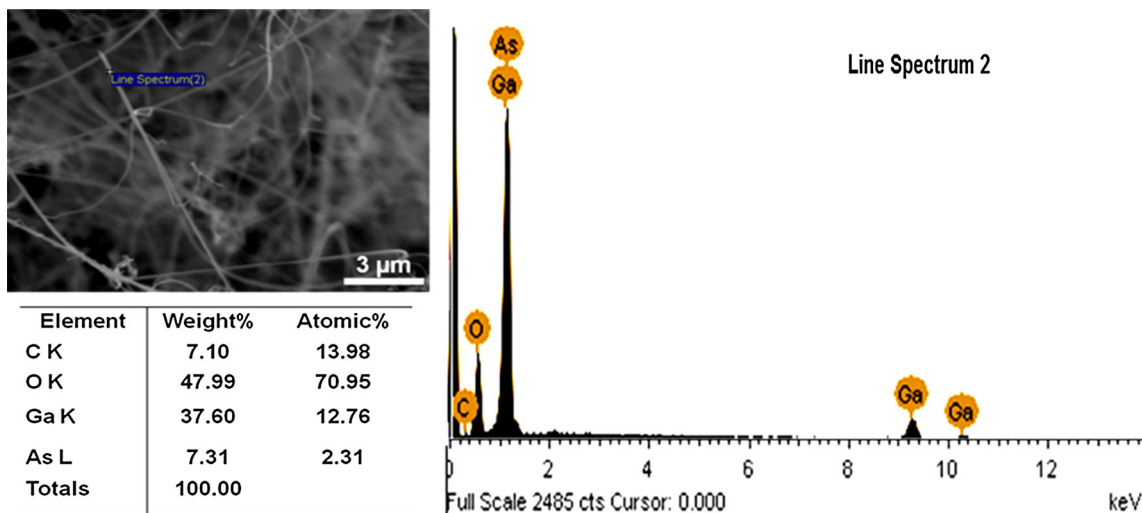
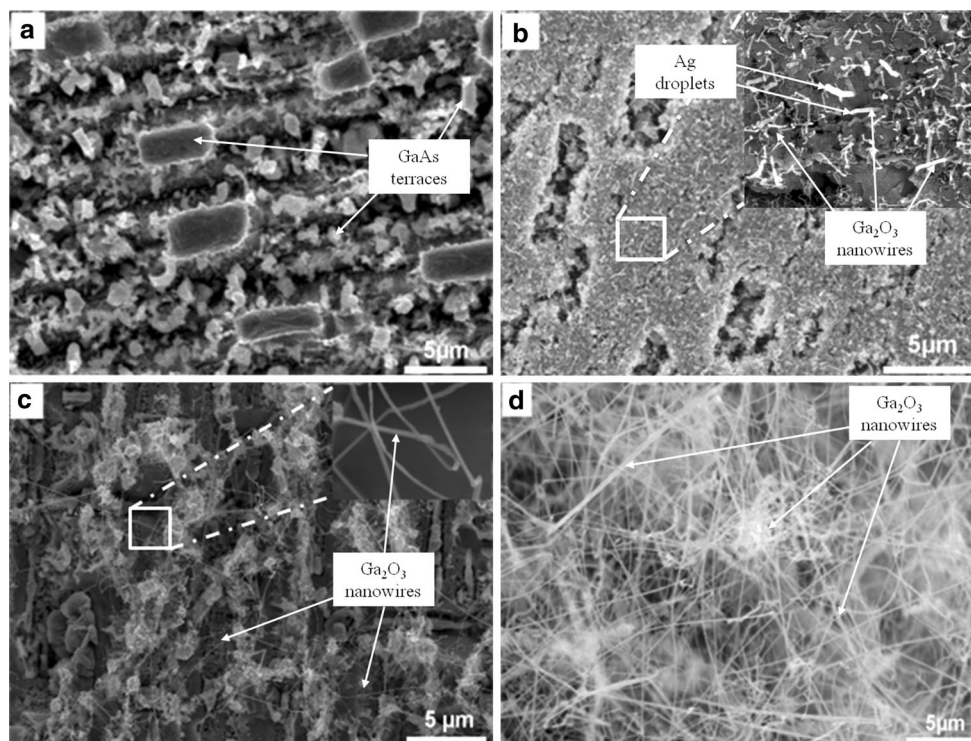


Fig. 5 EDX results of Ga₂O₃ NWs grown at 830 °C for 30 min with line scan on AG159 sample

4 Conclusions

In summary, we have successfully synthesized Ga₂O₃/GaAs NWs using VLS method based on Ag catalytic metal NPs deposited on the GaAs substrate by chemical deposition of HF/AgNO₃ solution and investigated the effects of Ag catalyst as well as the NW growth properties. During investigation process, we finally found that: (a) the NW can random grow at anywhere of GaAs wafer surface area and the NW morphology strongly depend on

the AgNP density, (b) the NW growth temperature is found around the T_e: 700–830 °C, (c) the two-step temperature modes for dividing Ag catalyst metal particles into smaller size and grow NW at low vacuum–pressure (~10⁻¹ Torr), at which can synthesis longer of length and control diameter of NWs depend of AgNP size. These results indicated also that the VLS mechanism is still dominated with Ag droplet on the top of NW. Therefore, in future, these Ga₂O₃ NWs are good candidate for the micro/or nano device applications.

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